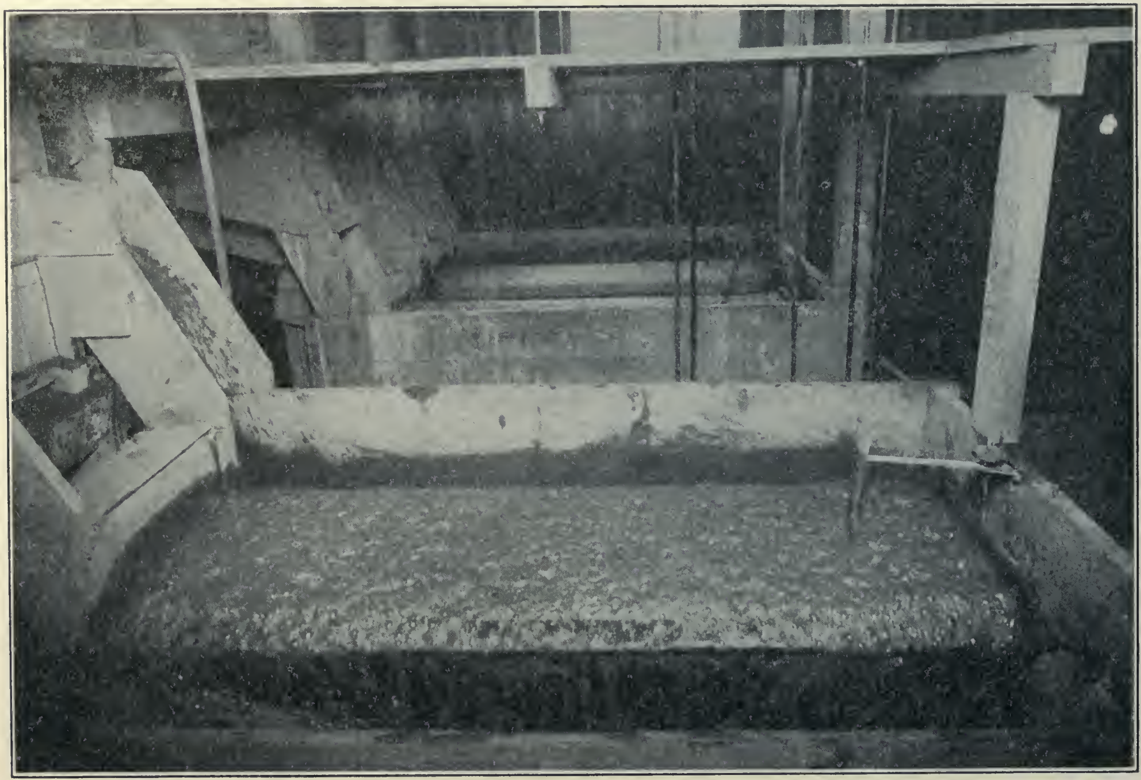
FLOTATION



THE FROTH ON A CALLOW CELL

THIS BOOK
is
Dedicated
to
JAMES M. HYDE
the Pioneer
of the
Froth-Flotation Process
in America

FLOTATION

BY

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PREFACE

This is a report on recent progress in the application of flotation to metallurgic practice. It does not pretend to be a last word. No final treatise can be written on an art that is growing as flotation has grown during the last two or three years. We have tried to give the worker the latest obtainable information on the technology of the subject, believing that the imperfection of our presentation will be disregarded in his eagerness to learn; he will neither misunderstand our purpose nor belittle our intention. To those that expect either to hear or to say the last word we do not appeal; we offer this book in the belief that it will be useful; that is all.

T. A. Rickard.
O. C. Ralston.

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A GLOSSARY OF FLOTATION

Absorb. To drink in, to suck up, as a liquid by a solid, like a sponge or fuller's earth.

Adsorb. To condense and hold a gas on the surface of a solid, particularly metals. Also the holding of a mineral particle within a liquid interface. From L. *ad*, to, and *sorbeo*, suck in.

Adhesion. A molecular force by which bodies of matter are caused to stick together.

Agitation is the act or state of being shaken, stirred, or moved with violence. From L. *agitatus*, *agito*, the frequentative of *ago*, to drive.

Baffle. That which defeats or frustrates, hence the projections or wings that divert or interrupt the flow of pulp in a vessel.

Bubble. A globule of air or other gas in a liquid; also a vesicle of water or other liquid inflated with air or other gas.

Buoy. To keep from sinking, to keep afloat in a liquid.

Coagulation. The state of a solute in a solvent, or of a colloidal gel, resulting from clotting or curdling; the act of changing to a curd-like condition.

Coal-tar is a thick, black, viscid, and opaque liquid condensed when gas is distilled from coal. This product consists of soluble and insoluble substances.

Cohesion. That force by which molecules of the same kind or of the same body are held together, so that the body resists being pulled to pieces.

Colloid. A state of matter supposed to represent a degree of sub-division into almost molecular dimensions, dispersed in a solvent. Colloidal particles possess the property of carrying electric charges, and also of failing to diffuse through a membrane, this being the original distinction between colloids and crystalloids.

Concentrate. To draw or gather together to a common centre. To reduce to a purer state by the removal of non-essential matter. From L. *con* or *cum*, with, and *centrum*, a centre.

Contaminate. To make impure by contact or admixture. A substance that performs the function, in an ore-pulp, along with oil, of promoting the emulsification or the de-emulsification of the oil, and thereby exerts an influence upon the making of froth for the flotation of minerals.

Dispersoid. A body that has been dispersed in a liquid.

Emulsion. Milkification. A liquid mixture in which a fatty or resinous substance is suspended in minute particles almost equivalent to molecular dispersion. From L. *emulgeo*, to drain out, in turn from *e*, out, and *mulgeo*, milk.

Fat is a white or yellowish substance forming the chief part of adipose tissue. It may be solid or liquid; it is insoluble in water; when treated with an alkali, the fatty acid unites with the alkaline base to make soap.

Film. A coating or layer, a thin membrane.

Flocculent means resembling wool, therefore woolly. Coalescing and adhering in flocks. A cloud-like mass of precipitate in a solution. From L. *floccus*, a lock of wool.

Flotation is the act or state of floating, from the French *flottaison*, water-line, and *flotter*, to float, to waft.

Froth. A collection of bubbles resulting from fermentation, effervescence, or agitation.

Gangue. The non-metalliferous or non-valuable metalliferous minerals in the ore; veinstone or lode-filling.

Gel. A form of matter in a colloidal state that does not dissolve but nevertheless remains suspended in a solvent from which it fails to precipitate without the intervention of heat or of an electrolyte.

Granulation is the state or process of being formed into grains or small particles. From L. *granum*, a grain.

Grease. Animal fat when soft, that is, in a semi-solid state, and oily or unctuous. From the French *graisse*.

Hydrophilic. A property possessed by colloids whereby they take up water in conjunction with the molecules of the colloid in a manner analogous to a closed hydrated molecule. Hydrophilic colloids are valuable dispersing mediums for the making of emulsions.

Levitation. The act of rendering light or buoyant. L. *levitas*, lightness, from *levis*, light.

Metallic. Of or belonging to metals, containing metals, more particularly the valuable metals that are the object of mining. From L. *metallum*, ore.

Mineral. Inorganic constituent of the earth's crust. As used in flotation the terms 'mineral' or 'metallic' refer to those valuable constituents in the ore that it is the object of the process to separate from the non-valuable constituents, or gangue.

Molecule. The smallest part of a substance that can exist separately and still retain its composition and characteristic properties; the smallest combination of atoms that will form a given chemical compound. From F. *molecule*, diminutive from L. *moles*, mass.

Occlude. To shut or close in pores or other openings. From L. *ob*, before, *claudo*, close.

Oleic acid is the fatty acid contained in olive-oil combined with cresoline. Although called 'acid,' it is an oily substance and functions as oil in flotation operations; it is contained in most mixed oils and fats, from which it is obtained by saponification with an alkali. From L. *oleum*, oil.

Oil includes (1) fatty oils and acids, (2) essential oils, mostly of vegetal origin, such as eucalyptus and turpentine, (3) mineral oils, such as petroleum products, including lubricating oils.

Osmose. The tendency of two liquids or gases to mix by passing through a membrane or porous wall separating them. From G. *osmos*, pushing.

Pulp is powdered ore mixed with water.

Saponification. Conversion into soap; the process in which fatty substances form soap, by combination with an alkali. From L. *sapo* (n–), soap.

Scum. Impure or extraneous matter that rises or collects at the surface of liquids, as vegetation on stagnant water, or dross on a bath of molten metal.

Skin. An outside layer, coat, or covering. From A. S. *scinn*, ice.

Solute. The substance dissolved in a solution.

Surface-tension is the contractile force at the surface of a liquid whereby resistance is offered to rupture.

Viscosity is the property of liquids that causes them to resist instantaneous change of shape or of the arrangements of their parts; internal friction; gumminess. From L. *viscum*, birdlime.

THE HISTORY OF FLOTATION

By T. A. Rickard

(From the *Mining and Scientific Press* of March 17, 1917)

Introduction

The various flotation processes depend upon the successful application of a number of physical principles, of which three may be instanced as underlying the methods successively invented.

1. Film suspension. This is typified by the floating of a needle on water. In the familiar experiment a small needle is greased, either intentionally or by the natural oil on the fingers; but when pains are taken to prevent contact with anything greasy, the needle will still float, if not too large and if carefully manipulated.[1] If the needle is too large it will not float, no matter how skilfully handled, because the force of gravity overcomes the force of surface-tension, which is the cause of this kind of flotation. Surface-tension is the force that causes the surface of a liquid to resist rupture. This, in turn, is due to the fact that the molecules at the surface have a greater coherence than the molecules within the body of the liquid. In consequence, the surface acts as if it were an elastic film.

2. Oil-buoyancy. This is a simple manifestation of gravity, whereby an oil, being lighter than water, will rise to the surface of a pulp and carry with it any mineral particles that have become immersed in it. The oil plays the part of a raft or boat. In order to effect flotation the volume of oil must be such that its smaller specific gravity will overcome the greater specific gravity of the burden it is to bear to the surface. Most oils have a specific gravity of about 0.9, as against the 1 of water; therefore the flotative margin is 10% only. If the specific gravity of a mineral is 5, then the volume of oil required to buoy it must weigh more than 40 times as much. When an ore contains 4% of a mineral having a specific gravity of 5, then more than 3200 pounds of oil will be required to raise the mineral in a ton of ore to the surface of the pulp. It remains to add that oil exhibits a preference for certain kinds of metallic particles, so that it attaches itself readily to them, while passing the particles of gangue. The lat-

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[1] 'The Flotation Process.' See 'Simple Problems in Flotation,' by T. A. Rickard. Page 357.

ter, therefore, are quickly wetted by the water, and sink. The oiling of the metallic particles enables them to resist wetting and lessens their specific gravity so that in the presence of sufficient oil they are enabled to float.

3. Bubble-levitation. This phase of flotation depends upon the aid of bubbles of gas, which, by attaching themselves to particles of mineral buoy them to the surface, like cork-belts or the bladders that children use when learning to swim. Various gases have been tried, but air is now generally used for the making of bubbles. The attachment of the bubbles to the metallic minerals in preference to the gangue has been said to be due to an affinity or selectiveness, like that of the oil, and the presence of oil is said to enhance it, but the oiliness of the bubble-film is now believed to be the chief factor.

In order that the bubbles generated in, or introduced into, a pulp may perform their metallurgic function they must last long enough to carry their freight not only to the surface but over the edge of the containing vessel. They must not burst untimely. This necessary prolongation of bubble-life is effected by lowering the surface-tension of the water, of which their envelope or film is composed. The bursting is due to the contractile force of surface-tension, and it must be moderated if the bubble is to last long enough. A decrease of surface-tension is produced by putting some impurity or contaminant in the water. Heretofore oil has been the contaminant chosen, as soap is used by a school-boy to blow his bubbles, he having discovered that the bubbles blown in pure water are too fragile for his play. The use of oil was inherited from the prior art, but other re-agents are likely to be found adequate for the purpose.

Thus the third and most successful phase of flotation has grown out of the second, although it is more nearly the logical development of the first phase. Film-suspension involves the aid of air, for the floating of pulverized minerals on the surface of water is helped by the air entrained in the ore. The attempt to invent an effective method out of oil-buoyancy instead of film-suspension goes far to explain the delay that marked the development of this metallurgic process.

EARLY ATTEMPTS

The story of the slow and toilsome development of this metallurgical process may claim to be 'historical' if only for the fact that the use of oil for collecting metals was mentioned by Herodotus. The recovery of gold from the mud of a lake by means of feathers daubed with pitch and held in the hands of apocryphal virgins is as pertinent to the subject as the yarn, 2000 years later, of a young school-teacher in Colorado who was washing oil-stained ore-sacks in her brother's assay-office when she noted that the pyrite floated on the water contaminated by the oil. We know now that the Carrie Everson fabricated in the course of litigation is a myth and that while there was a lady of that name, she was the wife of a Chicago doctor. Indeed, there is reason to believe that Dr. William K. Everson, of Chicago, not his wife, was the originator of the method that was patented. The death of the husband—the real inventor—prevented the development of the process, which fell into the hands of less competent persons, Thomas Criley and Charles Hebron, in collaboration with whom Mrs. Everson devised a method based on "the chemical affinity of oils and fatty substances for mineral particles"[2] and obtained a patent in 1885. She and her husband did ascertain that "acidification of the ore-pulp is necessary for the sharp oil-differentiation of mineral from gangue."[3] But the method patented by her in 1885 was a complete failure as a metallurgical process, although it probably did serve to suggest some of the later investigations and it was used freely in the attempt to disprove the originality of subsequent inventions. The odds were greatly against Mrs. Everson: she was a woman, her idea seemed absurd, she had no mechanical ingenuity herself nor was any at her command, and she had no financial backing. If we consider these circumstances, we shall not wonder at her failure to develop a concentration process.

The first patent employing oil for a metallurgical purpose was that obtained by William Haynes in England in 1860. This is of academic interest as being a prelude to flotation. By mixing coal-tar and resin with crushed ore, in the proportion of 5:9, he made a "dough" that held the metallic particles, while the gangue was removed by the help of water and "frictional trituration." The idea proved wholly impracticable and is only worthy of mention as the first recorded use of oil—an oil partly soluble—in the concentration of ores. The next attempt is that of Hezekiah Bradford, an American, who, in 1885, two months before the date of Mrs. Everson's patent, obtained a patent for the first method that was based upon a recognition of the surface-tension of water in contact with air. His method was one for "saving floating materials in ore-separation," such as escaped from arrest by tables, vanners, and jigs. He stated:

"These floating particles appear to possess some peculiar quality

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[2] As stated by her son. 'Carrie J. Everson and Flotation,' M. & S. P., January 15, 1916.

[3] H. L. Sulman, Presidential address. Trans. I. M. & M., Vol. XX, page 14.

which repels water from their surface, especially when such particles are exposed even momentarily to atmospheric air, and when such exposure takes place the water is repelled from a sufficient portion of their surfaces to cause such particles to float off on the surface of the waste water from the other particles that sink in the water.''

He had the germ of an idea pregnant with metallurgic possibility, but it was still-born. Haynes and Bradford had inklings of the physical phenomena underlying the flotation process, but they were pioneers that blazed no trail and crossed no range of fruitful discovery. Carrie J. Everson comes next in point of time. Her groping after a practical process is noteworthy by reason of the introduction of acid, but her trail also stopped at the foot of the talus on the slope of the range. The patent records disclose other abortive attempts in the same direction during the ensuing decade, but none is of any consequence except H. L. Sulman's British patent of 1893, in which he describes a means for saving 'float' gold by adding something to the mill-water that will diminish its surface-tension. This is interesting as recording scientific curiosity concerning the physics of flotation on the part of a metallurgist that was destined to contribute so greatly to the decisive development of the process. His successful participation is due, in part, to his having been formerly engaged professionally in the chemistry of the oil and soap industries, for thereby he acquired knowledge of a kind that proved of great value to him at a later date.

So far no workable method had been invented—only ingenious schemes and impracticable proposals.

The next incident in this story brings us to the edge of real achievement. In 1894 George Robson, for himself and Samuel Crowder, patented a process for separating sulphides from gangue. He disclaimed ''the use of acid or salts and also the method of washing away the gangue with water,'' and appears therefrom to have been aware of the earlier patents. He effected ''the separation of the metallic matter by the mixture of oils alone.'' Thus he followed in the track of Haynes. The proportion of oil was large: as much as three times the weight of ore. It was a method of buoying the sulphide particles with oil. The process was tried on a working scale at the Glasdir gold mine in Wales and was commended by James Brothers, a firm of experienced metallurgists. But it did not succeed and apparently led nowhere. Yet it opened the way for a decisive event namely, the technical participation of the Elmore brothers.

ELMORE

Francis Edward Elmore was a trained engineer with an inventive mind. His father, William Elmore, bought the Glasdir mine from Samuel Crowder, in 1896. The conventional concentrating plant, of jigs and shaking tables, had proved unable to make a good recovery of the gold-bearing chalcopyrite in the ore from this Welsh mine. The elder Elmore sent his two sons, Francis Edward and Alexander Stanley, to investigate. It has been stated[4] by Stanley Elmore that, on the occasion of one of their visits to the mill, his brother Frank noticed copper adhering to the oil that had dropped from a shaft-bearing, and thus obtained the idea of his invention: ''Finely-divided wet copper-pyrite would adhere to a greasy surface, whereas finely-divided wet rock would not.'' But no accidental demonstration of the action of oil was necessary to arouse Mr. Elmore's interest in face of the fact that Robson had conducted experiments in oil-flotation on the same spot. We have the testimony of Mr. Crowder himself,[5] now a very old man, that Robson's experimental oil-concentration plant was on the mine when it was purchased by William Elmore, and we know also, from Mr. Crowder, that he wrote to Stanley Elmore in 1897 urging him to use oil as a means of concentration. In 1898 Frank Elmore obtained his first patent. A working unit of full size was erected at the Glasdir mine. Walter McDermott, Hennen Jennings, and Wernher, Beit & Co., gave the Elmores their financial support and formed a syndicate, which became known as the Ore Concentration Syndicate.[6]

In his patent Frank Elmore describes the process as ''mixing the pulverized ore first with water in considerable quantity, then adding to the mixture an oil of the kind described, which adheres to the metallic constituents but not to the wet rocky constituents.'' He used a thick oil and introduced the idea of the freely flowing pulp as against the mixing of oil with crushed ore in the presence of only a small proportion of water, as Robson and Crowder had done. By using more water, he also entrained more air, so essential to success, although he did not then recognize this fact.

In the first plant, at the Glasdir mine, the mixture of crushed ore and water was fed at the upper end of a slowly revolving drum, provided with annular helical ribs and tranverse blades, so as to mix the pulp and oil without producing emulsification. The oil was introduced through a separate pipe. The mixture was discharged into a V-shaped vessel, where the water and sand subsided, while the oil buoyed the sulphide particles to the top. An oil-residuum of 0.89 specific

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[4] M. & S. P., September 23, 1916.

[5] M. & S. P., February 24, 1917, and June 16, 1917.

[6] In 1905 it acquired the Elmore vacuum patents and became the Ore Concentration Company.

gravity was used in equal parts by weight with the ore, ton for ton. The oil was so viscous as to require the aid of small rotary pumps to move it forward. The temperature of the oil and water was kept between 54° and 57° F. The loss of oil was 2 gallons per ton of ore. A concentration of 14:1 was achieved with a recovery (in the concentrate) of 69% of the gold, 65% of the silver, and 70% of the copper from chalcopyritic ore assaying 1.12% copper, 0.49 oz. gold, and 0.8 oz. silver per long ton. These details are taken from a paper by C. M. Rolker read before the Institution of Mining and Metallurgy, on April 25, 1900. Mr. Rolker described the process as "somewhat dirty and nasty," but he stated that "the mechanical contrivances brought into action by the inventor are excellently adapted to the work demanded, and bespeak very careful thought, as well as patient, systematic, and highly intelligent work."

The discussion of Mr. Rolker's paper, as recorded in the Transactions of the Institution, shows clearly that nobody at that time recognized the part played by air in the process of flotation. Stanley Elmore has cited the use of a Gabbett mixer, which causes a violent agitation with indrawing of large "quantities" of air[7] as proof that he and his brother were "quite cognizant of the fact that it was the air entrapped in the bulk of the oil which rendered it capable of carrying more than its theoretical load of concentrate." But this use of the Gabbett machine was made in 1902, by which time the action of air had begun to be understood. During the discussion of the Rolker paper, two years earlier, nobody present had been able to explain why the actual load of concentrate had been 150% more than was accountable to the difference in specific gravity between the oil and the water. The manager, John Bevan, had testified that the flotative efficiency of the oil was 25%, against the theoretical load of 10%, on an oil of 0.9 specific gravity; whereupon Frank Elmore remarked: "It seems rather strange that there should be such a difference between theory and practice." On the same occasion Mr. Rolker said: "The viscosity of the oil is the all-important point." Neither H. L. Sulman nor H. F. K. Picard, both of whom took part in the discussion, made the slightest reference to the agency of air, which was entrained with the ore and water while they were being mixed in the revolving drum. As late as January 1903 Stanley Elmore took out a patent for an improved apparatus wherein air was *excluded* from the operation of concentration by oil. But his is not the only attempt to read the past in terms of the present—all the litigants have done it and many of their witnesses.

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[7] M. & S. P., September 23, 1916, page 452.

The fact is clear that in 1900 the agency of air was *not* understood by any of the exponents of flotation.

In 1901 the Elmore syndicate established a demonstration plant in London and the free access thereto given to the mining profession, together with the frequent publication of information concerning the process, did a great deal to stimulate interest and curiosity, contributing thus to the later improvements whereby the process was turned inside-out and made supremely valuable to the mining industry. A number of plants were built to apply the bulk-oil process, at mines scattered all over the world, notably the Namaqua, in South Africa, the Le Roi No. 2 in British Columbia, the Tywarnhaile in Cornwall, and the Sygun in Wales, but it cannot be said that any one of them was an unquestioned metallurgical success.

At this time the treatment of low-grade complex zinc-lead ore at Broken Hill, and more particularly the beneficiation of dumps of similar material discarded in the course of large-scale milling operations, began to stimulate efforts to add some form of flotation to the conventional concentration process. Hence the next chapter of the story concerns itself mainly with the work of a group of Australian metallurgists.

FLOTATION AT BROKEN HILL

After various attempts at magnetic separation had failed, an effort was made to employ flotation for the purpose of treating the huge accumulations of tailing, which averaged 16 to 20% zinc, 5 to 10% lead, and 5 to 15 oz. silver per ton.

In January 1902, Charles V. Potter, an Australian engineer, obtained a British patent for the flotation of sulphides in a hot acid solution. He used a stirrer and claimed that the solution would "react on the soluble sulphides present to form bubbles of sulphuretted hydrogen on the ore particles and thereby raise them to the surface." Here we have the first suggestion of the bubble idea. In November of the same year Guillaume D. Delprat, manager of the Broken Hill Proprietary mine, applied for a similar patent, except that he used salt-cake instead of sulphuric acid. In his first American patent, No. 735,-071, filed on January 2, 1903, Mr. Delprat states that his process "depends upon the ore particles being attacked by the acid to form a gas. Each ore particle so attacked will have a bubble or bubbles of gas adhering to it, by means of which it will be floated and can be skimmed or floated off the solution." In another place he says specifically: "The sulphides in the ore are rapidly attacked by the acid and gas-bubbles formed on them, that quickly carry them to the surface.'' In this and in Potter's patent we have the earliest recognition of bubble-levitation. It is true, we have been told[8] of 'bubbles' being mentioned in connection with an experiment made in 1889 at Baker City, Oregon, where the Everson method was the subject of experiment, but the word was applied to the champagne that was the penalty of a bet, rather than the process itself. A story told in 1915 is apt to read into the happenings of 1889 much that was unknown at the earlier date. Oil and acid were the agents in those futile efforts at flotation made by Thomas F. Criley at Baker City, but it is worthy of mention that the fine grinding of wet ore in the presence of sulphuric acid must have been accompanied by the generation of hydrogen and probably of carbon di-oxide also, if the pulp contained either calcite or metallic carbonates.

Potter and Delprat were mistaken in the reactions that were supposed to follow the introduction of the acid, whether it was the sulphuric, the nitric, or the sodium bi-sulphate that they used variously. At that time it was believed that the sulphuric acid reacted with the sulphides to form hydrogen sulphide without attacking the gangue.[9] Then it was suggested that carbon di-oxide was generated by decomposition of a carbonate encrustation on the sulphides, due to weathering of the ore, arguing therefrom that it was necessary for the gas to be produced at the surface of the sulphide particles. Such explanations overlooked the simple fact that the Broken Hill ore contains a considerable proportion of carbonates, notably calcite, siderite, and rhodocrosite. From any of these a warm acid solution would release the carbon di-oxide gas that promptly attached itself to the surface of the metallic particles.

The processes of Potter and Delprat have been labeled under 'acid-flotation' and 'surface-tension' methods. In their original form, it is true, they did not include the use of oil, and the apparatus pictured in Delprat's patent (U. S. No. 768,035) suggests the surface-tension method of Bradford, but the use of a baffle ''to insure the total immersion of all particles of ore in the fluid or liquor'' indicates that surface-tension in its simplest form, as used later by H. E. Wood, for example, was not a principal agent. In Potter's apparatus—a pointed box—the feed has to pass under the surface and is wholly submerged, so that surface-tension again is not given free play, although, of course, it is a factor in the formation of the bubbles that buoy the sulphides to the

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[8] Ben. S. Revett, M. & S. P., October 16, 1915, page 590.

[9] 'The Physics of Ore Flotation,' J. Swinburne and G. Rudorf, M. & S. P., February 24, 1906.

surface after the pulverized ore has been mixed thoroughly with the acidulated water.

In August 1904, Auguste J. F. De Bavay patented a process resembling that of Bradford. He used neither acid nor oil, depending entirely upon the effect of surface-tension to form a film of sulphide particles while allowing the particles of gangue to sink. The company formed to exploit his patents claimed that the process worked without either oil or acid, but it was admitted that the flotation was improved thereby, and both oil and acid were used at a later date. In 1910 his rights were transferred to Amalgamated Zinc, Ltd., and in 1912 this company was annexed by Minerals Separation, Ltd. De Bavay's method was employed on a large scale at the North Broken Hill mine and in a plant for treating the dumps of the South and Block 10 mines. It is also used on current zinc-tailing produced at the North and South mines. Treatment is confined mainly to material free from slime. Indeed, none of the earlier processes, the Potter, Delprat, De Bavay, Cattermole, or Elmore did good work on slime—at Broken Hill.

The operation of some of these Australian methods of flotation without oil is an interesting feature. Most of them treated old dumps and it is well to note T. J. Hoover's suggestion[10] that "there may be organic substances in the ore which, upon the addition of acid, yield gummy organic compounds that selectively adhere to the ore." The research of recent years has disclosed the fact that a large variety of soluble frothing agents are effective and that a number of shrubs yield derivatives capable of replacing oil in the flotation-cell.

In 1903 a Potter plant was erected to treat middling from the lead-concentrator on Block 14.[11] Concurrently the Delprat process was adopted by the Broken Hill Proprietary, the plant being increased successively from its original capacity of 3500 to 6250 tons per week. Litigation ensued between these two Australian patentees. This ended in a compromise whereby Potter was eliminated; but it is worthy of note that Potter's method was the first flotation process to be used successfully on a working scale.

In 1905 the Zinc Corporation was formed to purchase and treat several large dumps. In 1906 the Potter process was used by this company on the British Broken Hill Proprietary dump, from which a concentrate was obtained containing 44% zinc, 8% lead, and 8 oz. sil-

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[10] 'Concentrating Ores by Flotation.' Page 101.

[11] The superintendent of this mill was Henry Lavers, whose name is notable in the history of the process.

[12] These figures refer to the final test made by W. E. Simpson on a mixture of tailings from all the dumps owned by the Zinc Corporation.

ver, representing a recovery of 81% zinc, 55% lead, 55%[12] silver, at a cost, including transport, of 50 cents per ton. H. C. Hoover testified in court that the Potter process, as used by the Zinc Corporation, "proved a commercial failure; for the later results, after the mill was remodeled, were not as good as those just quoted." In 1907 the Minerals Separation process was adopted in a plant erected under the direction of the patentees, but, as Mr. Hoover says, it "also proved a failure,[13] and after exhaustive trials the Elmore flotation process was introduced and found successful." He refers, of course, to the Elmore vacuum process, which was used by the Zinc Corporation chiefly on jig-middling from the Block 10 mill, until 1910, when, on the advice of his brother, T. J. Hoover, the improved Minerals Separation process was substituted, because it promised to give better results on slime and because most of the coarse material of the tailing-dumps had been milled by that time.

As early as 1902, while working with the granulation, or Cattermole, process in the Central mill, the scum of slime made from recrushed tailing was saved by floating it over a spitz-box. W. Shellshear and F. A. Beauchamp suggested the application of this idea to correct the failure of the granulating process caused by floccules of mineral breaking away from the granules on the tables. The suggestion was put aside until 1903, when a small spitz-box was tried. It was ascertained that the flotation effect was produced while using 9 lb. oil and 22 lb. acid per ton of ore. The proportion of oil was decreased gradually to 2 lb. per ton. This was the real beginning of froth-flotation.[14]

The first mill to use the Sulman & Picard modification of the agitation-froth process, as recorded in U. S. patent 835,120, was the one at the Central mine, built in 1905, as previously mentioned. In 1907 a new mill was finished and by 1908 the recovery had been improved to 85.5% of the zinc, 82.5% of the lead, and 83.8% of the silver, on a material assaying 21.4% zinc, 6% lead, and 8.6 oz. silver per ton, yielding a concentrate assaying 42.5% zinc, 11.4% lead, and 16.6 oz. silver per ton. Concentration was in the ratio of 7 : 3.

FROMENT

The scene shifts from Australia to Italy. At the time when Pot-

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[13] Partly because the plant was over-loaded to about double its capacity.

[14] It has been asserted that this method was discovered by the mill-men in the Central plant at Broken Hill and that the M. S. representative then cabled to the London office about it. The account given by Mr. Hebbard is not contradictory.

ter and Delprat introduced their methods at Broken Hill, another investigator was about to contribute his quota to the development of flotation. The Elmore bulk-oil method had been seen by Alcide Froment at the Traversella mine, in Italy, where he was engaged as an engineer in 1901, when he invented what he himself termed "a modification of what is known as the oil process of concentration." His modification—patented in June 1902—was to introduce a gas into the freely flowing oiled pulp used by Elmore. He argued, in his patent, that "if a gas of any kind is liberated in the mass the bubbles of the gas become coated with an envelope of sulphide and thus rise readily to the surface of the liquid where they form a kind of metallic magma." The phrase "gas of any kind" is important, for, although he generated his bubbles of gas by the reaction between sulphuric acid and the carbonates of the gangue or between the acid and the limestone that he added to the pulp, he hit upon one of the fundamental principles of the flotation process as we know it now. If he had specified air as the particular gas to be used he would have been acknowledged as the pioneer of present-day flotation. Air was present, of course, and played an important part in the operation, for in his description he specified the use of a centrifugal mixing device "in which two stirrers work in opposite directions, making 300 revolutions per minute." In his patent he explained that "the sulphide particles when moistened by a fatty substance" have a tendency "to unite as spherules and to float upon the surface of the water." He stated also that "the rapidity of the formation of the spherules and their ascension is in direct ratio to the quantity of gas produced in a given time." As to oil, his patent mentions "a thin layer of ordinary oil," but in the instructions given by him to the Minerals Separation people he specified as little as "1% of oil for ore containing up to 5% of metals" and up to 3½% "for ore containing 50% of metallic lead."

MINERALS SEPARATION

Before proceeding further it will be necessary to trace the origin of Minerals Separation, Ltd. At the end of 1901, John Ballot, W. W. Webster, and James Hay formed themselves into a syndicate to take an option on the Australian rights to the Elmore bulk-oil process. They engaged the firm of Sulman & Picard to act as advisory metallurgists. Acting on their advice, the syndicate did not exercise the option. In December 1902 John Ballot purchased the patents of Arthur R. Cattermole and assigned them to his syndicate, which became known as the Cattermole Ore Concentration Syndicate. On December 31, 1903, this syndicate was succeeded by a company, called Minerals Separation, Ltd., the directors being John Ballot, J. H. Curle, W. W. Webster, S. Gregory, H. L. Sulman, and H. F. K. Picard.

Now we return to Froment. His work appears to have been unknown in England until an abstract of his British patent was published in the Journal of the Society of Chemical Industry and was seen by Mr. Sulman in August 1903. Whereupon negotiations for the purchase of Froment's patent were opened by Mr. Ballot. He went to Milan to meet Froment, who, on November 7, 1903, sold his rights for £225. On December 29 Froment sent some drawings, with descriptions and instructions explaining his mode of operation. Early in 1904 a small plant designed by him was forwarded to London, but the apparatus was discarded, and destroyed subsequently, by the Minerals Separation people. Froment was in poor health at that time, and he died soon afterward. His patents had been taken out in Great Britain and Italy, but not in the United States, and when Mr. Ballot acquired them it was too late to obtain American rights, more than a year having elapsed since the grant of the British patent, on June 9, 1902. So the Froment patent was set aside as of no immediate value.

Cattermole's patents had been duplicated in the United States. In his American patent, No 777,273 of September 28, 1903, Cattermole prefaces his description by reference to the selectiveness of oil, when emulsified, for sulphide particles, such selective action being intensified by acidulation of the water. He then proceeds to say that if the mixture be agitated thoroughly there is a tendency for the metalliferous particles, now well coated with oil, to adhere together, forming 'granules' that sink and are readily separated from the lighter gangue by an up-current of water. In his description of the operation he says that "the granules, with a certain amount of heavy sands, sink to the bottom and are discharged (See Fig. 1) through a pipe G^1 into the vessel A^5, while the lighter sands are carried away by the upward current and discharged through outlet G^2 to a light-sands tank J." In the drawing, A^1, A^2, A^3, A^4, A^5, and A^6 are mixing-vessels; G and K are classifiers; E is a tank containing oil-emulsion. He refers to the proportion of oil several times in vague terms, explaining, however, that it should be insufficient to materially lessen the specific gravity of the metalliferous mineral particles." Finally, he specifies the proportion as "usually an amount of oil varying from 4% to 6% of the weight of metalliferous mineral matter present in the ore." This can be interpreted variously; if it refers to the sulphides to be concentrated, then an ore containing 20% blende would require from 0.8 to

No. 763,259. PATENTED JUNE 21, 1904.

A. E. CATTERMOLE.

CLASSIFICATION OF THE METALLIC CONSTITUENTS OF ORES.

APPLICATION FILED SEPT. 29, 1903.

NO MODEL.

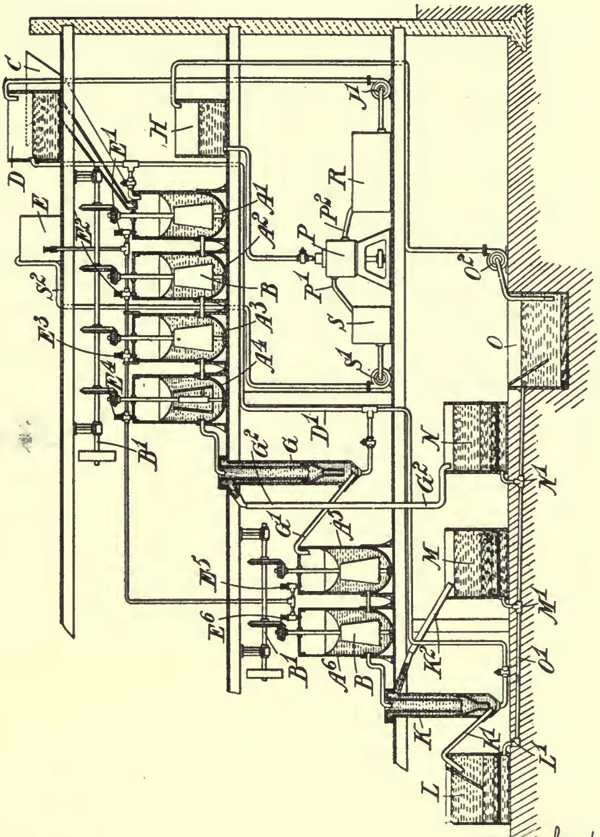

FIG. 1. THE CATTERMOLE PATENT

Witnesses:

Inventor:
Arthur E. Cattermole,
By Knight Bros
Attorneys

2% of oil, or from 16 to 24 lb. per ton of ore. On the other hand, a 2% chalcocite ore would need only 1.6 to 2.4 lb. of oil per ton of ore, which is as little as is now used. Such was the method from which patent 835,120 of Minerals Separation is claimed to be a logical development.

Much of the early experimental work of Minerals Separation was done in the laboratory of Sulman & Picard, at 44 London Wall, but in March 1904 Mr. Ballot established his own laboratory on Aldermanbury avenue, and it was there that decisive results were obtained. In 1903 a model 50-ton plant, to use the Cattermole process, was constructed and sent to the Central mine at Broken Hill, Australia.

The Minerals Separation people, notably the chief metallurgists, Messrs. Sulman & Picard, were experimenting with Cattermole's method and trying to develop a workable process at the time when their attention was called to Froment's patent. When they acquired this patent, they made experiments in accord with the specifications and the later instructions sent by Froment. To the detached spectator it would seem more logical to assume that Froment's floating 'spherules' rather than Cattermole's sinking 'granules' would lead to something like the froth-flotation process of today. But that is not the story told in the courts of law. The metallurgists identified with Minerals Separation testify that they had discarded Froment's patent and his instructions, having found them worthless, and were trying various modifications of the Cattermole method when suddenly they happened upon the particular combination essential to the froth-agitation process. Messrs. Ballot, Sulman, and Picard agree in stating that protracted experiments were being conducted in their London laboratory under the immediate charge of Arthur H. Higgins, who had been instructed to try all sorts of variations in temperature, acidulation, oiling, and mixing. Nothing noteworthy happened until the proportion of oil was reduced, whereupon the 'granules' began to rise instead of sinking and "the quantity of floating material increased rapidly when the oil was reduced below a certain point, this point being 0.62% of the oleic acid on the ore." So testifies Mr. Ballot. Thus happened "the startling discovery of the agitation-froth process," according to W. H. Ballantyne, Mr. Ballot's patent lawyer. The date was March 3, 1905. Then followed the British patent No. 7803 of April 12, 1905, and the American duplicate, No. 835,120—the date of application being May 29, 1905, and the date of issue November 6, 1905.

Before leaving this part of the story it is worth noting that the Cattermole 50-ton plant, already mentioned, had been erected in the Central mill early in 1904, and experiments were made there under the direction of G. A. Chapman. Tests showed that when using 0.75% of oil on the ore "the results were excellent, with all float concentrate, no granular material being formed." So says James Hebbard, the manager of the Central mine.[15] The adjective "excellent" is used in the

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[15] Proceedings Aust. Inst. of M. E., November 10, 1913. The same engineer

light of later events, for floating of the mineral was incompatible with the granulation upon which the Cattermole process depended. The importance of the floating does not seem to have been appreciated until a year later—early in 1905—when "a remarkable development in the operation was discovered (strangely enough, at the same time here [Central mine] and in the Patent Co.'s [Minerals Separation] laboratory in London), which had for its main principle the reversal of all previous operations, and consisted in the complete flotation of each particle of mineral independently in place of granulating the mineral particles and causing them to sink, thus not only revolutionizing the process, but greatly simplifying and cheapening it. The developments noted were mainly along the line of decreased consumption of oleic acid, for example, from 3% oleic on ore, resulting in very little float, down to 1%,[16] giving practically a complete float." According to this, the Higgins 'discovery' was made independently and contemporaneously at Broken Hill, but the underlying principle was detected a year earlier by Mr. Chapman, who had experimented with the Froment process in the London laboratory of Minerals Separation during 1903—again the suggestion that Froment had pointed the way to the agitation-froth process.

Next we revert to the first contact between the Elmore brothers and the Minerals Separation people. As already mentioned, in 1901 the Ore Concentration Syndicate gave Messrs. Ballot, Webster, and Hay an option on the Australian rights to the Elmore bulk-oil process. In accordance with this agreement, Mr. Ballot and his associates sent ore to be tested at the Elmore laboratory, to which they had free access while the experimentation was in progress. In the agreement it was stipulated that the holders of the option "and their assigns" should notify the Elmore syndicate of any "improvement, addition, or discovery" that they might make and the Elmore syndicate was "to be entitled to every such improvement, addition, or discovery whether the same shall be patented or not."

Mr. Ballot and his associates made tests and held the option for 11 months, that is, until late in 1902. Messrs. Sulman and Picard were

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relates how, before 1901, "it had been long observed that a froth was formed containing high metallic values, in silver and lead particularly, whenever conditions were favorable, as for instance, where the rotation of trommels, or the splash of the elevators or raff-wheels, or the motion of the jig-plungers, produced a violent agitation of the mill-water containing slime." The use of oil tended to make such froth more persistent. I have mentioned the suggestion made by Beauchamp and Shellshear in 1902 while at work in this same mill.

[16] Not below 1%, apparently.

engaged by Mr. Ballot to supervise the tests. They were "treated with the greatest frankness," says Stanley Elmore. The option was not exercised. Then followed Mr. Ballot's purchase of the Cattermole patents and in the succeeding year the acquisition of the Froment and Sulman & Picard patents, followed immediately by the organization of Minerals Separation, Ltd., as a process-exploiting company. In 1905 the Elmores brought suit to enforce the clause above quoted, in the agreement of 1901, claiming that they were entitled to the benefit of the improvements following upon the insight into the process given to the Minerals Separation people during the tests made under the option. The case went against the Elmores, the Court of first resort deciding that the particular clause had been introduced into the contract without sufficient authority after it had been signed. In the second trial, Messrs. Ballot, Hay, and Webster presented evidence to show that the Cattermole and other patents had never been in their possession but had passed from the inventors through a trustee to the syndicate that became Minerals Separation, Ltd. Whereupon the proceedings were stayed. The affair left a feeling of bitter animosity between the two factions; the Elmores showed so keen a sense of betrayal as to resign from the Institution of Mining and Metallurgy when Mr. Sulman was nominated for the presidency of that professional society in 1911. This incident indicates the bitterness, rather than the merits of the quarrel, but it must be recorded in this history of the process because it helps to explain the acerbity of the litigation that ensued and that still animates the protagonists in this metallurgical vendetta.

For three years, from 1906 to 1909, the Elmores fought the Minerals Separation's attempt to hold a patent in Germany. The patent was granted, but it was annulled subsequently by a higher court.

In 1907 Minerals Separation brought suit against the Ore Concentration Company, alleging infringement of Froment's patent, but in 1909 the Minerals Separation company discontinued the action, paying costs.

In 1909 the Elmores and the British Ore Concentration Syndicate brought suit against Minerals Separation for infringement of Frank Elmore's bulk-oil patent of 1898 and Stanley Elmore's patent of 1901, specifying the use of acid in the bulk-oil process. They lost in the first court, they won on appeal, but lost on final resort to the House of Lords. Both the use of oil and of acid were held to have been anticipated, and the Minerals Separation froth-agitation process was held to be entirely different from the bulk-oil method. Subsequently a new suit was started in Australia, the claim of infringement against the Sulphide Corporation, a licensee of Minerals Separation, being based on acidulation. The Australian court decided against the Elmores, who appealed, unsuccessfully, to the Privy Council, in 1914.

AIR-AGITATION METHODS

It is important to note that these suits dealt only with the bulk-oil patents of 1898 and 1901, and had no reference to the vacuum process of 1904. To the agency of gas in flotation we now return. So far the fact that bubbles of air would do the work of bubbles of chemically generated gases had been overlooked. In September 1903, Sulman & Picard described the use of air ''or other gas'' in British patent No. 20,419, which was duplicated in the United States as No. 793,808. In this they pictured a perforated coil of pipe through which either air is introduced into pulp with which oil has been already mixed or air and oil are admitted simultaneously in the form of a spray. The latter scheme has not proved practicable, whereas the procedure in which the oil is previously mixed with the pulp and then subjected to aeration by the introduction of air through the perforations in the pipe is a practical method. They said, ''The oiled metalliferous particles resulting from either of the processes above described have the power of attracting to themselves with a greater comparative strength than the gangue particles, the films or bubbles of gas which exist in the mass and are thus raised to the surface of the liquor by gaseous flotation.'' They did not claim the use of air as a discovery and they seem not to have known how near they were to the later phase of flotation, in which the making of a multiplicity of air-bubbles, or 'froth', is the principal feature.

In June 1904 Frank Elmore applied for a patent to use electrolysis in order to generate gas in a freely flowing pulp, and in August of the same year he obtained British patent No. 17,816, in which he described the performance of flotation in a vacuum, so as to liberate ''the air or gases in the milling water.'' Thus six years after the date of his first bulk-oil patent Elmore had learned to put the air to purposeful use. He subjected the oiled and acidulated pulp to a vacuum, thereby releasing the 2.2% of air normally absorbed in water. By lowering the pressure and raising the temperature this air is released, thereupon attaching itself, in the form of bubbles, to the oiled sulphide particles, which rise to the surface. For example, the air in a ton of pulp consisting of 6 parts of water to 1 of ore suffices to lift 360 pounds of zinc-lead sulphides in a Broken Hill ore. In actual practice, however, the weight of sulphides floated is considerably greater than the theoretical proportion as based on the efficacy of the air released from absorption in water. Part of the work is done by the gaseous carbon di-oxide liberated by the reaction between the acid and the carbonates, such as calcite, either in the gangue or added in the form of limestone. But a larger part of the bubbling is caused by the air entangled in the ore particles and entrained in the pulp during energetic mixing. In this process the quantity of oil added to the pulp was reduced from the ton used at Glasdir to 10 pounds per ton of ore, and finally to as little as 3 pounds per ton of ore. The machine devised by Mr. Elmore for the performance of his vacuum process was remarkably ingenious and to it the success of the process was largely due. It was applied at several Scandinavian copper mines, notably the Sulitelma, and also in the Zinc Corporation's mill at Broken Hill, as already mentioned.

This vacuum method of Elmore was a notable step toward the recognition of the part played by air in flotation, and in so far as he used air in a pulp that had undergone agitation with a relatively small proportion of oil he furnished a metallurgic sign-post that pointed to the final success of the process.

FLOTATION IN AMERICA

So far flotation had received scant attention in the United States. The old Elmore bulk-oil method had been tried, unsuccessfully, at the Boston Consolidated and Mammoth mines in Utah in 1900 and 1901. In 1906 a surface-tension process of great ingenuity, invented by A. P. S. Macquisten, was used in the Adelaide mill, at Golconda, Nevada, and in 1911 a similar plant was erected at the Morning mine, in Idaho, but these interesting efforts were mere ripples on the calm surface of American apathy, which at the time gave no promise of the full tide of metallurgical advance that since then has swept over base-metal mining in the West.

Another American patent must be mentioned, as linking the Elmore bulk-oil process with the later frothing methods. The patent of Edmund B. Kirby is No. 809,959 of December 14, 1903. He used from 25 to 75% of oil in a flowing pulp; but he depended upon thin oil—kerosene—and violent agitation, so that he departed from the Elmore type of flotation. The more interesting feature of his claim, however, is "the injection of a gas, preferably air, into the mass," which statement, if taken with his reference to "allowing the hydrocarbon-coated particles to float to the surface of the mass," seems indeed to be a forecast of froth-flotation. The patentee—Kirby—himself says: "It is thought that the use of a gas to assist in the flotation of the coated particles * * * is radically new in this art.'' He adds: ''The employment of the gas in the manner stated brings in a more powerful floating agency than anything before used.'' How prophetic! His gas was ''preferably air.'' Moreover, he knew of the use to be made of the air ''dissolved'' in water, as adopted a year later by Francis E. Elmore, for he says: ''The air-bubbles not only tend to attach themselves directly to the coated particles, and thus float them to the surface, but the air becomes dissolved in the water to its maximum capacity. This dissolved air tends to again separate itself from the water and attach itself in minute globules to the coated particles.'' Mr. Kirby tried his process on a number of British Columbian ores, but no working plant was erected; nevertheless, it is apparent that he has not received proper credit hitherto for his ingenuity, and it is a pleasure to make the correction here.

The credit for bringing the froth process to the notice of the American public belongs to J. M. Hyde, who had been in the employ of a subsidiary syndicate organized by Minerals Separation for the exploitation of flotation in Mexico. Mr. Hyde was introduced to Mr. Ballot by Theodore J. Hoover, who, in October 1906, had been engaged by Mr. Ballot as technical adviser and general manager for the Minerals Separation company. In 1910 Mr. Hyde went to Mexico and early in 1911 he resigned, at the conclusion of his one-year contract with the syndicate. Shortly afterward he went to Montana, at the instance of H. C. Hoover, to inspect the property of the Butte & Superior Copper Co., this company having offered Mr. Hoover a participation in a bond issue. The business proving unattractive, Mr. Hoover withdrew from it, but Mr. Hyde commenced to investigate the metallurgical problem presented by the zinc-lead ore of the Butte & Superior company's Black Rock mine. After making the necessary tests with the slide machine, he erected a trial plant in disregard of the Minerals Separation patents. This was in August 1911, and not until the Butte & Superior company had negotiated with E. H. Nutter, the American manager for Minerals Separation, who demanded a prohibitive royalty. In October 1911 suit for infringement of patent was brought by Minerals Separation against Mr. Hyde.

Meanwhile, in December 1910, T. J. Hoover had severed his connection with Minerals Separation, after having been instrumental in the successful development of the company's business in Australia and in improving the various apparatus employed in the froth-flotation process, especially in that country. His resignation was accompanied by some friction with Mr. Ballot, into the details of which it is not necessary to go, but the fact is a part of the history of the process. In December 1912 Mr. Hoover published his book, 'Concentrating Ores by Flotation,' after a grudging consent had been obtained from his former employers, in return for which he excised parts of the original manuscript trenching too deeply into patent matters. This is recorded here in order to remove the impression, still persisting, that Mr. Hoover wrote and published his book while connected with Minerals Separation.[17]

We now return to Mr. Hyde and the commencement of a big litigation. The suit started against him in 1911 was tried first in the District Court of Montana and judgment was given against him in August 1913. On appeal, before the U. S. Circuit Court of San Francisco, this judgment was reversed in May 1914. By writ of certiorari the case was brought before the Supreme Court of the United States, which on December 11, 1916, reversed the decision of the Appellate Court and decreed that patent 835,120 was valid, but confined the scope of the patent to violent mechanical agitation, the use of less than 1% of oil, and a persistent kind of froth.

It is worthy of note that the first successful froth-flotation plant erected in the United States, by Mr. Hyde in 1911, did not start until six years after the grant of patent 835,120 and not until 20% of the world's production of zinc was being made by aid of the group of other flotation processes in use at Broken Hill. This may be compared with the statement of the U. S. Supreme Court, in its final review of the Hyde case, that "the process in suit promptly came into extensive use for the concentration of ores in most, if not all, of the principal mining countries of the world, notably in the United States."

The first successful application of the froth-flotation process in the United States was made at Butte, on a zinc-lead ore, as we have seen. The later development of the process has been based on the treatment of copper ores, especially the chalcocite disseminated in the immense orebodies disclosed in Arizona, Utah, and Nevada. This part of the story begins with the tests made by Minerals Separation in their London laboratory and in plants erected at sundry copper mines in other countries, such as the Caucasus Copper and the Great Fitzroy, with results generally poor. In his book, dated July 4, 1912, Mr. Hoover re-

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[17] In mentioning these and other personal incidents, like the Elmore-Sulman & Picard affair, I am prompted solely by the desire to state facts essential to a correct understanding of the conditions governing the patent litigation, because they played a decisive part in the technical development of the process.

[18] 'Concentrating Ores by Flotation,' first edition, page 157.

fers to the limitations of the process and says:[18] ''The fourth limitation is one for which at present no adequate reason can be given. An ore in which the valuable minerals are wholly or partly bornite or chalcocite, as those of Bingham canyon, will probably give trouble to flotation processes, although not always, for among the many ores tested the one which gave the most uniformly satisfactory results was a copper ore assaying 2.8% copper, all in the form of microscopic specks of bornite.'' He proceeds to remark: ''It may be that only those ores where bornite and chalcocite are of secondary occurrence give trouble.'' In Mr. Hyde's report of January 8, 1911, given as an exhibit in the lawsuit, it is stated that the tests carried out in the Minerals Separation laboratory proved that ''the copper ores of a good part of the Southwest and also of at least a portion of the Utah region contain chalcocite, *which is not floatable by any of the methods so far tested.''* This summarizes the opinion held by the Minerals Separation staff at that time. However, they discovered their mistake two years later. Tests on chalcocite ore from the Inspiration mine, in Arizona, were made in Mr. Nutter's laboratory at San Francisco during 1912, but the results were not good enough. At the end of that year, however, an 87% recovery on a 2% copper ore was obtained in a 15% concentrate. The telegram sent to the New York office of the company was mutilated in transit so as to state that a 50% concentrate had been obtained, and premature rejoicing followed.[19] Nevertheless the Minerals Separation staff promised good results and erected a 50-ton experimental plant at the Inspiration mine. The company took out a license early in 1913. On March 23 an experiment on low-grade chalcocite ore was made by T. A. Janney at the Arthur mill of the Utah Copper Company. This proved satisfactory. During that same month, March 1913, the Minerals Separation staff, at the Inspiration mine, had demonstrated a 90 to 92% recovery and a 35 to 40% concentrate on a 2% ore, with a 0.15 to 0.2% tailing. The presence of a colloidal kaolinized mineral diverted the oil from its proper function and interfered with the recovery of copper until G. A. Chapman suggested the addition of the oil to the ore in the tube-mill, where the metallic particles became oiled at the instant of exposing fresh fractures. These experiments warranted the expectation that on a 1.58% ore there would be obtained a 27½% concentrate with a recovery of 92% and a tailing loss of only 0.13%. A 600-ton Minerals Separation test-plant was erected in January 1914; in July of that year a pneumatic equipment consisting of five Callow cells and one Pachuca tank was added and between August and Oc-

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[19] M. & S. P., March 18, 1916.

tober a Towne machine was in use. In 1915 the Inspiration Consolidated Copper Co. built a mill of 18 sections, each of 800 tons capacity, or a total of 14,400 tons daily. Since then this mill has treated as much as 21,000 tons in a day.

In June 1914 Mr. Chapman started flotation experiments at Anaconda in a 200-ton plant, obtaining 90% recovery. On February 1, 1915, the Anaconda and Inspiration companies signed a contract with Minerals Separation by the terms of which they agreed to pay royalty on a sliding scale ranging from 12 cents per ton on 4000 tons daily to 4 cents per ton on the treatment of more than 30,000 tons daily. By a curious proviso in the contract no royalty was payable on the 5000 tons between 10,000 and 15,000 tons daily. The tonnage coming under the terms of this agreement included the ore treated by sundry subsidiary companies, the consequence being that the maximum tonnage and minimum royalty specified in the agreement were reached by the close of 1916 at which time the Anaconda flotation plant was treating 14,400 tons daily. As an example of the saving made by aid of flotation, it is worth mentioning that whereas the tailing from the water-concentration mill used to assay 0.62% copper, the residue now after treatment in the flotation annex assays only 0.15% on a 3% ore; that is, out of 60 pounds of copper per ton only 3 pounds goes to waste, as compared with 12.4 pounds formerly. The recovery is 95%. Moreover, the metallurgical improvements made at the Washoe plant during 1915 were so effective as to enable an increase of 55,000,000 pounds per annum to be made in the production of the Anaconda company "without increasing the tonnage or grade of ore that has been mined in the past." So testified Mr. John D. Ryan, the president of the company, in his annual report.[20] Further, he stated that "approximately 40,000,000 pounds of this increased production will be made without adding to the cost per ton of ore treated." This is the equivalent of the output from a big mine.

Meanwhile preliminary tests had been started at the Miami mine, which is a near neighbor of the Inspiration. From December 1913 to August 1914 the testing was directed by R. C. Canby, who used various types of apparatus, notably the Minerals Separation and Towne machines. On August 7, 1914, a pneumatic flotation plant was erected. The remodeled mill, having a capacity of 4200 tons, went to work on March 15, 1915. On July 14, 1914, Minerals Separation brought two separate suits based on patents 835,120 and 962,678, but these suits were dismissed on request of Minerals Separation, and on October 10,

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[20] M. & S. P., February 26, 1916.

1914, a single suit was started for infringement of three patents, the two already mentioned and No. 1,099,699.

Instead of using the blade-impeller type of agitator, the Miami Copper Company adopted the Callow machine, essentially a sloping launder with a canvas bottom through the pores of which air under small pressure is admitted into the pulp previously oiled. Such oiling of the pulp was aided at first by the use of a Pachuca tank, but in the spring of 1915 this type of agitator was found superfluous and since then the oil has been simply added to the pulp while flowing through a launder to the flotation-cell. In the trial of the suit before the District Court of Delaware, the defendant claimed that he was not using the agitation-froth process of patent 835,120 but a bubble method similar to that of patent 793,808, which was granted to Sulman & Picard on July 4, 1905, on an application dated October 5, 1903. In this patent a perforated coil of pipe is described, the idea being to admit air and oil in the form of spray, so that the globules of oil attach themselves to the metallic particles in the ore and float them to the surface. The pneumatic machine used at Miami was devised by J. M. Callow and patented as No. 1,104,755 of July 21, 1914. The idea had been used already in T. J. Hoover's British patent No. 10,929 of 1910. Mr. Hoover's patent was not duplicated in the United States and Mr. Callow was unaware of it. Another investigator, R. S. Towne, had patented the idea previously, in the form of a carborundum wheel, the central hole of which he plugged, so that the wheel served as a porous medium. The admission of air to make froth, without the aid of mechanical agitation, was developed in several machines at a later date—in 1915 and 1916—as has been duly recorded in the technical press.[21] The kind of froth produced by blowing bubbles of air through the pulp is claimed to be different from that made by beating air into the pulp with a mechanical stirrer; in the one case the froth is said to be thin, tender, and evanescent while in the other the froth is described as thick, coherent, and persistent.

However, the first trial-court decided in favor of Minerals Separation's contention that the Miami Copper Company was infringing its patent, 835,120, and also 962,678. The judgment was delivered on September 30, 1916, an appeal being filed at once by the defendant.

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[21] 'The Kraut-Kollberg Flotation Machine.' By Max Kraut, M. & S. P., July 1, 1916. 'An Improved Pneumatic Flotation Machine.' By James M. Hyde, M. & S. P., November 25, 1916. 'The Porous Bottom.' By Rudolf Gahl, M. & S. P., September 30, 1916. 'Flotation in the Clifton-Morenci District.' By David Cole, M. & S. P., October 14, 1916. 'Flotation at the Calaveras Copper Mine.' By Hallet R. Robbins, M. & S. P., November 25, 1916.

Patent No. 962,678 is important and interesting because it involves an idea to which no reference has as yet been made in this brief history of the process: I refer to the varying solubility of oils and the use of soluble agents for that modification of the surface-tension of water to which the phenomena of froth-flotation or bubble-levitation are so largely due. The idea is not recent. Haynes, in his British patent of 1860, used coal-tar from gas-works in a rudimentary process of oil-flotation. Coal-tar contains as much as 20% soluble products. In U. S. patent 788,247, dated April 25, 1905, Cattermole, Sulman, and Picard used cresol and phenol, both soluble in water, as modifying agents.

On June 29, 1910, Sulman & Picard obtained U. S. patent 962,678 for a "soluble frothing agent," and this is the patent that the Miami company is charged with having infringed by reason of using cresol with pine-oil in its flotation operations. Application for this patent was filed on April 30, 1909. The illustration shows a beater form of agitator and "beating air into the mixture" is specified. Mention is made of "an organic compound in solution" and "amyl acetate" is instanced. No particular proportion of this "mineral frothing agent" is specified and an increase of the soluble substance is held not to interfere with the operation. The decision of the higher court on the validity of this patent will have an important bearing on the future of the flotation process, for it is manifest that the term 'soluble frothing agent' is extremely comprehensive and will frustate legitimate attempts to avoid the embargo on the use of oil. Meanwhile the Supreme Court's recent decision validating the patent on the use of a 'critical' proportion of oil, namely less than 1%, has been stultified by successful concentration on a scale of 1000 tons or more per day when using 22 to 23 pounds of oil per ton of ore. At the same time comes the news of the Freeman process, in which soda-cake is being used successfully at Broken Hill as a modifying agent instead of oil. The litigation is far from ended and before it is closed it will be likely that oil will have been discarded in favor of other contaminants capable of lowering the surficial tension of water so as to permit the formation of a metallugic froth.

In 1914 the flotation of oxidized lead ores became the subject of successful experiment, the method being to sulphidize the exterior of the oxides by means of sodium sulphide. This was accomplished so successfully that an effort was made in 1915 to apply the method to oxidized copper ores, which, however, are not readily amenable because the sulphidization penetrates the ore-particles so deeply as to interfere with the differential treatment and to consume an excessive amount of the sulphidizing agent. The treatment of zinc-carbonate ores by sulphide-filming has been even less successful, owing to the fact that such ores contain enough zinc silicate to interfere with flotation.

The story of flotation flows by devious ways and is broken by many cross-currents. Patents serve to record the high-water marks of ingenuity but they fail to disclose the movement between given points, and, what is much more important, they ignore the slow increase of manipulative skill. It is to manipulation, learned empirically in the laboratory and mill, that the flotation process owes its metallurgic success. Given the directions to be found in Kirby's or Froment's patents, the flotation expert of today can produce an effective result, without, apparently, borrowing from any later inventor. That is why the experiments made in Court have proved almost anything it was desired to prove. The manipulation to which success in the mill is largely due contravenes no patent and trespasses no man's preserves. A proof of this is to be found not only in the slow application of the flotation idea in metallurgy but in the delay that marked the fruitful use of the latest phase of the process. The froth-flotation that is claimed to be a new discovery is said to have been discovered in 1905; yet it was not introduced into an American mill until 1911, and even after that event the most skilful engineers, whether in the employ of the patent-mongering company or not, failed to apply it successfully for several years, not until 1914.

Haynes and Bradford left no trail. Everson failed to arrive, but it is likely that her patent put the idea of flotation into the heads of others, for example, Robson. He did not succeed, but he gave the clue to Elmore, who then prompted Froment and Kirby. Sulman was experimenting with the Cattermole method when he heard of Froment's scheme, and from that, I believe, he got the notion of using air to make a froth. Hoover, Callow, and other technicians, by the patient empiricism of the mill and laboratory, developed a workable process. Such, in brief, I believe to be the true pedigree of the flotation process.

PRINCIPLES OF FLOTATION

By T. A. Rickard

(From the *Mining and Scientific Press* of July 7 and 14, 1917)

Introduction. The understanding of the principles governing flotation has been delayed mainly because the explanation of the phenomena—or appearances—characteristic of the process is to be found in physics rather than in chemistry. Modern metallurgy has been in the hands of men primarily chemists, rather than physicists. Cyanidation and chlorination, for example, may be explained by chemical formulas, even if they cannot be expressed in their entirety by the language of elemental symbols; but flotation is not to be interpreted in that way; it is controlled by physical laws that are obscure and that hardly came within the cognizance of the metallurgist until the need for study was felt by him within a period so recent that the full results of scientific research are not yet available.

To understand the rationale of the flotation process we must return to the amusements of our boyhood; in the soap-bubble and in the greased needle we shall find an inkling of the forces at play in the flotation machine. Everybody knows the trick of the greased needle. If a needle be greased and then placed carefully on the surface of tap-water in a bowl it will float, despite the fact that steel is eight times heavier than water. Even the natural oil on the fingers, or that obtainable by passing the fingers through the hair, will suffice for the purpose of assisting the needle to float.

The first idea is that the buoyant effect of the oil adhering to the needle prevents it from being drowned. However, the quantity of oil thus attached to the needle is not enough to buoy it; the specific gravity of the oil is, say, 0.9 as compared with water, which is the unit of specific gravity; therefore the flotative margin is only one-tenth, and for the oil to float a piece of steel, having a specific gravity of 8, its volume would have to be more than 70 times that of the steel. So the buoyancy of the oil does not do it. Moreover, an ungreased needle also will float. This experiment must be conducted carefully. To be certain that the needle was free from grease[1] I held it in metallic pincers, dipped it in a solution of washing-soda (sodium carbonate,

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[1] New needles are slightly greasy, as I ascertained by means of the camphor test, described later. The grease protects the needles from rusting.

which is a solvent for grease), and then dried it, taking care to use a clean cloth and not to touch it with my fingers. Then I placed a piece of tissue-paper on the water in a cup and laid the needle, held in the pincers, upon the paper, which was depressed gently into the water by the point of a wooden match, until the paper became soggy and finally sank, leaving the needle floating. It lay in a depression of the water-surface, which appeared to be bent under it.

The needle that will float after being greased is larger than the one that floats without being greased,[2] so the oil seems to aid flotation; but when the needle is too large it cannot be made to float, greased or not. It is too heavy; that is, the force of gravity multiplied by mass is sufficient to overcome the peculiar resistance offered by the surface of the water. What causes that resistance?

Surface-Tension. The force responsible for the floating of the needle is called 'surface-tension.' It is a manifestation of cohesion, which is the attraction that binds molecules of like kind to each other. Each molecule within the interior of the liquid is imagined as surrounded by molecules like itself to which it is attracted and which it attracts equally in every direction, whereas the molecules at the free surface of the liquid are attracted only by those internal to themselves, the result being to constrict the free surface of the liquid. In consequence, the surface acts as if it were a stretched membrane or an elastic film. These molecular conditions may be represented graphically. See Fig. 2. The attractive forces acting on a molecule (A) in the body of the liquid may be represented by four resultant axial components, which are equal, so that the molecule is perfectly free to move, except for viscous resistance. At the surface itself the upward

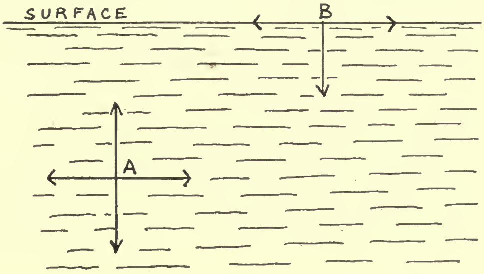

Fig. 2

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[2] I tried five large greased needles, all of which floated; then I tried the same needles after they had been washed in the soda solution and wiped dry on a clean cloth. One time all five sank; the other time four sank.

component disappears and the pull downward on the molecule (B) is uncompensated, any extension of the surface being opposed by a force the horizonal component of which is 'surface-tension'.

This can be illustrated in another way. Each particle of water is attracted by all the particles that lie within its range, which is definitely small, about 0.00000015 cm.; therefore the scope of molecular attraction may be considered as a sphere of influence. Thus A in Fig. 3 is attracted, and attracts, within a definite sphere, while B, which is close to the surface, is more attracted inward than outward, since a part of its sphere of attraction lies outside the water.

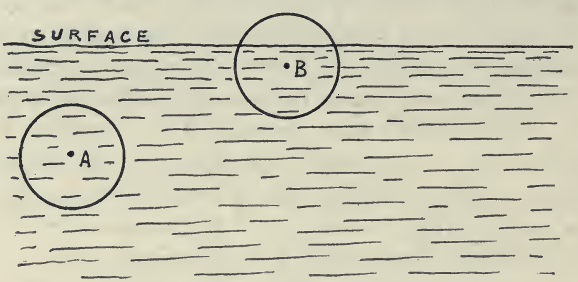

FIG. 3

Such a hypothesis is largely an abstraction; a concrete idea of the nature of surface-tension can be obtained by noting some of its various manifestations.

1. The drawing, or 'soaking up', of water by a sponge.
2. The penetration of wood by varnish.
3. The rising of oil in a lamp-wick.
4. The clinging of ink to a pen.
5. The running of the ink from the pen to the paper.
6. The absorption of the excess of ink by blotting-paper.
7. The cohesion between two plates that have been wetted.
8. Dip a camel's hair brush in water, remove it from the water, and observe how the hairs cling together. Immerse the brush in the water and note how the hairs separate.
9. Watch the water-spiders running over a pool, like boys skating on thin ice. H. H. Dixon actually measured the pressure exerted by the spider's feet on the water. He photographed the shadow of the dimple, then mounted one of the spider's feet on a delicate balance, and made it press on the water until it made a dimple of the same depth as that previously recorded.
10. Pour colored water in a thin layer over the bottom of a white

dish; then touch a part of its surface with a glass rod that has been dipped in alcohol. The colored water shrinks from the part touched, leaving an irregular patch of white bottom dry. This is due to the tension of the pure water being greater than that of the alcoholized water, so that the liquid is pulled away from the place where the tension is weak to the place where it is strong.[3] The lively movements of the particles of dye in the water indicate the conflict between the forces of diffusion and surface-tension.

11. The formation of a drop at the end of a tube or from the small mouth of a bottle is another example of surface-tension. Note how the drop grows slowly until it has attained a definite size, and then breaks away suddenly. The size of the drop is always the same for the same liquid coming through the same orifice. It hangs as if suspended in an elastic bag that ruptures when the weight becomes excessive. The contractile character of surface-tension is manifested in the formation of the drop, the force tending to draw the fragment of liquid into the most compact form, that presenting the least surface in relation to volume, namely, a sphere.

Similarly, if we admit air through a glass tube of given size into various liquids, we shall obtain the biggest bubble in the liquid with the highest surface-tension. If various liquids in succession are allowed to run out of an opening of given size, the largest drop will be that of the liquid having the highest surface-tension.

12. When an iron ring is dipped into a solution of soap and then taken out, it will be seen that a film of solution stretches across the ring, covering the whole interior circular space. If a small loop of cotton, previously moistened in the soapy solution, is placed on the film stretched across the circle of the ring, this loop can be made to assume, and to retain, any form, such as is shown at A in Fig. 4. If, however, this film within the loop is broken, the loop immediately assumes the form of a perfect circle, as shown at B; and if it is now deformed in any way, it springs back at once to a circle as soon as it is released. Evidently the surface of the solution assumes the shape covering the smallest area. The surface-tension of the liquid acts equally on both sides of the cotton so long as it is wholly immersed, but when the film of liquid inside the loop is broken, the tension acts on one side only—on the open side, where it is in contact with air—and hence draws the loop into a circle, which involves the minimum of extension.

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[3] This simple experiment is a fascinating exhibition of surface-tension and it should be made by every student of flotation.

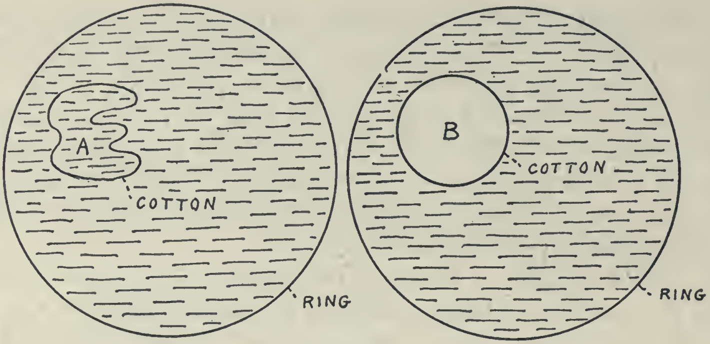

Fig. 4

13. The contractile force of surface-tension is shown in a simple way by blowing a soap-bubble on the large end of a pipe and then holding the other end of the pipe to a candle, whereupon the air escaping from the shrinking bag of the bubble will extinguish the flame, as in Fig. 5.[4]

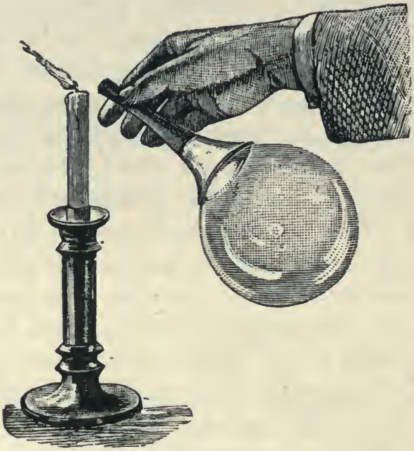

Fig. 5

14. When water is sprinkled on a dusty floor, the dust prevents the wetting of the floor by obstructing the coalescence of the drops, that is, the spreading of the water over the floor. The water draws itself into rolling spherules that become armored by particles of dust. They are nearly round, the larger ones showing a flattening, because

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[4] C. V. Boys in 'Soap Bubbles'.

the gravitational stress overcomes the contractibility or sphericity of the film. This flattening is shown by a drop of mercury on glass or by the beads of gold on an assayer's cupel.

15. The globular form assumed by water when spilled on a hot stove is another manifestation of these forces. The water is protected from the hot iron by a film of steam, which, as it is formed, decreases the size of the globule until it disappears. If the iron is not sufficiently hot, it becomes cooler and therefore wetted, by spreading of the water, which is instantly converted into steam.

16. Some of the physics of flotation can be illustrated at the dinner-table.

A. Fill a glass a little over-full of water and note the convex surface, indicating the play of a force that prevents the liquid from spilling. It is a contractile force.

B. Fill a wine-glass half-full with port and observe how the wine climbs up the side of the glass, forming a meniscus around the circumference of the surface. This liquid consists of alcohol and water, both of which evaporate, the alcohol faster than the water, so that the surficial layer becomes watery. In the middle of the glass the surficial layer recovers its strength by diffusion from below, but the film adhering to the glass, being more exposed to the air, loses its alcohol by evaporation more quickly and therefore acquires a surface-tension higher than that of the undiluted wine. It creeps up the side of the glass dragging the strong wine after it, and this continues until the quantity of fluid pulled upward collects into drops—called the 'tears of wine'—that run back into the glass.

C. Fill a a glass two-thirds full from a 'siphon' containing water that is effervescent because it contains gas in solution. Take three or four small grapes, preferably of the Californian seedless variety. The grapes will sink to the bottom of the glass, but soon they become restless and rise to the surface, one after the other. They do not remain there long; first one and then the other sinks. They will continue the performance for half an hour, bobbing up and down; their activities slowly diminish, and eventually they are left inert at the bottom of the glass. What happens is simple enough. The siphon has come from the refrigerator; the warmth of the room and the lowering of pressure release the carbonic-acid gas, which, in the form of minute bubbles, attaches itself to the grapes, buoying them to the surface as mineral particles are raised to the surface of a pulp in the Potter process. There the bubbles burst, causing the grapes to fall back. If a couple of grapes collide, the bubbles become detached, dropping their freight, and themselves rising to the surface. At first the grapes rise rapidly and rebound from the surface of the water as if it were an elastic membrane. This is a remarkable effect and should be noted carefully. After the evolution of gas has diminished the bubbles become too few to buoy the grapes, and the performance ends.

Surface-tension is identified with 'capillarity', because it is so marked in a tube the bore of which is only large enough to admit a *capillus*, or hair. When the lower end of a wide tube is held in water, the water inside rises to about the same level as that outside the tube, in accordance with the law of hydrostatic pressure; but when the lower end of a glass tube of small bore, say, 1 mm., open at both ends, is inserted into water, the water rises within the tube and stands at a level higher than the water outside. If, again, the tube be held vertically with its lower end immersed in mercury, the liquid metal inside the tube sinks to a level below that of the mercury outside. See Fig. 6. This is explained by saying that the molecular attraction of water to glass is greater than that of water to water; whereas the attraction of mercury to glass is less than that of mercury to mercury. The forces of cohesion in a substance and of adhesion between various substances have been measured. Quincke and others have ascertained by experiment that the effect is sensible within a range of one thousandth and one twenty-thousandth of a millimetre. Such is the scope of molecular attraction. The liquid rises in a capillary tube until the weight of the vertical column between the free surface and the level of the liquid in the tube balances the resultant of the surface-tension.

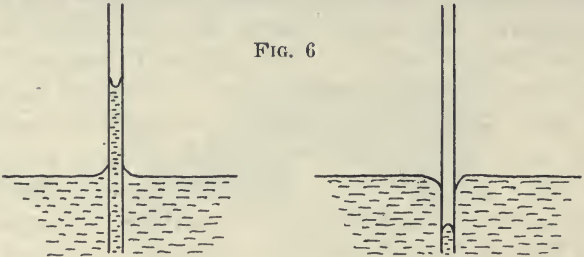

FIG. 6

GLASS TUBE IN WATER

GLASS TUBE IN MERCURY

The surface-tension of liquids can be modified. It is decreased by a rise of temperature. For example, place two matches an inch apart on the surface of pure water in a bowl and then touch the water between them with a hot wire. They draw apart promptly, because the surface-tension of the water between them has been lowered relatively to that of the rest of the liquid in the bowl, so that the pull of the water-surface under normal tension is stronger than that of the surface of the warm water between the matches.

The addition of an impurity or contaminant will lower the surface-tension of water. We have seen how this effect is caused both by alcohol and soap. Distilled water has a maximum surface-tension, which is lowered by almost any substance that is soluble or miscible in it. The soluble substance, or solute, modifies the tension directly, whereas the minutely divisible substance, forming an emulsion, creates a great number of interfaces, or surfaces of contact, each having a lower tension. The particular contaminant, or modifying agent, associated with the early history of flotation was oil, which is partly soluble and readily dispersible. The oil generally used at first was a heavy oil, like oleic acid.[5] By the addition of sufficient oil the surface-tension of water is lowered from 73 to 14 dynes per linear centimetre. The following experiment illustrates this fact. If a wooden match be laid on the surface of tap-water in a pan, so that it remains at rest, and if then a drop of olive-oil be placed on the surface of the water near the match, the match will draw away smartly, because the oil has reduced the tension of part of the water-surface and caused the uncontaminated water to pull away. This modification of the surface-tension of water by a contaminant is one of the fundamental factors in flotation, as we shall see.

Let us now go back to the floating needle. If it is greased, does the grease lower the surface-tension of the water? That can be ascertained by a pretty experiment. If camphor is whittled with a knife above a bowl of water the shavings, dropping on the water, will dance on the surface in a life-like manner suggesting insects in a fit. This phenomenon, as shown by Marangoni, is due to the dissolving of the camphor—a crystalline vegetal distillate—preferably at the pointed end, where the largest area per unit of volume is presented for solution. The dissolving of the camphor lowers the surface-tension of the water in contact and thereby causes the uncontaminated water, with its stronger tension, to pull away from the spot affected by the camphor—as in the colored water and alcohol experiment, No. 10. This causes the chips of camphor to turn and move spasmodically. In order to incite such activity the surface-tension of the water must be greater than that of the camphor solution. As soon as enough camphor has dissolved to modify the whole surface of the water in the bowl or cup,

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[5] No wonder the judges were puzzled by the technical terms used in flotation lawsuits. 'Oleic acid' is called an oil, whereas 'oil of vitriol' is an acid.

the chips become inert. Likewise if the surface-tension be lowered by the addition of grease the camphor remains quiet. For example, if, while the chips of camphor are lively, the water be touched by a greasy finger—all fingers are slightly greasy—the camphor is quieted immediately. No ordinary 'clean' cooking-utensil is sufficiently free from grease to allow an exhibition of the camphor dance.

Here we have a simple means of detecting the presence of grease or oil in the water upon which the needle is floating. I introduced some camphor chips into the water on which the ungreased needle was floating and they became lively. Then I repeated the experiment with a needle that was slightly greased, by rubbing it with the fingers that had touched my hair, and the camphor appeared unaffected thereby; it was lively. Finally, I smeared the needle with olive-oil; an iridescence on the surface of the water indicated diffusion of the oil. This time the chips of camphor fell dead as a door-nail and remained wholly inert on the water. Apparently, therefore, the needle will hold to itself a limited proportion of oil, which adheres so selectively as not to contaminate the water; but an excess of oil, more than the needle can hold, will be set free at once to modify the water and lower its surface-tension.

This is a classic experiment, as I ascertained afterward. Raleigh showed that the decrease of surface-tension begins as soon as the quantity of oil is about half that required to stop the camphor movements, and he suggested that this stage may synchronize with a complete coating of the surface with a single layer of molecules.[6]

A reference has been made already to the measuring of surface-tension. It can be done in several ways. For example, a framework, such as is shown in Fig. 7, is constructed[7] out of a transverse bar *AB* and two grooved slips *CD* and *EF*, so as to allow a piece of wire *GHIJ* to slip freely up and down. The wire *HI* is pushed against *AB* and some of the liquid is applied between them. The little pan *X* is loaded with sand so that the wire *HI* is pulled gently from *AB*. The minimum force required to do this is *mg,* the weight of *M* grammes. This weight suspended on the film of liquid between *AB* and *HI* equals the tension of the film on the wire. If the film stretches until the wire *HI* is at *p,* then the film has an area *CE, CP.* The total weight *mg* is distributed over the breadth *CE,* whence if *T* represents the surficial tension across the unit of length *CE,* then

$$mg = T.\,CE, \text{ or } T = \frac{mg}{CE}$$

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[6] The Encyclopædia Britannica. 11th Edition. Page 267.

[7] Alfred Danniell. 'A Text Book of the Principles of Physics'.

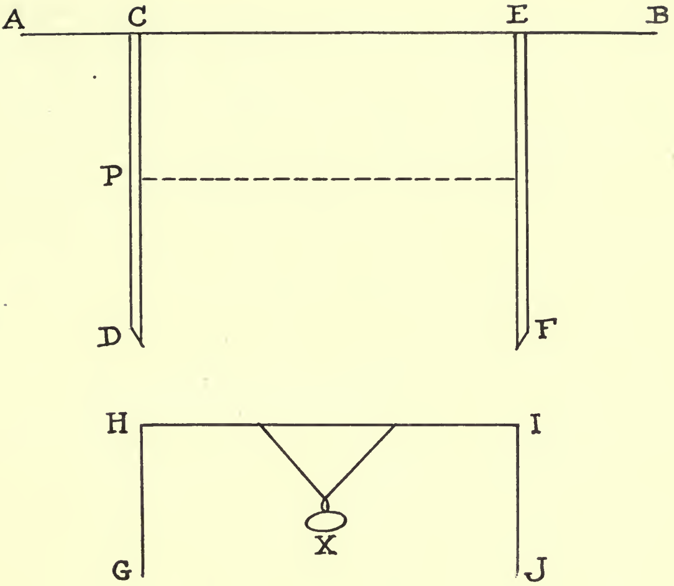

FIG. 7

Another simple way of measuring surface-tension is to make a wire-frame of which one side is movable; thus (Fig. 8) let *ABC* represent a bent wire and *DE* a straight piece. If a film of liquid is spread

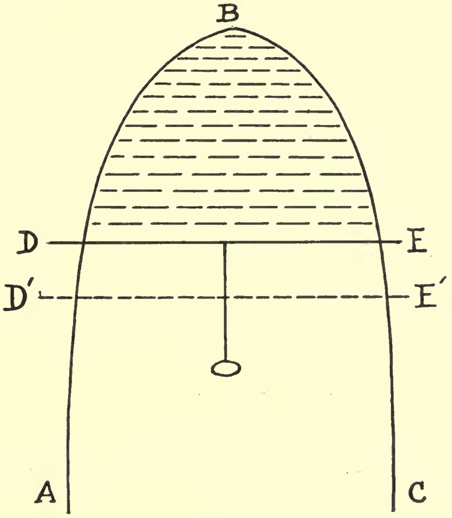

FIG. 8

over the space DBE then the surface-tension acting on DE will support not only the weight of the wire DE but also a small weight X. If W be the mass of the cross-wire DE and its attached weight, then the surface-tension of the film supports W and exerts a force Wg. The surface-tension acts all along that part (l) of the wire DE that lies in contact with the film, and it acts at right angles to DE. Since the film has two surfaces, if the force exerted on a unit length of DE and on one side of the film be T, then the upward force on DE due to surface-tension is $2Tl$. Hence[8] if there is equilibrium $2Tl = Wg$, or $T = \frac{Wg}{2l}$

This method was suggested by Clerk Maxwell. An ingenious mechanical model for illustrating the definition of surface-tension has been devised by Frank B. Kenrick, of the University of Toronto. He gives the definition as ''the maximum quantity of work that can be gained when a surface is decreased in area by one square centimetre'', and describes his device as follows: ''A projection cell 40 mm. by 10 mm. and 60 mm. high, the upper edges of which have been coated with a film of paraffine-wax, is filled almost to overflowing with water. On the surface is floated a thin shaving of cork 30 mm. by 5 mm. by 1 mm., to which is attached a fine cotton thread about 40 mm. long terminating in a little glass hook. The thread passes over a small pulley made from a pill-box and a pin resting in a double Y-shaped glass bearing. Three weights of glass or bent wire weighing about 0.1 gramme, 0.07 gm., and 0.04 gm. may be hung on the hook. The middle weight approximately balances the surface-tension, while the lighter one on being pulled down with a pair of tweezers is lifted again by the surface-tension. A fall of 1 c.c. produces one square centimetre of surface, namely, 0.5 cm^2 on the forward under side of the cork that is wet with water and 0.5 cm^2 on the upper surface of the liquid in the cell.''[9] For the accompanying sketch (Fig. 9) I am indebted to Professor Kenrick, who sent it to me on request. The waxing of the upper edge of the glass cell allows the water, which does not wet paraffine, to rise slightly higher than the level of the glass without overflowing.

By such experiments the force of surface-tension between water and air has been determined to be 3.14 grains per linear inch or 72.62 dynes per centimetre at 20°C.[10] Many disturbing factors enter into

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[8] W. Watson. 'A Text-book of Physics', p. 182.

[9] *Jour. of Phys. Chem.*, Vol. XVI, page 513.

[10] Theodore W. Richards and Leslie B. Coombs. 'The Surface-Tension of Water, Alcohols, etc.' Jour. Amer. Chem. Soc., July 1915. One dyne is equal to 1.02 milligrams.

the measurement of this force, so that divers figures, ranging from 70.6 to 81 have been announced at various times.[11]

This force may seem small, yet the actual tensile strength per unit-area of cross-section of the film is about one-fourth that of the iron or mild steel used in the shells of steam-boilers, although its density is not much more than one-eighth as great as that of the iron.[12]

The surface-tension of a liquid must be stated with reference to the fluid—gas or liquid—in contact, for it is modified by the nature of the substance on either side of the interface. An interfacial tension exists at any surface separating two substances and it has a particular value for each pair of substances. For example, the tension separating mercury from water is 418 dynes per centimetre whereas that separating olive-oil from air is only 36.9 dynes. A drop of water will not spread over the surface of mercury but oil will spread over water. The balance of forces is different in the two cases. When a globule of oil is placed on water, the tension of the water-air surface exerts a pull of 73 dynes as against the joint pull (37 plus 14) of the air-oil and

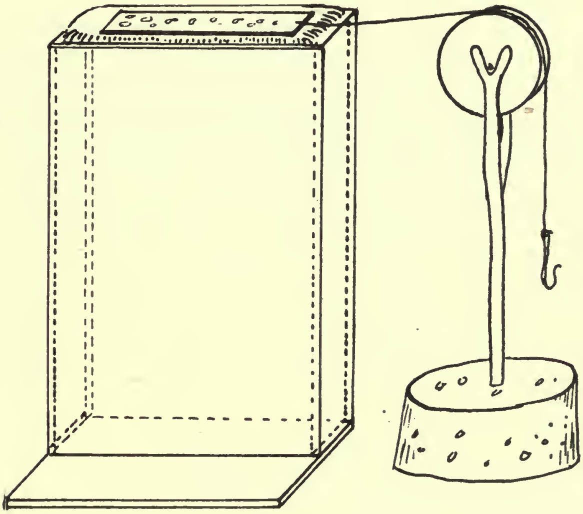

FIG. 9

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[11] T. J. Hoover in his valuable book 'Concentrating Ores by Flotation' quotes from Clerk Maxwell's article on 'Capillarity' in the Encyclopædia Britannica and gives the figures as 81, but he makes the mistake of saying that it is 81 dynes "per *square* centimetre." It is a tension, not a pressure.

[12] M. M. Garver. *Jour. Phys. Chem.*, Vol. XVI, page 243.

oil-water surfaces. Thus $14 + 37 < 73$. (Fig. 10). The oil spreads. If soap, in the form of ¼% sodium oleate, be added to the water its surface-tension will be lowered to 26 and the oil-water tension will also be decreased, how much I do not know, but certainly decreased, say, to 12; therefore $37 + 12 > 26$, and the oil will not spread over the water. On the other hand, the tension of the mercury-air surface has been given as 436 dynes and that of the mercury-water surface as 418.

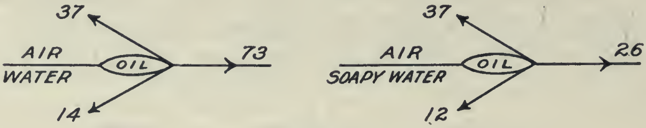

Fig. 10

If this be so, then a drop of water will not spread, because $418 + 73 > 456$. But Quincke showed long ago that pure water will spread on pure mercury, although the presence of an impurity, such as a slight greasiness, on the surface of the mercury will prevent spreading. According to later determinations of the interfacial tensions, by Freundlich, that of mercury-air is 445 dynes and that of mercury-water 370, so that $73 + 370 < 445$, and the pure water ought to spread on the pure mercury, as Quincke stated. If the water be contaminated, so as to lower its surface-tension, it will spread readily even on ordinary mercury, which is not chemically pure and on which pure water will not spread.

Wetting. A steel needle floats on water, but a glass rod of the same size sinks immediately; yet the specific gravity of steel is to that of glass as 8 to 2.75. The surface of the water resists rupture by the steel but it is readily broken by the glass; in other words, the glass is readily 'wetted,' while the steel is not. Again, if the glass rod be greased it will float; it ceases to be easily wetted. Here we face one of the underlying phenomena of flotation. The understanding of what constitutes 'wetting' is essential to the subject.

If a drop of pure water be placed on a clean piece of glass, it will flatten itself out so as to increase the space it first touched. If a similar drop of water be placed on a cabbage-leaf, it will not spread, but will retain its spherical form. We say that water 'wets' a glassy surface and does not 'wet' a waxy vegetal surface. A drop of mercury spreads eagerly over gold, but does not spread on glass; mercury wets gold but not glass. The statement is not absolute; it is a question of degree.

If I press the surface of water with a piece of glass the water rises to meet the glass, forming a mound, whereas if I make the same test with a piece of steel the water shrinks away from it, forming a depression. The tendency is for the water to lap the glass but to avoid the steel; the one substance is easily 'wetted,' the other not. The glass and the steel typify the gangue and the sulphide respectively in an ore treated by flotation. If we look carefully at the steel and glass, at the instant of touching the water, we see the conditions sketched in Fig. 11.

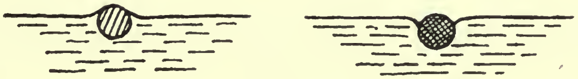

FIG. 11

Note how ink from a pen will not run on paper that is at all greasy. The paper refuses to be wetted where it is greased. That is why new pens are refractory; the steel has been greased to prevent rusting, like the needles. I used to burn the point of a new pen by aid of a match in order to cause it to deliver the ink to the paper comfortably. That burned the grease, but spoiled the temper of the pen-point.

The free surface of a liquid is horizontal, but at the contact with a

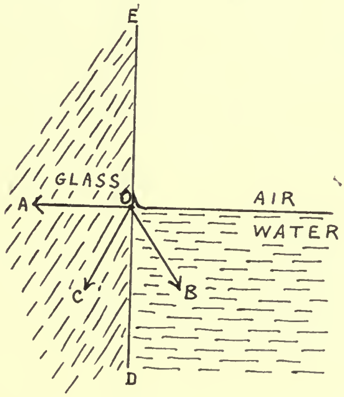

FIG. 12

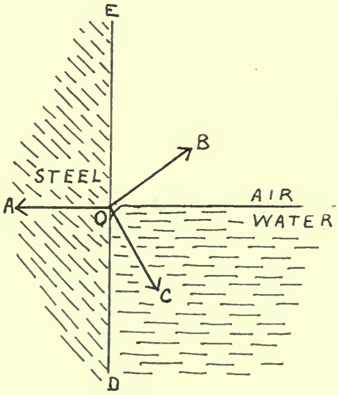

FIG. 13

solid the surface is curved, the direction and amount of curvature varying as between different liquids and solids. The water curves upward against glass, whereas it curves downward against steel; it tends to drown the one, but to float the other until gravity overmasters surface-tension. The way in which a liquid impinges on a solid is called the 'angle of contact.' For example, in Fig. 12 water is shown in contact with glass. Consider the conditions at the point *O*. The gravitational pull on a minute quantity of the water is negligible in comparison with its own cohesive force; so we can disregard the effect of gravity. The force of adhesion exerted by the surface of the glass is reperesented by *O A,* the force of cohesion in the water is represented by *O B,* and the resultant of these two forces is *O C.* If the adhesive force of the liquid to the solid exceeds the cohesive force of the liquid, the resultant will lie to the left of the vertical, *E D,* that is, within the solid; and since the surface of a liquid assumes a position at right angles to this resultant force, the water rises on the face of the glass. If, on the other hand, as in Fig. 13, where steel is shown in water, the cohesion of the liquid is greater than the adhesion of the liquid to the solid, then the resultant force lies to the right of the vertical, or within the liquid, which accordingly is depressed at the face of the solid.

In Fig. 12 and 13 the contact-angle is *DOB.* Since the surface of the liquid always assumes a position at right angles to the resultant force, the water will tend to rise on the glass and to sink on the steel. This angle of contact between a liquid surface and a solid is usually the same for the same pair of substances, but there is a subtle variation, which is called 'hysteresis' and it is said to play an important part in flotation. The variation is connected with the ability of a solid to condense a film of gas upon its surface. This gas-condensing power, or adsorption, can be modified, by acidulation, for example. Sulman has stated that "whereas the angular hysteresis of silica in plain water may exceed 30°, thus indicating that substance to have a definite power to occlude gas and to float, it drops from 4° to nil in water acidulated with sulphuric acid. Galena, on the other hand, retains its full measure of angular variation, or is but slightly affected."[13] This effect of the surface-energy of solids is apparently an important factor in flotation, and it is a pity that the exigencies of patent litigation have prevented Mr. Sulman from contributing more to the technology of the subject.

The angle of contact between water and glass is so acute as to be more nearly zero the purer the water and the cleaner the glass; between turpentine and glass it is 17°; between mercury and glass it is 148°. In a general way, subject to the variation already noted, the size of the contact-angle measures the capacity for 'wetting.' This angle can be changed by modifying the surface-tension of the water by means of a contaminant, such as oil, or the angle can be altered by modifying the surface of the solid, also by oiling. The oiling of the steel needle

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[13] H. L. Sulman. Presidential address. Trans. I. M. & M., Vol. XX. p. XLVII.

increased the angle of contact with the water so that it did not impinge as directly on the needle, and it did the same to the glass rod, but the effect was relatively less on the steel than on the glass because of the higher specific gravity of the former. The force tending to prevent sinking depends upon the radius of the needle, its density relative to that of the water, the surface-tension of the water, and the cosine of the contact-angle.[14] In metallurgical practice the pull of gravity is decisive in so far as it limits the size of particle that can be floated in water. If our needle is too large, it sinks, no matter how favorable the other conditions may be. So the flotation of a particle of mineral is conditioned on the size to which it has been reduced by crushing in the mill. The oiling of the needle increased the upward component of the surface-tension by enlarging the angle of contact, but the use of an excess of oil, that is, more than the needle could hold of itself, served to lower the surface-tension of the water and therefore to diminish the resultant force operating against wetting and in favor of flotation. Thus the oil used in flotation has two possible functions, and they may interfere with each other.

If to the water in which a needle is floating I add a drop of pine-oil, the needle sinks at once because the lowering of the surface-tension enables the water to wet the needle, that is, to diminish the angle of contact so that the water envelopes the steel. Let us make some other simple experiments. Take a piece of chalcocite that presents a smooth surface. A drop of water will not spread over it as it will on glass; the globule of water flattens itself on the glass but tends to retain its spherical form on the chalcocite. The glass may typify quartz or some other gangue-mineral. A drop of flotation-oil, such as coal-tar creosote, flattens on the chalcocite, whereas water maintains its sphericity. Coal-tar spreads less on glass than on water, but water spreads more on glass than on chalcolite. Thus water wets mineral less easily than gangue, whereas oil coats mineral more readily than gangue. So we say that gangue has a greater affinity for water than mineral, which, on the contrary, has a greater affinity for oil.

Water drips off oiled copper more quickly than off the unoiled; there is more adhesion between the water and the unoiled metal; the oil prevents wetting by the water. The effect of the density of the surrounding medium is shown by placing a piece of glass under water, dropping a globule of coal-tar upon the glass, and then raising it out of the water. The globule of oil spreads when lifted out of the denser

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[14] Joel H. Hildebrand. 'Principles Underlying Flotation.' M. & S. P., July 29, 1916.

medium and shrinks when returned to the water, although not quite to its first shape, on account of the adhesive surface. The oil on the galena replaces the water on its surface, but the oil on the quartz is unable to prevent the water from pushing itself underneath and over the surface of the quartz. Thus we have "an instance of the selective action of oil on a metallic sulphide in the presence of water, and the selective action of water on a gangue-mineral in the presence of oil."[15] On this phenomenon largely depends the process for separating valuable mineral from worthless gangue by flotation.

If a piece of galena and a piece of quartz are placed under water on the bottom of a beaker and if a few drops of oil, such as wood-creosote, are dropped upon the water, they will descend through the water owing "to their momentum and the releasing of the surface-tension of the water"[16] until one may fall on the galena, on which the oil will spread, while another falls on the quartz, on which it tends to draw into globular form, instead of spreading. Flotation is essentially a selective process. If I throw powdered ore on water, the particles of gangue sink and the particles of mineral float, in accord with our expectation, based on the foregoing experiments and the deductions therefrom, but some of the small particles of gangue will float and some of the larger particles of mineral will sink, because the play of forces is so complex that any single one of them is not uniformly decisive. Flotation is preferential, not absolute.

BUBBLES. We saw how the floating of the needle was aided by bubbles of air attached to it. That suggests, but does not explain, the latest and most successful phase of flotation. To understand it we must go back to the small boy's soap-bubble. The man that understands the physics of a soap-bubble has mastered the chief mystery of flotation. The boy, who, as pictured by Milais, watches the birth, ascent, and disappearance of the iridescent sphere of his own making, is the type of our modern metallurgist, who makes the multitudinous bubbles constituting a froth and then wonders to what natural laws his filmy product owes its existence.

To put it briefly, the boy, having dissolved soap in water, holds a little of the liquid in the bowl of his clay pipe while he blows through the stem. The soapy water forms a film that is distended by the boy's warm breath into a lovely sphere, which is lighter than the surrounding air, and therefore rises, while the sunlight falling upon it undergoes refraction into the colors of the spectrum. When the boy blows

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[15] A. F. Taggart, as witness in the recent trial, at Butte.

[16] Taggart, *op. cit.*

through his pipe into pure water, he makes bubbles likewise, but they burst instantly. The high tension shatters them. They do not burst explosively by expansion of the air within their envelope, but by lateral displacement of the substance composing their incompletely elastic films. To prevent such immediate collapse it is necessary to lessen the tension, that is, to diminish the contractile force at work in the watery substance constituting the exterior of the bubble. This can be done by introducing an impurity or contaminant. Water has the highest surface-tension of any common liquid, so that the addition of almost any other liquid—such as oil, alcohol, or acid—will lower the tension. The boy rubs the soap between his wet hands and dissolves it in the water. The soluble soaps contain an alkaline base, such as potash or soda, combined with a fatty acid, such as oleic or palmitic, extracted from tallow or oil. The boy uses oleate of soda, a compound of soda and oleic acid. The flotationist uses oleic acid, and much of the early work was done with this thick oil. In both cases, boy or man, playing at bubbles or working at metallurgy, the oil serves to lower the surface-tension of the water and to prolong the life of the bubbles that are made out of this modified water.

Two phases of the subject may be compared: The needle that floats on tap-water will sink in distilled water, because the latter lacks the air-bubbles that assist flotation. Although the tap-water has a lower surface-tension on account of its slight impurity, that effect is less decisive than the aeration. The bubble blown in pure water will break almost as soon as it comes into existence, but the solution of a little soap in the water will enable a boy to blow bubbles that sail away beautifully. The lowering of the surface-tension by the contaminant lessens the tendency of the bubbles to collapse. We have seen, in the camphor experiment, how the oil would lower the surface-tension not only of the bubble-film but also of the water in which it might be generated; that lowering of the surface-tension promotes wetting, which is antithetic to floating. If, to water on which mineral particles are floating, an addition of alcohol or caustic soda be made, or even the vapor of alcohol be allowed to play over the surface of the water; the mineral particles sink. The intense local contamination of the water has decreased its surface-tension so much as to increase the relative effect of gravity. Instant wetting ensues. It is evident therefore that oil can be used effectively in flotation in two ways: Either in such large quantity as to raise the mineral by sheer buoyancy or in such small quantity as to coat the particles of mineral, in preference to the gangue, and also decrease the surface-tension of the water in such a way as to promote the formation of a stable froth. Luckily the increased wetting power of the water due to the solution or emulsification of the oil is rendered largely ineffective by the oiling of the mineral particles themselves, on the surfaces of which the oil displaces the water and thus prevents wetting, while the lack of adhesion between oil and gangue serves differentially to aid the wetting of the latter by the water.

The changing colors of the bubble indicate that the thickness of the film is not constant; on the contrary, it may vary within wide limits without noteworthy variation of the surface-tension. That makes an important difference between a liquid film and any ordinary elastic membrane. "The tension in a liquid film is independent of the stretching, provided that it is not so great as to reduce the thickness of the film below about five millionths of a centimetre."[17] This result is promoted by the use of a solute that will be strongly adsorbed at the surface of the solution.[18] As the film is being stretched, the new surface formed at the thinner portion will contain less solute, owing to the time needed for adsorption, so that the new surface will be stronger than the old. Likewise, when water has been modified by a relatively insoluble contaminant, the components of the film can so dispose themselves that the surficial forces will be the same everywhere, that is, they tend to remain in equilibrium, including the force of gravity, which otherwise would pull them apart. Thus the tension at the surface of a contaminated liquid is able to adjust itself within fairly wide limits, and a film made of such a liquid can remain in equilibrium, whereas a film of pure liquid breaks at once. A soap-bubble will last for hours, a pure-water bubble persists for the fraction of a second. Moreover, the presence of a contaminant in water may also affect its viscosity, or internal friction, whereby it offers resistance to change of shape. This strengthens the film of a bubble generated in modified water. It has been asserted[19] that a concentration of the contaminant occurs at the surface of such a liquid, causing the viscosity to be magnified as compared with the body of the liquid. This statement is well founded.

An interesting experiment[20] to illustrate this phase of the subject

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[17] Poynting & Thompson, *op. cit.*, page 137.

[18] Hildebrand. Fig. 2, page 169, M. & S. P., July 29, 1916. Also Willard Gibbs' 'Thermodynamics,' page 313.

[19] Samuel S. Sadtler, in Minerals Separation *v.* Miami suit, 1915. Emphasized recently in the Butte & Superior case.

[20] How variously it can be seen and interpreted is shown by the descriptions given by Messrs. Durell, Norris, and Rickard, in 'The Flotation Process,' pp. 137, 315, 358; also by Messrs. Taggart and Beach in Trans. A. I. M. E., September 1916.

can be made by floating kerosene over blue-colored water and then passing air into the lower liquid. When bubbles are formed in the oil, they are short-lived, but they last long enough to indicate that the oil is not a pure and perfectly homogeneous liquid. In such a liquid, the bubble would break on arrival at the surface. The fact that two bubbles touch without coalescing (*K, K,* Fig. 14) proves that there is a film of variable composition between them. When I blow air gently into the colored water,[21] the bubbles that rise into the oil are colorless. They accumulate at the upper surface of the oil, where they show an attraction for each other and also for the sides of the glass vessel. They last longer than the bubbles blown in oil because they are made out of a liquid containing a decided contaminant, the dye. Next, I blow air more energetically, and I note that when the bubble is about to escape from the blue water it raises the surface into a mound (*A* in

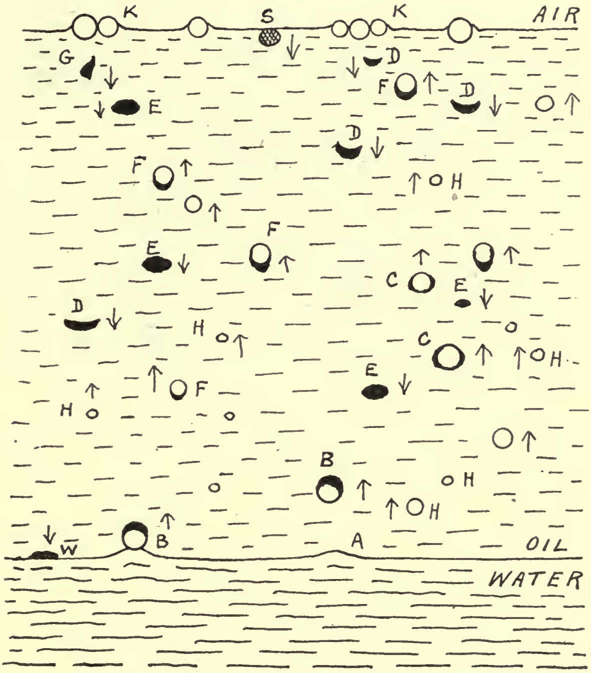

FIG. 14

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[21] Some of these experiments may seem almost childish to the supercilious, but I can commend them not only as giving insight into fundamental principles but as likely to stimulate thoughtful discussion.

Fig. 14), emerging at the point of it (as at *B*) as if the air had dragged the water in an effort to overcome a viscous layer. This indeed is the fact. I caught one bubble in the act; it came slowly through the little heap of water and remained poised at the top of the mound, finally breaking away, while the water subsided sluggishly to its level. Finally, I introduced air more rapidly into the water. The bubbles broke through the viscous water-oil interface and carried portions of water with them. These portions slipped from the north (*B, B*) to the south pole (*F, F*) of the bubbles and fell away, sometimes not until the bubbles had reached the upper surface of the oil. An intermediate stage is shown by *C, C*. This water that detached itself from the air-bubble was not a stable film but a viscous coating. It assumed various forms, crescent, hemispherical (*D, D*), lenticular, flatly globular (*E, E*), or even shapeless (*G*). The retention of a form that is not spherical is proof that the force of surface-tension is overcome by the high viscosity of the film at the water-oil interface.[22] Occasionally

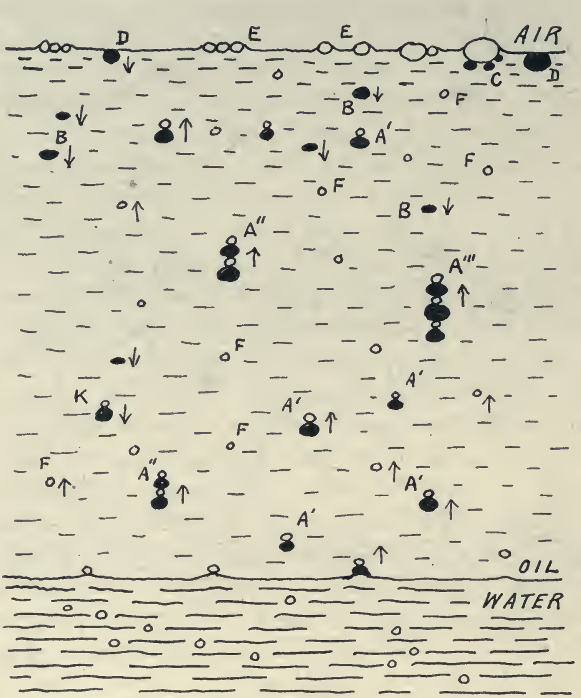

Fig. 15

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[22] As elucidated recently by A. F. Taggart in the Butte & Superior case.

some of the blue water remains as a globule attached to the surface of the oil, as at *S*. On reaching the oil-water interface the globule (as at *W*) will merge itself slowly with the liquid from which it originated.

If a similar experiment is made with carbonated water, in which minute bubbles of nearly equal size are generated quickly, one can see the little bubbles, like bright colorless beads, leading a much bigger globule of blue water upward (as at A', A' in Fig. 15) through the oil to the surface, where the bubble breaks and the globule of water falls back through the oil in oblately spheriodal shape (*B, B*). Sometimes two, or even three, couples rise tandem (as at A'' and A'''). At the surface of the oil the coalescence of several bubbles may leave one large bubble to which several small globules of water are attached (as at *C*), or globules of blue water (*D*) may remain floating in the oil, as if hanging from the surface of it. Sometimes the bubble may be over-weighted and, after rising a little way, it descends (*K*). If the couples collide, the bubbles are released and leave their freight of water, which drops back. The interesting feature is the air-bubble's ability to lift a water-globule so much larger than itself. This is due to the fact that the water comes from the water-oil interface and includes oil.

The amount of the contaminant in the froth of a flotation-cell can be measured by analysis. The concentration in a film may proceed so far as to form a solid, as when using hard water. The use of oil as a modifying agent is advantageous because it is not prone to enter into chemical reactions with impurities in the mill-water even when thus concentrated in the bubble-films; otherwise some other contaminant might be used. Indeed, it is likely that oil will be replaced by some contaminant that is cheaper and that may also induce some desirable chemical reaction. Several such substitutes are now being tried in flotation plants.

The question has been asked, when a bubble is formed in a liquid, is it a spherical hole filled with gas or is it a sac; in short, has it a skin or not? The reply to this question involves the whole theory of surface-tension and bubble-making. When a pure gas is blown into a pure liquid, the bubbles rise rapidly to the surface, where they burst instantly. The gas injected into the liquid is subject to the gas-liquid tension, therefore the surface of the liquid enclosing the portion of gas assumes a spherical shape in obedience to that tension, because a sphere occupies the least space. The liquid in contact with the gas will have a different orientation of its molecules and it will be slightly denser than the internal liquid. These conditions will accompany the globule of gas in its passage upward. The form of the liquid periphery persists but the substance of the liquid in contact with the gas is changing as the bubble rises. An analogy is furnished by the motionless cloud on a mountain. The cloud retains its shape, although its substance is fleeting. Ascend the mountain and you find yourself surrounded by a mist that is traveling at the rate of 20 or 30 miles per hour, or even faster; yet as seen from the valley the cloud seems fixed. The explanation is that the moisture-laden air sweeps into the cold area on one side, either the snowy or shady side of the peak, and there the moisture is condensed to globules of water constituting a fog or mist; these are visibly driven forward, to be expanded suddenly and dissipated into clear air as soon as they pass beyond the cold area, but their place is taken by others coming on behind, so the shape of the cloud persists although the substance of it is rushing forward at the speed of a railway-train.

Now the important question arises: What is the substance of the film of the bubble as it passes from one liquid into another? The attachment of blue water to the bubble in the water-oil experiment is confusing, because it obscures the fact that, as the coating of water slips away, the bubble acquires an oily film and when temporarily at rest on the surface it is enveloped in an oily film. No blue tinge can be detected, if the effect of reflection from below be avoided. On the other hand, if the experiment be repeatd with heavy oil (colored by 'oil orange') and alcohol, it will be found that the bubbles that come to roost at the upper surface of the alcohol are orange-colored. Thus, as scientific theory would suggest, the bubbles take a film of the liquid having the lower surface-tension or less molecular cohesion. In passing from water to oil or from oil to alcohol the bubble has an oily film at the end of its journey. If a bubble were generated in water and passed successively through oil and alcohol, it would have a water, oil, and alcohol film in sequence. If the bubble passed in the reverse direction it would have an alcoholic film in the alcohol, the oil, and the water alike, because alcohol spreads over oil and oil spreads over water, the liquid having the less cohesion or surface-tension being pulled by the molecular attraction of the liquid having the stronger cohesion or surface-tension. There is this to be added, however, that the bubble generated in water would have some water in its oily film when in the oil, and some oil in its alcoholic film when in the alcohol. Each liquid in turn serves slightly to contaminate. On the return journey, the alcoholic film, contaminated slightly by the air and by any impurity in the alcohol-air interface, would resist modification by the oil and by the water (forming the lower layers of liquid) because the alcohol would spread over both the oil-air interface and the water-air interface. Imagine a globule of oil in an air-bubble enclosed by water (Fig. 16): the oil spreads and forms a film to enclose the air.

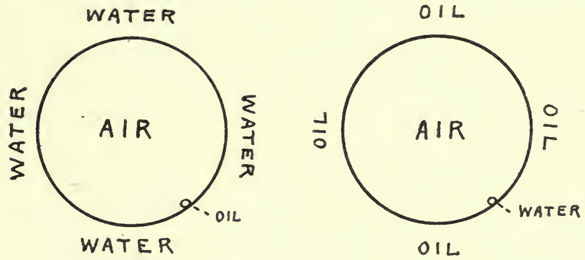

Fig. 16

Now imagine a globule of water in an air-bubble surrounded by oil; the water does not spread, because the pull of the air-water and water-oil surfaces is greater than that of the oil-air surface; therefore a water-filmed bubble will acquire an oil film when passing into oil; on the other hand an oil-filmed bubble will retain its film in making the same entry through water.

We have seen that mineral has a selective adsorption for oil rather than for water and that in this respect it differs from gangue. Metallic particles adsorb air, but this fact is relatively unimportant in flotation because the air approaches them when it is enclosed within a liquid envelope that is contaminated by oil. Therefore the adhesion of oil for the metallic surface becomes the dominant factor. The older notion that the affinity of air for metallic surfaces played an important part in flotation has been set aside, because of the absence in the flotation-cell of any direct contact between air and mineral. Metallic surfaces, such as those of minerals, are supposed to adsorb air and that is why they are not readily wetted. It may be due to molecular density, coupled with reduction of inter-molecular distance, which is practically the same thing as a reduction of sub-capillary porosity. Adsorption of air would also bear a relation to the higher density of the mineral. Such adsorption plays its part in the older surface-tension processes, such as those of Wood and Macquisten, but in the later flotation processes there is present insoluble oil or a soluble frothing agent, and this renders it impossible for the globule of air to come into direct contact with the mineral. It is not the air, but the film around it, that provokes the attachment of the bubble to the mineral.

Now let us consider the air-bubble made in water containing an impurity that decreases its surface-tension. In the language of flotation we would say that this impurity is a contaminant modifying the water. As soon as the air enters the water it assumes a globular form as before, but when the bubble reaches the surface it persists; it does not burst at once. The bubble in the water is a spherical hole occupied by air; the air has displaced the water and is enclosed by it; the water-surface in contact with the air is in a state of tension as compared with the interior body of water, and that causes contraction into spherical shape. The surface-tension has been lowered by the contaminant so that the bubble-film is in a state of less strain than a similar film of pure liquid, hence a diminution in the tendency to contract and to collapse. Moreover there is a tendency for the contaminant, whatever it be, to concentrate at the air-water surface; there is a differentiation of the constituents of the liquid, causing the surface to differ slightly in composition from the bulk of the solution and so to accentuate the modification due to the presence of the impurity. The bubble-film or air-liquid contact adsorbs the contaminant until equilibrium is established, and the contaminated liquid of the film carries some of the contaminant all the way to the surface, despite the interchange between molecules or particles of the contaminant on the way up. This differentiation and concentration of the contaminant at the surface of the water in contact with the air-bubble may indeed be likened to a film or membrane, so that the bubble may be regarded as a sac, but it is a sac the substance of which is not fixed while the bubble is moving upward through the water. It cannot be regarded as enclosed within a definite film until it reaches the end of its journey, and even then the film is coterminous with the surface at which it rests, and the play of light upon it shows that the rearrangement of its substance is still in progress, as the excess of liquid drains to the south pole. The variability in the surface-tension due to the shifting of the contaminating particles is essential to the longevity of the bubble-film. That brings us to a recognition of an important factor: viscosity.

Viscosity. This is defined as the internal friction of a liquid or its resistance to a change of shape. Two years ago the part played by viscosity in establishing a bubble-film was subordinated to emphasis on the lowering of the surface-tension of the water in the ore-pulp.[23]

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[23] However, I pointed to the probability of viscosity contributing to the tenacity of the film, even in the needle experiment on tap-water, and quoted Boys to show that increase of viscosity was involved in the lowering of surface-tension in enabling a bubble to persist. M. & S. P., Sept. 11, 1915, p. 385.

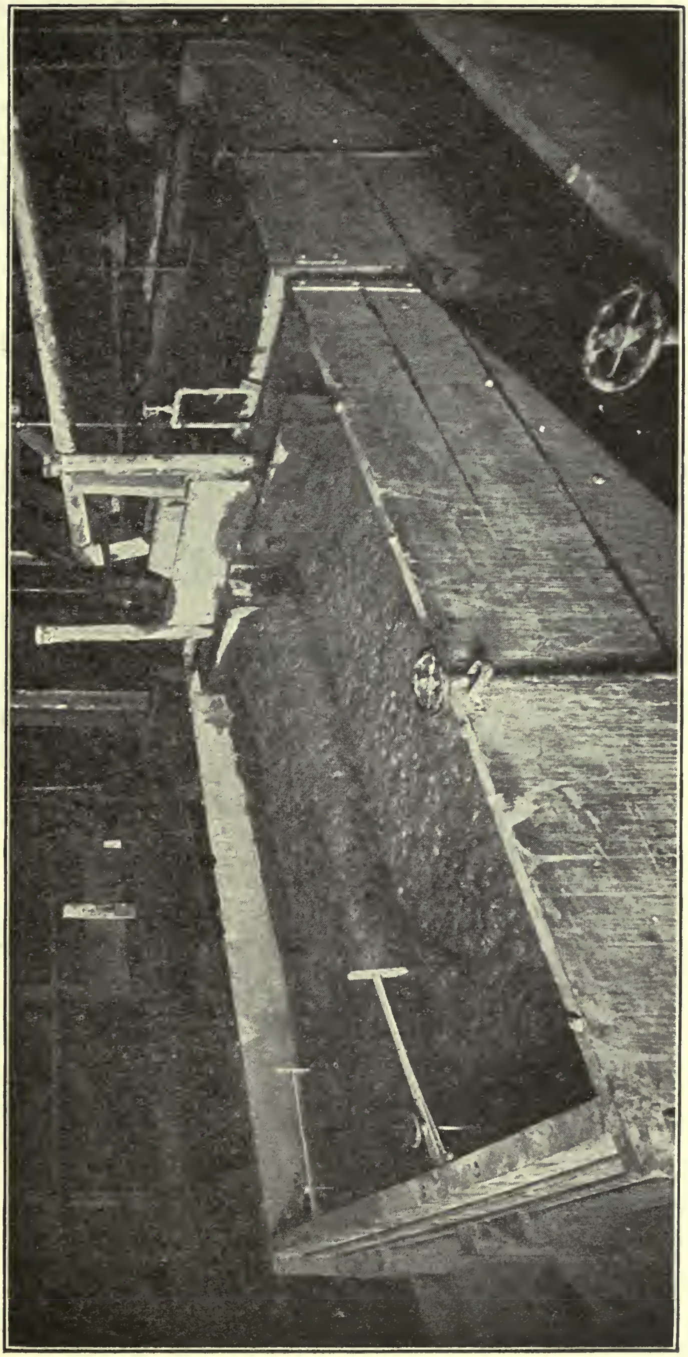

FIG. 17. THE FROTH IN A CALLOW CELL

Since then this branch of the theory has been elucidated by Messrs. Taggart, Beach, and Bancroft.[24]

The addition of alcohol increases the viscosity of water up to about 47%, after which the further addition decreases the viscosity. Alcohol, of course, lowers the surface-tension of water, but an experiment[25] will prove that the change of viscosity is the dominant factor in making a froth. If alcohol, to which 5% water has been added, be stirred violently in the glass-jar machine familiar to flotationists there will be no formation of froth, but if the experiment be repeated with tap-water, to which 1% of alcohol is added, then a froth is produced at once.

Such an alcohol-water froth is non-persistent, because the absolute viscosity is low. To increase it we must have a colloidal suspension; for example, the foam on beer. The colloidal protein of beer yields a froth that lasts longer than the bubbles on champagne, which are short-lived, like the alcohol-water foam of the experiment just described. To obtain a froth sufficiently persistent to serve a metallurgic purpose it is necessary to increase the viscosity of the bubble-films. This is one of the functions of the oil, and it is one that follows upon its affinity for metallic surfaces. It adsorbs or concentrates (at the surface of the bubbles) the mineral particles in the pulp so as to form an interface that is more viscous than either the oil or the water or the mixture of the two.[26] It is the presence of solid matter that contributes to the viscosity of the bubble-films in the froth.

If a needle be floated on water by means of a raft made of wooden matches and if a chip of wood be floated to one side of it, one can use a magnet to turn the raft and needle on the surface of the water without moving the chip. This shows that the surface, or water-air interface, has no noticeable viscosity.[27] If, however, the surface be dusted with finely pulverized ore, then the magnet will cause the chip to move with the rafted needle. The viscosity has been so greatly increased by the addition of solid matter to the interfacial film that the surface behaves as if it were solid. Next, if a drop of oil, sufficient to lower its surface-tension, be added to the water, the chip will not turn when the rafted needle is moved by the attraction of the magnet.

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[24] More particularly in their expert testimony at Butte, from which I have quoted already.

[25] Described by Wilder D. Bancroft in his testimony at Butte.

[26] Taggart.

[27] Taggart. He pointed to the fact that the addition of the oil increased the viscosity of the surface so as to cause it to act as a solid within small distances, close to the raft, but considerably less than when the powdered ore was sprinkled upon the oiled surface.

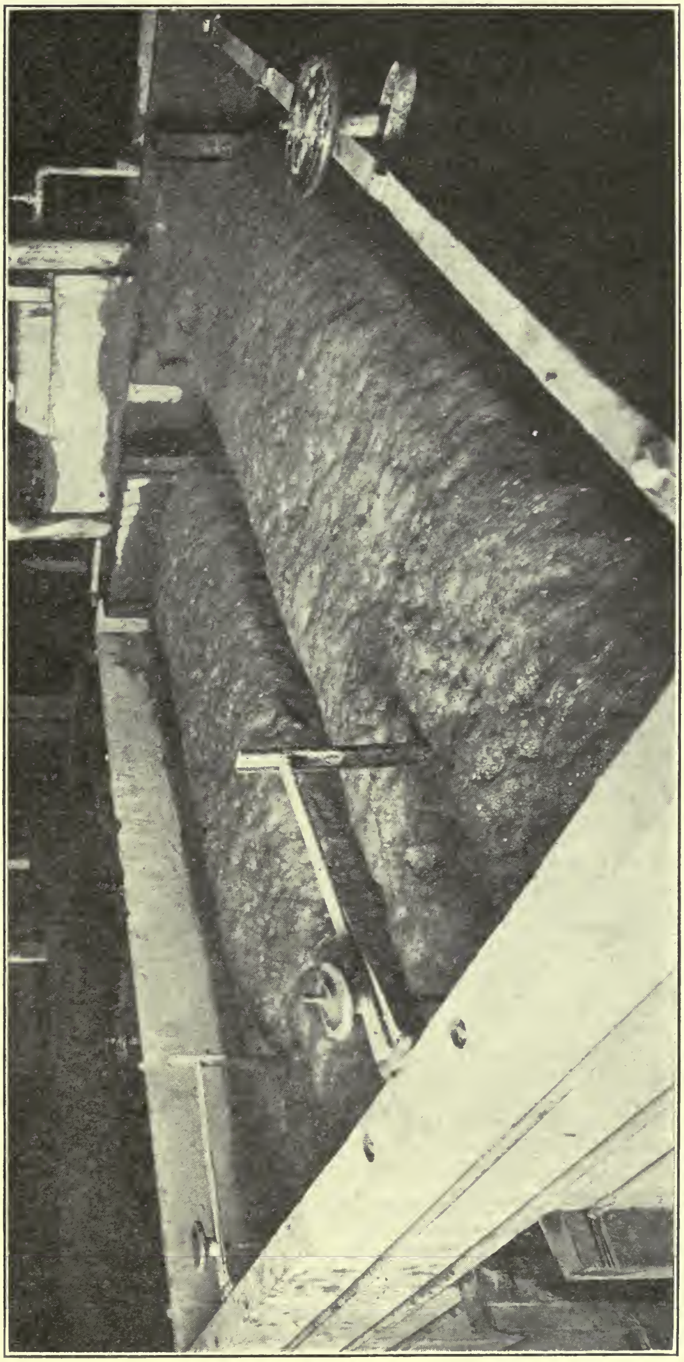

FIG. 18. ANOTHER PHOTOGRAPH, SHOWING THE FROTH OF TWO ADJACENT CELLS

Such increase of viscosity as has been caused by the oil is insufficient to form a resisting medium. Finally, if powdered ore is dusted upon the oil-contaminated surface, again the chip does not move with the raft, because ''the surface has been stabilized and made highly viscous.''[28]

If water and kerosene be poured successively into a glass bottle, and if then finely-divided copper, called 'bronze powder', be introduced and the contents of the bottle be subjected to vigorous shaking, and then allowed to remain quiescent, the copper powder collects at the oil-water interface and from it slowly a bronze film will separate itself and become pendant. This, when viewed by transmitted light, is seen to be a lace-like fabric, like a cobweb that has been long exposed to dust.[29] It is a film of particles of kerosene and water so viscous, owing to the inclusion of the powdered copper, that it hangs like a curtain; it is an adsorption layer of bubble-film matter hanging from the oil-water interface. The presence of the powdered copper has stabilized the film.

It is important to note that such increase of viscosity as prolongs the life of the bubble-film need not be metallic. When pine-oil is added to water, and the mixture is agitated, the froth that comes to the surface of the water is thin and evanescent. When to this there is added lycopodium powder, which is of vegetal origin, being the spores of club-moss, the froth becomes thick and lasting.[30] If the lycopodium be used without the pine-oil, no persistent froth is made. In this case, as with the bronze powder, the effect of the solid is to stabilize the froth by making the bubble-films more viscous. The gangue would serve for this purpose if the particles of gangue could pass into the oil-water interface, but it happens, as we have seen, that the oil exhibits a choice for the particles of mineral, so that they are adsorbed preferentially.

Another experiment:[31] When a needle was floated on water in a beaker and a drop of caster-oil was added, the needle did not sink. When another drop of the same oil was added, the globule moved to the needle and adhered to it. But it continued to float. When a drop of pine-oil was allowed to run down the side of the beaker, the needle sank as soon as the pine-oil touched the water, while the globule of oil

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[28] I am quoting from Mr. Taggart's testimony, from which the description of the experiment also is taken.

[29] F. E. Beach, who performed the experiment in the court-room at Butte. R. B. Yerxa repeated it for me at Miami.

[30] Bancroft, who performed the experiment in the court-room at Butte.

[31] Made for me by Mr. Yerxa in the laboratory at Miami.

remained afloat. Apparently the increase of viscosity due to the thick oil counteracted the lowering of the water's surface-tension.

The effect of saponine, noted in Hoover's book as being so detrimental to flotation, can now be explained. Although it does not increase the surface-tension of water, but tends rather to decrease it very slightly, according to Freundlich, it causes a marked increase of viscosity. The result is a good froth; but it exhibits no essential adhesion, that is, the saponine solution is not adsorbed by the mineral. Therefore the froth does not persist and the mineral is not floated.

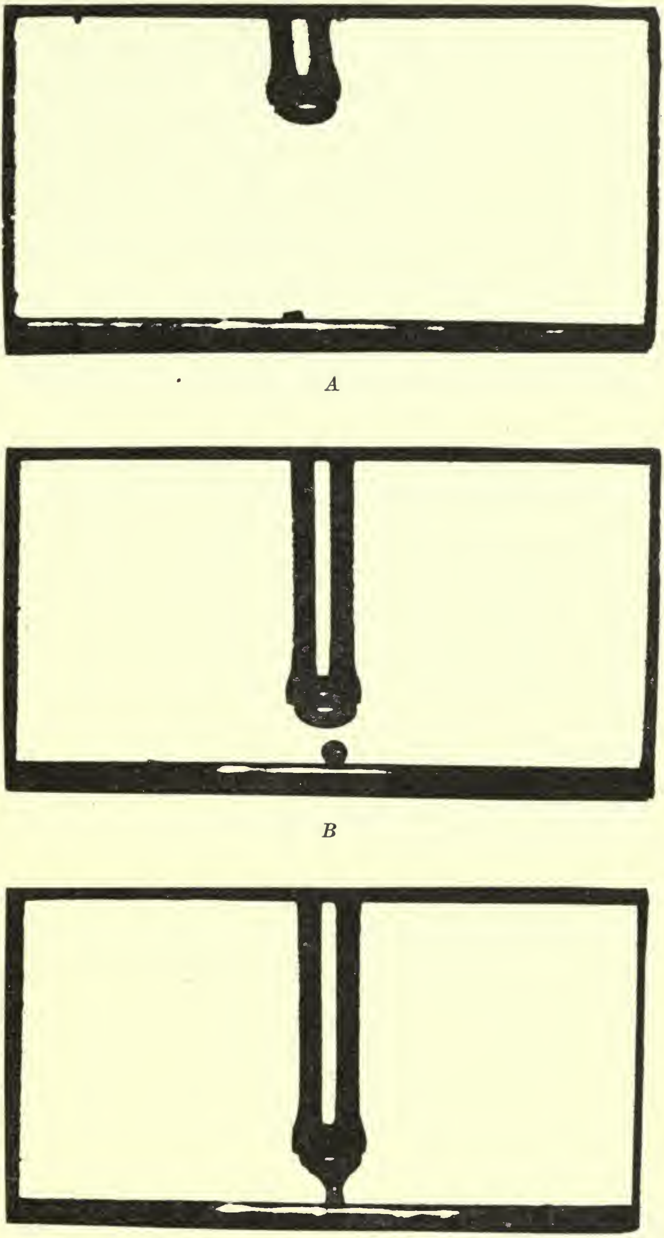
Any substance that is adsorbed into the oil, or the oil-water interface, of the bubble will pass into the film. If it does that the substance will be floated. Mineral goes into oil in preference to gangue.

Fig. 19

If a particle of sulphide is in the vicinity of oil and water, the oil-surface of the sulphide grows larger and the water-surface grows smaller, until the sulphide at the last takes a position within the oil. Reversely, a particle of quartz takes a position within the water. The greatest possible area of sulphide that can be covered by the oil is when the sulphide is within the oil; therefore the particles of sulphide tend to encase themselves within the oily substance of the bubble-film and so not only stabilize it but give themselves the opportunity of being floated to the surface in the froth.

Oil-Films. In the course of the first trial of the Miami lawsuit, at Wilmington, a series of demonstrations was made in court for the purpose of argument. These experiments were photographed and placed in the record. Some of them are of scientific interest. Fig. 19 shows the curved pipette employed to pass an air-bubble to the bubble-holder, which is a bell-mouthed glass tube. Fig. 20 shows the play of a bubble on the oil placed upon a particle of galena lying at the bottom of a vessel containing water. In A the particle of galena and the bubble-holder are shown. In B a globule of oil rests on the galena. The oil is 1½ times the volume of the galena particle. In C the air-bubble is adhering to the oil on the galena and drawing it up, forming a neck of oil between the bubble and the galena. The photographs exhibit the affinity of the oil for the air-bubble. If the bubble failed to raise the particle of galena, this should not occasion surprise, as it was much too large—several thousand times bigger than the average pulp treated in flotation. In Fig. 21 similar experiments on particles of unoiled galena of a reasonable size—about 20 mesh—are recorded photographically. In the first of this series the bubble-holder is approaching one of three particles, in the second it is moving away with one of them, and in the third with another. In Fig. 22 another series of experiments is shown, but with oiled particles of galena, of plus 20-mesh size. In the third member of this group it will be noted that all the galena particles are being carried away by the bubble. Two of these particles are adhering to the third particle, which is attached directly to the bubble. Ordinary tap-water was used. These experiments, and others like them, showed that particles of galena will adhere to an air-bubble, whether they are oiled or not. The adhesion takes place even when the mineral carries an excess of oil. Particles of chalcocite do not adhere so readily to the air-bubble when they are unoiled as when they are oiled, but the evidence given in this suit was incomplete; moreover, it was not shown whether a bubble made out of water suitably modified will, or will not, adhere to an unoiled particle of chalcocite. The motion-pictures of these demonstrations cost a great deal of money, but it will be acknowledged now, I believe, that they threw but little light on the theory of flotation.

The adhesion of air, as a bubble in water, to mineral particles is easy enough to prove, but such bubbles, as far as I have been able to ascertain by experiments, will adhere to almost anything that happens to be near-by. Trying some of these experiments recently with Mr. Yerxa, at Miami, I found that a large air-bubble would not lift an 8-mesh particle of chalcocite without a good deal of coaxing, but when a minute (accidental) air-bubble became poised on the chalcocite then the big bubble attached itself to the small one and thereby raised the mineral particle. When the chalcocite was oiled the bubble was lifted without hesitation. Examining the bubble-film, it will be seen (Fig. 23 that the particle of chalcocite hangs from it when in the water, but as soon as the bubble is taken out of the water into the air, the



A

B

C

Fig. 20

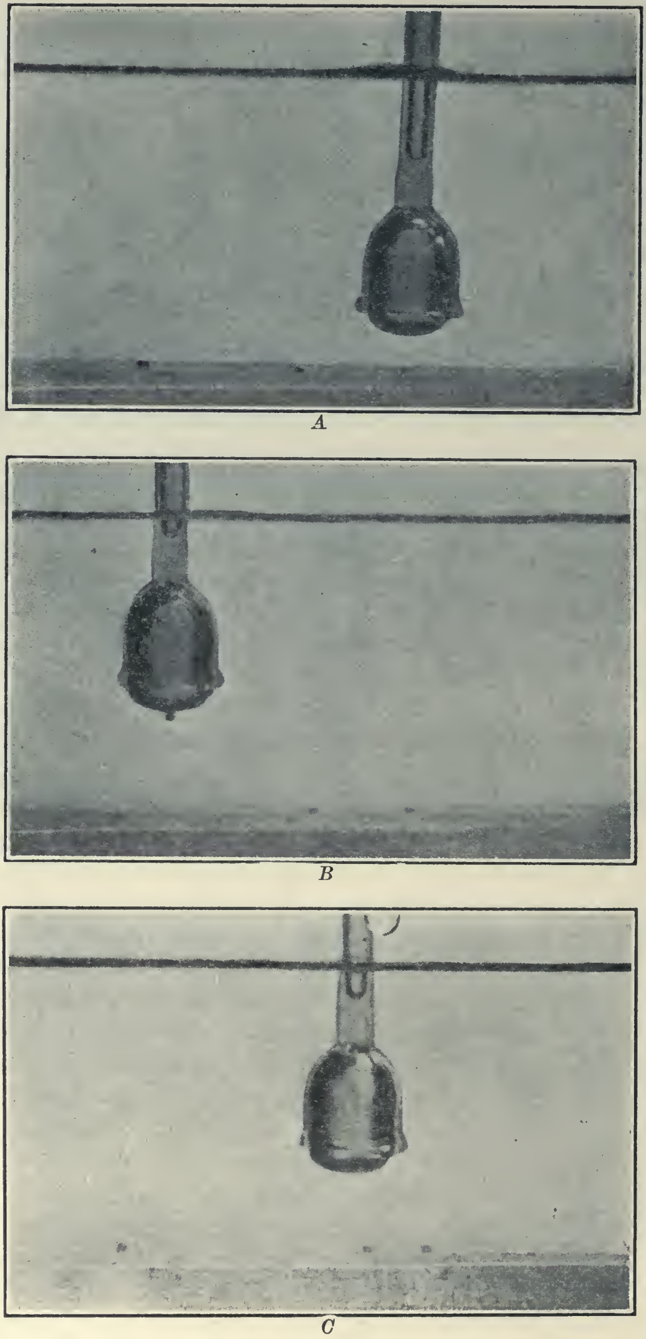
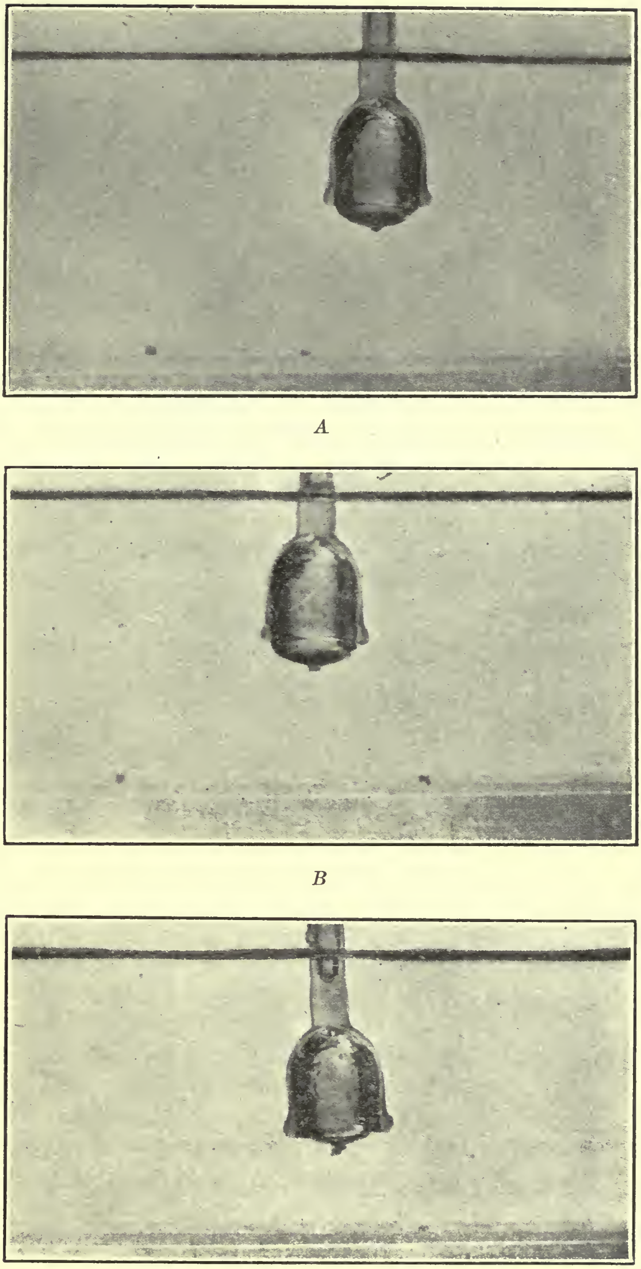


Fig. 21



A

B

C

Fig. 22

chalcocite is enclosed between an inner and an outer surface,[32] in both of which the oily contaminant is so concentrated as to form an adsorption layer.

The nature of this oil-water interface is indicated by another experiment. If water and pine-oil are poured successively into a test-tube and a particle of chalcocite is dropped into it, we shall find (Fig. 24) the particle floating at the oil-water interface in such a way that the mineral seems to be in the water, when it is really enclosed within a downward protrusion of the oil.

FIG. 23

When a bubble is in oily water it has only one contaminated surface, or adsorption layer, but when it emerges it has two. See Fig. 25. The oil is concentrated at the surfaces in contact with the air, outside and inside, leaving the less modified water between.

FIG. 24

Again, when a globule of pine-oil was placed on the smooth surface of a lump of chalcocite under water, the pine-oil was held by the chalcocite as against a bubble brought in contact with it, but when the globule of oil lay on a piece of quartz the pine-oil was adsorbed by the bubble. A particle of mineral and a bubble show mutual attraction and if the mineral particle is minute it becomes drawn into the interface of the bubble-film. That may be why larger particles are not

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[32] As elucidated by Taggart at Butte.

floated easily; they are too big to be enveloped in this way. The mineral particles are carried within the bubble-film; they are not attached to it outside. That may explain why fine pulverization is essential to the success of flotation. Thus we arrive at the idea that it is not the air in the bubble only, but the nature of the film, that affects the floatability of the metallic particles.

The addition of oil to water—in a beaker, for example—causes an oily film to appear at the interface between water and air. When an air-bubble meets an oil-glouble they will be mutually attracted and some of the oil will pass into the interface between water and air. When air occupies a hole in water, forming what is called a bubble, the periphery of this hole presents a surface—exposed to the air within—like the surface of the water in the beaker. In each case the oil tends to concentrate at that air-surface.

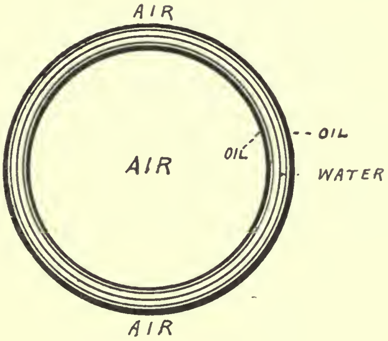

FIG. 25

The old idea that the mineral particle attached itself directly to air is now relegated to one side; while this mutual attraction may exist, it plays a minor part because the air when it approaches the mineral in a pulp is always enclosed within a watery film contaminated by oil or some substance that functions similarly. This statement has been made previously and is repeated here for emphasis.

It has been disclosed by microscopic examination[33] that the mineral particle is not in direct contact with air, but so enclosed within the film as not to be in touch with air either inside or outside the bubble in a mass of froth. The film raises itself over the particle and wraps itself under the particle, so that the mineral is enclosed within a watery interspace. The film itself consists of an exterior surface in

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[33] Taggart.

which the oil is concentrated, and of an interior surface in which oil also is concentrated, both of these oily concentrations grading toward the water that lies between them. The oil is concentrated at each gas-liquid interface, just as oil concentrates at the surface of water in contact with the atmosphere.

The various experiments described in the foregoing pages have shown that the oil in a pulp, consisting of crushed ore and water, performs three distinct functions:

1. It lowers the surface-tension of the water.
2. It assists in the selection of the mineral particles.
3. It promotes the formation of a stable froth.

Water is a convenient liquid for flotation work because it has a surface-tension so high that the addition of almost any other liquid will lower it. The lowering of the surface-tension diminishes the contractile force in water and lengthens the life of the bubbles that are formed by the injection of air; but this lowering of the surface-tension has another important consequence: it creates such a variable concentration of oil in the watery film of the bubble as to enable the film to adjust its strength to external forces. This variability of tension is even more important than the lowering of the surface-tension, because it serves to strengthen the film where necessary by lessening the proportion of contaminant at any weak spot. The contaminant will concentrate at the surface of the liquid because by doing so it will decrease the potential energy.

Next comes the selective adsorption of mineral particles by the oily film. The oil wets mineral in preference to gangue; it envelopes the mineral, by which it is 'adsorbed' or attracted. This causes the particles of mineral to be drawn into the oily film of the bubbles, which in turn are strengthened by reason of the increase of viscosity imparted to their films by the inclusion of mineral particles. The electro-static hypothesis has been discarded in the latest investigations.

Any substance that will lower the surface-tension of water and be adsorbed by mineral particles would appear to promote flotation. The value of a flotation agent depends upon its ability to 'adsorb' mineral. Most 'frothers' or bubble-makers by themselves are not satisfactory because they lack this ability, and, in order to correct the deficiency, it is customary to add a 'non-frothing' oil, which is adsorbed strongly by the mineral, thereby promoting successful flotation.[34] A froth made with a relatively soluble oil, like pine-oil, can be stabilized by adding a relatively insoluble viscous oil, like fuel-oil. The idea of

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[34] Bancroft. In his testimony at Butte.

agitation, whether of the violent and mechanical kind or of the gentle and pneumatic kind, is to bring the particles of mineral in contact with the oily films of the air-bubbles. Whether the oil is emulsified before or after it is added to the pulp does not matter at this stage, but the oil must have been presented to the bubbles in a minutely subdivided condition, so that they may acquire oily films and so that those films may come in touch with the mineral particles. In doing so the globules of oil and the bubbles that they contaminate beneficially come in contact with particles of gangue as well as particles of mineral, but owing to the tendency of oil to replace water at the surface of the mineral particles these will be coated with oil and adsorbed into the oily film of the bubbles and rise, whereas, by reason of the tendency of water to displace oil on the surface of gangue-particles, those will become wetted and sink.

'Mineral,' 'metallic,' even 'ore,' are used interchangeably in the technology of flotation. The misuse of 'ore' has caused great confusion, for the object of the process is not to recover the 'ore', but only the valuable mineral in the 'ore,' rejecting the valueless portion, called 'gangue'. As between 'metallic' and 'mineral,' the reference is not so much to substances containing metals, for that would include much of the gangue, such as rhodonite and feldspar, but particularly to minerals having a metallic lustre, which feature appears to be favorable to the adhesion alike of air and oil. 'Sulphide' is another synonym, because the sulphur compounds with the base metals are particularly the object of flotation, but 'sulphide' would exclude the tellurides. At least one sulphide without metallic lustre is amenable to flotation, namely, cinnabar. So is graphite, which is neither sulphidic nor metallic, except in lustre. Likewise certain forms of scheelite respond to flotation, and it has been shown by experiment that a stable froth can be made with lycopodium powder, which is of vegetal origin. So we must be careful in our use of terms. The use of 'metallic' and 'mineral' as adjectives to designate floatable substances is based on a concept of flotation that may soon be discarded. No classification of floatable minerals can be made yet and when it is made it must be based on a better understanding of the physical conditions governing flotation.

The amount of oil required in froth-flotation depends upon three factors: the proportion of mineral to be concentrated, the amount of water, and the degree of aeration. Air and water are needed to make bubbles; these bubbles must be oiled in order that they may engage the mineral in the pulp. The more numerous the mineral particles the greater the number of oily bubbles needed to arrest them. If the amount of water is doubled, there will be only half the number of mineral particles in a unit of space; therefore more oily bubbles will have to be sent in search of them than if they were herded within the smaller volume of water. The idea that a 'critical' proportion of oil—somewhere under 1%—is required to perform successful froth-flotation has no basis of evidence outside the imaginings of a group of patentees and it has been stultified by the operations of 1000-ton plants using 22 or 23 pounds of oil per ton of ore, in Utah and Montana. As Wilder D. Bancroft has said: "The hypothesis of a 'critical point' rests on unverified and unverifiable statements."

THE HYPOTHESIS. Let us recall the principal points in the evidence before venturing upon a summary of our conclusions. I write in the plural advisedly, for the evidence has come from many sources and the suggestions explaining it have been borrowed from many writers; the theory, like the practice, of flotation is the joint work of a large number of investigators.

(1) The needle that floats on tap-water will sink in distilled water. Although contaminants have lowered the surface-tension[35] of the tap-water, it has more sustaining power on account of its aeration.

(2) The bubble blown in distilled water will break as soon as it emerges, but the solution of an oily substance will enable a boy to blow bubbles that sail away beautifully.

(3) The addition of oil lowers the surface-tension and thereby promotes wetting, but the adhesion of the oil to the surface of the mineral particles causes the water to be displaced, so that the gangue preferably, not the mineral, is wetted, and drowned.

(4) Emulsification of the oil provides a means, through the subsequent breaking of the emulsion, for imparting oil in a minutely subdivided state, as needed, for oiling the bubble-films and the mineral particles.

(5) The contaminant, such as oil, in water concentrates at the air-surface and by doing so affords a surface-tension sufficiently variable to be adjustable to shock.

(6) The oil-water interface is more viscous than the body of either liquid.

(7) Oil is attracted and adsorbed by mineral particles, which therefore are pulled into the oily film of the bubbles.

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[35] The layer of liquid subject to surface-tension has a thickness less than the radius of molecular action. R. S. Willows and E. Hatschek. 'Surface Energy,' page 8.

(8) Bubbles will break when they collide unless there is a stable film between them, preventing coalescence. Such stability is furnished by a dissolved substance that adjusts the surface-tension and also increases the viscosity of the film.

(9) A multiplicity of bubbles, or 'froth,' will serve a metallurgic purpose if it floats valuable mineral matter long enough to facilitate a separation from the valueless components of the pulp.

The recent trend of hypothesis—it has hardly the status of a theory— is to subordinate sundry ideas prominent a year ago.[36] The direct 'adhesion' of air to mineral particles is not so vital as was supposed, because air and mineral rarely come in direct contact in the flotation process; usually either the air-bubble has an oily film or the mineral itself has undergone oil-filming. The lowering of the surface-tension of water is still a fundamental factor, but this modification of the water is recognized as chiefly important not for the first consequence, which promotes the wetting of the mineral, but for its secondary result, which is to create a variable tension on the surface of a bubble-film, and thereby strengthen it greatly. The addition of acid has ceased to be essential, it having been found that alkaline water is better for the treatment of many ores. The acid, like the oil, is supposed to serve more than one purpose:

(1) To adsorb on the gangue and aid the wetting of it.

(2) To promote the flocculation of gangue-particles and the separation of them from the valuable mineral.

Fine grinding of the ore is recognized as necessary, not only to separate the mineral from the gangue, but to assist the making of a froth rich in mineral. No longer is the mineral supposed to be buoyed by the bubbles, as if tied to a cork, but the minute particles of mineral are believed to be drawn into the bubble-film, so that, to pursue the simile, the life-preserver of cork surrounds and encases the thing to be floated. The idea that a fixed proportion of oil to 'ore' is necessary has gone with the supposition that 'oil' only will perform the absorptive function necessary to a stable froth. Colloidal sulphur, sulphur dioxide, and salt-cake have been proved effective agents in froth-flotation; and we may expect a steady increase in the discovery of such substances until oil, which is expensive, is discarded. The parts played by emulsification and by the formation of colloid hydrates are becoming recognized as possibly important factors. The violent type of agitation has been found unnecessary, and, thanks to recent litigation,* it is

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[36] 'The Flotation Process,' 1916.

*See chapter on 'Litigation' elsewhere in this volume.

likely that the use of compressed air under low pressure will supplant the power-consuming devices of an earlier period. The trend is toward simplicity both of treatment and apparatus. When air and a cheap modifying agent are found adequate for the making of a mineral-bearing froth then the flotation process may be deemed fully developed.

ATTENTION may be drawn to the interesting statement made by H. Hardy Smith, elsewhere in this book, that natural grease, soluble in ether, was detected in the centre of a large uncracked piece of sulphide ore from a mine at Broken Hill. This may explain T. J. Hoover's interesting observation, quoted on page 21 of this volume. It remains to note the opinion of W. E. Simpson that the natural flotative agent is gelatinous silica formed by the reaction between fluorspar and quartz with the hot sulphuric acid used in the Potter process. Such gelatinous silica is said to have a selective adhesion for lustrous bodies, similar to those of oil or grease.*

AMONG recent patents for flotation-agents are No. 1,228,183 and 1,228,184, of May 29, 1917, issued to Henry P. Corliss for the use of alpha-naphthylamine and nitro-naphthalene respectively. The second of these is non-oleagenious and solid, but it can be dispersed in pulp so uniformly as to perform its frothing function most effectively. Only a quarter of a pound is needed, as used at the Magma mill, where also alpha-naphthylamine has reduced the copper tailing from 0.6 to 0.3% on a 4 to 4½% feed.† This may prove a discovery of the greatest importance, because, being neither 'oil' nor 'soluble', these substances can be used without conflict with the basic patents of the Minerals Separation company.

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*'The Potter Process at Broken Hill,' W. E. Simpson. M. & S. P., May 26, 1917.

†M. & S. P., July 14, 1917.

TESTING ORES FOR THE FLOTATION PROCESS

By O. C. Ralston and Glenn L. Allen

(Revised from the *Mining and Scientific Press* of January 1 and January 8, 1916)

Introduction. Although the subject of testing for flotation has been well presented in T. J. Hoover's book on 'Concentrating Ores by Flotation,' there is need of later information on this timely subject. Much testing has been done in laboratories not connected in any way with the Minerals Separation company, with which Mr. Hoover was formerly associated as metallurgical engineer, and there have been developed methods of investigation that may prove suggestive to many experimenters.

On that account we have compiled data on the subject of testing both from the literature available and from our own experience, as well as from what we have seen in other laboratories. This paper is designed to present the results of this compilation, with a critical discussion of the more important methods now in vogue.

On account of the empirical state of the art of flotation a great deal of testing is necessary before large-scale practice can be commenced on any ore; therefore a small laboratory-machine is necessary in which many tests involving many variables can be made in a short time. The machine must be so designed and so operated that a close approximation to the results possible with full-sized flotation machinery will be obtained. In a mill-plant it is a matter of some difficulty to control conditions through a wide range of such variables as temperature, acidity, quantity of oil, percentage of solids in pulp, fineness of grinding, etc., and as the proper treatment of a given ore can be ascertained only through testing it first, a critique of the testing methods in use is in order.

Many people have had the experience of reading the available literature on flotation testing and of failing to get satisfactory results when the described testing was attempted. To actually witness some good test-work and learn thereby the appearance of froth, the exact manipulation of the machine and froth, goes far toward bringing the beginner to a point where he can test efficiently. None of the literature mentions the fact that it is difficult to get a high percentage of extraction and a high grade of flotation concentrate at the same time. The beginner often strives after both of these things in a single test, whereas he should determine how each can be attained before he attempts to obtain both simultaneously. Furthermore, it is difficult to manipulate a small machine to give as good results as a large one, until after considerable practice. So the small machine is generally pessimistic, compared with the large one. It is practically essential for the beginner to weigh and assay all of his products in order to see if the extraction and the grade of concentrate are satisfactory, where an experienced manipulator can often tell by aid of past experience and the use of a glass or microscope whether he is getting good results or not.

With these points in view, we shall describe first the satisfactory machines and their operation. Then we shall give a more general exposition on what variables to study and what points to observe.

Flotation test-apparatus must necessarily be classified in the same way as large-scale machines, namely, as film-flotation machines, acid-flotation machines, and froth-machines of both pneumatic and mechanically agitated types. Film-flotation, as exemplified in the Macquisten[1] and in the Wood machines, does not seem to have the same wide application as does froth-flotation; hence little need be said about them.

The Wood machine can be built in miniature and for several years a small machine of the type sketched has been used in the plant of the Wood ore-testing works at Denver.[2] This small machine was about two feet long and one foot wide. The method of operation is the same as that of the full-sized machine. (See Fig. 1.)

As neither of these machines has been much used in practice, they are merely mentioned for the sake of completeness. Hoover[3] has recommended a test on a vanning-plaque, so that the sulphides will float off onto the surface of the water, but we consider this test of practically no value. Hoover, however, acknowledges that it is merely a test illustrative of the film processes.

In testing ores for the Potter or the Delprat processes, Hoover's text is again the source of information. A 200-c.c. beaker is used with 100 c.c. of 3% H_2SO_4 and brought to nearly boiling temperature. The ore when introduced into this yields a froth composed of sulphides supported by bubbles of CO_2. In case the ore is deficient in carbonate, an addition of as much as 3% of calcite or siderite is made. The froth is skimmed with a spoon as fast as it forms. We have noticed that a

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[1] M. & S. P., Vol. XCVI, page 414 (1908).

[2] H. E. Wood. Trans. A. I. M. E., Vol. XLIV, pp. 684-701 (1912).

[3] T. J. Hoover. 'Concentrating Ores by Flotation,' 1st edition, page 77.

great deal of mineral is often lifted partly but never reaches the surface. Consequently extractions are low, although the grade of concentrate obtained is often very good. For practical purposes, however,

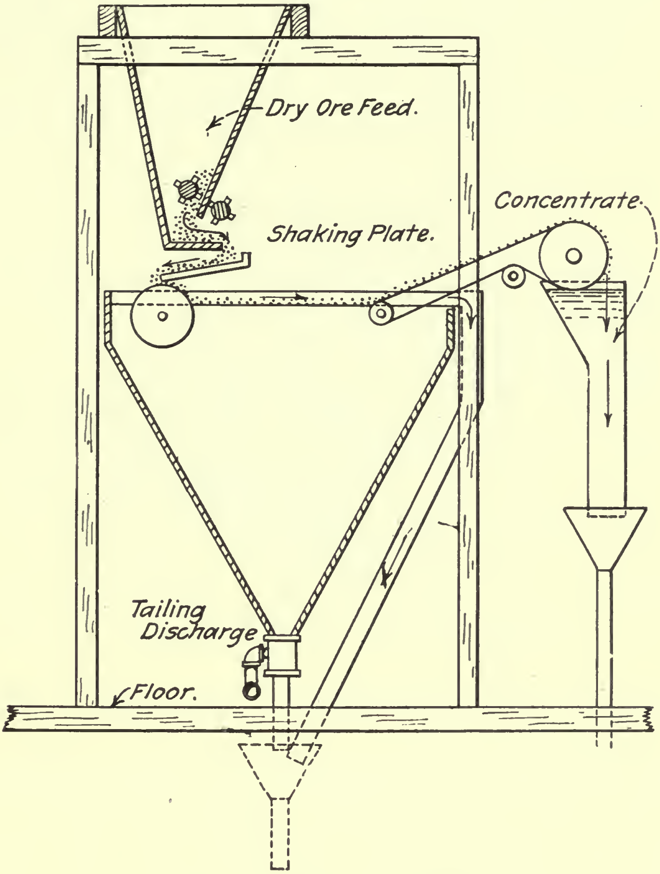

FIG. 1. THE WOOD MACHINE

the test is not of much value. A better test-machine is the small unit shown in Fig. 2. The acid should be allowed to run down through a section of garden-hose to within an inch of the surface of the ore and the ore should be kept stirred with a wooden paddle so that the bubbles of CO_2 generated by the action of the acid can lift the sulphides out of the body of the pulp. The froth formed should be skimmed with the paddle as fast as made, then filtered, dried, weighed, and analyzed. Not many ores yield gracefully to this treatment and slimes give poor extractions. Fines and Wilfley-table middlings are better adapted, and the presence of siderite in the pulp is desirable, as it reacts slowly with dilute acid. From 1 to 3% H_2SO_4 is best in testing and ½ to 1½% solutions on the large scale will give about the same results. The temperature of the pulp should be maintained at 70° C. by use of a steam jet. Five to ten pounds of ore per test is necessary. The extractions obtained are always lower than in full-sized units. While oil is not necessary in this process it will greatly assist in the flotation, and the addition of a small amount is often of much assistance in test-work.

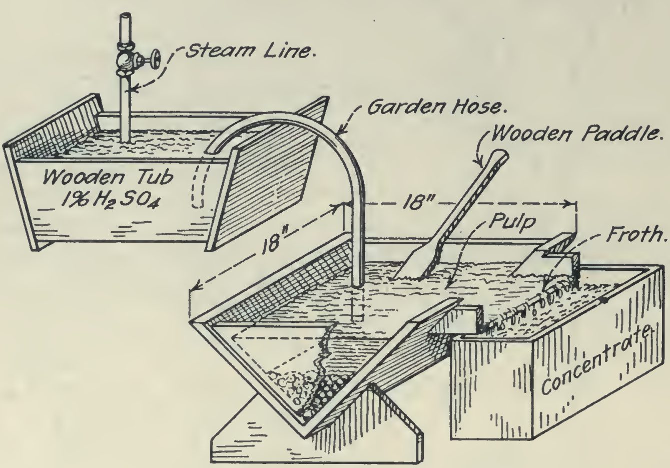

FIG. 2. A POTTER-DELPRAT TEST-MACHINE

MECHANICAL FROTHING as developed by the Minerals Separation company in England and Australia, and modified by many others, has been one of the most important methods of flotation. Therefore the laboratory machinery that has been developed is at as high a state of perfection as any such machinery now in use.

The Janney machine is probably the best designed machine for getting reliable quantitative results on a small quantity of ore. A sketch is appended (Fig. 3). It can be seen that the agitation compartment is cylindrical in shape and that its top is surrounded by a froth-box, which slopes into a spitzkasten, where the froth can be skimmed. The tailing sinks to a return-hole at the bottom, passing into the agitation-compartment again. To provide good agitation, four vertical baffles are attached to the wall of the agitation-compartment, against which the pulp is swirled by the two impellers. Lining the walls with expanded metal lathing or with a coarse-mesh iron screen adds to the thorough mixing that the pulp must receive. The two impellers are on a common shafting, which enters the machine through a stuffing-box in the bottom of the machine. The lower impeller with four vertical vanes is submerged; it agitates and emulsifies the pulp while the upper impeller, likewise with four vertical vanes, acts as a pump to lift the pulp and beat air into it. A pulley and belt connect the shafting with a variable-speed motor.

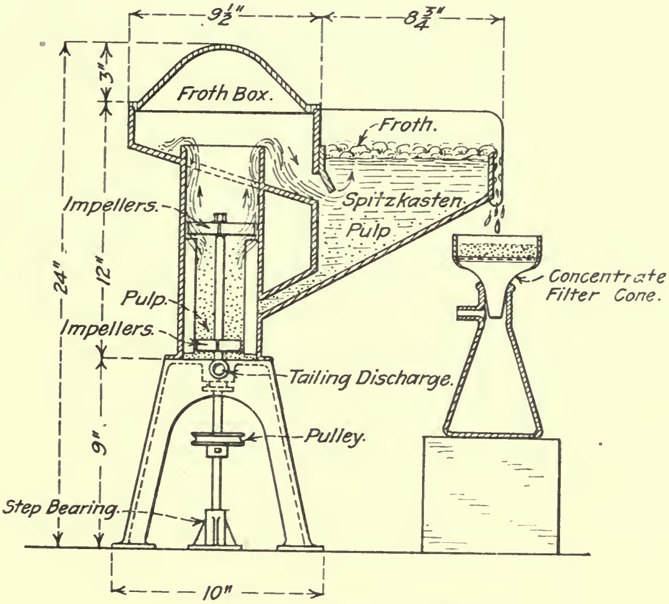

FIG. 3. THE JANNEY TEST-MACHINE

A dome-shaped lid is used on the machine. A small hole in the top of the dome allows the introduction of oil, acid, water, or other materials without the removal of the lid. The lid is so constructed that it can be turned upside-down with the dome extending down into the froth-box, and in this position it can act as a funnel. The dome rests then on the top of the agitation-compartment and no froth can escape into the froth-box. This allows a period of agitation of the pulp before the dome-top is turned right-side up to allow aerated pulp to overflow into the froth-box and down into the spitzkasten, where the froth can be removed.

A discharge-plug at the bottom of the machine allows the flushing out of tailing after the test has been completed. So careful has been the design of this test-machine that even this discharge-plug is beveled to fit flush with the bottom of the machine and thus afford no dead space in which the solids might settle.

The spitzkasten is long and narrow, in order to permit a deep froth to be formed and to travel over as long a space as possible, before reaching the discharge. This tends to allow more of the entrained gangue to settle out of the mineral froth. The sides of the spitzkasten are of heavy plate-glass, each fastened to a metal-frame by means of screws. The wrought-iron shaft projects through a brass stuffing-box and is supported by a ball-bearing beneath. All the other metal parts are of cast aluminum.

The small variable-speed motor may be of either D. C. or A. C. type. F. G. Janney recommends the use of a General Electric, shunt-wound, direct-current motor, for 230 volts, with a rated speed of 1700 r.p.m. and ¼ hp. The impeller-shaft is to be driven at 1900 r.p.m. maximum speed. For speed-control he recommends a General Electric direct-current field-rheostat, with an ampere capacity of 1.25 to 0.063 at 250 volts.

In our own laboratory it was desirable to use the ordinary city-lighting circuit of 110 volts, A. C. On that account we have found the following motor satisfactory: ¼-hp. General Electric repulsion induction motor, single-phase, 60-cycle, with full speed of 1780 and carrying 4.2 amperes at 110 volts, or 2.1 amperes at 220 volts, depending upon the voltage of the current supplied to the machine, either voltage being acceptable. Speed-control is obtained by the use of an ordinary field-rheostat in series with the motor. Such a motor has a speed varying with the load and with the voltage applied. As the load is practically a constant, the speed will depend upon the amount of resistance in series with the motor. As the majority of laboratories find a city alternating current more convenient to obtain, such a motor is recommended.

The operation of the machine is as follows: It is set up on a bench convenient to the sink and to running water. The motor is set up one foot to the rear with the switch and rheostat placed so that they can be easily reached while standing in front of the machine. A ¼-in. round-leather sewing-machine belt is used for drive. The bearings are well oiled, the stuffing-box is properly packed, and some attention should be given to it occasionally in order to see that it is kept screwed tight enough to avoid leakage.

Enough clear water is run into the machine to barely show in the spitzkasten and the motor is started at its lowest speed. A 500-gm.

charge of ore ground to at least 48-mesh is added and the cover placed on the machine in its inverted position. This is done to allow thorough mixing without circulation of the pulp. All or part of the oil and other reagents are now added and the motor brought up to full speed for 30 seconds. The speed is again lowered to the minimum and the cover is turned over into its upright position. The speed is then raised and water is added through the hole in the top of the lid until the froth in the spitzkasten is nearly at the overflow-lip. The ultimate speed of the agitator will depend somewhat upon the character of this froth, as some oils will give a deep persistent froth, while other froths are thin and brittle and allow of more water being added to the machine, as well as more violent agitation in order to beat more air into the pulp. The froth may either be allowed to flow out of the spitzkasten of its own weight or skimmed with a small wooden paddle. It is a good idea to wet the glass sides of the 'spitz' with water while the froth is rising, so that none of the froth will stick to the glass.

The duration of the test is about five minutes with an ore that floats easily, while other ores will require a considerably longer time to allow the entrained gangue to settle out of the froth before it is discharged from the machine. In such cases it is best to hold back the froth until its appearance shows it to be fairly clean. Beginners are likely to dilute their froth with too much gangue. In a large-sized machine the froth can travel over from four to eight feet of spitzkasten before it is discharged, while in this test-machine it only has a travel of about 10 inches. Consequently, the small machine is liable to yield concentrate of too low a tenor. The same applies to most other machines for making tests on flotation.

The concentrate may be caught in a pan or on a filter. After the test the machine is brought back to low speed and the tailing-plug removed, so that the tailing can be caught in a pan or bucket, or run to waste.

If it is so desired, this rough concentrate can be put back into the machine and treated in the same way as the original sample, or the concentrates from several tests combined to give enough material for re-treatment. If this is done three products are made, namely:

A 'rougher' tailing, to waste.

A clean concentrate, for shipment.

A 'cleaner' tailing or middling, which in actual practice is returned to the head machine.

When these conditions are observed results only slightly lower than those possible with a big machine can be obtained. A test can be run in from 5 to 30 minutes in such a machine with 500 grammes of ore in anything from a 3:1 to a 5:1 pulp. The glass sides of the spitzkasten allow close observation of the condition of the froth, and this is a great advantage to the beginner. The small amount of ore necessary for a test is a matter of considerable convenience, as fine grinding of the ore in the laboratory is often irksome. The aluminum casting is little corroded by either acid or alkaline electrolytes. The return of pulp from the 'spitz' to the agitating-compartment allows the material to be treated until all mineral has been removed without stopping the machine, so that a single treatment yields a clean tailing. However, a second treatment of this 'rougher-froth' is sometimes necessary in order to get a high-grade concentrate. Clean tailings generally mean only medium-grade concentrates due to entrainment of gangue, in the removal of all the mineral.

The stuffing-box in the bottom will probably leak if not watched. However, this driving of the impellers from below, instead of from above, leaves the top of the machine free for the operator and is more convenient in every way. This is of importance in a laboratory-machine, and will excuse the use of a stuffing-box. In large-scale machines a stuffing-box underneath would not be tolerated, and the drive should be from above. We would also suggest a sheet-lead construction as being more easily built. A $\frac{1}{4}$-inch sheet-lead is sufficiently rigid to stand up well, while it is ductile enough to be worked readily into the desired shape. The joints are easily burned, and it is acid-proof.

The Hoover Machine, Fig. 4, was designed after a test-machine described in the second edition of Hoover's book, being copied from one of Lyster's patents, and has been much copied by people wishing to make flotation tests. An improvement over this construction was published by Ralph Smith[4] recently, and a modified form of the same

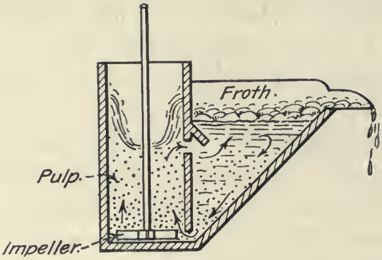

Fig. 4. ORIGINAL FORM OF HOOVER TEST-MACHINE

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[4] *E. & M. J.*, Vol. C, page 395 (1915).

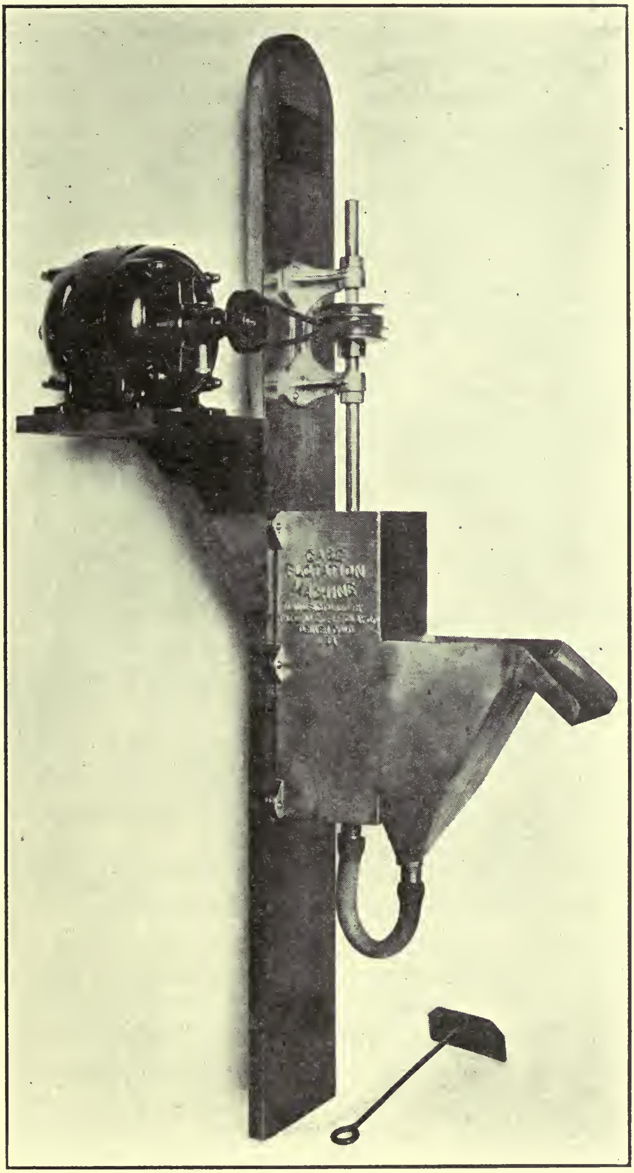

FIG. 5. THE CASE FLOTATION MACHINE

is shown in Fig. 5, which is that sold by the Denver Fire Clay Co. under the name of the Case machine, for $75. Either a variable-speed motor is belted to the pulley that drives the stirring mechanism, or a pair of cone-pulleys on a constant-speed motor is used. A less original machine but a fairly useful one is that described in the *Mining & Scientific Press* of April 15, 1916, which is said to be used at the Suan Concession, Korea. All of the dimensions are given in the drawing (Fig. 6) so that it can easily be built. Its capacity is said to be 100 lb. per hour and its total cost, including the motor, is under $50. It is used for checking small-scale tests and occasionally for separating chalcopyrite from scheelite in small lots. This construction has been popular because it can be made of wood, at small expense. The Janney machine will cost about $125, while the Hoover machine can be built for a small fraction of that amount. Mr. Hoover's original drawing does not show the spitzkasten drawn to a point, as only the front side was beveled. Our sketch shows both sides beveled. This is desirable, as it eliminates space in which fine sand can settle, and tends to minimize the amount of pulp lying inactive in the spitzkasten. In the agitation-compartment the pulp is swirled into the corners, where it is well mixed with air; hence the baffles sketched in the Janney machine are unnecessary. One objection, however, is that unless the agitation-compartment is very tall the pulp being swirled into the corners has a tendency to splash out, and a lid similar to the one on the Janney machine is desirable. However, it is difficult to attach one because the stirrer-shafting is in the way. The operation of this machine is practically the same as that of the Janney, except that without glass sides on the spitzkasten it is hard to get as clean a froth.

One very simple and inexpensive machine of recent development is the McPherson, shown in Fig. 7. As can be seen, it is of the ordinary agitating-box and spitzkasten type. A disc-drive from a countershaft, driven at constant speed, and capable of adjustment such that the driving disc may be moved in or out from the centre of the friction-disc, allows of variation in speed. Such a machine does not call for a variable-speed motor and this is its main claim to novelty. The body of the machine is of rather light construction being made of sheet-metal and painted with acid-proof paint. It is sold for $35 by the Calkins Company of Los Angeles.

A most interesting test-machine is that of Roy & Titcomb, of Nogales, Arizona, which is run by hand-power by means of gears and a balance-wheel. This machine is shown in Fig. 8. The impeller shaft

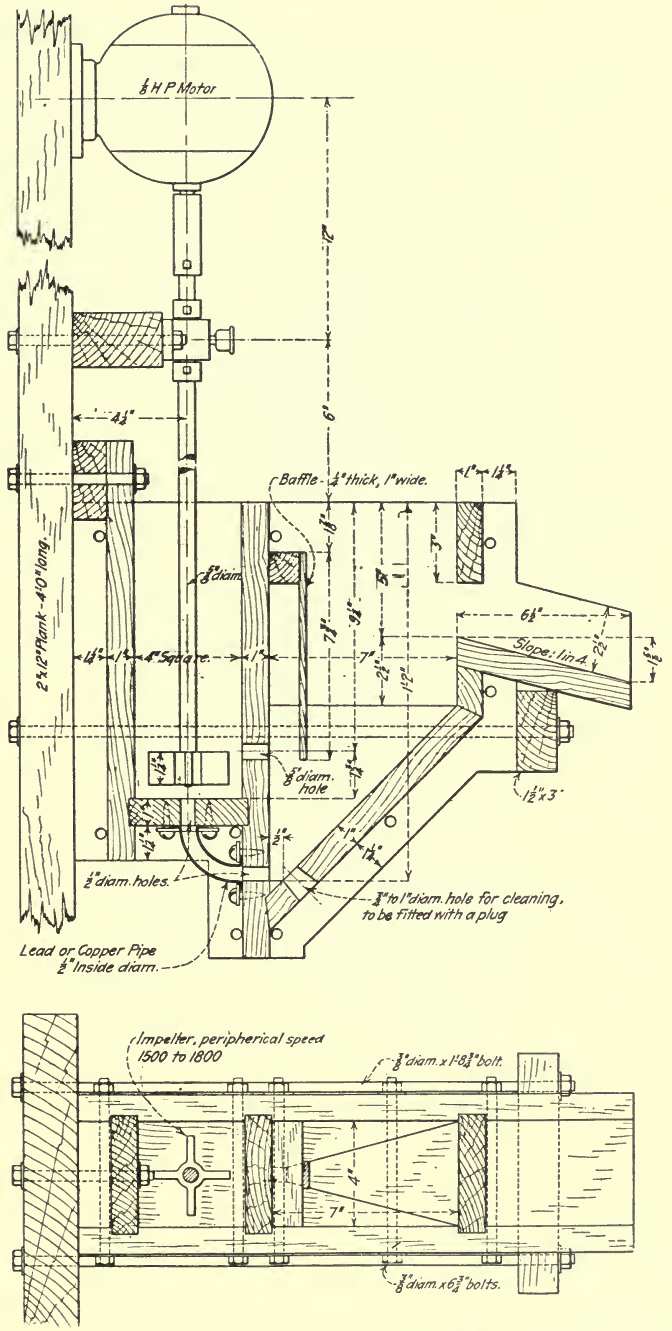

FIG. 6. FLOTATION MACHINE USED AT THE SUAN CONCESSION, KOREA

is suspended on ball-bearings and the cells are cast in one piece. The possibility of taking such a hand-driven machine into remote localities for test-work is immediately suggested. It costs $85.

The Slide Machine, as shown in Fig. 9 and 10, was designed by Hoover and perfected by many others. In recent practice it is motor-driven. A number of these machines were given by James M. Hyde to various universities in this country. Many people favor this apparatus for the reason that they have had little opportunity to use any other design. In this machine the agitator is driven from below through a stuffing-box, as in the Janney, with the consequent freedom of the top of the machine for the convenience of the operator. The top half of the machine is so constructed that it can be slid to one side, cutting off the froth formed in the agitation from the gangue, which is allowed to settle. The operation consists in agitating with oil and other reagents, then a period of quiet during which the froth collects at the top while

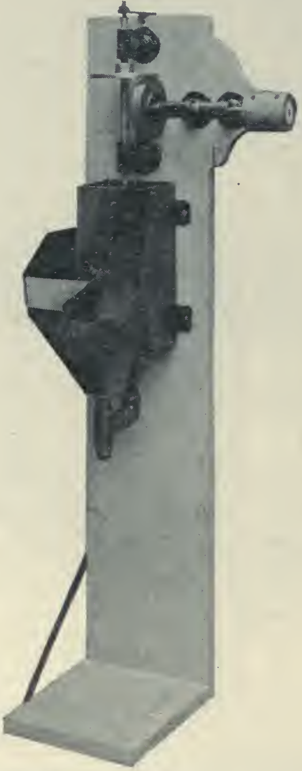

Fig. 7. THE M'PHERSON FLOTATION MACHINE

the gangue sinks. Two windows in the side enable the observer to see when the gangue has subsided sufficiently to allow the top half to be slid along the rubber gasket, cutting off the froth from the remainder of the pulp. The time necessary for the settling of the gangue is sufficient for much of the gangue to separate from the froth, leaving

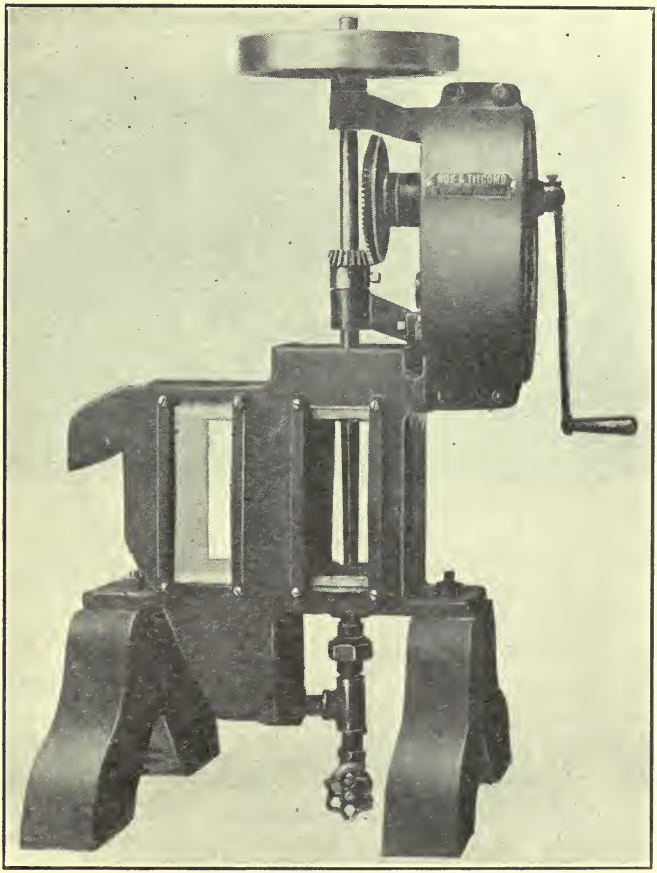

FIG. 8. ROY & TITCOMB TEST-MACHINE

only clean sulphides in the froth. This element of the machine has made it of some value in testing flotation-oils, but in a weak froth much of the sulphide mineral also settles out and is lost, so that the test results with this machine often show unnecessarily low extractions and a high grade of concentrate. On the other hand, when conditions are adjusted to give a froth persistent enough to hold all the sulphide mineral, considerable gangue is entrained in the stiff froth. Further, after skimming one froth we find it necessary to add more water and start the machine again to make more froth. It is hard to make the slide machine give a high extraction with only one agitation. The intermittent character of such work and the time necessary to wait while settling are disadvantages that make the Janney or the Hoover machines of greater utility, in our opinion. The parts are of cast aluminum with a rubber gasket between. A charge of 500 to 1000 grammes of ore is used.

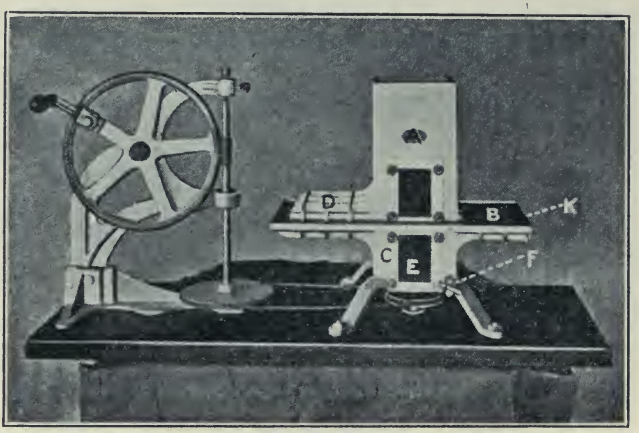

FIG. 9. THE SLIDE MACHINE

One other test-machine, designed more recently, is that of Kraut & Kollberg, often referred to as the K. & K. It is a reproduction of the larger machine of the same make (shown on another page) although it does not do the large machine full justice in the test-work done. It consists of a cylindrical rotating drum covered with longitudinal riffles contained within a cylindrical casing placed on one side of a spitzkasten, into which the agitated pulp is thrown by the motion of the rotating drum. It is adapted to a charge of about 2 lb. or 1000 gm. of ore. It is opened by loosening the hinged top which is held by thumb-screws. A great deal of time is necessary in cleaning out this machine after a test. The tailing can be drained out by pulling a stopper in the bottom. Oil and other reagents are introduced during a test through a small hole in the front. Sand will tend to accumulate, during a test, on the bottom of the machine. Fast and loose pulleys are provided and the speed recommended is 400 r.p.m. The machine is sold by the Braun Corporation of Los Angeles for $75.

Separatory Funnels. During the past year an article on practice in Mexico[5] mentioned the fact that much of the preliminary testing on the ore was done in separatory funnels, in which the charges of pulp, oil, etc., were shaken, after which the cock at the bottom of the funnel was opened and the tailing run into a second separatory funnel for further flotation tests, the cock being closed in time to catch the froth. The versatility of experiment shown by the use of such apparatus (Fig. 11) is commendable. Obviously, this arrangement is open to the same objections as is the slide machine, except that separatory funnels are simple and inexpensive.

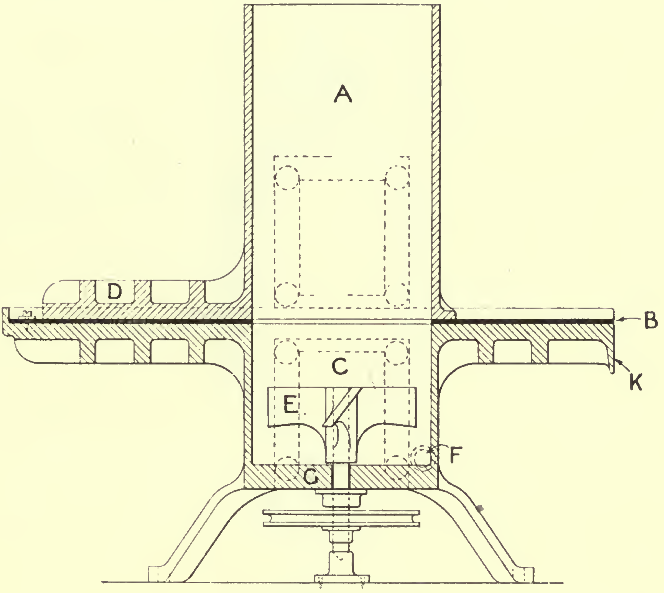

Fig. 10. THE SLIDE MACHINE

Elmore Machine. As far as we know, no small test-machine for the Elmore process has come into common use on account of the fact that the pulp must be lifted through a tube corresponding in length to the column of water equivalent to barometric pressure. This makes an awkward laboratory machine. Mr. Hoover (2nd edition, page 98), describes ''illustrative'' experiments with the pulp in a bottle connected with a water-pump for producing a vacuum, but no quantitative method of this kind has been developed.

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[5] M. & S. P., Vol. CXI, page 122 (July 24, 1915).

Other miscellaneous frothing tests are in the literature but most of them are merely ''illustrative.'' Putting a charge into a soda-water siphon, pumping in air to dissolve the water, and then releasing the charge into a beaker gives nice-looking froth. In some of the lawsuits square glass candy-jars (Fig. 12) with a motor-driven impeller have been used to show flotation phenomena in court. In a recent U. S. Patent (No. 1,155,836) taken out by T. M. Owen, one of the engineers of the Minerals Separation, Ltd., is a sketch of a simple test-machine made of an ordinary 2½-litre acid-bottle. (See Fig. 13.) This corresponds to the sub-aeration type of machine and is recommended by Mr. Owen for test-work when such a type of machine seems necessary, as in differential flotation. Air is led into the pulp through the stopper in the bottom and beaten into the pulp by the impeller. The four large baffles above the impeller prevent the swirling of the pulp from rising through them, so that there is a quiet zone in the top of the machine where the froth can collect. One great beauty of such a machine is that any froth formed will rise immediately to the

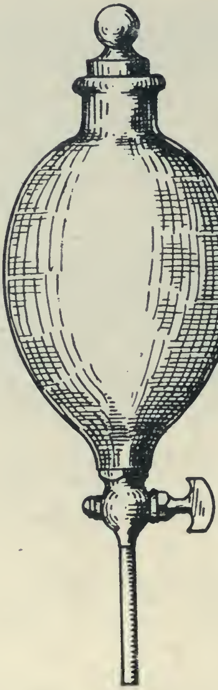

FIG. 11. SEPARATORY FUNNEL

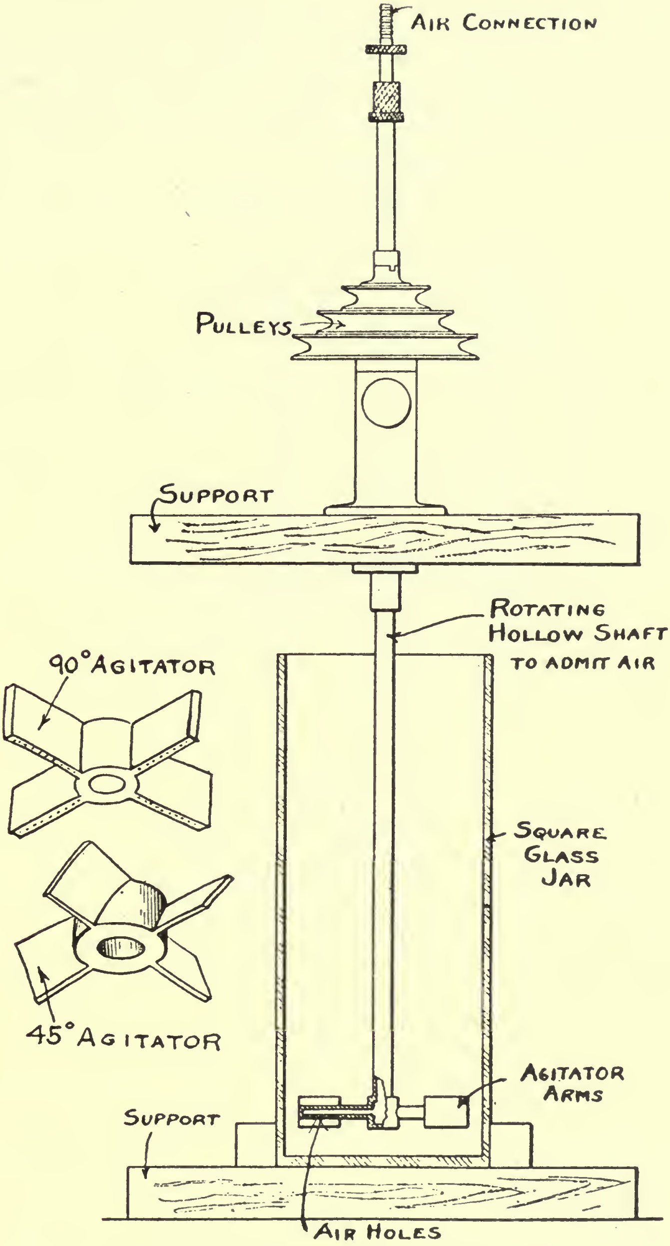

Fig. 12. THE SQUARE GLASS JAR MACHINE

discharge. However, we believe that the Janney and Hoover machines are the most useful of the mechanically-agitated type.

Pneumatic Flotation. Among the different pneumatic machines, as far as we are acquainted, the Callow test-machine is the only one of laboratory size that has been much developed. It is merely the commercial Callow machine reduced in size. (See Fig. 14.) Later development in the laboratory of the General Engineering Co., in Salt Lake City, has resulted in the reproduction of the whole plant in miniature, with Pachuca mixer, roughing-cell, cleaning-cell, vacuum-filter, and sand-pump to return middling to the Pachuca mixer. As seen in the drawing, the pulp is mixed well in a Pachuca tank of small size, over-

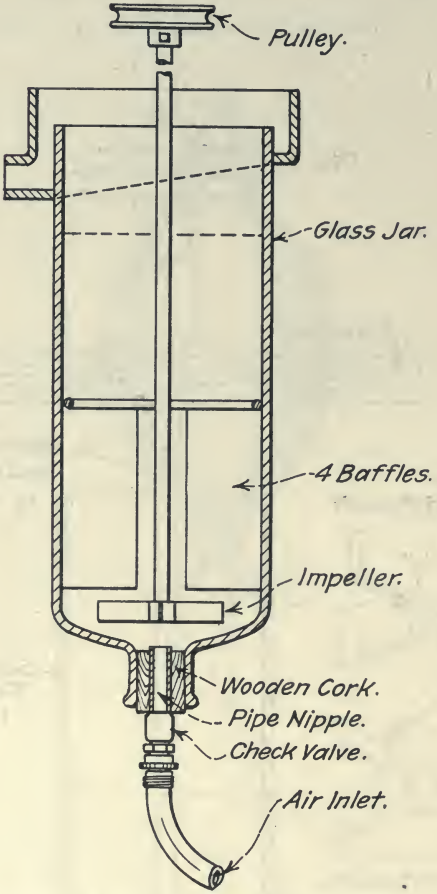

Fig. 13. OWEN TEST-MACHINE

flowing into the rougher flotation-cell. The tailing from this rougher goes to a sand-pump and is returned to the Pachuca. The froth is treated in a second and smaller pneumatic-flotation unit, giving a concentrate that overflows into an ordinary laboratory vacuum-filter actuated by a water or aspirating pump. The tailing from the 'cleaner-cell' consists of a middling that likewise flows to the sand-pump and back to the Pachuca.

A novice will have no small difficulty in operating such an installation, as there are a number of things to be kept in operation at the same time. The mixture of ore, water, oil, and any other reagents is fed either into the suction of the sand-pump or into the top of the Pachuca after air has been started into the various machines. The overflow from the Pachuca into the rougher-cell accumulates until a nice froth is coming up and nearly overflowing. Then the tailing-discharge valve on the rougher is gradually opened and froth allowed to overflow from the cell into the 'cleaner'-cell. It is best to get most of the charge circulating before much concentrate-froth is allowed to overflow, the overflow of froth being controlled by the main air-valves leading to each unit. After the valves into the individual wind-boxes beneath the machine have been once adjusted they should never be disturbed, and all control of air supplied should be at the valves in the main pipes. When everything is going well, the air-pressure in the cleaner can be increased until concentrate-froth is overflowing into the vacuum-filter. A wooden paddle to stir any settled material in the flotation cells is of value, as well as a small jet

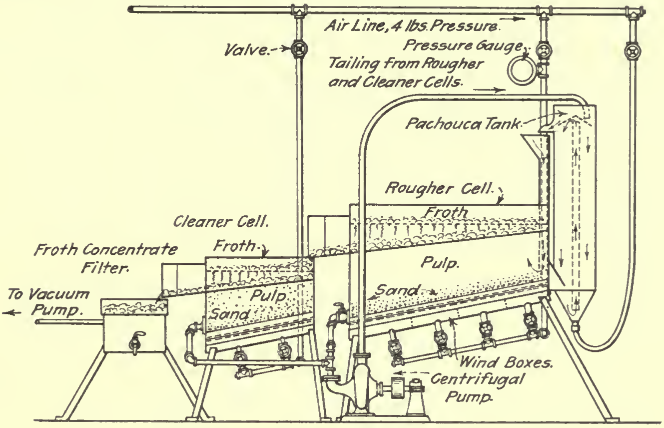

FIG. 14. CALLOW TEST SET

of water from a rubber hose for washing concentrate along the froth-launders and for beating down froth when occasional too-violent rushes of froth from the cells take place. After a test is complete the pulp should be drained completely from all parts of the machine while the air is still blowing, so that solids will not settle in passages or clog the canvas blanket in the cells. Only practice will allow anyone to get reliable results with this machine. A watch-glass for catching and panning occasional samples of froth is another necessary auxiliary to this equipment. The cost of installing such a set of apparatus is from $100 to $150. At least 1000 grammes of ore is required for a test and about 30 minutes to 1 hour is spent. It can be seen that nothing but a finished concentrate and a tailing are obtained. The machine is said to give results closely paralleling those obtained with larger-scale apparatus. A source of supply of compressed air at 3 to 5 lb. per sq. in. is necessary and the main valves on the air-pipe leading to each machine should be of some type of needle-valve in order to ensure exact control.

Laboratory Manipulations. Turning from the description of the machines used to the operations on the ore before and after the flotation operation, we have in general the problems of crushing the ore and of drying the froth-concentrate.

As a rule laboratory machinery for the pulverization of ore is of the dry-grinding type, with the exception of small ball-mills that can crush from 1 to 100 lb. charges in the wet. Consequently, most people start with weighed charges of finely-ground dry ore, a known quantity of water, of oil, and of acid or alkali. Our experience has been that most dry-ground ore must be treated in an acidified pulp to get good flotation. Doubtless the surfaces of sulphide particles become somewhat oxidized in, or shortly after, dry grinding and the function of the acid would be to clean the slightly oxidized surfaces. Wet grinding usually does not call for so much acid. One interesting experience is that of L. B. Pringle, working on ores from south-east Missouri. He found that drying of a sample of mill-slime before floating in a laboratory machine gave a much higher tailing and a lower-grade lead concentrate. On that account the laboratory samples were kept under water and the proper weight of pulp was obtained for each test by the use of a graduate and a hydrometer, always taking enough of the pulp to get 500 grammes of solid. Sulphuric acid did not seem to rectify the oxidation effect obtained in drying because calcium and magnesium carbonates tended to float with the concentrate in the acid pulp.

In nearly all laboratory work finer grinding than is used in practice seems to be necessary. This may possibly be due to the smaller amounts of froth that are formed. Such small quantities of froth cannot form layers as deep as those made in the large machines. If a big particle of sulphide can be entrained with a number of smaller particles, it can be floated, but with a thin froth the chance of such entrainment would seem to be less. Some experimenters have informed us that they were able to float even as large as 30-mesh material, but our own experience is that 60-mesh material is often hard to float with any chance of getting a high extraction, while the operation is performed with much more ease and expedition when the ore is crushed somewhat finer.

Wet grinding is more desirable, as it parallels conditions in practice, where most of the finer grinding of ore is in Chilean, tube, and other mills. However, wet grinding is harder to manipulate in a small laboratory and requires more time. The dry weight of the feed to the flotation machine must be known; hence a weighed charge of dry ore crushed to about 10-mesh can be introduced into a porcelain or iron pebble-mill for grinding and ground for the length of time found necessary to reduce the pulp to sufficient fineness—15 minutes to 24 hours. The charge can then be poured and washed through a coarse screen (to retain the pebbles) into a bucket and thence into the flotation machine. The oxidation of sulphide surfaces is thus avoided, but separate grinding of each charge, in order to know its exact weight, is rather tedious and requires a number of small mills if many tests are being run, on account of slow speed in grinding. A mill with iron balls rather than pebbles is of greater service. It is possible to introduce the flotation-oil before grinding, to be sure that it will be thoroughly mixed. For thick viscous oils this is highly beneficial, as a ball-mill gives about the best conditions for agitation and mixing. Usually 1 to 2 lb. charges are used and a small laboratory mill of the Abbe type serves well, although a good mill can be made with a 10-in. length of 8-in. iron pipe and two heavy iron caps for the same.

Practice in our laboratory has been standardized to a laboratory-gyratory breaker crushing to 10-mesh, splitting into weighed samples kept in paper bags and reduced to smaller size by either wet or dry grinding as occasion demands.

A short-stemmed tin funnel about 6 inches in diameter with a one-inch opening is found to be about the most convenient means of pouring a charge of ore into a laboratory flotation-machine.

The measuring and testing of flotation-oils in the laboratory has been very inexact in many instances witnessed by us. It is common

FIG. 15

practice to count the number of drops of oil falling from a small piece of glass tubing. We are using a Mohr pipette of 1 c.c. total capacity for measurement of the amount of oil used in each test. Such a pipette is shown in full size in Fig. 15. It will be seen that this pipette allows measurement of the oil to the nearest 0.01 c.c., which is as close as will ever be desired. If the density of the oil is known, the volume as measured by this method is quickly converted into the weight of oil used.

The testing of oil samples for flotative power is a matter that needs standardizing. It is desirable to classify oils according to flotative power, but just how to do this is not exactly clear. A unit of 'flotativeness' might be established and each oil referred to that unit in terms of percentage. But it has to be remembered that the best oil for one ore may not prove to be the best oil for another, although two such series of oils might roughly parallel each other. For any given ore, it would be permissible to make such a measurement on a series of oils and group them according to some definite standard. A standard oil might be chosen and the value of a second oil expressed in percentages of the flotative power of the first as determined by using equal quantities of the two oils in tests on an ore under identical conditions. This test could not be fair for the reason that different amounts of two different oils are necessary to accomplish the same results. Further, the conditions of acidity or alkalinity might favor one oil and handicap another. If we measured the amount of oil necessary to give a fixed percentage of recovery the first of the above objections would be satisfied but conditions of acidity or alkalinity could make the test unfair for some oils. Hence the dilemma as to a standardized test of a flotation-oil.

No single test could definitely place an oil in any scheme of classification and nothing can be done but run a series of tests using varying amounts of the oil to be tested and with varying acidity or alkalinity. The temperature of the pulp must be kept constant although it has a minor effect.

Coutts gives about the only directions on oil-testing that are to be found in the literature of the subject.[6] He states rightly that the

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[6] J. Coutts. E. & M. J., Vol. XCIX, page 1079 (1915).

first thing to do with an oil is to measure its density, for future calculations, as it will be measured by volume in the laboratory and must later be reduced to weights. He recommends the use of a burette for measuring the oil, but we favor the Mohr pipette mentioned above. He chooses a standard ore on which all tests are to be run and classifies three different kinds of standard tests: (1) for mixed sulphides, (2) differential separation, and (3) flotation of copper and iron sulphides. He states that oils high in phlanderene have proved best for differential separation of zinc-lead sulphide ores. While this is helpful, he does not state just how the oils are to be classified after the tests have been made.

Much work with oils is needed in order to determine if there are any definite constituents in oils that give them flotative power. Research is also needed in the preparation of oils from the wood, coal, and mineral oils in such a manner that they will have maximum efficiency in flotation. Work on this subject has been initiated in our own laboratory and it is known that several of the larger companies have employed oil-chemists to look into such problems. We understand that most excellent work is being done on methods of modifying and reconstructing oils that can be had cheaply. By this we mean more than mere mixing of a good flotation-oil with a cheaper non-selective oil. Sulphonating the oils, dissolving them in acids, dissolving modifying substances in the oils, etc., are some of the ideas being tested with varying success. It is on account of all this oil-testing that considerable progress has been made in flotation during the past few years, so that now most of the larger companies are using cheaper oils than they were formerly.

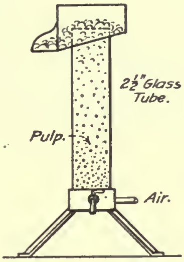

FIG. 16. CALLOW QUALITATIVE TESTER

When starting to work with a new ore, there is needed a rapid qualitative method of choosing an oil that seems well adapted to the flotation of the ore in question. Such a scheme is in use in the laboratory of the General Engineering Company in Salt Lake City. Their qualitative tester is designed to test oils for use in the Callow pneumatic flotation cell and consists of a glass tube of about two inches diameter and two feet long. (Fig. 16.) This can be set on end and closed at the bottom with a one-hole rubber stopper through which passes a glass tube into a small canvas bag. The small bubbles of air coming through the canvas are similar to those used in large-scale machines and can be observed through the glass walls of the tube. With some pulp in the tube, oils, acids, salts, etc., may be added in very short tests until the proper appearance is obtained. An overflow lip is provided in case it is desired to examine the mineral in the froth. A slight adjustment of the air will provide an ample overflow of froth. Two alternative methods of making the bottom of such a cylinder, as published by Alfred T. Fry, of Broken Hill, in the *Mining and Scientific Press* of February 3, 1917, are shown in Fig. 17.

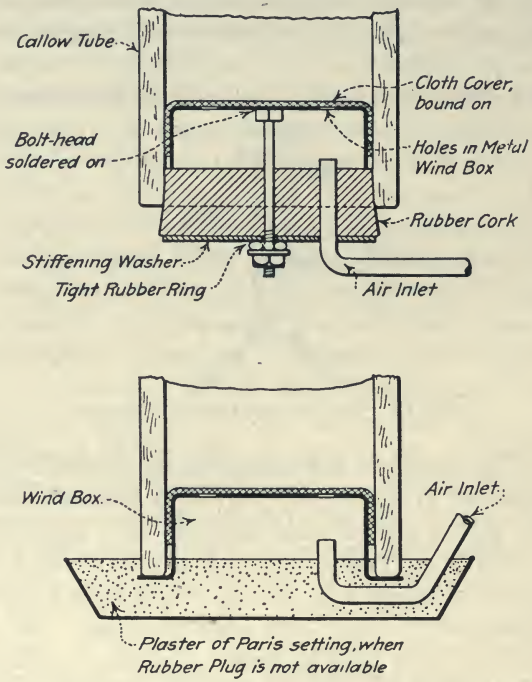

FIG. 17. METHOD OF PLACING POROUS BOTTOM IN OIL-TESTER

DISPOSAL OF THE FROTH. The handling of the flotation froth in the laboratory finds difficulties which are reflected in practice. It is often very slow to settle and filters with difficulty. A vacuum-filter, connected with a laboratory aspirating pump, is a very convenient method of getting the concentrate out of the froth. A large porcelain Buechner funnel fitted into a filtering flask, as shown in Fig. 3, is used at present in our laboratory. A copper vacuum-filter of much the same type, provided with a porous false bottom of acid-proof wire-cloth, resting on a punched plate, is shown in Fig. 14 of the Callow test set. Filter-papers can be laid over the bottom of either of these funnels to collect the concentrates and the vacuum beneath sucks out the water and oil of the froth. Such a filter can be placed under the froth-discharge of a flotation machine so that a fairly dry cake of concentrate is ready for further drying at the end of the flotation test. By loosening the outer rim of the filter-paper and then turning the funnel upside down over a pan, the filter-paper with the concentrate can be dropped into the drying-pan by gently blowing into the stem of the funnel. This is set aside in a warm place to dry and later weighed against a filter-paper tare.

If it is desired, the froth can be collected in a glass beaker or other vessel and allowed to stand over-night. A layer of clear water can then be siphoned off and the thick pulp remaining filtered or dried direct. In some laboratories the froth is dumped onto a shallow pan on a hot plate and the water evaporated. Occasionally such a sample of froth will be left too long, and will be ignited and roasted. We once used a numbered set of shallow pans for such evaporations but prefer filtering before drying the precipitate. A numbered tag is now put in each pan along with the cake.

The products coming from the flotation machine should be watched closely and occasionally panned or examined with the microscope to see what kind of work is being done. This is fairly easy to determine as the sulphides are most of them distinguished easily from the gangue under the miscroscope, and likewise gangue particles in the froth concentrate can often be distinguished. A microscope is a most useful adjunct in a flotation laboratory or mill.

General Considerations. We have mentioned at various places the relation of the laboratory tests to the large-scale operations and now repeat that in almost every instance the laboratory results are somewhat pessimistic as compared to large-scale work. The reasons are made apparent by the smallness of the machine and the shallower layer of froth often formed under these conditions. Moreover, laboratory operations seem to call for greater amounts of oil, acid, etc., than do the large-scale operations.

Only one of the above machines is adapted to 'roughing' and 'cleaning' operations in a single test. Present-day practice tends toward re-treatment of at least part of the froth in order to make cleaner and higher-grade concentrates. Consequently, it may be desirable to collect enough froth from a series of tests to be re-treated in a 'cleaning' test. Of course, this is provided for in the Callow test set, where only 'cleaned' concentrate is discharged from the machine. It is further found desirable to weigh and analyze some of the successive fractions of the froth being discharged from a flotation machine, as the tailing becomes leaner, and determine at what point it may be desirable to re-treat such froth.

Many reports of flotation test-work with mechanical-agitation machines give the speed of the rotation of the agitating-blades. We have found that it was possible to get much the same work done with quite a variation of speeds, the only effect being to lengthen or shorten the time of treatment. We feel that the importance of this matter has been much exaggerated. Some means of speed-control is necessary and the speed can be adjusted in each case until the froth presents the proper appearance as to depth, size of bubbles, color, etc. Speeding toward the end of a test in order to give a deeper froth with a faint line of concentrate on the very top is often advisable. We recommend adjusting the speed in each test to suit the other conditions, rather than running a series of tests with different speeds. Only in the slide machine, where operation of the impeller must be suspended in order to allow froth to collect, is the speed of much importance. Here we recommend agitation for a definite length of time, and then a period of settling. The effect of variation of speed during a definite length of time may be a considerable variation in the amount of froth collected during the quiet period. Hence we are prejudiced against the use of the slide machine except for oil-testing.

When a good set of conditions has been found for the flotation treatment of an ore, it is best to recover the water from each test to see what effect a closed circuit of the mill-water will have. Some oil and chemicals are thus recovered, cutting down the amounts necessary for operation. In fact, a carboy or two of the water to be used in the large mill should be used to make certain that no deleterious contamination will ensue from this source. Under these conditions filtration of the concentrate and tailing for recovery of the water is necessary. Such conditions are provided for in the Callow apparatus, above described, and can be applied easily to any of the other machines.

Oil samples for test purposes can be obtained from the various wood-distilling companies now advertising in the technical press, from gas companies and from petroleum-refining companies.

In attacking refractory ores, there are a number of ingenious things that can be done to the pulp both in and out of the machine. The trouble may be due to deleterious substances, which sometimes can be washed out, rendered harmless by boiling, or by acidifying, or by making alkaline with lime before entering the machine. Occasionally, the ore will not work well under ordinary conditions but will yield beautifully after finer grinding. Sometimes extra reagents are necessary, such as powdered charcoal, modified oil, argol, soap, calcium sulphate, alum, etc. A rational method of devising the proper tests in such cases must be based on some theory of flotation. Colloid chemistry is a branch of knowledge that we believe to be very necessary for such work, as it has facilitated a more intelligent control of our tests and has given wonderful results in a number of instances.

Finally, it is well to be prodigal in the amount of analytical work connected with flotation testing in order to discover interesting differences in gangue-constituents carried into the concentrate, as well as to find the best conditions for leaving out some gangue constituent that is less desirable than the rest. If an experimenter does his own analytical work he can be expected to spend three-fourths of his time analyzing what has been done during the other fourth.

DIFFERENTIAL FLOTATION

By O. C. Ralston

(Written especially for this volume)

Introduction. Many names are used to express the fundamental idea conveyed by the above title. 'Preferential' is used more particularly to designate the process claimed in patents issued to E. J. Horwood of Australia. 'Differential' implies that one mineral is being floated to a greater degree than another flotative mineral also present. Moreover, it is a broader term than 'preferential' because the latter is coming to mean the process, patented by the man who used it first, equivalent to fractional roasting and flotation. 'Differential' has found acceptance in England and in Australia but it has not yet been adopted in the United States.

For the benefit of those who have not read my earlier compilation misnamed 'Preferential Flotation,'* it may be well to abstract a portion and to state that differential flotation is now obtainable in three ways:

I. By fractional roasting and flotation.

II. By the use of certain dissolved substances in the pulp.

III. By close control of the physical conditions regulating flotation.

I. Fractional Roasting. H. A. Wentworth, in U. S. patent No. 938,732, of 1909, claimed the fractional roasting of "ore mixtures containing several sulphides," so that one mineral would be deadened while the others would float. He seems to have meant film-flotation.

A. S. Ramage, in U. S. patent No. 949,002 of 1910, stated that the "principle of my process is founded on the combination of fractional roasting with chemical floating;" in other words he had particularly in mind the warm-acid methods of DeBavay, Potter, and Delprat.

E. J. Horwood, in U. S. patent No. 1,020,353 of 1912 and No. 1,108,440 of 1914, claims "preferential flotation," which depends on deadening the surfaces of such minerals as galena and pyrite by a short flash-roast, while sphalerite and chalcopyrite are unaffected and can be later removed by flotation. This process† has been employed on the Broken Hill mines of the Zinc Corporation and the flotation

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*M. & S. P., June 26, 1915. Also 'The Flotation Process,' by T. A. Rickard, p. 71.

†The operation of this process is well described by Allan D. Rain in a separate paper elsewhere in this volume.

used has been the modern air-frothing method of the Minerals Separation company.

Fractional roasting and flotation are said to be in use in the North Star mill of the Federal Mining & Smelting Co., near Hailey, Idaho. The most serious objection to it is the large amount of sulphuric acid necessary in order to obtain good flotation of the zinc sulphide after the roasting. The iron sulphides are effectively deadened.

In the mill of the Progress Mining & Milling Co., near Robinson, Colorado, a complex zinc-iron-lead ore is receiving table-treatment to make a good lead concentrate and a zinc-iron middling. This middling is roasted, ground, and treated in a mechanical agitator for flotation of the zinc.

In U. S. patents 1,197,589 and 1,197,590 of September 12, 1916, Raymond F. Bacon calls attention to the fact that in such fractional-roasting processes part of the minerals that it is desired to have deadened will not be oxidized and part of those that are not wanted to oxidize are nevertheless oxidized. Besides, in some ores the sulphides are so intimately mixed that a clean separation is impossible by any crushing process. He inclines toward more complete oxidation of the ore, followed by sulphidizing with a soluble sulphide, or even getting one of the constituents into solution and then sulphidizing. Thus, for pyritic ores containing some copper, the treatment recommended is to roast long enough to completely decompose the iron sulphides, although part of the chalcopyrite will resist roasting. During the roasting part of the copper minerals will also be roasted and lost if treated directly by most of the previously mentioned methods of fractional roasting and flotation. Bacon treats the fractionally roasted ores with enough sulphuric acid to get the copper into solution and then adds hydrogen sulphide to precipitate it as sulphide. The flotation treatment that follows will then recover both the natural and the artificial sulphides of copper.

In the case of copper-zinc sulphides the same idea can be applied. A complete roasting of the ore is necessary, and then copper and zinc are taken into solution by sulphuric or other acid. The application of hydrogen sulphide to the pulp containing this solution will precipitate only copper sulphide. After flotation of the copper sulphide the pulp is neutralized and an alkaline sulphide is added to precipitate zinc sulphide, which is then likewise floated to remove it from the gangue. In commenting on this process, I would say that in the first place the complete roasting of zinc sulphide is a difficult and expensive operation. Secondly, there would almost certainly be some iron dissolved from the ore and it would accompany the zinc, being precipitated as iron sulphide with the zinc sulphide. This is undesirable from the standpoint of the zinc smelter. Moreover, the flotation of copper sulphide in the presence of large amounts of zinc and iron sulphides in solution presents considerable difficulty. Since Dr. Bacon also claims the application of this method directly to oxidized ores, as well as to the abovementioned sulphide ores, and as oxidized ores nearly always contain considerable amounts of acid-soluble iron compounds, I am inclined to believe that he has obtained a 'paper patent.'

Numerous other separations of this kind are claimed in his patent. Nickel-copper ores and lead-silver-zinc ores are mentioned. The use of sulphurous acid in place of sulphuric acid is also specified.

While the underlying chemical ideas described in this patent are excellent, I feel justified in stating that the practical details of flotation in such solutions, the cost of the large amount of chemicals required in many cases, and the difficulties of roasting in other cases, are enough to make the process too costly.

I have recently unearthed a British patent containing a somewhat different idea. It was granted to Sulman & Picard, consulting chemists to Minerals Separation, Ltd., and is numbered 8650 of 1910. While its claims are more broad than here indicated, the particular application is to roast mixed sulphides to oxides; then to treat the roasted ore at about 600° C. with carbon or a reducing gas. Only the easily reducible metals, such as lead and copper, will be reduced to metallic form, while zinc and iron are not affected. Hence, theoretically, at least, it should be possible to obtain a separation. Whether the process works satisfactorily I do not know. It should be a good method for recovering lead and copper left in a zinc concentrate, but it would, of course, be undesirable where the zinc concentrate contains much iron. However, to roast completely, to an oxide, an ore containing zinc sulphide, is a long and costly operation and it has yet to be proved that the subsequent reduction gives a product capable of economical separation by flotation. It is now generally known that metallic copper, in a finely divided condition, can be floated satisfactorily, and it is possible that the same can be done with freshly reduced lead, but there is no certainty that the ore will be in such a physical condition after reduction that these reduced metals can be separated from the other metallic oxides in the ore.

II. USE OF DISSOLVED SUBSTANCES. The first mention of the use of dissolved substances in obtaining differential flotation was contained in British patent 23,870 of 1910, granted to Henry Lavers, E.

H. Nutter, and Minerals Separation. This was probably the first truly differential method on record. Most of the patent is devoted to claims of differential flotation by varying the physical conditions, such as dilution and aeration, but there is also mention of the fact that differential flotation can be obtained by adding soluble substances to the water of the pulp. This patent was also granted in the United States, No. 1,067,485 of 1913. As no specific mention is made of the dissolved substances that effected good differential separation and as the number of dissolved substances that might possibly be used is infinite, it is hard to see why such a patent should have been granted.

Chromates. The next important process of this kind was that of H. H. Greenway and A. H. P. Lowry, British patent 11,471 of 1913 (also U. S. 1,102,738 of 1914). This consists of treating the ore with a solution of a bi-chromate either before or during flotation. Such minerals as galena and pyrite will be wetted by this solution and minerals like molybdenite, sphalerite, and chalcopyrite can then be floated differentially from their mixtures with either pyrite or galena. The inventors of the process soon learned that much better work could be done by performing the flotation in an alkaline pulp, in the presence of a bi-chromate, and the result of their discovery was embodied in British patent 16,302 of 1913 and U. S. 1,142,820 of 1915. For example, the pulp may advantageously contain an amount of sodium carbonate equivalent to 1% by weight on the ore. This combination of a chromium salt and alkalinity in the pulp is claimed to give particularly good results. Two examples of its success are mentioned in the patent specifications.

The first example is that of an ore containing 9.0% lead, 28.2% zinc, and 14.2% iron, which was finely crushed and then subjected to froth-flotation in apparatus of well-known type by being agitated vigorously with four times its weight of water at 130° F. containing in solution sodium carbonate amounting to 22 lb. per ton and sodium bichromate amounting to about 6 lb. per ton of ore. The oil used was a mixture of half a pound of eucalyptus oil with an equal weight of kerosene per ton of ore. The flotation product contained 50.1% Zn, 4.25% Pb, and 8.3% Fe, while the bulk of the iron and lead was left in the residue. Of course, the reaction of sodium carbonate on sodium bi-chromate would be such as to produce sodium chromate, for bichromates do not exist in alkaline solution. It is also to be noticed that the percentage of zinc remaining in the lead and iron product is not specified. My own experience in the laboratory with this process is that it is difficult to make as clean a separation as might be desired unless the pulp is heated. In the cold it does not seem to work well unless a long treatment with the chromate solution is given and even then low extractions of zinc are the general rule.

The second example is of slime containing 11.6% lead and 13.4% zinc. This was introduced into an agitator with four tons of water per ton of ore and 24 lb. of sodium carbonate. One pound of eucalyptus oil per ton of ore was used and the flotation was done at 130°F. with the formation of a floating concentrate containing 22.2% Pb and 27.4% Zn. The concentrate was then subjected to differential bi-chromate flotation in pulp containing 24 lb. sodium carbonate and 6 lb. sodium bi-chromate. The oil consisted of 0.75 lb. kerosene and 0.25 lb. eucalyptus oil per ton of ore. The flotation contained 48.6% Zn and 7.5% Pb, while the residue contained 8.9% Zn and 55.9% Pb. This is particularly interesting as it shows that, even after oiling and flotation, the minerals can be so modified by an addition-agent that only one will float. Further, the separation is commonly regarded as good. It is a matter of considerable ease, however, to juggle tests so that they look as well as these in comparison with the test in which only sodium carbonate was used in the pulp. I have noticed that in the flotation of such a mixed ore in an alkaline pulp it is not unusual for the galena to float first, particularly if a small amount of oil is used, and by further addition of oil the zinc can be floated, so that the composite concentrate is much like the first above mentioned. For purposes of obtaining a patent, however, such an experiment is excellent.

NEUTRAL OR ALKALINE CHLORIDES OR SULPHATES. F. J. Lyster was the next successful inventor to patent a differential flotation process of this kind, which was assigned to Minerals Separation. His process was first tried by the Zinc Corporation at Broken Hill. It purports to be only an improvement on the fundamental differential patent 23,870 of 1910, mentioned above, and is British patent 11,939 of 1913; also U. S. 1,203,372 of October 31, 1916. This process applies ostensibly to the separation of galena and sphalerite. No heating of the solution is required; it must contain a sulphate, chloride, nitrate, or hydrate of calcium, magnesium, sodium, or potassium, or a mixture of them. It is also possible to use manganese, zinc, or ferrous sulphates, barium chloride, or the carbonate or bi-carbonates of sodium. Under these conditions only the galena floats; the zinc sulphide does not float. The zinc may be caused to float later by continued agitation and aeration of the pulp, an operation that is rather slow, or by dewatering and mixing the residue with fresh water. The effect of excess of alkalinity is to cause poor differentiation of the galena from the zinc. No fixed rule as to alkalinity can be given but the water should always contain enough alkalinity to react well with methyl orange.

The water from the mines at this particular plant happened to be of such an analysis as to be well adapted to this process. It contained

	Gr. per gal.	
Total soluble solids		666
Volatile organic matter	57.2	
Silica	2.2	
Calcium oxide	78.2	
Magnesium oxide	53.0	
Sulphur tri-oxide	205.0	
Chlorine	178.0	
Manganese	30.3	
Zinc	5.0	
Alumina	4.0	
Carbon di-oxide	9.3	
Total	622.2	

Lyster names the different reagents that can be used with success on the Broken Hill ore with which he worked and which contained 11% zinc and 13% lead. A few of these mixtures are

	Gr. per gal.
Calcium sulphate	160
Calcium sulphate	160
Calcium hydrate	3.6
Calcium chloride	160
Calcium hydrate	1.8
Magnesium chloride	300
Sodium sulphate	800
Calcium hydrate	18
Ferrous sulphate	300

Lyster has recently been granted four American patents covering this process, namely 1,203,372 to 1,203,375, inclusive, of October 31, 1916. In these patents we find the following statement: "I have further discovered that the residue obtained as before described, containing the bulk of the zinc sulphides, may be further treated by flotation separation to produce a concentrate rich in zinc by first dewatering and thickening the pulp and then submitting it to a repetition of the flotation separation, using, however, sufficient water in lieu of the solution previously described, or by further continuing the process herein described, after the recovery of the lead sulphide (galena), in a separate dezincing unit until the zinc sulphides (sphalerite) appear upon the surface of the solution and are carried over into the launder. In operation I prefer the former to the latter method for the recovery of the zinc sulphide. In this way, a zinc concentrate may be obtained and thereby both the lead sulphide and zinc sulphide recovered in separate products by flotation separation without recourse to separation by gravitation on tables or vanners as heretofore.''

Acidulated Alkaline Chlorides. These were introduced by Leslie Bradford, whose process was taken up by the Broken Hill Proprietary Co. It is protected by British patent 21,104 of 1913 and U. S. 1,182,290 of 1916. It aims at the flotation of pyrite or of sphalerite in the presence of galena. A solution of one or more chlorides of the alkalies or the alkaline earths, preferably feebly acidulated, is used as a 'wetting medium' for galena. If used neutral or akaline the concentrate would contain too much galena and would require re-treatment.

A temperature of 120-160°F. is preferred, although some ores work well in the cold. Usually, a concentrate produced in cold solution will have to be re-treated. Bradford is unable to indicate the degree of acidity required for all ores but with the ores on which he has experimented he states that if the acidity is increased to 1%, galena begins to float again and usually he has obtained good results in solutions containing 0.1 to 0.2% sulphuric acid. This must be over and above the amount of acid that is consumed by the ore. The amount of salt can be varied within wide limits but a 10% solution of sodium chloride is a good strength to use.

Owing to the fact that the Proprietary company is using a modification of the Potter-Delprat process, no oil need be added when treating a crude ore containing calcite and siderite, as the gas generated by the acid accomplishes the flotation. However, the addition of oil is not objectionable. After treatment in this way, the pulp has to be drained (or dewatered) and re-floated in order to obtain a concentrate carrying the galena. Hence, it may be preferable to make first a mixed concentrate of the two minerals, galena and sphalerite, and then treat the mixed concentrate by this process. In case the mixed concentrate has been obtained by the use of oil, the oil should be removed from the surfaces of the particles by the use of a solution of sodium hydrate, sodium carbonate, or by treatment with ether.

Fine ore often tends to flocculate too fast and the floccules of sphalerite entrain particles of galena. Hence Bradford found it necessary to use an agent that would check or slow down the 'flotation tendency.' This idea was patented in British 19,844 of 1914. The best substances to use are sulphites and thio-sulphites of the alkaline metals or sulphurous acid, as the latter is generated by the action of the acid in the pulp on these sodium salts. Such a reagent is added to the acidulated brine just before flotation. Too much of these agents spoils the flotation but just the right amount gives a much cleaner concentrate.

British patent 19,373 of 1914 was granted to the Minerals Separation and De Bavay companies for differential flotation applied to zinc and lead sulphide ores, in which the amount of acid largely controls the mineral floated, although a simultaneous control of the amount of oil greatly assists the differentiation. Galena is first floated by the use of a limited amount of oil and too small an amount of acid to effect a separation of both galena and sphalerite from the gangue. On the addition of more acid and more oil the zinc can be separated by another flotation treatment.

When using a circuit-water already containing some oil, the lead can be floated without the addition of oil and the slight acidity of this water does not injure the flotation. The sphalerite can then be floated by addition of oil and sulphuric acid. If fresh water is used a small amount of oil must be added in order to float the galena.

As an example of the application of this invention the patentees cite the results from treating the slime-dump of a Broken Hill mill. It contained 10% lead and 21% zinc and was used in a circuit-water containing some oil to which was added 22 lb. sulphuric acid per ton of ore. The galena concentrate contained 66% lead and 8.8% zinc from the first flotation-cell, and the average from all the 12 cells of the machine was 50.5% lead and 21.2% zinc. The recovery of the lead amounted to 62.9%.

Commenting on this process: it is probable that any oil in the return-water is only the soluble portion of the oil used. The fact that a great portion of the galena can be floated by the use of this oil is interesting. Sphalerite is known to require more oil than galena and it often requires the presence of acid in the solution. The large amount of zinc in the above concentrate and the low extraction of the lead from such a high-grade heading indicates that the process is not a flattering success.

ACID AND REDUCING AGENT. Bradford's work with a 'retarder,' in the process ascribed to him above, must have brought about the development of this present process. In his first process Bradford floated sphalerite and pyrite in the presence of galena. In this process, covered by British 21,880, of 1914, he floats galena and pyrite in the presence of sphalerite. A slightly acidulated mill-water is used and to this is added a small amount of a reducing agent, like sulphur di-oxide, sodium thio-sulphate, sodium sulphite, or hydrogen sulphide. Bradford has worked almost entirely with sulphur di-oxide or its compounds and states that he does not know much about the action of other reducing agents. He does not confine himself to any particular proportion but states that he has used from 8 ounces to 8 pounds of reducing agent per ton of ore. This renders the zinc sulphide "temporarily immune" to flotation.

Sphalerite can be floated from the residue by dewatering and re-pulping with fresh water, or by the addition of an oxidizing agent or by warming and aerating until the sulphur di-oxide and sulphites are oxidized. An excess of reducing agent delays the flotation of both galena and sphalerite, because the excess of reagent has to be oxidized by the aeration given the pulp in the machines until the galena can float, and later, when further oxidized, the sphalerite can float. Only enough reducer should be added to render the blende temporarily immune. Heat is not required but assists greatly, as the oxidation of the reducing agent takes place much faster and thereby the sphalerite is all the sooner ready to float after the galena and pyrite have been floated. The apparatus recommended by Bradford is a string of centrifugal pumps and separating-boxes in order that aeration can be controlled. Occasionally, the results are greatly enhanced by giving the pulp a previous digestion with acid and the reducer before flotation.

This patent quotes a number of excellent examples of tests made according to the method described. In one test a 500-gm. lot of ore was treated in three litres of water containing one gramme of sodium thio-sulphate and enough sulphuric acid to make the water react acid, and enough of the regular frothing-agent. This ore was a Broken Hill weathered dump-slime, which was partly oxidized. The results were as follows:

	Gm.	Zn, %	Pb, %	Ag, oz.
Heading	500.0	18.2	15.2	18.3
Lead concentrate	79.5	9.6	60.0	69.0
Zinc concentrate	166.5	46.4	6.3	15.7

The zinc concentrate was obtained after the lead concentrate had been taken off by the addition of 0.1 gm. of potassium permanganate to oxidize the sodium thio-sulphate.

In another test with a pyritic blende ore the use of sulphurous acid prevented the flotation of the blende while the pyrite was removed. By thickening the pulp and discarding the sulphurous acid solution, it was possible to obtain a residue from which the zinc could be floated after re-pulping with fresh water. The table of results is as follows:

	Gm.	Zn, %
Heading	500	28.3
Pyritic concentrate	148	13.4
Zinc concentrate	220	51.6
Tailing	120	3.7

HYDROCHLORIC ACID AND ZINC CHLORIDE are supposed to sink galena and sphalerite in the presence of other sulphides, supposedly pyrite and chalcopyrite, as well as the sulphides of silver. This combination is mentioned in a German patent, 282,131 of 1915, granted to E. Languth of Neerpelt, Lembourg, Belgium. Nothing seems to be known of it beyond the statement that an acidified zinc-chloride solution is used.

Alkaline Solutions. British patent 9049 of 1914 was granted to the Amalgamated Zinc (De Bavay's Ltd.) for the use of alkaline and other solutions. Galena is wetted differentially in the presence of sphalerite. The patent recommends that a combined zinc and lead concentrate be obtained by ordinary flotation and that the combined concentrate of galena and sphalerite be re-treated in dilute sodium-carbonate solution. The galena, wetted by the solution, sinks while a froth rich in sphalerite is obtained. It is also recommended that if a mixed concentrate has been obtained by the use of an organic frothing-agent it should be first treated with a solution of hydrogen sulphide, sodium sulphide, sodium sulph-hydrate, or other such agent added to the sodium-carbonate solutions.

I do not pretend to understand this process, as all my experience tends to prove the contrary: that galena is more easily floated differentially in the presence of sphalerite in a slightly alkaline solution. A reference to the paper‡ of Palmer, Ralston, and Allen on the subject of 'Some Miscellaneous Wood-Oils for Flotation' will show that in neutral and in alkaline solutions most of the oils tested gave differential flotation of the galena.

In U. S. 1,203,373 of October 31, 1916, Lyster claims the use of solutions containing alkalies like sodium carbonate (500 gr. per gal. water) or sodium bi-carbonate (600 gr. per gal.). This patent accompanies others claiming the use of alkaline solutions of chlorides or sulphates of the alkalies and alkaline earths.

Alkaline Sulphides. British patent 8746 of 1915, granted to Minerals Separation, covers the use of sodium or similar sulphides in the differential flotation of galena in the presence of sphalerite. It also mentions that occasionally the addition of sodium carbonate or of a bi-chromate is helpful, and that a frothing-agent may or may not be used and that the solutions may be heated if so desired. Pyrite is also said to be floated differentially in the same manner, and the sub-aeration machine is recommended. Beyond the mention of bare facts and claims this patent does not tell much; no statement of general principles is given and it is only claimed that the "chemicals are varied to

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‡Bull. 116, A. I. M. E., Aug. 1916, pp. 1387-1396.

suit the ore used,'' with no suggestion as to how this point can be determined except by ''experiment.'' It is not even claimed that sodium sulphide has any advantage over other alkaline reagents and nothing is said about the fact that sodium sulphide is a reducing agent. We have seen the use of a reducing agent, such as the sulphur di-oxide, or sodium sulphite under acid conditions, patented by Bradford. The result is the same as in Bradford's patent, the differential flotation of galena and of pyrite in the presence of sphalerite. These patentees say:

''The process is usually carried out in a circuit containing in solution about from 0.1% to 1% of a sulphide of an alkali-metal or earth, such as sodium sulphide. The solution is preferably heated to 130 to 140°F. and is used with or without a frothing-agent. In certain cases, the addition of a small amount of about 0.1% to 0.5% of an alkaline substance, such as sodium carbonate, may be made, while in other cases the addition of a small quantity of a bi-chromate of an alkaline metal, such as potassium or sodium bi-chromate, will be found advantageous.''

In giving the details of a number of illustrative tests, mention is made of the use of a ''sub-aeration vessel constructed of wood or iron'' but no reason is given for this stipulation. Evidently cast-bronze or aluminum test-machines are taboo.

MANGANESE COMPOUNDS. T. MacKellar Owen has been granted U. S. patent 1,157,176 of 1915 for the use of alkaline permanganates in solution for accomplishing differential flotation of various sulphides. ''In the froth-flotation treatment of mixed sulphide ores containing, for instance, lead, copper, zinc, and iron sulphides, or any two or three of these sulphides, the introduction of a small quantity of an alkaline permanganate into contact with the slime, makes the flotation operation selective in the case of a large range of representative slimes. In the case of lead-zinc slime the galena and the blende are raised in successive order; the galena is floated first, the bulk of the silver if present, accompanying the galena, and the blende is subsequently floated from the residue after acid has been added to the pulp. If copper is present it usually comes up with the lead.

''The proportion of alkaline permanganate required is less than the quantity that would be necessary to change permanently the reducing character of the mass of the pulp. Relatively minute quantities of free alkaline permanganate will substantially affect the behavior of certain metallic sulphides in the flotation liquor. * * * The pretreatment of the water with permanganate to neutralize its reducing quality does not produce the same effect as having the permanganate present in the pulp acting on the slimes during its dissociation.'' It is most advantageous to add the permanganate after the slime has been mixed with the flotation liquor as, otherwise, it seems to be wasted in oxidizing impurities of the water and more quickly results in 'sickening' of the circuit-liquor. ''Manganese di-oxide may be used to procure effects of the same order as alkaline permanganate.'' When the slime is of a very reducing character and quickly decomposes the permanganate, it is advantageous to conduct the process at a temperature of approximately 120° F.

''I quote the case of a weathered slime obtained from the treatment of an ore obtained at Broken Hill, N. S. W., said slime containing approximately by assay 16% Pb, 13.5% Zn, and 17 oz. Ag per ton. In this treatment, using 2.5 lb. of potassium permanganate, and 3 oz. eucalyptus oil per ton of slime, a lead concentrate was obtained containing 60.5% Pb, 54 oz. Ag, and 11.8% Zn, and after adding 15 lb. of sulphuric acid per ton of original slime, a zinc concentrate containing 6.2% Pb, 11.2 oz. Ag, and 43.4% Zn, leaving a residue containing 2.0% Pb, 3 oz. Ag, and 1.6% Zn.''

Owen describes the operating details of his process most frankly. The patent specification is pleasant to read and I regret that it is too long to be reproduced in full. If acid is added in any quantity to the pulp before the lead is removed it is impossible to get differential flotation, the lead and zinc sulphides tending to float together. In practice Owen recommends the use of a separate circuit-liquor containing the manganese compounds for flotation of the lead, followed by dewatering and re-pulping with new water for the flotation of the zinc. This makes two water-storage tanks necessary. Since the manganese liquor tends to 'sicken' with repeated use, an effort is made to exclude contaminations and to introduce fresh water at this point rather than some other in the system. Certain cases, which cannot be definitely defined, are found in which the process is commercially ineffective, notably a few cases of mixed iron and copper sulphides. Only a laboratory test will tell. For some slimes a preliminary weathering of a few hours will greatly improve the results, and hence it is advisable to make experiments in the laboratory and take account of this possibility.

Copper or Mercury or Their Compounds. British patent 4974 of 1915, to Minerals Separation, covers the use of metallic copper or mercury or a compound or alloy of either of the metals, in differential separation of a froth rich in zinc from a mixture of the sulphides of lead and zinc. Preferably the operation shall be carried on in a brass or a bronze vessel. The invention is applicable to other differential processes patented by Minerals Separation or its engineers, one example being the use of chromium compounds mentioned by Lavers. The copper metal can be placed in the flotation machine in any convenient form such as a sheet-copper lining, or it may be introduced with the pulp in finely divided form.

Copper Sulphate. The above mention of the use of metallic copper and copper compounds for differential flotation evidently does not extend to the use of soluble compounds of copper. A minute amount of copper sulphate in solution in the mill-water seems to improve the flotation of sphalerite. It has been used for this purpose in the mill of the Hercules Mining Co., at Wallace, Idaho, with only indifferent success, as the object is to drop some of the pyrite, which tends to enter the zinc-lead concentrate. While improved results are obtained, there is still too much iron in the zinc concentrate.

Chlorine and Chloride of Lime. The use of chlorine in an active form, such as is obtained by the use of chloride of lime, seems to be successful in the treatment of products containing sphalerite. In one Canadian plant iron sulphides are wetted by such a solution. Its use in the United States has been kept secret. However, the employment of chloride of lime for flotation of galena in the presence of sphalerite has been patented in England (10,478 of 1915, granted to Minerals Separation). Considerable success has been claimed for this reagent and it is hoped that information will be forthcoming in the near future. It may be that chloride of lime has much the same effect as that observed in the use of ordinary slaked lime at the Midvale plant, Utah, where some lessees of an old dump claim to have prevented the flotation of iron by the use of 8 lb. of lime per ton of ore, both sphalerite and galena being floated.

III. By Physical Control. One of the most important and fundamental processes for obtaining differential flotation is disclosed in the patent of E. H. Nutter, Henry Lavers, and Minerals Separation, (U. S. patent 1,967,485 of 1913, and British 23,870 of 1910. This patent probably grew out of observations on the changes of froth produced by varying physical conditions during flotation. The factors mentioned are "agitation, aeration, chemical constitution of the solution employed, the degree of dilution of the pulp, the temperature, and the amount and character of the frothing-agents." The purpose seems to be to claim the idea of differential flotation in general and the Minerals Separation people evidently regard it as their basic patent in this line. In fact, most of their subsequent patents in differential flotation refer to this one, stating that they are improvements and that they merely supplement it.

The best idea contained in the patent is that occasionally, by controlling physical conditions in just the proper way, a froth containing the minerals in certain ratios of size will be obtained, such as a froth containing most of the copper sulphides of an ore, some fine sphalerite, and some still more finely divided gangue. After breaking down such a froth the mixed froth can be tabled to separate the various minerals. After obtaining several different froths by close attention to any of the above conditions it may be possible to separate a complex ore by tabling.

One of the important physical conditions affecting differential flotation seems to be the variety and amount of the oil or frothing-agent. For example, the process in the patent of T. M. Owen (British 16,141 of 1913) taken out by Minerals Separation, is designed to treat a mixed zinc-lead sulphide ore. By the use of a limited amount of frothing-agent in a neutral or an alkaline pulp, the galena can be floated in the presence of sphalerite, and then by the addition of more oil, or by more oil and some acid, the sphalerite can be floated. This method is in general use throughout the North-west, both in the United States and in Canada. Most of the companies are secretive, however, and do not wish to allow publication of the details of their practice. Suffice it to say that they are making commercial grades of concentrate but that the separation is never quite clean, and too much zinc is left in the lead concentrate and too much lead in the zinc concentrate. I am informed that this process is at work in the Hewitt mill of the Silverton Mining Co., at Silverton, B. C. The gangue contains much siderite and the sulphides are galena, sphalerite, and silver sulphides. The ore is crushed, and the coarse galena tabled. The slimed galena is floated differentially in a 2-cell M. S. machine, giving a concentrate carrying 52% Pb and 6% Zn, while the zinc is removed in a 10-cell machine giving a product carrying 45% Zn and 2% Pb. The silver goes with the lead, and the extractions are said to be 85% of the lead, 90% of the silver, and 86% of the zinc. This is unusually good work.

Owen describes the treatment of slimes at the Broken Hill South mine. Ordinary temperatures suffice and no acid. The lead is removed in the first three cells of an 11-cell machine by the use of one ounce of eucalyptus oil per ton of ore. This gives a recovery of 85% of the lead in a product containing 60 to 79% lead. By the addition of more oil and some sulphuric acid 70% of the zinc in the ore can be recovered in a concentrate carrying 46% zinc.

Following Owen's patent came one taken out by the Minerals Separation and De Bavay companies, British 19,374 of 1914. It purports to be an improvement over Lyster's and over the basic differential patent 23,870 of 1910. It is designed for differential flotation of galena-sphalerite mixtures. The claim is that too small amounts of oil to float both sulphides will float only the galena and will give a clean separation in either neutral or alkaline pulp; in other words, flotation conditions are so poor that only the most easily floated mineral, the galena, is separated. The zinc in the residue can be caused to float by the use of more oil, with or without the addition of acid. Aeration and emulsification are claimed to have no effect on the zinc as long as the amount of frothing-agent is below the maximum required for the lead alone. This maximum is dependent on the condition of the circuit-water and the amount of dissolved salts therein. While aeration is said to have little effect on the zinc, it is to be noticed that usually the sub-aeration machine is recommended for the flotation of the galena in most of these patents and sub-aeration machines or pneumatic machines seem to be best adapted to the flotation of this mineral.

This method of flotation is in use by the Sulphide Corporation at its Central mine, treating the slime-tailing from the table-concentration in a Hebbard machine. The feed averages 4.2% lead and 18% zinc, while the lead concentrate assays about 50% lead. The residue from the first three boxes assays 0.53% Pb and 18.5% Zn. The zinc concentrate assays 6% Pb and 47.5% Zn and the tailing 1% Pb and 2% Zn. The recovery of lead is rather low.

It also happens that during grinding one mineral will be slimed while another will not be so thoroughly ground. Galena and chalcopyrite are two rather friable minerals and as galena usually accompanies sphalerite, and chalcopyrite usually accompanies pyrite, it is these two separations that are of interest. As a rule there is little difficulty in getting a marked separation of galena from sphalerite, owing to this fact alone, and likewise a separation of chalcopyrite from pyrite. For the flotation of chalcopyrite the plants of the Calaveras Copper Co., and of the Mountain Copper Co., in California, as well as that of the National Copper Co., in Idaho, are examples.

The Minerals Separation company has taken out a British patent, No. 5650 of 1915, that claims the addition of finely divided carbon to a pulp in order to gather the galena in preference to the sphalerite. Any finely divided form of carbon, charcoal, or coke is said to be satisfactory. Preferably an alkaline pulp should be used. The finely divided carbon probably depletes the pulp of oil so that a minimum amount of oil in a slightly alkaline pulp with excessive aeration can be obtained for the differential flotation of the galena. This is only a guess on my part but I believe that the absorbent power of the finely divided carbon for oil is the physical result involved. If the oil in the pulp is largely absorbed by the carbon, only the galena can get enough oil to float. The carbon goes into the froth and the galena accompanies it. Recent work at the Magma Copper Co., in Arizona, by the General Engineering Co., of Salt Lake City, has developed a fairly successful differential flotation of sphalerite from pyrite. A small amount of oil, together with an alkaline pulp and excessive aeration in Callow cells, aids the flotation of the sphalerite. This is improved by the addition of a small amount of copper sulphate. As little as a tenth of a pound of copper sulphate per ton of ore has a noticeable effect. A 45% zinc concentrate and a 4% tailing is made from a 15% zinc heading.

WHAT KIND of differential flotation is most desirable? The usual answer of the technical man is, ''That depends on circumstances.'' The circumstances under which a slime needing differential flotation is generally produced are those obtaining in a gravity-concentrating mill. It is awkward to dewater the slime and give it the fractional roasting demanded by some of the patentees. There is no point in dewatering the pulp, roasting it, and then putting it back into the water for further flotation if there is a possible method of getting the same results without so much trouble. The simple addition of a small amount of some chemical to the pulp or the careful control of the amount of oil used offers a much less expensive process. The dewatering and filtration of a slime often costs 20 cents per ton and a roast might cost all the way from 25c. to 75c., with attendant dust-losses. Against these costs are to be set the amount of chemicals consumed or the extra power expended when minute amounts of oil are being used in order to obtain flotation of only one mineral. However, where the ore can be obtained in a dry state with no special effort it may pay to use the roasting method of modifying the easily burned minerals before flotation. Dust from an electro-static or an electro-magnetic plant, or from other dry-concentration processes, is already in a condition for such treatment. Moreover, roasting is the only sure way of rendering iron pyrite non-flotative. In the case of zinc ores this may be well worth while, as the smelters do not like to take much iron in the concentrate. The wonderful resistance of zinc sulphide to roasting grieves the zinc smelter-men but the above method takes advantage of this resistance. A mixture of zinc and iron sulphides can be roasted at about 600° C. for as much as two hours, causing but little oxidation of the zinc sulphide and almost complete oxidation of the pyrite. The ore does not even have to be finely ground for this work and can be more easily pulverized for flotation after the roast than before. I have witnessed a separation of one particularly difficult ore containing marmatite and pyrite. The purest piece of marmatite contained 12% iron and much of it contained more. Of course, the iron in the marmatite could not be separated, but by roasting till the iron from the pyrite was almost completely converted into red oxide the marmatite could still be floated. The concentrate assayed 49% zinc and 21% iron, and looked almost blood-red. This was made from ore containing 13% zinc and 19% iron, which could not be separated by any other means, and while the flotation product was still far too high in iron to be acceptable at the zinc smelter, the point to be noted is the wonderful resistance of zinc sulphide to alteration.

The question arises how best to apply differential flotation. Shall a mixed flotation concentrate of the several sulphides be made first and then only this small bulk of higher-grade product be subjected to differential flotation or would it be better to apply the differential-flotation methods to the crude ore?

It is probable that a flow-sheet in which only a concentrated product is treated by the specialized methods described here would allow of more careful work, closer supervision, and the use of more expensive chemicals than could be applied to the bulk of the crude ore. This principle should apply to all the methods in which the previous concentration by flotation does not spoil the mineral particles for one of the differential schemes. Such a process as the one in which only a minute amount of oil is added to float the galena of the ore, followed by the addition of more oil to float the remaining sulphides, would be impossible if applied to a mixed flotation concentrate because this concentrate already contains too much oil for the application of the process. It is doubtful if the oil in a flotation concentrate can be removed by any of the proposed methods sufficiently to warrant the application of this process. The use of powdered carbon might be of value in this connection for absorbing some of the excess oil.

The Elements of Simplicity should be sought in differential work. Any of the methods of differential flotation that involve dewatering and re-pulping should be avoided, if possible, on account of the space and cost of thickeners and the large amount of water used. Some method requiring a simple addition of oil or acid in order to float one mineral after a first has been floated will commend itself. Avoid also the use of a solution that can be so changed by continual use that it sickens and has to be discarded. It will be recalled that Owen's process, using alkaline permanganates, is one of this type. A sodium-sulphide solution is likely to oxidize to thio-sulphates or sulphites, which, if present in sufficient amount, entirely inhibit flotation. Avoid the use of a solution of a valuable chemical that must be washed out of the tailing and recovered. The solution containing zinc chloride or the one containing chromates is an example. Avoid the use of addition-agents that, in order to be effective, require some length of time in contact with the ore. Heating of solutions, unless by waste heat from some other operation, is also to be avoided. Finally, do not use a method of differential flotation that is sensitive and requires constant attention.

When differential flotation depends on the addition of some chemical, the supply of that chemical and the facilities of transportation to the mill have to be considered. Sulphuric acid is not well adapted to carriage by wagon in mountainous districts. Many of the reagents are expensive when bought on the market but they can be cheaply made at the mine. For example, I have heard Owen's alkaline permanganate solution decried on the ground that "potassium permangante is entirely too expensive a chemical for commercial work." No one said that the potassium salt had to be used and Owen's claim was that most manganese compounds were suitable. Manganese ores are often available locally and the fusion of some of this ore with crude soda will give an inexpensive sodium manganate. Lime is a cheap chemical, easily available in most mining districts, and hydrogen sulphide can be made from pyrite, other sulphides, or even elemental sulphur. Likewise, sodium chloride, common salt, is well distributed over the face of the earth and is not far distant from most mines. The chromates are the only reagents recommended that might be difficult to obtain.

There is only one case where a substitute for differential flotation seems to be having any success, namely, in the separation of the zinc and lead sulphides. A pulp that will not separate well by ordinary tabling methods may yield to a method wherein the mixed sulphides of zinc and lead are floated together, the froth broken down, and the pulp passed over a Wilfley or other table. Under these conditions a streak of lead, well-defined and sharply differentiated from the zinc, can be obtained, whereas the gangue-slime may prevent any gravity-separation before flotation. Some people have gone so far as to believe that the oiling of the surfaces of the particles has improved the tabling qualities. It is probable that the only effect is the breaking up of the lumps of mixed mineral during the agitation for flotation.

The most pressing problem in differential flotation is the removal of pyrite from a sphalerite concentrate made by flotation. Mixtures of zinc and lead sulphide are not so hard to get apart. If a previous fractional roast is given before milling there is usually no difficulty from the flotation of iron, and the zinc will still float; but if flotation is used in a wet mill to treat only the slime, and a zinc concentrate badly contaminated with iron is formed, the separation of the iron will be difficult indeed. The most successful addition-agents for dropping the iron during flotation seem to be oxidizers like the chromates and chloride of lime. Chlorine improves the flotation of sphalerite and lime tends to drop iron. Copper sulphate likewise seems to improve the flotation of sphalerite but at the same time tends to improve that of pyrite. Fortunate is he who has the ore in which the pyrite does not tend to slime to the same extent as does the sphalerite, or where the pyrite is already weathered to a condition in which it is difficult to float. At Crown King, Arizona, a mixed flotation concentrate of zinc and iron sulphides is passed over a Wilfley table with the result that the oil is washed off of the pieces of pyrite. On subjecting this pulp to a second treatment only the sphalerite is floated.

SUMMARY. The factors used in differential flotation either to assist the flotation of one particular mineral or to retard its flotation are tabulated for four of the principal sulphide minerals. These are the factors on which the various processes are based. The abbreviations 'As' and 'Ret' mean 'assisted' and 'retarded' respectively.

	Sphalerite		Galena		Pyrite		Chalcopyrite	
Factor	As.	Ret.	As.	Ret.	As.	Ret.	As.	Ret.
Acids	*				*		*	
Weakly alkaline solutions		*						
Lime						*		
Sodium sulphide					*			
Chloride of lime	*					*		
Chlorine	*					*		
Limitation of oil		*				*		
Chromates				*		*		
Permanganates, etc.		*						
Neut. or alk. chlorides		*						
Weakly acid chlorides				*				
Sulphur di-oxide, etc		*						
Roasting or weathering				*		*		
Dry grinding						*		
Heated solutions	*							
Fine grinding			*				*	
Zinc chloride and HCl		*		*				
Metallic Cu and Hg	*							
Copper sulphate	*							
Reducing solutions		*	*		*			
Oxidizing solutions	*			*		*		
Aeration			*					
Washing in fresh water						*		

FLOTATION-OILS

By O. C. Ralston

(Written especially for this volume)

Introduction. Recently there have been developed methods of flotation by gas-bubbles, without a frothing-agent; however, most of the successful frothing methods depend more directly on the oil than on any other factor. The term 'oil' is retained because most of the substances now in use are of oily consistence even though they may not be true oils. For example, carbolic acid, which is soluble in water, is rarely called an 'oil' but in flotation it functions as one.

Perhaps the deepest mystery in flotation is the real function of the oil. While we have theorized successfully in many directions we are still much in the dark as to just what it does. We know that if a certain oil is added in small amount to an ore-pulp the valuable minerals are caught by air-bubbles introduced into the pulp, and carried by them to the surface in the form of a froth. It has also been noticed that sundry 'oils' cause a great deal of foaming but they seem to carry very little mineral with them to the surface. Moreover, it has been found that there are oils which cause very little froth but the froth formed is heavily laden with mineral. Therefore, frothing-agents have come to be placed in two general classes, 'frothers' and 'collectors.'

(1) Frothers. These oils (and other agents) seem to be necessary in order to give some oils a frothing quality. It is believed that their principal function is to form froth of a more or less persistent nature by giving the water in the pulp a variable surface-tension. Literature on the physics of foaming solutions informs us that a pure liquid will not froth or foam. The addition of the proper contaminant will modify it so that it can form a foam. Such a contaminant must not only alter the surface-tension of the liquid but must be capable of adjusting itself in concentrations so that the surface-tension developed at any particular portion of a bubble will be just sufficient to balance the strain put on the bubble. To illustrate, let us assume a soap-bubble hanging from the pipe on which it was blown. It is evident that the portion of the bubble near this point of support must carry the weight of the bubble below and that it is under a greater strain than the portions of the film at the bottom of the bubble. If the soap adjusts itself into the different parts of the bubble in the right amount

to cause the surface-tension of the water to change enough to balance the strain put on the film at each point, we have the conditions for persistence of froth. In the case considered, since soap reduces the surface-tension of the water, the greatest concentrations of soap will be found in the lowest portions of the bubble where the strain is least and consequently it is there that the surface-tension is lowered the most. The common frothers now used are the products of the distillation of wood, such as pine-oil, pine-creosote, hardwood-creosote, turpentine, and resin-oil, as well as certain coal-tar fractions like phenol. cresol, and the tar-acids.

(2) Collectors. As mentioned above, some oils seem to be adapted to making froth yet do not collect much mineral into the froth. Other oils seem to be specially adapted to collecting the mineral but little adapted to frothing. The addition of a collecting-oil to a frother usually results in a froth more heavily burdened with mineral. As a rule, the frothers are either soluble in the water or form colloidal emulsions, which also alter the surface-tension of water. The collectors are usually much less soluble in water and seem to concentrate on the surfaces of mineral particles so as to 'oil' them. The common collectors are coal-tar, coal-creosote, pine-tar, hardwood-tar, crude petroleum and many of its fractions.

All oils possess both some frothing and some collecting ability and many of them are acceptable for performing both functions. Eucalyptus-oil and pine-oil are examples of this latter type.

Condition of the Oil. It seems necessary to distribute the oil intimately through the pulp before successful flotation takes place. In doing this the oil almost entirely disappears for the reason that it is rarely used in amounts of over four pounds per ton of ore and often less than a pound of oil per ton of ore is used. Flotation-men call this distribution of the oil through the pulp 'emulsification,' but a question has been raised as to the correctness of this terminology. Undoubtedly the oil is very finely divided but whether 'emulsified,' as the chemist would see it, is doubtful. In fact, G. D. Van Arsdale shows[1] that there are generally present in a flotation-pulp enough dissolved electrolytes or other agents to prevent emulsification. The flocculation of suspensions and the coagulation of emulsions by certain electrolytes are well known in colloid chemistry. Materials, such as tanninc, which promote emulsification, seem to prevent flotation. Van Arsdale has also made an interesting observation on mixing a collecting and frothing oil. If a film of collecting-oil is formed by placing a drop of

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[1] *Eng. & Min. Jour.*, May 13, 1916.

it on the surface of water, it spreads over a large area. By dropping in a small amount of a frothing-oil the immediate retraction of this film is claimed and the collecting-oil "takes on a circular globular form with a definite positive contact-angle." This leads Van Arsdale to believe that if a collecting-oil has adhered to a particle of mineral and a frothing-oil is later added, flotation should be immediately improved.

Wilder D. Bancroft, with his usual lucidity, seizes on what Van Arsdale says and recognizes in it the condition for the formation of emulsions of water in oil instead of oil in water. He deduces that any addition agent which tends to increase dispersion in the oil phase and to decrease it in the water phase, will assist flotation. Hence we can understand why Bancroft believed that flotation was "nothing but a special case in emulsions."[2]

It is highly probable that some of the frothing-oil is dissolved in the water. Where mills dewater the tailing and return the water to the mill, often this water needs no addition of a frothing-agent. However, a collector must be added because flotation in this water brings up very little mineral. Hence, the supposition that the collecting-oil is insoluble and that it has adhered to the sulphide and thereby left the frothing-agent in the solution. A striking confirmation of this is found in a couple of experiments performed in court in the Miami case by Dr. Liebmann, witness for Minerals Separation. He concentrated Broken Hill tailing with oleic acid (insoluble) as a flotation-agent and then repeatedly washed the concentrate with hot water. On submitting this concentrate to flotation in fresh water and without the addition of any more flotation-agent the mineral was re-floated, showing that the oleic acid had stuck to it. When phenol was used in a similar experiment only 20% of the concentrate could be re-floated, showing that the soluble phenol had been washed away from the concentrate.

Persistence of Froth. The prime requisite for a persistent froth is a variable surface-tension of the water. Some practical observations on the conditions favorable to either brittle or persistent froth are next in order. Pine-oil and many other single oils tend to give a fairly brittle froth. Oils that contain a great many different substances and mixtures of oil yield a more persistent froth. The wood-creosotes usually give a more lasting froth in which the bubbles obtain a larger size than is the case with pine-oil. As a rule, the better the oil is distributed through the pulp the more stable is the froth.

The persistence of the froth in a 'mechanical' machine, as com-

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[2] *Met. & Chem. Eng.*, June 1, 1916.

pared with the evanescent froth produced in the 'pneumatic' machine, has led to much conjecture concerning the cause of the difference. The following proposed explanation is rather simple. In the pneumatic machine so much air is introduced that only a few mineral particles are found clinging to each bubble. At the surface of the froth these numerous bubbles, in bursting, drop their burdens on the bubbles below them and if the froth is allowed thus to collect mineral without overflowing it usually assumes the condition of the more persistent froth in a mechanical agitator; in other words, a pneumatic froth carries less mineral but contains more water and air. In the mechanical agitator each bubble of air is usually well loaded because there are fewer of them and the mineral particles come so close to each other that they mat together and tend to support the arch of the bubble. If allowed to dry without disturbance they will dry into mud of the same shape as the original bubbles of froth. In fact, many persistent froths could almost be called mud-froths. Of course, the proper frothing-agent will give the desired variability of surface-tension to the water, irrespective of the mineral burden. Instances are known of the proper oil-mixtures being obtained to give such a tough froth that the mill-floor would be flooded many feet deep with it before the trouble could be righted by cutting down the oil-feed or changing its composition.

Over-Oiling. In any mill that has been brought to a high state of efficiency by use of a definite proportion of an oil mixture and under given conditions of agitation, an excess of oil causes a bad effect. This effect is much less pronounced with collecting-oils than with frothing-oils. When the over-oil effect is noticed the froth is usually 'dirty;' it contains too much gangue. The remedy is more agitation (at least a change in agitation) in order properly to distribute the excess of oil. The basic patent of Minerals Separation was recently held valid in the Supreme Court on the ground that they had shown a new effect when less than 1% of oil was used, and hence they were entitled to patent-rights. Many people have held the opinion that the over-oil effect plainly showed that more than 1% would give a poor metallurgical result and a different kind of froth. As a matter of fact, the over-oil effect appears only when changing the amount of oil used and not the other conditions of flotation. Just as it usually takes considerable adjustment of plant to get good results when using one pound of oil per ton, a similar adjustment of conditions is necessary before 25 or 50 pounds of oil per ton of ore can be used with success. Since the decision of the Supreme Court was published several companies have been using more than 1% of oil without making any apparent difference in the froth produced. In fact, the data given out on the operations of the slime-plant at the Arthur mill of the Utah Copper Company show that a somewhat higher extraction and a higher grade of concentrate is now being produced with 32 lb. of oil as compared with the former 2 to 4 lb. per ton of ore. Moreover, the machines are not as sensitive to changes in the feed. The metallurgical result is the same or better; the physical appearance of the froth is the same, and only the increased odor of oil in the mill would indicate the use of any more than the usual proportion of oil. Of course, the 'emulsification' had to be taken into account when the amount of oil was increased. The oil used is a crude-topped petroleum with a small amount of coal-tar and of pine-oil. This is a large-scale verification of the claim made by the defendants in the Hyde case that the use of less than 1% of oil was merely for economy and hence not a patentable process. The defendants produced the regular froth in an experimental machine before the court, when using successive increases up to 25% of oil on the weight of the ore. However, the plaintiffs succeeded in convincing the judges that this was merely a laboratory trick and that there was a new effect produced by the use of less than 1% of oil. Minerals Separation claimed to have made 75-ton tests on the use of more than 1% of oil and that the results showed a low extraction and a poor grade of froth. It is probable that they operated the large plant long enough to produce only the 'over-oil' effect and that they did not adjust the operation of the plant to the increased amount of oil. This was merely negative evidence.

Raw Oil Effect is a striking phenomenon, which was first mentioned by W. A. Mueller.[3] A good froth can be killed instantly by pouring on it a small amount of the same oil that was used in making the froth. It not only makes a hole through the froth in the immediate neighborhood of the raw oil but the oil may even spread over the whole surface of the cell. Not until this raw oil has been well stirred into the pulp can a good froth be formed again.

Choice of Oil. The maximum economic effect requires that the oil or mixtures of oil chosen must produce the highest grade of concentrate with the highest possible recovery for the minimum cost and at the maximum profit. In copper work a low tailing is a greater desideratum than a high-grade concentrate, while in zinc work everything must be done to obtain as high a grade of concentrate as possible. In any case, where the concentrate has to be shipped a long way, an oil

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[3] 'Froths Formed by Flotation-Oils,' *Eng. & Min. Jour.*, July 1, 1916.

must be used that will allow the preparation of a clean concentrate. In order to obtain a cheap oil it is now quite common in most copper work for the mill-men to mix a high-grade pine-oil, or other frother, with a great excess of a cheap petroleum or a coal-tar as a collecter.

The classes of oils used are as follows:

PRODUCTS OF WOOD DISTILLATION—

Pine-oil, both steam-distilled and destructively distilled.

Pine-tar oil.	Pine-creosote.
Rosin-oil.	Hardwood-oil.
Pine-tar.	Hardwood-creosote.
Turpentine.	Hardwood-tar.

PRODUCTS OF DISTILLATION OF COAL—

Coal-creosote.
Cresol.
Phenol.
Coal-tar, from gas-works and by-product coke-ovens.
Water-gas tar.

PETROLEUM PRODUCTS—

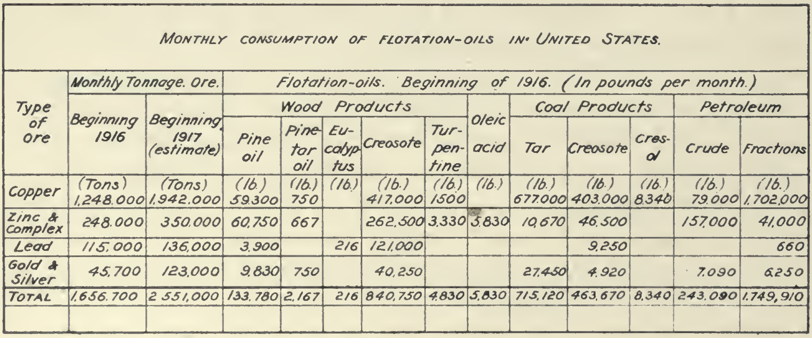
Crude petroleums (California, Texas, Kansas, Illinois).
Distillate, after removing gasoline and fuel-oil.
Fuel-oil, a topped petroleum.
Kerosene acid-sludge.

ANIMAL OILS OR DERIVATIVES—

Oleic acid.

Many other oils have been tested but they are not in general use. Among the coal-products the creosote and tar are the only two that are important in flotation. Hardwood-creosote is the only hardwood fraction that is in general use. Eucalyptus-oil and fir-oil are used in Australia and Canada, but hardly at all in the United States.

CONSUMPTION OF OIL. A statement was issued by the Bureau of Mines in May 1916 giving the market conditions and the consumption of flotation-oil in the United States at the beginning of 1916 and the estimated consumption by the beginning of 1917. The following table is taken from that statement.



MONTHLY CONSUMPTION OF FLOTATION-OILS IN UNITED STATES.

Type of Ore	Monthly Tonnage. Ore.		Flotation-oils. Beginning of 1916. (In pounds per month.)										
			Wood Products					Oleic acid	Coal Products			Petroleum	
	Beginning 1916	Beginning 1917 (estimate)	Pine oil	Pine-tar oil	Eucalyptus	Creosote	Turpentine		Tar	Creosote	Cresol	Crude	Fractions
	(Tons)	(Tons)	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)
Copper	1,248.000	1,942.000	59.300	750		417,000	1500		677.000	403.000	8.340	79.000	1,702,000
Zinc & Complex	248.000	350.000	60,750	667		262,500	3.330	5.830	10,670	46,500		157,000	41,000
Lead	115,000	136,000	3,900		216	121,000				9,250			660
Gold & Silver	45,700	123,000	9,830	750		40,250			27,450	4,920		7,090	6,250
TOTAL	1,656.700	2 551,000	133.780	2,167	216	840,750	4,830	5,830	715,120	463,670	8,340	243,090	1,749,910

These figures are the best estimates that can be prepared to give an idea of the tonnage of ore now treated and to indicate the new demand on the oil-producers. Three years ago very few flotation-mills were in existence in the United States. The sudden development of the process upset conditions in the various oil-markets so that for a time the producers questioned their ability to supply the demand. The beginning of the War cut off the supply of German-made coal-creosotes. Now every company that is producing any of the best types of oils is figuring how to capture a goodly share of the supply. Here is such a large outlet for some products that an entirely new market condition has arisen. Take the case of pine-oil, as an example. Before flotation called for it, pine-oil was a drug on the market and could be bought at reasonable figures. The demand from flotation men became too great and other oils had to take its place. All the available pine-oil is still sold for prices rarely below 50c. per gallon. Many of the oils now called 'pine-oils' are not the pine-oil of the U. S. Navy specifications, but simply oils prepared by distilling pine-wood.

DISTILLATION OF PINE-WOOD. Undoubtedly some of the most valuable oils for flotation today are the various oils that come from the distillation of pine-wood. The wood-distillation industry in the eastern South is taking for a crude material what is known as the fat lightwood—the dead timber and the stumps from former logging operations. Only the dead wood contains much pine-oil, as a result of the oxidation and other changes that take place in the sap.

Two main methods of distillation are recognized, steam distillation and destructive distillation. In the steam-distillation of pine-wood, the wood is 'hogged' into chips and live steam is passed through the wood in a retort. A crude turpentine is distilled and the chips are then ready for the extraction of the resin by means of a solvent like gasoline, after which they are made into paper, thrown away, or burned. The crude turpentine is the only distillate produced in this case and is condensed with the steam issuing from the retorts. This crude turpentine is then separated into pure wood-turpentine and pine-oil. The latter is the 'steam-distilled' pine-oil of commerce. It has a higher boiling-point than the turpentine and is easily separated from it. This steam-distilled pine-oil is one of the best flotation-oils made in the United States and only about 175,000 lb. of it is produced per month. Of this three-fourths goes into the chemical trades and the remainder into flotation.

In the destructive distillation of pine-wood it is placed in closed retorts and heated with a fire. The wood is reduced to charcoal and the crude distillate is composed of four things: gas which escapes, crude pyroligneous acid, crude turpentine, and crude tar. The turpentine is in the first fraction distilled; the tar settles out of the pyroligneous acid, which consists mostly of water but contains acetic acid and wood-alcohol as the principal dissolved constituents. The crude turpentine, which is all distilled by the time the retort reaches 275° C., is separated by distillation into what is known as destructively distilled turpentine and destructively distilled pine-oil. Much more of this kind of pine-oil is available than there is of steam-distilled pine-oil and it can be purchased for a lower price. Being a destructively distilled product it naturally contains some of the other products of destruction of the wood, such as pine-tar oil and resin-oil. The crude tar—distilled from the wood—is re-distilled to give some of the crude turpentine that was caught with it some more crude pine-oil, a great amount of pine-tar oil, and finally pine-pitch. Much of the pine-tar oil is used by the flotation trade under the impression that it is pine-oil. From one cord of 4000 lb. of pine-wood there is usually obtained about 10 gallons of 'd.d. turp.,' 3 gal. pine-oil, 40-50 gal. pine-tar oil, and 20-25 gal. pitch. The pyroligneous acid amounts to 125-150 gal. and the charcoal weighs 800 lb. It can thus be seen that the principal oil-product produced by the resinous-wood distiller is pine-tar oil. Pine-tar oil is not pine-tar. It is an oil obtained by distilling pine-tar. Likewise, resin-oil is an oil obtained by distilling resin destructively and is usually contained in pine-tar oil. True pine-oil and turpentine existed as such in the wood before it was distilled. The other products result by the breaking up of the wood.

In the distillation of hard wood much the same thing happens as in the destructive distillation of resinous wood. A charcoal, a tar, and a gas product are obtained together with the pyroligneous acid. The pyroligneous acid is worked-up into acetic acid and wood-alcohol. The tar settles out of the pyroligneous acid and is called the 'settled tar.' There is also a portion of the tar dissolved in the pyroligneous acid and called dissolved tar, which is recovered by boiling away the alcohol, water, etc. This dissolved tar is different from the settled tar. The settled tar is distilled by use of steam-heat and a light 'wood-oil' separates from the rest of the tar. The remainder is distilled over a direct fire, giving a 'light' oil, a 'heavy' oil, and pitch. The heavy oil is emulsified in water with sodium hydrate, the insoluble portion withdrawn, and the solution then mixed with sulphuric acid, which throws out 'creosote' and leaves a solution of sodium sulphate.

Nearly all of the above-mentioned fractions from wood-distillation are sold on the market for flotation work and in many cases the crude intermediate products are acceptable without further refining. The hardwood-creosotes and tars can be obtained cheaply as several million gallons of each are annually used merely as fuel.

Physical and Chemical Properties of some of these oils have been given in the trade-circulars of a number of dealers. These have been prepared in an honest attempt to standardize the oils sold and prevent the difficulties met in the flotation-mills when oil shipments cannot be duplicated.

The Pensacola Tar & Turpentine Co. is a distiller of soft wood, using destructive distillation. I quote the table of physical constants of their flotation-oils. These constants represent the properties of similar wood-oils sold by other dealers.

No.	Name	Specific gravity	Distilling points	Refractive index	Viscosity	Non-polymerizable
75	Crude wood-turpentine..	0.887	65–217°C.	1.456	0.9	10–12%
80	Crude pine-oil	0.911	70–232	1.4894	1.1	8
90	Pine-tar oil, re-distilled.	0.982	160–368	1.5636	5.8	Note
200	Refined wood-creosote...	0.965	105–275	1.5096	1.7	7–8
400	Crude wood-creosote....	1.025	190–360	1.4977	2.9	Note
15	Thin resin-oil	1.017	170–368	1.5631	6.1	Note
350	Crude pine-wood oil....	1.019	70–345	1.525	2.9	4
1580	Combination pine-oil....	0.980	85–352	1.5361	2.3	Note

The non-polymerizable matter is that which will not be dissolved in concentrated sulphuric acid. The test mentioned in the last column is the one used by organic chemists in order to give an idea of the amount of mineral-oil that may have been added as an adulterant. The greater the non-polymerizable residue, the more mineral-oil probably present. The test is particularly adapted to testing turpentine and light oils, and is conducted as follows:

"Place 20 c.c. of concentrated sulphuric acid in a graduated narrow-neck Babcock flask, and place in ice-water or other cold water to cool. Add slowly about 5 c.c. of the oil to be tested. Gradually mix the contents, cooling from time to time, not allowing the temperature to rise above 60°C. When it no longer warms on shaking, agitate thoroughly. Place in water-bath and heat to 60° or 65° for about ten minutes. Keep agitating four or five times during the heating. Cool to room temperature and fill the flask with concentrated sulphuric acid until the unpolymerizable matter rises in the neck. Allow to stand 12 hours or more for light oils and 48 for heavier ones, and read unpolymerizable matter in graduated neck for percentage. Note: The longer period is to be preferred, as it often takes time to make the separation. All the organic oils contain some unpolymerizable oil, which should be deducted.''

A second test is for heavier oils, such as tar-oils and resin-oils. It is known as the acetic acid test and is conducted as follows: ''Weigh about 40 grammes of the oil into an evaporating-dish, then add 100 c.c. of 10% alcoholic potash solution and heat on a water-bath for 15 minutes, stirring well. This mass is then poured into a separating-funnel and the soap washed out with water. The unsaponifiable matter is then run into a flask with 100 c.c. of glacial acetic acid and heated to 52°C., shaking the flask to dissolve the soluble matter. This mixture is then run into a separating-funnel, using a little acetic acid to wash out the flask, and allowed to stand about 30 minutes, when most of the mineral-oil will be separated on top. After separating, the solution should be put back into the funnel, as there may be more separation, in which case it is separated and added to the rest of the mineral-oil, which has been run into a weighed beaker and placed on the water-bath to evaporate the acetic acid. The beaker containing the separated oil is weighed and is considered mineral-oil; this can be ascertained by the odor and by treating with concentrated sulphuric acid.''

Both of the above tests are now commonly used in the laboratories of the larger companies using flotation. Their utility has been great and has enabled these companies to refuse shipments of adulterated oil, the adulterants commonly being non-polymerizable mineral-oils.

The General Naval Stores Co. has likewise compiled some useful data about oils from which the following is abstracted. It gives an excellent idea of the particular field in which each oil has proved of practical utility. (See next page.)

The sludge-acids from refineries treating petroleum, coal-tar, and other oily products constitute another series of products that have been misunderstood by mill-men. They are mixtures of concentrated sulphuric acid with portions of the oils that have been refined. For instance, in the refining of kerosene the treatment with strong sulphuric acid will dissolve certain tarry or asphaltic constituents, leaving it water-white. These sulphonated oil compounds are commonly wasted by the refineries. The material can be bought cheaply as a thick black liquor, often containing the equivalent of 50% sulphuric acid by weight. Of course, other oils than kerosene are treated by this method during refining, but it so happens that the kerosene-acid sludge has proved of greater value than the others. Kerosene sludges

PROPERTIES OF COMMON FLOTATION OILS

Oil	How made	Color	Sp. Gr. at 60° F.	Flotation value		Nature of froth	Use
				As frother	As collector		
Pine oil (steam)	Steam distillation of pine wood	Straw yellow, transparent	0.925 to 0.940	Excellent	Fair	Voluminous, brittle, small bubbles	As frother, with petroleum, coal tar, etc. Good on zinc ores.
Pine oil (D. D.)	Destructive distillation of pine wood	Dark yellow, transparent	0.920 to 0.940	Excellent	Fair	Voluminous, brittle, small bubbles	As frother, with petroleum, coal tar, etc. Good on zinc ores.
Pine tar oil..............	Distill pine tar	Dark brown, opaque	1.025 to 1.035	Good	Good	Profuse, permanent, large tough bubbles	To make froth permanent. Good on copper, lead, and pyrite ores.
Pine tar oil (refined)	Re-distill pine tar oil	Reddish brown, transparent	0.965 to 0.990	Good	Fair	Profuse, fairly permanent, elastic, moderate-sized bubbles	As frother. Use where ordinary pine tar oil gives too much froth.
Crude turpentine	Destructive distillation of pine wood	Reddish brown, translucent	0.980 to 1.000	Excellent	Good	Large quantity elastic, moderate-sized bubbles	As frother, with coal tar, pine tar, hardwood tar, petroleum. Good for zinc ores.
Thin pine tar............	Destructive distillation of pine wood	Brownish black, opaque	1.060 to 1.080	Fair	Good	Scant, brittle, large bubbles	As a collecting oil. Used mostly on copper ores.
Resin oil	Destructive distillation of resin	Brownish red, translucent	0.955 to 0.975	Excellent	Good	Large quantity elastic, moderate-sized bubbles	As a frother. Often used on zinc ores.
Hardwood oil	Destructive distillation of hardwoods	Black, opaque	0.960 to 0.990	Excellent	Poor	Voluminous, brittle, small bubbles	As a frother. Very good on lead ores.
Hardwood oil (heavy)	Destructive distillation of hardwood	Black, opaque	1.06 to 1.08	Good	Good	Moderate quantity of tough, medium-sized bubbles	Used alone on lead, zinc, and copper ores.
Coal-tar creosote (neutral).	Distillation of coal-tar	Brownish black, opaque	0.990 to 1.010	Poor	Good	Negligible, thin	To dilute coal tar or other heavy oils.
Coal-tar creosote (acid)....	Distillation of coal-tar	Brownish black, opaque	0.995 to 1.015	Good	Good	Voluminous, brittle, medium-sized bubbles	As a frother. Used on copper, zinc, lead, and pyrite ores.
Coal tar (thin)...........	Destructive distillation of coal	Black, opaque	1.080 to 1.110	Poor	Good	Negligible, thin	As a collector with any frothing oil. Used on copper ores.

produced by different refineries differ in their flotation value, and the Californian oil-sludges are the only ones that seem to have given satisfaction in flotation plants.

It is probable that credit for the discovery of the flotative value of these sludges belongs to Minerals Separation. At least this company owns the patents covering its use (U. S. 1,170,637, granted to A. H. Higgins). The patent specification claims the sulphuric acid derivatives of fats, oils, alcohols, phenols, and their homologues. Flotation in the slightly acid pulp with the above compounds as frothing agents gives different results from the use of these oils after sulphonating with strong acid. A second patent, covering the use of sludges obtained from petroleums, kerosene, gas-tar, etc., was granted to E. H. Nutter (U. S. 1,170,665). This patent cites the use of kerosene-acid sludge at Anaconda, which is the greatest user of the product. Not over a half-dozen other companies are using it. In every case a pyritiferous mineral is being floated. These sludges are said to do good work in sub-aeration machines. Sometimes they work better if they have been standing awhile, or after they have been mixed with water.

In case sulphuric acid will not dissolve an oil, it is sometimes possible to dissolve it in strong acetic acid and then add the sulphuric acid. Most significant is the fact that most of the good frothing-oils are almost completely polymerizable by this method. This indicates that the sludge-acid is nothing but a concentrated form of the polymerizable material present in small amounts in crude petroleum and other oils. A further conclusion is that the presence of 'double bonds' in the molecules of the oils used is essential to their becoming good frothers. The fact that carbolic acid is a better flotation-oil than oleic acid should be interesting to organic and physical chemists.

Another bit of theory in connection with the acid-sludges and the sulphonated oils has to do with the idea that acid is necessary to clean the surfaces of sulphides that have commenced to oxidize. By using a sulphonated oil the acid cleans the surface of a sulphide particle and the oil is present in the most advantageous position to 'oil' the cleaned surface.

The search for new flotation-oils is still keen. Because we do not yet know what differences in oils makes one good and the other bad, the only method available for carrying on this work is to obtain samples of the thousands of products and mixtures that are on the market and test them on a given ore in comparison with oils of known value for flotation. In Australia it was found that many of the eucalyptus-oils high in phlanderene were best, especially for differential flotation, but phlanderene cannot be found in many of the American pine-oils that are standard.

Sage-brush oil was discovered to be an excellent flotation-oil through some co-operative work between Maxwell Adams, of the University of Nevada, and the Salt Lake City station of the Bureau of Mines. G. H. Clevenger also took up the distillation of sage-brush and tested the oil resulting therefrom. Papers by both Adams and Clevenger were read at the Globe meeting of the American Institute of Mining Engineers and published in Bulletin 117 of the Institute. My own discussion of the probable cost of production of sage-tar appeared in Bulletin 119. It is there shown that it can probably be produced for from 30 to 50 cents per gallon, and since it is the full equivalent, if not the superior, of steam-distilled pine-oil, its future production in the semi-arid regions where sage-brush is abundant would seem justified. It is particularly valuable for the flotation of sulphidized 'carbonate' ores.

It is difficult to utilize coal-tar in plants using flotation supplementary to gravity concentration, on account of the fact that it is not easy to effect a good amalgamation of tar with the pulp in agitating-tanks, and even in mechanical flotation-machines. The use of coal-tar lends itself very well indeed to the system of feeding tar into the grinding machines, a system that, as mentioned above, had been worked out in our small test-mill and patented by G. A. Chapman.

The company is indebted to Mr. J. M. Callow for proving the merits of coal-tar creosote as a flotation agent by using it, in his demonstration plant at Inspiration. After we had established the value of coal-tar by laboratory tests, and while efforts were being made to obtain it commercially, he applied creosote successfully. We have continued to use it for a long time, mostly in combination with coal-tar, and have only recently dropped it, as we find crude coal-tar cheaper and better.—Rudolf Gahl, Trans. A. I. M. E.

ORE-FLOTATION

By Wilder D. Bancroft

*When discussing the theory of ore-flotation, people are apt to lay great stress upon surface-tension in general and upon contact-angles in particular. While this is entirely legitimate, it seems undesirable, because we cannot measure a contact-angle with any accuracy and because the actual existence of a contact-angle is a matter of doubt.[1] The problem of ore flotation is a very simple one or a very complex one, depending on our point of view. It has been customary to consider it as a very difficult problem, but the other attitude rather appeals to me. There is nothing strange to us in the fact that water wets glass and that mercury does not. We also know that water does not wet greasy glass readily. If one wishes to say that these facts are mysterious, I concede it willingly, because everything becomes mysterious if one follows it back far enough. All I claim is that this is no more mysterious than anything else, and that if we start with these bits of every-day knowledge as given, there are no other serious difficulties in connection with ore flotation. Ore flotation is not a unique phenomenon, it is merely a special case under the broad heading of emulsions.

If a liquid wets a solid, it is adsorbed by the solid, forming a liquid film on the surface of the latter and displacing the air film that was there. If a liquid is not adsorbed by the solid, it does not wet the solid. The formation of a liquid film over the surface of a wetted solid accounts for the experimental fact that the rise of a liquid in a capillary tube is independent of the nature of the walls of the tube. This has always seemed a very improbable state of things, and one that could be justified only by the fact that it was so. It becomes quite simple, however, the moment we consider that the rising liquid does not come in contact with the walls of the capillary tube at all. We are really dealing with the rise of liquid in a liquid tube, and it makes no difference what material is used to support the walls of the liquid tube. That this is the real explanation may be seen from the fact that concordant results are not obtained when a liquid is allowed to rise in

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*A paper read at the joint meeting of the New York sections of the American Institute of Mining Engineers and the American Electrochemical Society on May 12, 1916.

[1] Rayleigh, Scientific Papers III, 354 (1902).

a dry tube. To get good results it is important to immerse the tube in the liquid and then to raise the tube.

Since the wetting of a solid is a case of selective adsorption, we should expect that one liquid would wet a given solid more readily than another liquid does, and consequently that the first liquid would displace the second from contact with the solid. No systematic study of this phenomenon seems to have been made, but we know that alcohol will displace oil in contact with metal[2] and that water will displace kerosene in contact with quartz.[3] If we shake a finely divided solid with water and a liquid which is not completely miscible with water, an oil for instance, we can distinguish three cases. The solid is wetted entirely by water, in which case it stays in the water phase and settles to the bottom of it. The solid is wetted entirely by the oil, in which case it stays in the oil phase and sinks to the bottom of it. The solid is wetted simultaneously by oil and water, in which case it passes into the interface separating the two liquids. If the oil is less dense than the water, as is usually the case, it is a little difficult to distinguish between the last two cases. If the non-aqueous liquid is denser than water, chloroform or carbon tetrachloride for instance, it is difficult to distinguish between the first and third cases. The particles will float if the mean density of solid plus adherent oil film is less than that of the water. They may also float if the action of gravity is not sufficient to overcome the surface-tension of the water and thus to pull them through the surface. The maximum weight of substances which can be floated can be calculated from the surface-tension under ideal conditions. This calculation applies only when the solid passes into the upper liquid, and does not hold for the case where the solid passes into the interface.

Since we are dealing with selective adsorption, we should expect to find that certain substances would float readily, some others less well, and still others not at all, both the nature of the solid and of the liquid having an effect. This is the case experimentally. Hofmann found that lead iodide, silver iodide, mercuric iodide, mercuric sulphide, and mercuric oxide were floated by ether, butyl alcohol, benzene, kerosene, and amyl alcohol. Copper sulphide, lead sulphide, and calcium carbonate were floated only partially by ether, but completely by the other liquids; while zinc sulphide and tin sulphide did not float readily in ether or butyl alcohol, and calcium sulphate was not floated by any of the liquids.

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[2] Pockels, *Wied. Ann.* LXVII, 669 (1899).

[3] Cf. Hofmann, *Zeit. Phys. Chem.* LXXXIII, 385 (1913).

An interesting experiment, which has been done in my laboratory,[4] is to shake copper powder or aluminum powder with kerosene and water. The metallic powder goes into the kerosene and into the interface, producing an effect of molten copper or molten aluminum, as the case may be. When the bottle is allowed to stand after having been shaken, the metallic powder in the interface creeps up the side of the bottle above the surface of the liquid, rising higher if a little alcohol has been added. I have seen an apparently coherent metallic film rise three inches above the surface of the upper liquid phase. If too much copper or aluminum be added, the kerosene cannot hold all of it up and a portion falls to the bottom of the flask, carrying drops of kerosene with it. If the mixture be poured out on a piece of wood, the copper spreads over the surface of the wood just as it did over the surface of the glass. This experiment illustrates the principle involved in all bronzing liquids. A bronzing liquid consists of a volatile liquid which will hold up the metal, and some substance which will keep the metallic powder from rubbing off too readily after it has been applied. The aluminum and copper powders on the market are coated with stearin. This makes them difficult to wet with water, but special experiments have shown that the behavior of copper or aluminum with kerosene is qualitatively the same whether the stearin coating is removed with ether or not.

Similar results can be obtained with colloidal solutions. Isobutyl alcohol[5] was added to a colloidal gold solution obtained by reducing gold chloride with carbon monoxide. When the two liquids are shaken, the gold forms a thin film at the interface. This film is violet-blue to blue-green by transmitted light and golden by reflected light. A thin water film forms between the isobutyl alcohol and the glass, and the gold concentrates in the dineric interface thus formed, making the alcohol appear uniformly gold-plated. With ether the gold film rises high above the level of the two liquids. With carbon bisulphide the adherent film of gold appears blue. When the carbon bisulphide is broken into drops by shaking, each drop appears blue. When a blue gold was obtained by reducing gold chloride with phosphorus dissolved in ether, the gold went into the dineric interface. When a brownish-red gold was obtained in this way, it remained in the water phase and showed no tendency to pass into the interface. This difference is undoubtedly due to an adsorption of something at the surface of the gold, because Reinders found that 0.005% gum arabic prevents

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[4] Bancroft, Trans. Am. Electrochem. Soc. XXIII, 294 (1913).

[5] Reinders, *Zeit. Kolloidchemie* XIII, 235 (1913).

colloidal gold from passing into the ether-water interface. With carbon tetrachloride, carbon bisulphide, or benzene, the gold goes into the interface as before, but the gum arabic prevents its changing from red to blue.

Colloidal arsenic sulphide goes into the dineric interface with amyl alcohol or isobutyl alcohol, but stays in the water phase when carbon tetrachloride, benzene, or ether is the second liquid. India ink goes completely into the interface with amyl alcohol, carbon tetrachloride, or benzene; it goes partly into the interface with isobutyl alcohol, and stays entirely in the water phase when ether is the second liquid.

Winkelblech[6] has shown that mere traces of gelatine in water can be detected by shaking with organic liquids, the gelatine concentrating at the interface to form a film. ''A heavy precipitate was obtained when 10 c.c. of a solution containing 0.234 gm. gelatine per litre was shaken with benzene. Precipitates were also obtained when the gelatine solution was diluted ten-fold, twenty-fold, and even forty-fold, provided 10 c.c. solution were taken for the test. At the highest dilution the concentration of the gelatine was 0.06 gm. per litre, and there were consequently 0.06 mg. in the 10 c.c. taken for the test. This seemed to be about the limit at which a precipitation could be detected definitely. * * * Some other colloids behave like the glue colloid (glutin), and can be shaken out of their solutions. Other hydrocarbons are also effective, so that the phenomenon seems to be a general one. Precipitation was obtained with albumin, water-soluble starch and soap, as well as with resin dissolved in very dilute caustic soda. The colloids grouped as mucin can be precipitated from urine and the proteins from beer. It is worth noting that tannin can be precipitated but not gallic acid.

''The hydrocarbons which can be used are : kerosene, liquid paraffine, benzene, chloroform, and carbon bisulphide (in addition to benzene). The result varies from case to case. With the hydrocarbons which are lighter than water, the precipitate floats on the water; with the denser hydrocarbon the precipitate is below the water layer. The emulsions which form seem to have very nearly the same density as the organic liquid used. It is not possible to get the precipitation with all liquids which are non-miscible or slightly miscible with water. Experiments with ether were entirely unsuccessful.

''As a complement to the action of hydrocarbons on aqueous colloidal solutions it was found that fats dissolved in hydrocarbons or similar liquids can be precipitated in the surface film by shaking with

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[6] *Zeit. angew. Chem.* XIX, 1953 (1906).

water. Precipitations were obtained with butter, olive-oil, lanolin, and vaseline. It was also found that the emulsions of heavy hydrocarbons or carbon bisulphide with the fats of low specific gravity also accumulate below the water layer, only a small portion being carried to the surface by adhering air bubbles. When water is used for shaking out, the precipitation is very slight. With a slightly alkaline solution such as dilute lime-water, heavy voluminous precipitates were obtained while a transparent layer of fat is obtained when a slightly acid solution is used. With concentrated alkali or acid solutions, viscous emulsions are obtained which hold fast considerable amounts of solution.''

Winkelblech patented the use of such organic liquids as kerosene for clearing sewage by shaking out the colloidal oxidizable matter. The method was not a success commercially, because less than 40% of the oxidizable matter was removed.[7]

Briggs[8] has shown that sodium oleate is removed from solutions of different strengths during the process of emulsifying benzene, and that the amount of this removal depends upon the strength of the soap solution and the specific surface of the benzene phase. Rayleigh[9] has observed an interesting case in which dust goes into the water layer. ''In the course of some experiments last year, in illustration of Sir George Stokes' theory of ternary mixtures, I had prepared an association[10] of water, alcohol, and ether, in which the quantity of alcohol was so adjusted that the tendency to divide into two parts was almost lost. As it was, division took place, after shaking, into two nearly equal parts, and these parts were of almost identical composition. On placing the bottle containing the liquids in the concentrated light from an arc lamp, I was struck with the contrast between the appearance of the two parts. The lower, more aqueous, layer was charged with motes, while the upper, more ethereal, layer was almost perfectly free from them. Some years ago I had attempted the elimination of motes by repeated distillation of liquid in vacuum, conducted without actual ebullition, but I had never witnessed as the result of this process anything so clear as the ethereal mixture above described.

''The observation with the ternary association, which happened

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[7] Biltz and Kröhnke, *Zeit. angew. Chem.* XX, 883 (1907).

[8] *Jour. Phys. Chem.* XIX, 210 (1915).

[9] Scientific Papers, III, 569 (1902).

[10] *Association* is here employed as a general term denoting the juxtaposition of two or more fluids. Whether the result is a *mixture* depends upon circumstances.

to be the first examined, is interesting, because the approximate equality of the liquids suggests that the explanation has nothing directly to do with gravitation. But the presence of the alcohol is not necessary. Ether and water alone shaken together exhibit the same phenomenon. It would appear that when the two liquids are mixed together in a finely divided condition, the motes attach themselves by preference to the more aqueous one and thus when separation into two distinct layers follows, the motes are all to be found below.[11] * * *

"I have lately endeavored to obtain some confirmation of the views above expressed by the use of other liquids. It would evidently be satisfactory to exhibit the selection of motes by the upper, instead of by the lower, layer. Experiments with bisulphide of carbon and water, and also associations of these two bodies with alcohol, which acts as a solvent to both, gave no definite result, perhaps in consequence of a tendency to the formation of a solid pellicle at the common surfaces. But with chloroform and water, and with associations of chloroform, water and acetic acid (acting as a common solvent) the experiment succeeded. The motes were always collected in the *upper,* more aqueous, layer, even when the composition of the two layers into which the liquid separated was so nearly the same that a few additional drops of acetic acid sufficed to prevent separation altogether."

The reverse case appears to occur with white lead. J. Cruickshank Smith[12] says: "During recent years the practice has been adopted, largely among white-lead corroders who grind their own white lead in oil, of doing away with the final drying of the white-lead pulp as it comes from the washing process, and grinding or beating up the pulp (exhausted of water until the proportion of the latter does not exceed about 20 per cent) with a suitable quantity of refined linseed oil. This process depends on the greater surface attraction which white-lead particles offer to linseed oil than to water. It enables considerable economies to be effected in the manufacture of ground white lead, and it eliminates risk of lead poisoning during one of the most dangerous parts of the white-lead manufacturing process." Not enough oil is added to float the white lead and consequently the white lead carries the oil down with it,[13] leaving the water as upper phase.

That the adhesion between the solid and the liquid may be very

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[11] The clearness of the upper layer, after a mixture of ether and alcohol has been shaken up with dust, had already been observed and explained, much as above, by Barus, *Amer. Jour. Sci.* (3) XXXVII, 122 (1889).

[12] 'The Manufacture of Paint,' 92 (1915).

[13] My attention was first called to this by T. R. Briggs.

marked is shown by the behavior of the so-called water wings. These consist of a closely woven fabric readily permeable to air when dry. When thoroughly wetted, the film of water is strong enough to permit of the wings being blown up enough to float a person with ease. Though I know of no direct experiments on the subject, it seems probable that the gas pressure in some sandstone anticlines may result from the oil being displaced by water, which would wet the porous rock more readily than does the oil.

In many of the cases where oil flotation has been employed we have a sulphide ore, which is much more readily wetted by oil than by water, in the presence of a silicious gangue, which is much more readily wetted by water than by oil. Consequently the gangue tends to stay in the water phase while the ore is carried up by the oil. The use of an acid solution is natural, because oil adsorbs hydroxyl ions,[14] and these latter cut down the adsorption of the solid. Nagel[15] found that when precipitated chromic oxide is shaken with water and benzene, it goes into the dineric interface, but is precipitated from it by the addition of caustic alkali. Zinc sulphide is also precipitated from the dineric interface of kerosene and water by addition of alkali. I am aware that modern flotation practice is tending to the use of neutral or slightly alkaline solutions, but in such cases air plays an important part, and the use of mixed oils may introduce a new set of factors. It must also be remembered that acid in ore flotation does not act because of a replaceable hydrogen atom, but by cutting down the concentration and consequently the adsorption of hydroxyl ions. If calcium ions, for instance, cut down the adsorption of hydroxyl ions sufficiently, calcium hydroxide would behave like an acid, so far as ore flotation is concerned, though it would be alkaline to litmus paper. Somewhat similar cases are known. Under electrical stress albumin moves to the cathode in acid solutions, and also in calcium chloride solutions. The effect is not a question of acidity. The direction in which the albumin moves depends upon the charge of the ion adsorbed in excess. The hydrogen cation and the calcium cation are each adsorbed more than the chlorine anion, and consequently the albumin moves to the cathode in these two solutions. I do not know whether anything of this sort is a factor in modern flotation practice.

Since no systematic experiments have been made to determine the exact effect of temperature, we do not know to what extent the apparent advantages of a heated solution are due to a relative change in the

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[14] Twomey, *Jour. Phys. Chem.* XIX, 360 (1915).
[15] *Jour. Phys. Chem.* XIX, 570 (1915).

selective adsorption, to a change in the relative densities of the two liquids, or to a change in the viscosities. It seems probable that all three changes are factors, but that the change in the selective adsorption is the important one. Of course, the absolute adsorption must decrease with rising temperature, but the selective adsorption may, and probably does, increase with rising temperature. At still higher temperatures the decrease in absolute adsorption becomes too serious and there is therefore a maximum temperature which is not necessarily the same under varying conditions.

We now have to consider the part played by air in flotation. Since the density of air is low, it is clear that a film of adsorbed air or an attached bubble of air will be very effective in floating a solid particle. If we like, we may consider air as an extreme case of a second liquid phase, in which case we may have the solid remaining in the air phase under suitable conditions, concentrating in the interface, or remaining in the water phase. If a piece of metal covered with an air film be laid very carefully on the surface of water, the water may wet it so slowly that the metal will float if it is not too heavy. If the surface of a copper wire be converted to sulphide, it will float more readily because the adsorption of air is more marked. If we have a stearin surface, as in the case of copper powder or aluminum powder, the water has still less tendency to wet the solid, and it becomes quite difficult to cause the commercial copper powder or aluminum powder to sink in water. This difference in readiness to wet is made use of in the film flotation processes of Wood and Macquisten.

The concentration of the solid at the interface occurs when a skin forms over the surface of boiled milk or of cocoa or of a peptone solution. I do not know of any case of ore flotation analogous to this, but doubtless one could be devised if anybody was interested in it. In the case of soap solutions we have a partial concentration at the surface, but the bulk of the soap remains distributed through the water phase. The soap, however, adsorbs so much air that boiling-point determinations on concentrated solutions are worthless.[16]

The selective adsorption of gases and vapors by solids is a matter of common knowledge.[17] The film of condensed gas shows itself in the abnormal mobility of very fine powders, in the fact that two pieces of a broken object will not re-unite when pressed together, in a resistance to the passage of an electric spark between solid terminals, and in the behavior of the crystal detector and the coherer as used in wireless tel-

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[16] McBain and Taylor, *Zeit. phys. Chem.* LXXVI, 182 (1911).

[17] Bancroft, *Jour. Phys. Chem.* XX, 1 (1916).

egraphy. All liquids show selective adsorption of gases and vapors. The most striking way in which this shows itself is in the form of the splashes when a drop of water, 5 mm. in diameter, falls on a sheet of water from a height of less than 1 metre. It is this film of adsorbed gas which tends to prevent the coalescence of two soap-bubbles or two impinging jets of water when there is no electrical stress.

Since water removes air more or less quickly from practically all minerals, selective flotation from already wetted ore is practically impossible, and one must have recourse to the combined effect of oil and air. It so happens that in acid or neutral solutions air seems to be adsorbed by organic liquids much more readily than by water.[18] Into 100 c.c. approximately normal caustic potash solution 0.5 c.c. chloroform was dropped from a 5 c.c. pipette. The chloroform did not seem to spread out on the surface before sinking so much as it did with water. The globules sank to the bottom and flattened out; they were distinctly not very mobile, and seemed to sink to the bottom of the vessel. When the chloroform was dropped into the water it broke up into a number of drops which did not agglomerate so easily as in the water solution. In fact, quite a little shaking was necessary in order to make them coalesce. At first no air bubbles could be detected, but after standing for five minutes a very small bubble appeared on the chloroform. Sulphuric acid was then added until the solution became acid. The flattened drop of chloroform at once assumed the shape of a round ball and became mobile. An air bubble also appeared in the centre of the drop.

''Into 100 c.c. approximately normal sulphuric acid solution 0.5 c.c. chloroform was dropped as before. The chloroform spread all over the surface and then sank through the solution in small drops, forming round globules with air bubbles clinging to each. It was hard to get rid of the bubbles on the chloroform drops by shaking; as soon as one was driven off another bubble appeared exactly in the centre of the drop. When the bubbles were dislodged from the drops, they rose to the surface carrying with them some chloroform, a part of which remained on the surface until it evaporated, while the rest sank back to the bottom of the solution. The globules were very mobile and coalesced readily. Caustic potash was added to the solution, making it alkaline. The chloroform globule flattened immediately and the air bubble in the centre disappeared. In still another experiment an acid solution was made alkaline, then acid, and then alkaline again. The re-

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[18] Twomey, *Jour. Phys. Chem.* XIX, 360 (1915).

sult confirmed Wilson's experiments,[19] for the drop of chloroform was always flat in the alkaline solution and always round in the acid solution. There is scarcely any difference to be noted between the shape of the drop in acid solution and in pure water. The same results were obtained when NaOH and HCl were substituted for KOH and H_2SO_4.

''In one experiment in a nitric-acid solution the temperature was raised to about 40° C. Bubbles seemed to shoot from all parts of the solution to the chloroform drop. When they had formed a large bubble in the centre of the chloroform, the air bubble rose to the surface of the solution as in the other cases.''

Of course, it does not follow that the relative adsorption of gas is always greater for oil in acid solution, but merely that this seems to be true in the cases hitherto studied. It is purely an empirical observation. Another interesting fact is the difficulty that is experienced in getting air bubbles to attach themselves in some cases to the oil films surrounding the solid particles. Some people have even claimed that nascent gas is essential, but this is absurd. If the air bubble comes in contact with the oil it will adhere; but it is not easy to bring about this contact. It can be done by vigorous agitation or by causing dissolved gas to come out of solution, but the essential thing is merely to bring the gas in actual contact with the oil. . . .

Anderson[20] classifies flotation-oils as ''frothing'' and ''collecting'' oils.[21] ''There is at times some difficulty in grasping the distinction between frothers and collectors as such, for one oil in itself may, and often does, possess both frothing and collecting properties. The action of a frothing oil is such as to produce froth in greater or less amount, dependent on the frothing power of the oil. A collecting oil has a collecting power for sulphides in preponderance over its frothing action, being therefore, so to speak, a poor frother; a collecting oil may have simply a collecting action and little or no frothing action. As stated in the foregoing, some oils combine both the properties of frothing and collecting in variable degrees of each.

''The most successful frothing oils include the pine-oils, cresylic acid and turpentines, and other pyroligneous products from the distillation of wood—notably methyl alcohol.[22] The coal-tar phenols and their near derivatives, and almost all of the so-called essential oils are

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[19] Wilson, *Jour. Chem. Soc.* I, 174 (1848).

[20] *Met. & Chem. Eng.* XIV, 136 (1916).

[21] Van Arsdale calls them "foamers" and "oilers."

[22] *Met. & Chem. Eng.* XIV, 136 (1916).

good frothers. The essential oil of eucalyptus finds favor, particularly in Australian practice, on account of relatively low cost and immediate supply. Castor-oil, to which reference has already been made, when mixed 1:4 with kerosene has found application. The more volatile products of petroleum, including kerosene and gasoline [?], have been successful frothing oils.

''So-called mineral-oils and tar-oils do not generally form good flotation froth, but have a marked selective action on the sulphide minerals. Among the mineral oils are included the following: asphaltum base, crude petroleum, refined oil, gasoline, burning oil, cresol, and coal-tar creosotes.

''It is found that thick oils tend to form viscous coherent flotation concentrates, while thin oils form less coherent masses. The action of coal-tar in stiffening a weak ephemeral froth is indicative of the former. In general the essential oils give a coherent froth and satisfactory extraction; oils like oleic acid or candle-maker's red oil, petroleum, and lubricating and engine oils have a strong tendency to produce heavy thick granules which will not float. Oleic acid has a well-marked power to float silicates.'' . . .

Since we are dealing with selective adsorption, we should expect to find that some oils would be better than others for certain purposes.

Anderson[23] states that ''oils derived from the destructive distillation of wood, such as wood-creosotes, pyroligneous acid, and the like, are found to give the best recovery on galena and zinciferous material; coal-tar products are better adapted to the successful flotation of copper-bearing minerals.'' There are no independent data from which this result could have been predicted.

Since flotation is due to selective adsorption, anything which will change the latter will change the degree and nature of flotation as far as the oil-water flotation is concerned. Adding a third liquid which is miscible with the other two will tend to make the oil and water layers more nearly alike in composition and therefore in properties. This gives us a possibility of varying the selective adsorption within certain limits and its possiblities should be determined, even though there may be no economic advantages. . . . . In some experiments recently made at Cornell by Mr. Briggs, it has been found that addition of salt made it easier to shake out colloidal ferric oxide with benzene. The reason for this seems to be that the salt makes the colloidal solution less stable. Any substance which prevents peptization in the water

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[23] *Met. & Chem. Eng.* XIV, 136 (1916).

phase or promotes it in the oil phase will tend to increase the flotation. I do not yet know to what extent this is applicable to ore flotation; but Anderson[24] reports that experiments performed on a 60-mesh product from the Joplin district containing pyrite and galena in a calcareous gangue showed: that potassium bichromate will deaden galena and permit the flotation of the pyrite; that sodium, potassium, and ferric sulphates promoted the production of clean concentrates; and that ferrous sulphate and cupric sulphate were very harmful to the successful flotation of this particular product, flotation being practically impossible in their presence. Anderson, of course, ventures no opinion as to why these salts act in this way; but it ought not to be difficult to work out a hypothesis if some data were forthcoming. The inadequacy of the present data is made clear by the statement of R. H. Richards that in the case of a certain Tennessee zinc ore the addition of a small amount of copper sulphate was necssary in order to bring about successful flotation. We have not yet made any experiments on the factors affecting the air-flotation when the oil is reduced to a minimum, so I will not discuss that point at all.

There seems to be no reason to suppose that ore-flotation has yet gone beyond the first stages of its development, and certainly a clear knowledge of the general theory should be a help in promoting the development.

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[24] *Met. & Chem. Eng.* XIV, 137 (1916).

THE THEORY OF FLOTATION

By H. Hardy Smith

(From the *Mining and Scientific Press* of July 1, 1916)

It appears to me that the problem of elucidating the theory of flotation could be greatly simplified by formulating some definite line of attack; the first consideration in which should be to segregate the various physical forces with their attendant phenomena, and to attack each in turn.

It is quite possible, in fact, most probable, that some of the forces come into play in all the phenomena, but by delivering a massed attack on each section in turn, perhaps success can be achieved more easily.

I suggest the following as a possible segregation:

(1) The physical forces governing the formation of bubbles in a pulp.

(2) The physical forces governing the attachment of bubbles to sulphide particles in a pulp.

(3) The physical forces governing the stability of the bubble attachment.

(4) The physical forces governing the stability of a bubble at the free surface of the pulp.

Leaving out of consideration those processes in which bubbles are formed in a pulp by the chemical action of one substance on another, and also Mr. Norris's unique process, in which minute bubbles are 'born' in a pulp which is super-saturated with a gas, and regarding only those processes in which a gas is introduced directly from an external source, segration No. 1 will be found to present a considerable problem.

Several of your correspondents appear to be laboring under the delusion that it is simply necessary to introduce air violently into a pulp either by agitation or blowing, and immediately bubbles of the right number and kind obligingly form themselves. Anybody who has had practical experience with flotation, especially with the so-called air-froth flotation, knows that most unfortunately this is not the case. No amount of agitation or blowing will produce bubbles of the right kind and number in absolutely pure water. A contaminating agent is necessary, and as some of the contaminating agents commonly used happen to be oils, concentration by frothing most unhappily has been named 'oil-flotation,' thereby masking the real significance of the use of the reagent. The action of certain substances in producing innumerable minute bubbles when air is introduced forcibly into a pulp, seems to be of fundamental importance, since without these bubbles the most common forms of froth flotation cannot be considered.

Professor Pollock of Sydney University, in Australia, has done some very interesting and useful work on this all-important subject, and I believe has formulated a theory. I once saw a set of instantaneous consecutive photographs of bubbles, taken by him, showing their formation after the introduction of a blast of air. With pure water the bubbles were mostly large, and even the small ones which were instantaneously produced had a tendency to collect together to form large ones. With contaminated water the reverse was the case, the instantaneously produced large bubbles seeming to break down into smaller sizes.

From my experience in the practical application of the froth-flotation process, I am inclined to believe that many of the troubles that crop up from time to time at flotation plants are due to the inability of the reagent used to produce the required quantity of bubbles, owing to the appearance of some reactive substance in the pulp. Hence practical, as well as theoretical, considerations demand a thorough understanding of the physical forces governing the production of bubbles in a pulp.

Coming now to segregation No. 2. More attention has been paid to this phase of the question perhaps than to any other, and rightly so, as it is of the utmost importance in all flotation processes, those employing the surface-film effect being excepted. Many writers pass lightly over the problem and simply state that the bubbles attach themselves preferentially to the oil or gas-filmed sulphide particles.

Let us now see whether this is possible if the two forces of surface-tension and adhesion are alone considered. In the following discourse surface-tension can be most simply defined as that force acting at the surface of all liquids which continually tends to reduce the surface area; and adhesion as that force which acts across the interface between two substances, which are in infinitely close contact, and tends to keep them from separating.

Consider a particle of sulphide mineral (which, for the sake of clearness, we may assume to be nearly spherical) and a bubble in close contact, in the interior of a pulp, but before the bubble has actually 'picked up' the mineral. (Fig. 1.) Even if the particle possesses appreciable adhesion for the water, the surface of the liquid in contact with the particle must be considered as tending to have surface-tension, although the tendency is opposed by the adhesion. (See T. J. Hoover's 'Concentrating Ores by Flotation,' pages 50 to 55).

In the first case, assume the adhesion to be negligible. The surface-tension forces that now come into play are shown in Fig. 1, where *Tg* is the gas-liquid, and *Ts* is the solid-liquid surface-tension. A glance at the force diagram will show that whatever the value and direction of the forces *Ts* and *Tg*, their component *Tc* can never be greater than *Tg*+*Ts*. Therefore surface-tension alone cannot rupture the intervening film, and cause the bubble to envelop the particle. If the particle possesses appreciable adhesion for the liquid, then the case

Fig. 1.

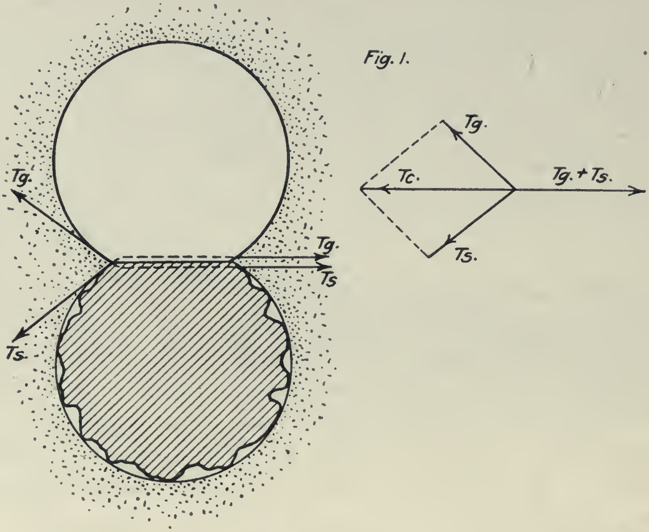
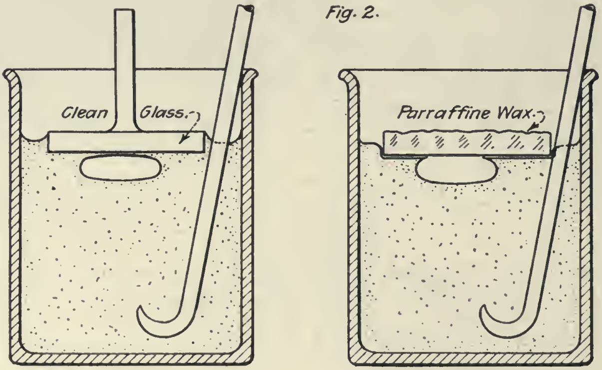


Fig. 2.



Bubble unattached
Bubble-Film continuous and
Bubble perfectly mobile.

Bubble attached and
Bubble-Film discontinuous.

is more hopeless still, as *Tc* must then be sufficiently strong to rupture the intervening film and also to tear it away against the action of the adhesive force between the solid and the film.

Once a rupture has been effected, bubble attachment resolves itself into a struggle between surface-tension and adhesion, the former strongly favoring a strategical retirement to the rear, from the salient, so as to straighten the line, and adhesion endeavoring to hold the right wing to its position.

As it is an established fact (see Fig. 2) (Mr. C. T. Durell notwithstanding) that a bubble contiguous to a surface with negligible adhesion does become attached almost immediately, so that its film forms part of a continuous film covering both solid and gas, there must be some force that causes rupture of the bubble-film at the point of contact.

In the case of two plain bubbles in pure water with their films in contact, the immediate coalescing can probably be explained by the difference in vapor-pressure existing in bubbles of different radii. But we add a contaminating agent for the very purpose of counteracting this force due to the difference in vapor-pressure so as to allow small bubbles to exist in the presence of larger ones; otherwise a froth would be an impossibility. Hence some force other than the difference in vapor-pressure must be present when one of the bubbles happens to have some, or all, of its interior space occupied by a sulphide particle.

In all probability this additional force manifests itself in the phenomenon known as the 'hysteresis' of the contact-angle. Hysteresis is defined as the lagging of effect behind cause, and a contact-angle is the "effect" that is "caused" by bringing a solid surface in contact with a liquid surface in the presence of a gas. With many substances the "effect" (the contact-angle) does not assume its full value immediately, but lags behind. The reason why the angle changes can be fairly well explained if we assume that there is a force acting between a solid surface and a gas, tending to concentrate the gas on the solid surface; and that this force is strong enough to act across a thin film of the liquid.

In Fig. 3 the solid is a piece of glass, which is clean, and has been immersed for some time in the liquid. On drawing it through the surface, a contact-angle is immediately formed, and for any given angle, the forces *Tsg, Tlg,* and *Ad* are in equilibrium (ignoring gravity). If now the solid possesses the power to adsorb the gas through the very thin film at the toe of the angle, the adhesion of the liquid for the glass will be lessened and a corresponding surface-tension *Tsl* set up in the direction shown. This additional force will be sufficient to upset the state of equilibrium, the toe of the angle will recede, and the angle will increase in size. The stable angle will be reached when *Tsg, Tlg, Tls,* and *Ad* have such magnitude and direction as to balance one another.

It has been found that those substances which possess the greatest power to vary the contact-angle also show the strongest tendency to float under suitable conditions, and it is reasonable therefore to assume that this power has something to do with the attachment of bubbles.

The problem presented by segregation (3) is not nearly so formidable as that just considered; it, as already stated, merely resolves itself into a struggle between surface-tension and adhesion. With most substances in their natural state, adhesion is altogether too strong, and, even if the film at the point of contact is ruptured, the bubble cannot attach itself on account of the inability of the surface-tension to tear the solid and the liquid surfaces apart. Hence either the surface-

Fig. 3.

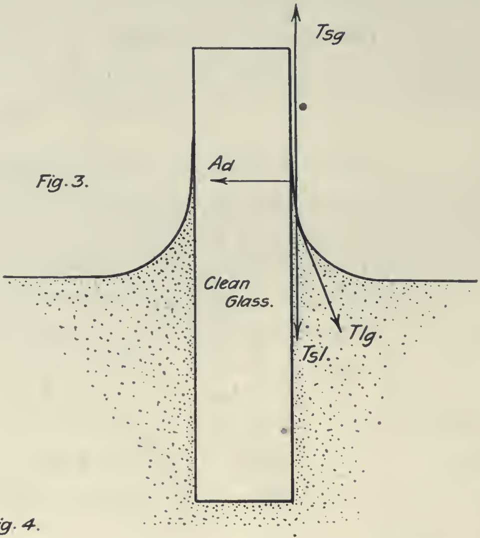
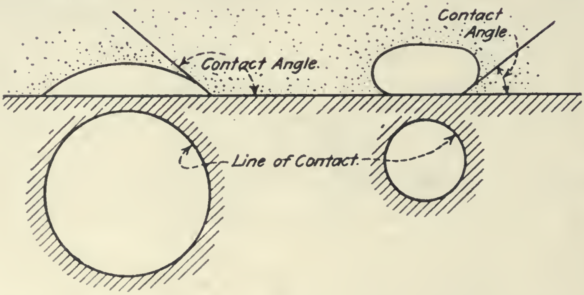


Fig. 4.



tension must be increased or the adhesion decreased. The latter course is usually adopted, as, with dilute solutions, the former is difficult; and except for very small amounts is an impossibility.

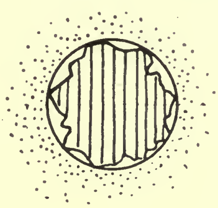
Although an absolute increase in the surface-tension is out of the question, a relative increase is possible by raising the temperature. Both surface-tension and adhesion decrease with a rising temperature, but the latter much faster than the former; one being zero at the critical temperature and the other probably zero at the boiling-point. This is one of the reasons why solids that will not collect bubbles at ordinary temperatures, will do so when the boiling-point is approached.

The usual methods employed for decreasing the natural adhesiveness of liquids for solids are:

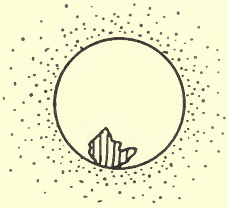
(a) To allow the solid to take on a film of gas by adsorption (or occlusion?).

(b) To allow the solid to take on a film of oil or other greasy matter by adhesion.

(c) A combination of both (a) and (b).



A



B

While collecting evidence for one of the patent lawsuits that are ever with us, an interesting discovery was made. A piece of Broken Hill sulphide ore, taken from the centre of a large uncracked block, was found to contain 0.0037% of natural grease, as obtained by an ether extract. Samples were taken from several other mines, and all gave an oily residue after extracting with ether in a most careful manner. Perhaps it is just as well to add that this was discovered accidentally and was not being specially sought as prospective evidence. This discovery goes a long way toward explaining the preferential adhesion of bubbles to sulphide particles.

The tenacity with which the bubble holds the particle depends on the length of the line of contact, which in turn depends on the size of the contact-angle, itself proportional to the relative values of surface-tension and adhesion. (See Fig. 4.)

If the adhesion is negligible, and the particle is large in comparison with the bubble, the result would be as shown in Fig. A.

If the particle is small, then the result would be as in Fig. B.

As adhesion increases, the tendency is for the particle to get more and more out of the bubble and into the liquid until the surface-tension does not act over a sufficiently long line of contact to hold the weight of the particle, and it falls off.

The problem presented by segregation (4) has been dealt with in a most excellent manner by Mr. W. H. Coghill in the *Mining and Scientific Press* of February 26, 1916. His remarks in regard to a lowering of the surface-tension *per se* not being essential to the formation of a froth are most timely.

The tension that exists in a pure liquid film is unlike all other tensions with which we are familiar, in that the stress is not proportional to the strain. Within the elastic limit (that is, the limit wherein the substance will return to its original shape when the contorting force is removed) a steel rod, or, taking what is more familiar still, a steel spiral spring, needs twice the pulling force to stretch it twice as much, and so on. The well-known spring balance depends on this fact. But with a liquid film the same force can continue to cause an extension until rupture takes place, in spite of the fact that the film, right up to the point of rupture, is within the elastic limit according to the above definition.

It is plain then that our common conception of a tension must be entirely revised when we come to deal with the tension at the surface of a liquid. For a system to be in a state of stable equilibrium it must offer a greater resistance to any force which tends to change its configuration, and as a pure liquid film does not fulfill this requirement it cannot possess stability.

The extreme instability of bubble-films is strikingly shown by the phenomenon in certain boiling liquids, with which we are all painfully familiar in our student days, called 'bumping.' In the absence of nuclei on which to form, the radius of a steam bubble when it first comes into being must be infinitely small, and the vapor-pressure to balance the surface-tension of these small bubbles is large. Therefore before the bubbles can expand and rise through the liquid (that is, before boiling can occur) the temperature must be raised above the natural boiling-point of the liquid. As soon as the bubble has expanded to appreciable size, the vapor-pressure of the liquid is in excess of that necessary to balance the surface-tension, and the bubble expands so rapidly that it literally explodes.

A boiler does not explode until its steel plates are actually ruptured, but the bubble explodes at the bottom of the beaker, that is, while its shell is actually in existence.

In the case of a solid, the greater the tension the greater the tensile stress developed; for a material of given strength, the greater the tensile stress, the greater the chance of rupture.

This line of reasoning does not hold in the case of a liquid film. The idea that a bubble film can be ruptured by the force of its own surface-tension is about equivalent to the idea that a man can lift himself by his own shoe-strings.

It is obvious from the nature of the molecular forces engaged, that the greater the surface-tension the greater the ultimate tensile strength of the film. The lowering of the tension in itself therefore cannot give greater stability to a liquid film; but the surface adsorption, which accompanies the lowering of the tension in the case of certain solutes, can.

For reasons that need not be gone into, a solute which lowers the surface-tension of a liquid, concentrates at the surface of the solution, but this process of concentration (called adsorption) takes a certain definite time to reach its full value. Now, if a film of the solution be stretched, new surface is produced, and this new surface at the moment of production possesses greater tension than the rest of the surface, because the surface adsorption has not had time to reach its full value. It therefore offers a greater resistance to the stretching force, and fulfills the conditions for stable equilibrium. So strong is the adsorption factor in certain cases, that practically the whole of the solute is concentrated in the surface layers, and therefore, although the absolute quantity in the solution may be exceedingly slight, the surface effect it produces is considerable. This explains the efficacy of the extremely small amount of contaminating agent used in some froth-flotation plants.

In a mineral-froth, it is strikingly obvious that those bubbles which have their films thickly studded with sulphide particles have their stability enormously increased. In some froths, one such bubble can be seen pursuing the even tenor of its way, amid a regular holocaust of its less fortunate brethren. The reason for this is not quite clear, but it is probably due to the adhesive force between the liquid and the solid.

The above remarks are given for what they may be worth, in the hope that they may be of some assistance to other mill-men, who, like myself, are anxious to see the inner workings of a flotation process clearly, as by the light of day, but at present, only perceive them dimly, as by the flicker of a candle at the far side of a 50-ft. stope.

THE FLOTATION OF MINERALS

By Robert J. Anderson

(From the *Mining and Scientific Press* of July 8, 1916)

*Many phenomena are supposed to contribute to the flotation of minerals, whether in whole or in part is a mooted question. I shall only sketch roughly the present tendency of ideas and make no reference to the first early and crude notions, which are now mainly of historical interest.

Surface-Tension has been well defined in articles appearing in the *Journal of the American Chemical Society* during the years from 1908 to 1913. The theory has been treated in particular by Laplace, Gaus, and more recently by Van der Waals, and by Willows and Hatschek.[1] As defined by Jones,[2] ''potential energy, present at the surface of liquids, produces a tension which is known as surface-tension.'' The phenomena invariably indicative of surface-tension are: Drops of a liquid not exposed to an external force, that is, either suspended in another liquid of the same specific gravity or freely falling, assume a spherical shape, the sphere being that form of body with the smallest surface per given volume; further, if water be placed in an open vessel its surface film will be a measurable quantity, and its thickness will vary with a number of factors of which temperature is one. Its thickness is observed as ranging from 4×10^{-5} cm. to 4×10^{-8} cm., and its density, when referred to the main bulk of the water below, will approximate 2.14. Surface-tension is not affected by the surface area. It is numerical in value and expressed in dynes per centimetre. It is a variable factor dependent on temperature, increasing numerically with falling temperature, for example, water at 18° C. has a surface-tension of 73 dynes per centimetre, and at 0° C. this increases to 75 dynes. At the critical temperature of a liquid its surface-tension becomes nil.

All liquids have a definite cohesion or tensile strength, which is ascribed to the mutual attraction of their molecules. This then is comparable to a pressure existing within a liquid, which has been termed the 'intrinsic' pressure. Naturally the value of the surface-tension of

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*Abstract of paper read at the Arizona (September 1916) meeting of the American Institute of Mining Engineers.

[1] Willows and Hatschek: 'Surface Tension and Surface Energy,' 1915.

[2] Jones: 'Elements of Physical Chemistry,' 1907.

solids is numerically high. The surface-tension of a pure liquid against its vapor is markedly affected by the addition of soluble contaminants. Some salts will raise the surface-tension of water while others will lower it; the fact that the salts of weak acids will lower the surface-tension of water is explained by the fact that free acid is liberated by hydrolysis. It is further known that all acids will lower the surface-tension of water, which is also decreased by the addition of oil, or, in other words, oil will reduce the interfacial tension between the water-air phases. A phenomenon for which no explanation has been given is the one showing that the addition of contaminants may either raise or lower the surface-tension of water, but such addition, while it may decrease that tension greatly, can increase it only slightly. Any lowering of surface-tension is more marked in a liquid that has a high surface-tension, such as water, than in liquids of low surface-tension.

There can be, of course, no surface-tension without adsorption, which produces, in the case of positive adsorption, an increased surface concentration resulting from a lowering of the surface-tension by the contaminating and dissolved substance, whatever it may be. The equation of Gibbs ($u = -c/Rt.do/dc$) gives the relationship between surface-tension and the distribution of the solute between the bulk of the liquid and the film interface. Here the notation is:

$u =$ excess of substance in the surface layer,
$c =$ concentration in the main body of the liquid,
$R =$ the gas constant,
$t =$ absolute temperature,
$o =$ surface-tension.

This shows that when the surface-tension is reduced by the addition of a contaminant, the quantity do/dc is negative and u is positive (from algebraic consideration). The surface film then contains more of the contaminant than the main body of the solution. If the surface film contains less of the contaminant than the main body of the solution it is a case of negative adsorption.

As given in the foregoing, the surface of a liquid against its vapor is in tension; the surface of liquid against another liquid, or a gas or solid, is also in a state of tension, termed interfacial tension. In the flotation machine the following conditions obtain: Pulp consisting of ore of approximately 80-mesh, water in ratio of 3:1 of ore, and oil in disappearingly small amount, is being violently agitated. For the sake of a specific case, the air is being forced mechanically into the swirling pulp by beaters or stirrers. The phases present in flotation by the oil-froth process are therefore: solid-liquid (ore-water), solid-liquid (ore-oil) solid-gas (ore-air), liquid-liquid (water-oil), liquid-gas (water-air), and liquid-gas (oil-air). Thus six tensions are present, but if the oil is soluble in the water the tensions are reduced to three. It is known that pure water cannot be made to maintain a persistent froth because its surface-tension is too high. Acid, if present, will lower the surface-tension of water, as will oil, if it is soluble.

Certain metallic sulphides, such as galena, have the power of floating on undisturbed water; they are not wetted and the curve of contact is convex. Some gangue minerals, such as quartz, possess an adhesive force of attraction for water that exceeds the intrinsic pressure of the water; they are therefore wetted and sink to the bottom, being drawn through the surface film. Such properties of the minerals are affected by the presence of oil, acid, and other reagents. Oil has a greater adhesive attraction for sulphide minerals than for gangue minerals; and the addition of acid and oil (if it is soluble) acts as a contaminant that will lower the surface-tension of the water and aid in the production of a persistent froth. Let us now look into the question of adsorption and see what part it plays in flotation, since it is so requisite to the production of a variable surface-tension.

ADSORPTION. Generally speaking, adsorption deals with the unequal distribution of substances at the interface between dissimilar phases such as, solid-solid, solid-liquid, solid-gas, liquid-liquid, liquid-gas, and gas-gas. It is purely a physical effect. Commonly, adsorption[3] is construed to be the result of the condensation of a disperse phase upon the interfacial boundary solid-liquid. Returning for a moment to the Gibbs equation quoted above, adsorption may occur if the interfacial tension solid-liquid is reduced, this being positive adsorption. If, however, such an interfacial tension is raised in value it is a case of negative adsorption, as the solute or disperse phase will be rejected from the surface. Any condensation, strictly stated, of a solute or disperse phase in the interfacial boundary separating liquid-liquid or liquid-vapor is held to be a special case of adsorption. However, in the general sense, the phenomenon is looked upon as being the result of condensation of a disperse phase in the interface of two immiscible phases. Adsorption is shown strikingly by colloid gels—the product obtained by the coagulation of sols—and certain cases of selective adsorption are most remarkable. Adsorption will naturally vary with the surface exposed. In Miss Benson's experiments with

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[3] Briggs: *Jour. Phys. Chem.*, Vol. XIX, No. 3, p. 210 (March 1915).

amyl alcohol in aqueous solution, amyl alcohol reduced the surface-tension of the water, and it was found by producing a voluminous froth that the alcoholic concentration in the froth exceeded that in the bulk of the aqueous solution by about 5%. A froth has a very large surface, and it would be expected that the adsorption would be greater. Such experiments prove the value, qualitatively, of the Gibbs rule.

Recent work shows that all solids do condense gases on their surfaces and retain them there with great tenacity. Liquids in like manner adsorb gases. Further, liquids and solids exhibit selective adsorption of gases. Although this selective adsorption obtains, no proof has been submitted indicating that the amount of gas adsorbed by one substance is largely different from the amount adsorbed by another substance. An electric charge on an adsorbed substance probably would influence the amount adsorbed. The adsorption of air plays an important rôle in flotation, for, as Breuer points out, the adsorbed air film is enormously responsible in preventing the coalescence of solid particles.

A comprehensive study of the adhesion of small particles of solid to the dineric interface (surface separating two liquid phases) has been made by Hofmann[4] based on the theory of Des Coudres.[5] From the standpoint of flotation this may be given as follows: If a solid particle, such as quartz, is wetted much more strongly by water than by another liquid, such as oil, the water will displace the oil, and a film of water will form about the quartz particle according to the relative forces of adhesion. Then the quartz particles will remain in the water phase if the water has a specific gravity greater than the oil, regardless of their size; but if now the oil has a greater specific gravity than the water, then the quartz particles will remain in the water phase until the size of the particles is such that the force of gravity will remove them from the water. Conversely, if a solid particle, such as galena, is wetted more strongly by oil than by water, the oil will form a surface film about the particle and hence prohibit the particle from being wetted by water, that is, from entering the water phase. Then the galena will only enter the water phase when the water is more dense than the oil, and, further, when the galena particles are of such a size that the force of gravity overcomes the adhesion of the oil film to the oil.

Returning to purely theoretical considerations, Hofmann draws certain conclusions that deal with the supposition that solid particles will then remain in the surface separating two immiscible liquids, if

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[4] *Zeit. Phys. Chem.*, Vol. LXXXIII, p. 385, 1913.
[5] *Arch. Entwicklungsmechanik*, Vol. VII, p. 325, 1898.

those particles are wetted partly by each liquid. I quote Bancroft at length on this matter.[6] "The solid particles tend to go into the water phase if they adsorb water to the practical exclusion of the other liquid; they tend to go into the other liquid phase if they tend to adsorb the other liquid to the practical exclusion of the water; while the particles tend to go into the dineric interface in case the adsorption of the two liquids is sufficiently intense to increase the miscibility of the two liquids very considerably at the surface between solid and liquid."

Any simultaneous adsorption of two immiscible liquids by a solid would tend to form a homogenous liquid phase at the surface of the solid.

In regard to the effect of contaminants or other impurities in contact with two immiscible liquids, this condition obtains: If the contaminant is soluble in one liquid but not in the other, and also lowers the interfacial tension of the two, the equation set forth by Gibbs exacts the requirement that the contaminant should obtain in the interface. Examples of this prove the validity of the law.

The terms adsorption and absorption have been used interchangeably in some writings, thus contributing to the already existing confusion of ideas.

ABSORPTION OR OCCLUSION. There are three ways by which gases can be held with reference to solids: (1) By surface adsorption; (2) in solid solution; and, (3) by occlusion. The term 'occlusion' has been applied indiscriminately to any of these methods by which gases are held by solids. Strictly speaking, by 'occluded' gas is meant gas that is absorbed and held in finely-divided pores or openings, which may be of microscopic size. A recent theory[7] holds that occlusion plays the operative rôle in the flotation of minerals by all processes. I am unable to reconcile myself to this explanation, for a number of reasons. Marked instances of occlusion at normal temperature are known only in certain amorphous substances, like charcoal. Many metals, of course, both in the liquid and solid states, have the power of occluding gases, often in marked degree. There may be and undoubtedly are fine pores in the floatable minerals, which may in a sense be considered as an assemblage of capillary tubes; these can and do occlude gas. Yet occlusion is marked only in amorphous substances and in certain metals as just stated. It is definitely known that occluded gases are re-

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[6] Bancroft: *Jour. Phys. Chem.*, Vol. XIX, No. 4, p. 287 (April 1915).

[7] Durell: M. & S. P., Vol. CXI, No. 12, p. 428 (Sept. 18, 1915) and Durell: *Met. & Chem. Eng.*, Vol. XIV, No. 5, p. 251 (March 1, 1916).

tained with great tenacity by the substances occluding them and therefore are expelled only with difficulty. It seems anomalous to hold that the occluded gas can depart from the mineral occluding it with sufficient speed to aid the air bubbles in the liquid in the process of flotation. I believe firmly that occlusion is not a cogent factor in flotation, and that a more consistent theory may be formulated without postulating these conjectures regarding occlusion.

COLLOIDS, in the original definition of the term by Thomas Graham, do not constitute a definite class of substances; a large number of different substances may be made to assume the colloidal state if proper precautions are taken. All of which reveals the striking fact that this colloidal condition is a *state* and not a *form* of matter. The ultramicroscope of R. Zsigmondy and H. Siedentopf has greatly increased our knowledge of colloids. A general statement may be made regarding colloids: that they do not show osmotic pressure in appreciable amount. Colloidal solutions—sols—are regarded as systems of two phases, in which the dissolved substance is the disperse phase and the solvent the continuous phase.

Since, in flotation, the ore is often as small in size as certain of the colloids, the pulp (ore, water, etc.) can be looked upon as a coarse suspension, and the laws of colloids apply here with equal force as in the realm of colloidal chemistry. So-called suspensions are systems consisting of solid particles of microscopic size distributed through a liquid. As mentioned by Ralston,[8] Reinders has treated at length the particular case of a solid phase maintained in contact with two liquid phases, that is, two immiscible liquids. His work is based on the different interfacial tensions existing, and his experiments and those of Hofmann, as mentioned in an earlier paragraph, have considerable bearing on the flotation problem.

EMULSIONS are fairly coarse dispersions of one liquid in another with which it is immiscible. The simplest and commonest emulsions are the pure-oil water emulsions, containing no emulsifying agent such as soap, proteids, etc. In such systems the oil globules can be coagulated by electrolytes, they show the Brownian movement strikingly, and can even be retained by some filtering media. Any process of emulsification is dependent on a lowering of surface-tension, or, to be more precise, on a lowering of the interfacial tension between the two phases. According to Briggs and Schmidt,[9] the two essential require-

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[8] Ralston: M. & S. P., Vol. CXI, No. 17, p. 623 (Oct. 23, 1915).

[9] Briggs and Schmidt: *Jour. Phys. Chem.*, Vol. XIX, No. 6, p. 479 (June 1915).

ments of an emulsifying agent are: (1) The property of condensing by adsorption in the dineric interface; and (2) the ability to form under these circumstances a strong coherent film. Temperature is a decisive factor in emulsification, for its effect is to reduce the interfacial tension between phases and also to lower the viscosity of the phases. In the production of emulsions, a considerable amount of surface energy is produced because of the relatively large surface area of the disperse phase; an emulsion is the more speedily effected if such surface energy be reduced by the use of a liquid having a low surface-tension as the continuous phase. Some emulsions, under certain conditions, display a great increase in viscosity over that of either of the immiscible phases, for example, the emulsions of the Pickering order—up to 99% of oil in 1% of soap solution—can be cut into cubes. Any emulsion produced with soap solution is at once destroyed by the addition of acid, as the latter will decompose the soap.

If solid particles are suspended in a liquid, they tend to increase the viscosity of that liquid gradually, depending on the amount of solid particles present. Experiments have shown that whenever a substance in suspension is wetted by two immiscible liquids simultaneously, it will go into the dineric interface in the manner already mentioned, and will tend therefore to produce an emulsion. If, however, the suspended particles cannot coalesce, owing to adsorbed oil film or for other reasons, and thus effect the production of a coherent film, the emulsion will not be stable. Few data are available on the production of emulsions by the oils used in flotation work, or on the matter of interfacial tensions between such oils and water. However, we are no doubt dealing with emulsified or partly emulsified pulp in some of the flotation processes, in the oil-froth process at least.

ELECTROLYTIC AND ELECTRO-STATIC PHENOMENA. Any substance placed in contact with water or many other liquids will assume an electric charge, the origin of which is, as yet, not set forth. Most substances when in contact with water become negatively charged, but these charges can be differed at will or reversed by the addition of the proper electrolyte in requisite amount. These electric charges are by no means confined to sub-microscopic particles, but are found also on the particles of a coarse suspension. Gangue minerals, such as quartz, when suspended in water, are negatively charged, and sulphide minerals, such as pyrite, are positively charged under like conditions. Oil drops are negatively charged, as are air bubbles under certain conditions. These charges are very minute when referred to the mass of the particle. Substantial evidence is at hand to show that floatable minerals have the positive sign of electricity when suspended in water or can be made to assume that sign by the addition of proper electrolytes in sufficient amount. As Callow[10] observes, there is a parallelism between electro-static characteristics and the flotative properties of ores. Many of the electro-static principles have either been carried too far or misapplied, as recent work shows.

Experiments in colloid chemistry indicate that the contact films are charged and that such charges affect the dispersion or coherence of the particles in suspension. Of course, oppositely charged contact-films will coalesce while similarly charged contact-films will repel each other, if the charges are sufficient in amount to overcome the force of cohesiveness; in the latter, dispersion is the result. The oil and air contact-films having negative charges would tend to attract the sulphide particles, but further than this possibility electro-statics probably plays little part in flotation.

It is admitted that only minerals that are good conductors are suitable to flotation. As the electrical theory contends, electrified bubbles must be supplied to float the conducting minerals that are attracted, leaving behind those that are not. The bubbles in flotation are simply air spaces contained by a mantle of oil or of water, and there is, therefore, nothing within to bear the charge. In case it could carry a charge, which would only be possible by the presence of contained ionized gases or water-vapor, the charge would be speedily dissipated by contact with the interfacial boundary. Then in order that a bubble may carry a charge it must be protected by a dielectric film. Further, electro-statics plays probably little part in holding the sulphide particles and the gas bubbles together, as neither the bubble nor the particle can have a charge of sufficient magnitude when referred to the size. The electrical theory has been strongly championed by at least one writer[11] and has been tolerated by some others. A recent article[12] indicates that the principles of electro-statics have been considerably misapplied. It is my belief that electro-statics may be a small contributing factor in flotation in a manner not as yet understood because of a lack of information concerning charges at the interfacial boundary between immiscible phases, for example, where the colloidal

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[10] J. M. Callow: Bulletin A. I. M. E., No. 108, p. 2334 (December 1915).

[11] Bains: 'The Electrical Theory of Flotation,' M. & S. P., Vol. CXI, No. 22, p. 824 (Nov. 27, 1915) and Bains: 'The Electrical Theory of Flotation,' II, *ibid.*, Vol. CXI, No. 24, p. 883 (Dec. 11, 1915).

[12] Fahrenwald: 'The Electro-statics of Flotation,' *ibid.*, Vol. CXI, No. 11, p. 375 (March 11, 1916).

state is introduced in oil-water emulsions. Apparently, the electric theory is not important.

FROTH AND BUBBLES. The idea has been abandoned by most people that a low surface-tension is the essential requirement for froth formation. As mentioned by Coghill in a recent writing,[13] the contamination of the liquid with an impurity that will cause a variable surface-tension is the real requirement. A bubble of air is spherical in shape and this shape can only be maintained if the external pressure exceeds the internal pressure. Since a bubble does not expand *per se,* large bubbles can only be accounted for by heat, coalescence, or electrification. Viscosity is an important factor in froth-persistence, as it increases the tenacity of the liquid film and thus prevents ready rupture. The rupture or bursting of bubbles is explained thus:

1. Concussion upon a surface film deficient in the requisite viscosity and variable surface-tension.
2. Relief of pressure—here the gas of the bubble in expanding exerts a pressure exceeding that of the liquid film.
3. Adhesive force of the entrained gas for the atmospheric air.
4. Evaporation of the liquid film.

Flotation bubbles will burst for any one or a combination of these reasons.

Solutions in which the continuous phase is a solution of soap, various products from the saponification of albumens, etc., will froth voluminously even in a very diluted condition; frothing never occurs in pure liquids and is a definite proof that the solute or disperse phase lowers the surface-tension of the solvent. A froth, which shows adsorption at the interfacial boundary of solution and gas, depends for its persistence on the production of a viscous film at that boundary; these viscous films are the direct result of surface adsorption of the disperse phase, that is, dissolved contaminants, the amount of which is small—disappearingly so. The work of Hall and of Miss Benson shows that in a foaming liquid the foam is richer in the dissolved contaminant than is the bulk of the liquid. Froth formation in the Callow cell is the result of the injection of air into the pulp (already emulsified); the froth persists as long as there is sufficient air injected into pulp of the proper consistence. The froth in the Callow cell is governed in nature by the kind of oil used and by the amount of air. A pneumatic froth is unstable or ephemeral; it dies rapidly when removed from the influence of the injected air. The mechanical froth, on the other hand,

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[13] 'The Science of a Froth,' M. & S. P., February 26, 1916.

is thick and persistent, and must be broken up in dewatering the concentrates.

OILS have a selective action for metallic sulphides, tellurides, and some other minerals. The fact that both the oil and the air or other gas have a selective adhesion for sulphides prevents them from being wetted by water. Conversely, the quartz and other minerals exhibit just the opposite characteristics. The gangue-minerals, generally, do not exhibit adhesion for either gas or oil; hence they are readily wetted by water. Gases have a well-defined adhesiveness for oils; therefore the air or gas adheres strongly to the oil film. The stability of a froth depends, in the main, on the kind of oil used, for example, pine-oil makes a weak brittle froth, and creosote makes a stable elastic froth. The work of Devaux[14] on oil films explains how so small an amount of oil as is used in the various flotation processes can be so efficacious. From a consideration of the immiscible oil-water interface, if any oil will film the internal surface of a gas bubble the sulphide particles would be contained in the oil-water interface no matter what the nature of the gas contained by the water film. The sulphide, if it enters the oil phase, would then present an oiled surface to the water phase. There are three conditions then: (1) The mineral enters the oil phase completely; or (2) the mineral enters the water phase completely; or (3) the mineral enters the oil-water interface.

Experiments made to determine the nature of the frothing, selective, and collective action of different oils show some interesting results. I made tests on a zinciferous slime from Joplin with different oils, the results obtained indicating that a definite mixture of oils will effect better recoveries than any one oil alone. The best combination consisted of pine-oil as a frother, plus wood-creosote as a frother and selector, plus refined tar-oil as a froth stiffener.

In general, pine-oil makes a brittle froth, which immediately dies; creosotes make a more elastic froth, the bubbles of which may expand to 3 in. diam. or more before rupture. Coal-tar products are poor frothing agents and if used must be aided by either creosote or pine-oil to produce a good froth. Oils of a lubricating nature seem to be of little value in flotation, while such light oils as gasoline and naphtha are of value only for thinning the heavy coal and wood tars.

AIR AND GAS. At this time, there are three ways by which a gas may be forced into a solution mechanically, as follows:

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[14] Devaux: 'Oil Films on Water and on Mercury,' *Smithsonian Report* of 1913, p. 261.

1. By beating it into the solution by means of paddles, as in the Minerals Separation and similarly mechanically agitated machines.
2. By pneumatic means, as in the Callow cell, where the air is divided by the porous blanket-bottom into minute sprays.
3. By so-called liquid jets, as in a process recently patented in which the air is introduced as a surface film surrounding a liquid jet by surface-tension.

Conversely, there are three methods by which dissolved gas may be expelled from a liquid:

1. When the liquid is super-saturated, the excess gas is expelled.
2. By heating the liquid, when some of the gas is expelled owing to an increase in its volume.
3. By pressure reduction, as in the Elmore vacuum process, where, according to the law of Henry,[15] ''the amount of gas dissolved by a liquid is proportional to the pressure to which the gas is subjected.''

An air or gas bubble on being introduced into a liquid is at once surrounded by a film of the liquid. Such a bubble will rise to the surface (carrying the metallic sulphides by reason of the forces already mentioned) on account of gravitation, by which is meant that the adherence of the air to the liquid is less than the force of gravity.

RÉSUMÉ. From a consideration of the foregoing, it is believed that the theory based on the different interfacial tensions involved is the dominating one at this time. Probably flotation is due to a combination of complex phenomena. The theory based solely on occlusion goes ''by the board,'' as it has been shown that the contributing effect of this phenomenon has been interpreted laxly.[16] The phenomenon of electro-statics may be a small contributing factor, but recent work indicates that the principles have been misapplied. An explanation more in consonance with fact can be given in terms of the interfacial tensions involved, without postulating either occlusion or electrostatics.

The main and essential requirements for froth flotation are: (1) the production of a persistent froth; (2) the attachment of the bubbles of air to the sulphides or other material to be floated; and (3) the maintaining of a selective action by the froth bubbles for the sulphides or other material to be floated.

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[15] Jones: *Elements of Physical Chemistry*, p. 177, 1907.

[16] Ralston: 'Why Do Minerals Float?' M. & S. P., Vol. CXI, No. 17, p. 623 (Oct. 23, 1915).

PRINCIPLES UNDERLYING FLOTATION

By Joel H. Hildebrand

(From the *Mining and Scientific Press* of July 29, 1916)

Introduction. *The phenomena involved in ore flotation are mostly effects of surface-tension, so that an understanding of this force and how it may be modified by various factors is fundamental to a scientific study of flotation.

Wherever different phases are in contact we have surfaces where the effects of surface-tension may be apparent. It will be convenient, for our purposes, to classify the boundaries between phases as follows: (1) liquid-gas, (2) liquid-liquid, (3) liquid-solid. The boundaries solid-gas and solid-solid will not be considered, being unimportant from the standpoint of our subject. Since the effects of surface-tension are increased as the surface between the phases increases in extent, we will be led to consider the systems encountered in flotation processes, in which one of the phases is highly dispersed. These systems, corresponding to the above classifications are (1) foams, in which the gas is highly dispersed in the liquid (the other system, fog, in which the liquid is dispersed in the gas does not here concern us); (2) emulsions; (3) suspensions.

Liquid-Gas Boundary. (a) *Definition and Measurement of Surface-Tension.* It is found that all liquids have a tendency to assume a form which will have the smallest surface. Where the liquid is supported by a surface that it does not wet it tends, for example, to assume a spherical form, manifest especially with small drops, where the influence of gravity is small. A soap-bubble tends to contract, expelling the air through the orifice of the pipe from which it is blown. A liquid that wets the walls of a tube will be drawn up into it. The magnitude of this force can be measured by various methods, such as the rise in a capillary tube, the shape of a drop under the opposing action of surface-tension and gravity, the weight of a drop that surface-tension will support as a liquid issues slowly from a tip of definite size. A general idea of the magnitude of this force may be obtained from the values given in Table I.

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*Abstract of an illustrated lecture delivered before a joint meeting of the San Francisco section of the American Institute of Mining Engineers and the California section of the American Chemical Society, February 15, 1916.

TABLE I

Liquid	Temperature, °C.	Surface-Tension, Dynes per Cm.
Hydrogen	−252	2
Carbon di-sulphide	20	33.5
Alcohol	20	22
Water	20	73
Ether	20	16.5
Mercury	18	436
Gold	1070	612
Sodium sulphate	880	187

(b) *Cause of Surface-Tension.* It must be noted that we can define and measure surface tension without making any assumptions whatever as to what causes it. The fact that the surface tends to contract with a definite force does not mean that the surface is coated with anything like a rubber membrance. The surface of a liquid, except for a slight difference in density, is doubtless the same as the rest of the liquid. The existence of surface-tension is to be attributed to inter-molecular attraction. Consider a molecule, such as *a* in Fig. 1, in the interior of a liquid. It will be attracted by the surrounding molecules, and these attractions may be resolved axially into four equal components, as shown in the figure. Consequently nothing but viscous resistance would oppose the moving of this molecule to another portion of the liquid, provided it remains in the interior. The moment, however, it approaches sufficiently near the surface, the upward component of molecular attraction is reduced, becoming zero at the surface at *b,* if we neglect any effect of gas or vapor above the surface. The result is that we have to do work upon each molecule brought from the interior to the surface of a liquid, and any considerable extension of its surface involves the doing of a considerable amount of work against a force the component of which along the surface of the liquid we call 'surface-tension.'

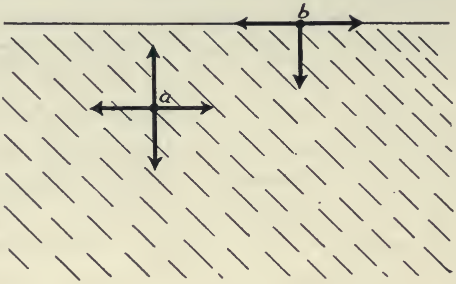

FIG. 1

(c) *Effect of Temperature.* Since the increase in kinetic energy of the molecules with temperature forces them farther apart we should expect inter-molecular attraction and hence surface-tension to diminish with increasing temperature, and such is indeed the case. At the critical temperature, where the density of the vapor becomes the same as that of the liquid, the surface-tension becomes zero, of course.

(d) *Effect of Dissolved Substances.* The surface-tension of mixtures of liquids is usually less than that which would be calculated on an additive basis, so that the more general tendency is for solutes to lower the surface-tension of the solvent. We find that the surface-tension of water is usually raised by dissolved salts, and lowered by other liquids, and especially by organic colloids, such as albumen, glue, soap, saponin, etc. Moreover, it is possible to show thermo-dynamically that solutes which lower the surface-tension of the solvent tend to concentrate at the surface, still further lowering the surface-tension there. For this reason very different figures are obtained for static and dynamic measurements of surface-tension with solutions of such substances. Table II shows the results of such measurements with sodium oleate (soap) solutions.

TABLE II

Concentration, %	Surface-Tension, Dynes per Cm. Static	Dynamic
0.025	55	79
0.25	26	79
1.25	26	62
2.5	26	58

It will be seen that where time is allowed for the concentration of the soap at the surface the tension is much less than in the dynamic method, where no time is allowed for the effect to be manifest. This behavior is exceedingly important in connection with the stability of foams, emulsions, etc., as we shall see.

(e) *Stability of Foams.* Since the production of a foam (or a mist) from a liquid involves an enormous increase in surface, and consequent performance of work against surface-tension, such a system is unstable unless stabilized by some means. Drops or bubbles tend to coalesce, hence pure liquids never foam. To produce a stable foam requires a film that is stable. The chief condition for this is the presence of a solute that will be strongly adsorbed at the surface of the solution, lowering its surface-tension, as explained above. How this will give a stable film may be understood by the aid of Fig. 2, which represents a film of solution, the shading indicating the greater concentration at the surface. If such a film should be stretched, becoming thinner at some portion, as at *a*, the new surface formed by

Fig. 2

the stretching would contain less solute, the time not being sufficient for adsorption, and hence would be stronger than the old surface. It is obvious that such a film would be stable, automatically becoming stronger wherever rupture is threatened. This is the action of the foaming agent, such as pine-oil, used in flotation processes. Here, of course, a foam of great stability is undesirable, as it must be broken down later.

Other factors of minor importance in foam stability are viscosity, which retards the draining of the film (hence the frequent addition of glycerine to soap-bubbles); small volatility, preventing evaporation of the foam where exposed to the air; and the protection of the bubbles from coalescence by the forming of a skin or armor about them. The particles of solid ore present in the foam in flotation processes undoubtedly act in this way.

Liquid-Liquid Boundary. Much that has been said applies here. Methods of measurement are similar. The magnitudes of these interfacial tensions are illustrated in Table III.

Table III

Boundary	Surface-Tension, Dynes per Cm.
Mercury-water	370
Benzene-water	33
Turpentine-water	12
Methyl alcohol-carbon di-sulphide	0.82

This surface-tension becomes zero at the critical temperature of mixing of the liquids, and it is affected by dissolved substances according to the same principles as apply to the simpler systems.

(a) *The Spreading of Drops.* The spreading of drops of oil upon water to form an exceedingly thin film is familiar to all. Whether or not this phenomenon takes place depends upon the magnitudes of the three surface-tensions indicated in Fig. 3, which represents a drop of a lighter liquid placed upon a heavier one with which

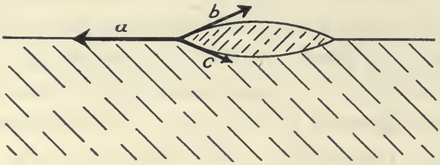

Fig. 3

it does not mix. Obviously the drop will spread out over the surface whenever the surface-tension represented by a is greater than the sum of b and c. When $a < b + c$ the drop will remain in lens form upon the other liquid. One of these cases may be converted into the other by the addition of suitable solutes to one phase. For example, although oil usually spreads upon water, where the surface-tension of the water is much lowered, as it is in meat-broth by the presence of albumin, gelatin, etc., the value of a is small enough to allow any oil present to remain as lens-shaped drops.

(b) *The Stability of Emulsions.* This is obviously favored by a low surface-tension between the phases, by viscosity, by the presence of a substance tending to form a skin preventing the droplets of the enclosed phase from coalescing, as they naturally tend to do, and most important of all, the presence in the phase that is to enclose the other of a substance that will be positively adsorbed at its surface, thus making stable a film of the liquid separating two droplets of the other, enclosed, liquid. The enclosed phase takes the place of the bubbles in the previous discussion of foam stability. By a suitable choice of solutes either phase may be made the enclosed phase. For example, when soap is added to water the films of water become stable, and a liquid like benzene may be made to form a stable emulsion in water. On the other hand, when a magnesium soap is dissolved in benzene, films of benzene become stable, and benzene will yield both stable foams and stable emulsions with water as an enclosed phase.

LIQUID-SOLID BOUNDARY. With a boundary of this sort direct measurement of surface-tension is impossible, but relative values may be inferred by noting the wetting power of a liquid for a solid, especially as indicated by the angle of contact. When, for example, a drop of water is placed upon a bright metal surface, instead of spreading over the surface of the latter as would kerosene, it remains in drop form, its surface meeting the metallic surface at a certain angle. When a drop of castor-oil is placed on the metal it forms a much flatter drop, the angle being different, corresponding to greater wetting power for the metal. The surface-tension between these phases can be altered as before by the addition of adsorbed solutes, so that a drop of soap solution will be much flatter when placed upon the metal than the drop of pure water. This wetting power is also different for the same liquid upon different solids, as is illustrated by the experiment shown in Fig. 4, where the angles of contact indicate that when chloroform and water are in competition the former has greater wetting power for a metal surface, while the latter has greater wetting power for glass. It would seem that determinations of these angles should offer a valuable preliminary to flotation experiments.

As a consequence of this relative wetting power, if a layer of kerosene is placed over water, and a powdered silicious material dropped into the vessel, it will stop only momentarily at the oil-water surface. As fast as the oil can be displaced by the water the particles drop through into the water phase. If, however, a metallic powder, or a sulphide with metallic lustre, be dropped into the vessel, it remains in the oil phase, supported, if the mass is not too great, by the surface-tension at the boundary.

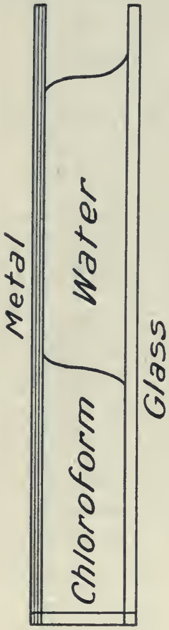

Fig. 4

The ease with which a solid particle can float on the surface of a lighter liquid depends upon its size, the difference in density of solid and liquid, and the angle of contact the liquid makes with the solid. The relationship is expressed in Fig. 5, where we assume, for simplicity, a cylindrical particle of radius r, height h, and density d, floating on a liquid of density d_2 and surface-tension s. The maximum effect that could be exerted by gravity upon the particle would obviously be $\pi r^2 hg\ (d_1 - d_2)$ dynes. If the solid were not wet at all by the liquid and the angle of contact were zero, the upward force tending to prevent the particle from sinking into the liquid would be $2\pi rs$. In an actual case, however, where this angle is a, the upward force is $2\pi rs \cos a$. It is obvious that the floating tendency would be greater the smaller the particle, the less its density relative to that of the liquid, the greater the surface-tension of the liquid, and the smaller a. In floating practice the densities are not to be altered, the size of the particles is made as small as is consistent with economical grinding and subsequent recovery, the surface-tension of the water cannot be increased, but is rather decreased by the agent added to produce foaming. The foaming gives a large surface, as the total quantity of ore floated is proportional to the surface of the water and not to its volume. The most effective modification that can be made in the above factors is to decrease the angle a as much as possible for the ore particles, while still leaving it greater than 90° for the gangue particles, the condition necessary that the latter should sink. This is the purpose of the small quantity of oil added during the grinding of the ore. The wetting power of oil for a metallic surface causes the oil, if the right kind, to spread over the metallic surface as it would over the surface of water. The water present at the same time wets the gangue preferentially, preparing for the separation that results when the large amount of water is added. It is obvious that the frothing agent necessarily added later works against the effect here desired of the least possible wetting of the ore, as it decreases the surface-tension both at the liquid-air and at the liquid-solid surfaces.

A word might be said in conclusion about the stability of suspensions. Besides the stabilizing influences important in the case of foams and emulsions, another here rises to great importance, namely, the electric charges on the suspended particles due to adsorbed ions.

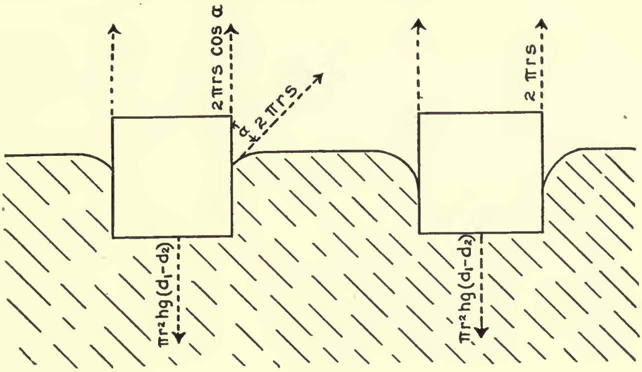

FIG. 5

This effect may be illustrated by dividing a suspension of fine silica into two portions, and adding to one a little acid and to the other a little alkali. It is found that in the second case the suspension is quickly flocculated and settles out, while in the acid solution it remains suspended for a long time. Reference must be made to works upon colloids for further discussion of the many interesting phenomena connected with such behaviors. In ore flotation, the effect of even slight amounts of acid or alkali may be, aside from that just mentioned, to clean the ore particles and thus expose a more truly metallic surface to the oil, and to affect the surface-tensions involved, especially by modifying chemically the other substances added, notably the frothing agent.

MOLECULAR FORCES AND FLOTATION

By Will H. Coghill

(From the *Mining and Scientific Press* of September 2, 1916)

The warning about young men specializing in flotation, as sounded by E. P. Mathewson in a recent number of the *Mining and Scientific Press,* should be considered by all who are directing these men in their education. It provokes the question that ever confronts the instructor in a technical school.

The student may be drilled on the design and construction of the various flotation machines, and the methods and results of the experimenters, and be sent into the field feeling that he is strictly up-to-date, but his school-work would not amount to much if he has been taught only the ever-changing art. He would have acquired something more enduring and be better prepared to benefit from his college course had he been taught natural laws with enough of the art to give a view of the field to which the laws could be applied, for man's methods are ever changing while Nature's laws are invariable. The processes of a few years ago are now obsolete, but the principles upon which they were founded will be applied to new methods for generations to come.

To the workers in flotation has fallen the problem of outlining the rudiments, and then by means of laboratory experiment, made by aid of the results of workers in the related sciences, developing flotation to the point where scientific reasoning may be applied to direct tests on ores as is now done in cyanidation. It took twenty years to develop the science of the cyanide process. It will take as long in flotation if we continue our antiquated methods. So far as I can learn, not more than two of the great number of recent contributors of articles on flotation have had an opportunity for a deliberate study of the related sciences. The rest of us have a job to look after and are busy enough attending to it. Advancement is, therefore, slow. The papers by O. C. Ralston and E. E. Free are, of course, excellent. But in many cases they shoot above our heads; for this we and not they are to blame.

The majority of the workers in flotation who have had the advantage of a school of mines training have taken only the prescribed four years and then hurried into the business of mining. Their love for science was none too great when they left school and the constant employment in the art has in no way tended to increase it. By a careful reading of the articles mentioned they might hope to glean some fact, the knowledge of which would be of aid in the art of metallurgy, but the material is entirely too heavy for one who has not had a special training in science.

We should learn to think—not parrot the statements of others—in terms of the molecules before science will be of aid to us in flotation. We cannot adjust ourselves to this in a moment. It requires time and effort. Many of us have sat aghast while an astronomer spoke of distances in terms of the diameter of the earth. We must now go to the other extreme and become familiar with molecular dimensions. This requires much study, but in it we acquaint ourselves with the observations of physicists and chemists so that we are not likely to spend valuable time in discovering something that is already known.

The mastery of science is not easy. While in school we had to learn the chapters page by page, but this does not seem to be the best way for those without an instructor. To advise one to go through a book rapidily, gathering only an idea here and there, and through it again, may seem to be superficial. But the aim is to master the subject and this is doubtless the way to do it. This method of study is endorsed by Dr. V. H. Gottschalk[1] when he says: ''After several readings of the short paper on . . . , read first the excellent summaries at the end of . . . before undertaking a rapid survey of the whole set; follow this by a more careful consideration of the summaries with re-reading of portions of the text when necessary; continue this process until the drift of the argument begins to reveal itself.''

One contributor has said that the scientific man has aided little in flotation. Indeed he is correct, and so is the old-timer who says that more mines have been discovered by simple prospectors than by mining engineers. The ratio of those who pursue the right methods to those who have no method at all is as 1:1000.

Have any of the big companies put their engineers on retainers so that they could review the fundamentals of science and pursue post-graduate work in a university where they could have access to a complete library? Probably none, because the American business man goes straight for the dollar and must see the wheels turning before he is assured of dividends.

Some of the blunders that have crept into the articles on flotation are a great drawback to those who wish to learn but find their library incomplete. One writer has said, for example, ''the cohesion of water varies as the temperature . . . and at the boiling-point there is no

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[1] Bibliography, 'Concentrating Ores by Flotation,' University of Missouri.

cohesion.'' This statement is misleading. Scientists had this problem pretty well in hand nearly a century ago and knew that surface-tension became zero at the critical temperature and not at the boiling-point, as we ordinarily use this term. Brunner[2] recognized this fact in 1847 and knew that surface-tension decreases with rising temperature until the critical point is reached, when liquid and vapor become identical and surface-tension is zero.

In the Smithsonian Physical Tables, the surface-tension of water at 100° C. is given as 61.5, and nothing is said about boiling-point.

Since critical temperature is so closely related to surface-tension it is obvious that we should acquire a working knowledge of it. At one time it was considered sufficient for us to be able to say that critical temperature was the temperature above which a gas could not be liquefied no matter how great the pressure. This served the purpose for which it was intended, but it is inadequate for us now. If we define it as the temperature at which the surface-tension between a liquid and its vapor becomes equal to zero, and any meniscus or bounding surface disappears, we have added to our knowledge of molecular forces.

It follows that when liquids are near their critical point, for example, condensed gases, they will have small surface-tension, while liquids far removed from their critical point, such as molten metals and fused salts, will have large surface-tensions.

Liquid carbon dioxide is an example of a liquid that is near its critical point at atmospheric temperature; the critical temperature is 31° C. Its surface-tension is therefore very small unless artificial refrigeration is used.

Mercury, on the other hand, at atmospheric temperature, is so far below its critical point that it would be expected to have a great surface-tension, as indeed it has.

To aid further in getting the relation of critical temperature to surface-tension, I quote from Ferguson.[3] He indicates their relation and the basis on which surface-tension of liquids should be compared, saying: ''In earlier researches on the subject, comparisons [surface-tension] were made at the same temperature, but it was recognized by Schiff that surface-tension should be compared at corresponding temperatures, that is, at temperatures which are equal fractions of critical temperatures of the liquids under consideration.'' Continuing, we find him stating the relation of critical temperature to boiling-point, thus: ''Unfortunately the critical temperature of comparatively few

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[2] 'Physical Chemistry.' Ramsey and Smiles.

[3] *Science Progress*, January 1915.

organic compounds have been directly determined, and it was supposed that these conditions were fulfilled at the boiling-point of the liquids examined. If this be the case the ratio of the boiling-point to the critical temperature of all liquids should be the same where temperatures are measured on absolute scale.''

The degree of exactness with which this condition is fulfilled is remarkable, as can be seen by an examination of tables published by Ferguson, also those in the 'Handbook of Chemistry and Physics,' and elsewhere. They show the value of this ratio calculated from a number of substances of very diverse boiling-points

An examination of these tables shows that it is a fairly accurate generalization to put

$$\text{Boiling point} = 0.656 \times \text{crit. temp.}$$

where temperatures are measured on the absolute scale; so that from the boiling-point we can calculate the critical temperature (subject to an error of not more than 5% in the case of the carbon compounds). For a proof that vapors as well as liquids are regarded as having molecular cohesion, one has only to refere to Van der Waal's modification of Boyle's law.

The toy-balloon theory[4] that each molecule of water is drawn toward the centre of gravity of its mass cannot be taken as a substitute for the accepted theory of surface-tension, for it is not in accord with physicists either here or abroad. They generally agree that the radius of molecular attraction is insensible but finite. They are of one accord in the opinion that ''every molecule[5] attracts every other molecule that may happen to be within a certain distance from it, which we denote as the sphere of molecular attraction. In the body of the liquid, this attractive force is more or less neutralized by the fact that the molecule we are considering is surrounded on all sides by others, all pulling in different directions. Hence the combined effort is practically zero. At the surface, however, all the molecules are below it, and there are none above to neutralize the force they exert. There is thus a strong downward force tending to drag the molecule into the surface. This force makes itself manifest in the phenomenon known as 'surface-tension' or 'capillarity.'

Methods of ore dressing today fall under one of two heads, gravitation or flotation. The fundamental law of the former was discovered by Archimedes, that of the latter by Leslie. Archimedes, as we know,

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[4] Dudley H. Norris, in M. & S. P., Feb. 12, 1916.

[5] 'Molecular Physics.' Crowther.

while in his bath, noticed the loss of weight of his own body and it occurred to him that any body immersed in a liquid must lose a weight equal to the weight of the liquid displaced. Leslie, a British scientist, was the first (1802) to give a correct explanation of the rise of a liquid in a tube.[6] Archimedes considered only the force of gravity on known masses; Leslie took into account the molecular force. It is Archimedes *v.* Leslie. Metallurgists have written much on Archimedes' law and very little on Leslie's, the latter having been left to the physicist and chemist.

It is surprising how little attention metallurgists have given to the application of the physical principle discovered by Leslie. Until recently they have been quite satisfied to call it 'capillarity' and let it pass. Capillarity has made itself manifest to us in many ways. Richards speaks of it in his 'Textbook of Ore Dressing' under the subject of amalgamation. He says that the capillarity of mercury is negative except with those metals with which it easily amalgamates; and the trouble due to grease is familiar to mill-men. In cupellation, the lead oxide is drawn into the pores of the cupel, while the lead ignores them and tends to shape itself into a sphere. Were it not for molecular cohesion the resulting silver bead would flatten and become so contaminated by the cupel that its subsequent treatment would be difficult. Galena[7] penetrates the fire-brick of the furnaces in which it is treated. Often a network of small veins of bright crystalline galena is found in furnace-linings. The molecular deportment of galena and litharge is quite different from that of lead itself.

In zinc smelting it is necessary to re-work the 'blue powder' because the film of oxide,[8] which coats each particle of zinc, prevents coalescence. The forces that control the films on blister-steel and blister-copper are identical with those that maintain the form of the soap-bubble.

The geologist has studied the bubbles in lava and has found that the vesicles[9] are roughly spherical. This spherical shape cannot be maintained unless the pressure on the inside is greater than that without. Only surface-tension can account for this excess. He is also aware that if the wick of a lamp touches water,[10] the latter rises

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[6] Some authorities state that Laplace first developed, about 1807, a theory of capillary action.

[7] 'Metallurgy of Lead.' Hofman. P. 8.

[8] 'Metallurgy of Zinc and Cadmium.' Ingalls. P. 526.

[9] 'Igneous Rock and Their Origin.' Daly.

[10] 'Rôle and Fate of Connate Water in Oil and Gas Sands,' R. H. Johnson, Bull. No. 98, A. I. M. E., p. 221; also 'Capillary Concentration of Gas and Oil,' C. W. Washburn, Bull. No. 93, A. I. M. E.

through the capillaries proviously filled with oil, makes the flame sputter, and often extinguishes the light. In the same way water will pass from the coarse spaces of the sand or from fissures into the fine capillaries of shale, displacing the oil, which is thereby forced into the sand through neighboring pores. The cohesion that holds together the particles of a crayon and adhesion of the chalk to the blackboard, or of dust to a mirror, are all evidence of molecular force. Many of the examples cited come under 'capillarity,' but since that is difficult to define and is therefore likely to be used to cloak ignorance, I shall not attempt a definition. Molecular cohesion and adhesion, and probably molecular repulsion, must be studied in detail.

A study of capillarity is of great aid in gaining a conception of the conduct of the molecular forces of cohesion and adhesion that cause some substances to float on the surface of a liquid while others sink. I quote from a high-school book on physics,[11] which, to my mind, gives one of the first lessons in the science of flotation. The discussion is as follows: "We must keep in mind two familiar facts: first, that the surface of a body of water at rest, for example a pond, is at right angles to the resultant force, that is, gravity, which acts upon it; second, that the force of gravity acting upon a minute amount of liquid is negligible in comparison with its own cohesive force. Consider then a very small body of liquid close to the point *O* (Fig. 1) where water is in contact with the wall of the glass tube. Let the quantity of liquid considered be so minute that the force of gravity acting upon it may be disregarded. The force of adhesion of the wall will pull the liquid particles at *O* in the direction of *OE*. The force of cohesion of the liquid will pull these same particles in the direction of *OF*. The resultant of these two pulls on the liquid at *O* will then be represented by *OR* (Fig. 1). If then the adhesive force *OE* exceeds the cohesive force *OF*, the direction of *OR* of the resultant force will lie to the left of the vertical *OM* (Fig. 2) in which case, since the surface of the liquid always assumes a position at right angles to the resultant force, it must rise up against the wall as water does against glass. If the cohesive force *OF* (Fig. 3) is strong in comparison with the adhesive force *OE*, the resultant *OR* will fall to the right of the vertical, in which case the liquid must be depressed about *O*. Whether then, a liquid will rise against a solid wall or be depressed by it will depend only on the relative strength of the adhesion of the wall for the liquid and the cohesion of the liquid for itself. Since mercury does not wet glass[12] we know that cohe-

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[11] 'A First Course in Physics.' Millikan and Gale.

[12] It is a well known fact that there is a slight adhesive force between

sion is here relatively strong, and we should expect, therefore, that the mercury would be depressed, as indeed, we find it to be. The fact that water will wet glass indicates that in this case adhesion is relatively strong, and hence we should expect water to rise against the walls of the containing vessel, as in fact it does. As soon as the curvatures just mentioned are produced, the concave surface *aob* (Fig. 4) tends, by virtue of surface-tension, to straighten out into a flat surface ao^1b. But it no sooner begins to straighten out than adhesion again elevates it at the edges. It will be seen, therefore, that the liquid must continue to rise in the tube until the weight of the volume lifted balances the tendency of the surface to flatten out. Similarly a convex surface *aob* (Fig. 5) falls until the upward pressure at *o* balances the tendency of the surface *aob* to flatten out.''

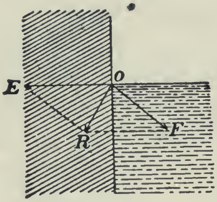

FIG. 1

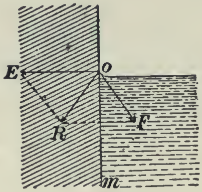

FIG. 2

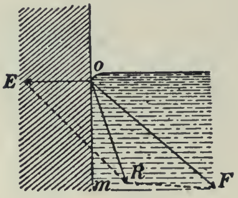

FIG. 3

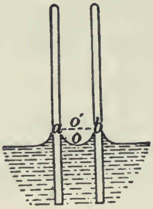

FIG. 4

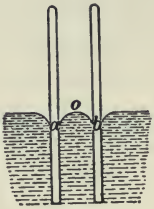

FIG. 5

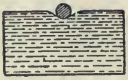

FIG. 6

If, in the case of water against glass, the water is pulled upward and in the case of mercury against glass the mercury is pulled downward, the converse must also be true, namely, that in the former the glass is pulled down and in the latter the glass is pushed up.

Now assume that you had two minerals so that they are partly submerged by a liquid and that with one adhesion is very great (relatively) and that with the other the adhesion is very slight. It is obvious

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mercury and glass and that mercury exerts an attractive force upon air, but the quotation suffices for the present.

that the surface of the liquid will turn up at the contact with the former and down and around the other, and that if these particles are so small that the force of gravity is negligible it is impossible for the former to float and just as impossible for the latter to sink. One of them cannot ride on the surface and is actually drawn into the liquid like gold into mercury, while the other cannot by any means enter the liquid unless its mass is sufficient to overcome the contractile force in the surface of the depressed liquid.

This process of reasoning is what I consider to be a natural and correct result of the study of the cause of capillary rise and depression as presented by Millikan and Gale, and to show that my conclusions are in harmony with their ideas I quote them again, where they discuss the floating of a needle. They say: "So long as the needle is so small that its own weight is no greater than the upward force exerted upon it by the tendency of the depressed liquid surface to straighten out into a flat surface, the needle could not sink in the liquid, no matter how great its density. If the water had wet the needle, that is, if it had risen about the needle instead of being depressed, the tendency of the liquid surface to flatten out would have pulled it down into the liquid instead of forcing it upward. Any body about which the liquid is depressed will therefore float on the surface of the liquid if its mass is not too great."

If the needle floats, the surface is turned downward, as in Fig. 3, where the resultant of the parallelogram of adhesive and cohesive forces lies in the liquid; and if it sinks, the surface is turned up, as in Fig. 2, where the resultant lies in the solid. Therefore, may we not say that if we can draw the resultant of the forces of cohesion and adhesion when a mineral is in contact with water, we can predict whether or not it is floatable; for if the resultant lies in the liquid (Fig. 3) it will float, and if it lies in the mineral (Fig. 2) it will sink.

We note next that when water is in contact with quartz the resultant lies in the solid; when it is in contact with galena[13] the resultant lies in the liquid. We can, therefore, separate galena from quartz by flotation. I believe it to be quite possible for us to use a contaminating substance in the water and thus vary the molecular attractive forces so that with some sulphides the resultant lies in the liquid and with other sulphides it lies in the solid. This, indeed, has been done, and I believe that this idea is essential to the understanding of selective and differential flotation. To be sure, the introduction of the paral-

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[13] Galena and quartz are here supposed to be in such condition that they are typical of floatable and non-floatable minerals.

lelogram of forces is only a shift from one series of unknowns to another, but it affords a means of stating the problem accurately, which is the first step in a solution.

The reader here exclaims: "Oh well, you are talking about film-flotation?" I think that anyone who will give serious thought to the above demonstration of capillary rise and depression will be convinced that there is nothing but film-flotation.[14] All flotation depends upon the film. If a piece of sulphide is brought to the surface by a bubble, it is, indeed, riding on the wall of a hole in the water, the only difference between this and what is commonly meant by film-flotation being that the hole is a sphere with finite radius while in 'film-flotation' the surface of the wall has an infinite radius.

If this is true, we go too far afield when we marshal osmosis, newborn gas, static charges, etc., for the first lesson in flotation.

Many writers have expressed a desire to discover the nature of the forces that cause a sulphide particle to cling to a bubble. I think their desire will never be appeased, for there is no such adherence, except in so far as there is a slight adhesion of the liquid film to the mineral as it rides in the cavity in contact with the wall or on a plane surface. With this exception, a bubble does not cling to a sulphide particle in a flotation-cell any more than butter clings to our fingers when we carry a pound of it from the store.

What has been observed, and not properly interpreted, is the coalescence of two cavities, one of which is filled with mineral and the other with air, where the mineral is brought to rest on the wall of the resulting cavity or, perchance, the walls of the two cavities do not break through but merely cling together.

A piece of submerged galena is just as surely surrounded by a surface-tension liquid film as is the air-bubble or submerged greased needle. If this is not plain look again at the familiar cross-section of the floating needle, Fig. 6. That the film extends below the needle there is no question, and it is just as sure that if the needle were submerged the film would surround it. It is obvious that any submerged solid is surrounded with a liquid film when the resultant lies in the liquid, for this resultant represents an inward drawing of the molecules that causes the contractile force known as surface-tension.

If a piece of quartz impinges against the wall of one of these cavities and has not sufficient kinetic energy to carry it through, as a bullet pierces a thin board, the rise of the liquid about it and the contract-

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[14] This statement applies to the processes now in operation, not the original bulk-oil method of Elmore.

ile drawing of surface-tension will cause it to retreat directly into the liquid just as surely as the glass tube in Fig. 4 is pulled into the water. If it has sufficient energy, so that it can pierce the wall where it first impinges and falls on the wall in another place, it will likewise be cast out of the cavity. When a piece of galena hits the wall the conditions are entirely different; for the galena fills a cavity that has walls just like those of the bubble and what happens is nothing more or less than the coalescence of two bubbles. If the impact is very slight they might only cohere, and thus give the appearance of a mineral grain clinging to the bubble, when in fact it is the bag about the mineral that has become attached.

It is commonly accepted that a hole in water filled with air is encased in a surface-tension film; by applying the principles set forth by Millikan and Gale one sees that a similar encasing film exists when the hole is filled with either a greased needle or galena. In the first case there is a wall of air; in the second, a wall of grease; and in the third, a wall of galena.[15] In every case the resultant of cohesion and adhesion is such that it lies in the liquid. A piece of glass submerged in mercury would be surrounded by an extremely strong film. If glass is submerged in water there is no surface-tension liquid film.

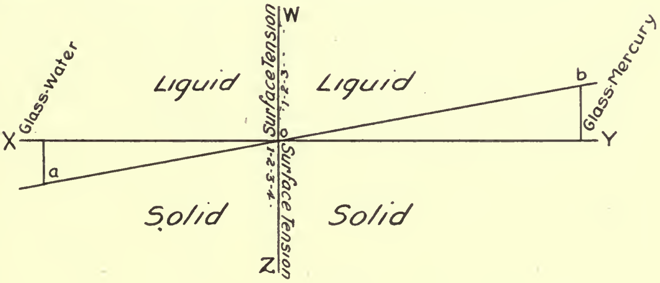

FIG. 6a

I have cited an instance where there is no liquid encasing film at all (glass-water interface) and one where the film is excessively strong (glass-mercury interface). May not these extremes be plotted and connected by a continuous curve with points to show the tension at the solid-liquid interface of various combinations of substances? Yes, and more than that. One end of the curve might represent great surface-tension in the surface of the solid and the other end a great surface-tension in the surface of the liquid. Fig. 6a is a diagrammatic sketch

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[15] Whether or not galena be surrounded by a film of adsorbed air or grease does not concern us now.

to show this. The surface-tension of the glass-water interface, where the resultant—and therefore the surface-tension—is in the solid, is placed at one end and the curve passes through a zero surface-tension to an extreme point representing tension at the glass-mercury interface.

If the resultant lies in the solid there is no liquid film, but, instead, a surface-tension solid film, and the surface-tension would plot on *ao* in the quadrant *xoz*; while if the resultant is in the liquid there is a liquid film and the surface-tension would be indicated by a point on *ob* in the quadrant *woy*. It seems to me obvious that the non-flotative minerals would plot to the left and the flotative minerals to the right of *zw,* and that such minerals as fluorite, garnet, and calcite, which have been described as at times inclined to float, would be placed very near *zw.*

Since I have said so much about the encasing surface-tension film, it might be well to see if the workers in colloid chemistry take cognizance of this sort of thing. Indeed, we find that there is no lack of precedents. The idea of films around small particles has long since been accepted, and furthermore, before the Wilfley table was invented, they knew that is was the coalescence of these films that caused aggregation. I quote from 'Colloid Chemistry' by Ostwald, page 88: ''Stress was laid upon the importance of these envelopes in phenomena of condensation early in the history of colloid chemistry. Thus, J. M. van Bemmelen wrote in 1888: 'I think it possible that the formation of the flakes which are precipitated in a liquid is dependent upon a change in the surface-tension of the liquid membranes surrounding the colloid particles, of such type that these membranes between the particles are torn at some point, thus permitting the particles to form aggregates.' ''

This excellent picture of aggregation tempts me to quote more of Ostwald's text, but we must leave it and finish the high-school book before taking up a more advanced work. In doing this let us make some simple tests. Touch the round end of a glass rod to the surface of water. No sooner does the smallest physical point come in contact with the water than the water seems to jump to the rod and spread over the end as if it were magnetized. We say, that is to be expected, that is capillary rise. Observing that there must be a great pressure exerted upon the film that is pulled to the glass rod with such manifest energy, we explain the spreading and consequent rise in the terms of John Leslie, who, in 1802, said: ''The result of this pressure if unopposed is to cause this stratum to spread itself over the surface of the solid as a drop of water is observed to do when placed on a clean horizontal glass plate; and this even when gravity opposes the action, as when the drop is placed on the under surface of the plate."

Since this plain and simple reasoning of Leslie's is credited by Clerk Maxwell as being a correct explanation of the rise of a liquid in a tube and, further, since it leads up to the same conclusions as does the 'component and resultant' method of Milikan and Gale, we feel an added security and proceed with a similar test using a different solid substance. Let us take for this test a fragment of galena and touch it gently to the surface of the water. Does a dimple appear immediately to indicate the presence of a membrance that is resisting rupture? Not so. The water jumps to the galena much as it did to the quartz, though probably not so vigorously. We argue that this is not in accordance with our expectations; thereupon we repeat the test and make sketches.

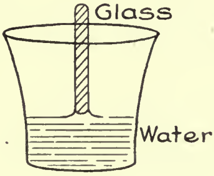

FIG. 7

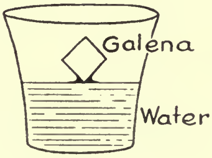

FIG. 8

Fig. 7 shows how the surface of the water is elevated to wet the glass rod, and Fig. 8 shows much the same sort of phenomenon when galena is used. Though badly confused, we decided to carry the test one step farther. To do this, press the end of the glass rod below the natural surface of the liquid and also allow the galena to float. Fig. 9 and 10 show a cross-section through the contact of liquid and the two solids.

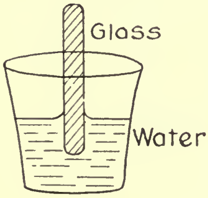

FIG. 9

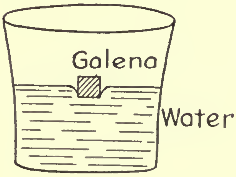

FIG. 10

The liquid is now plainly elevated around the rod and depressed around the galena. This seems perfectly natural and satisfactory; but how about the rise of the liquid in Fig. 8 where the galena seemed to be wetted? It is nothing more nor less than adhesion, a component that must be reckoned with, however small it may be, as, for example, in Fig. 3, where mercury is in contact with glass. Let us prove that there is adhesion between mercury and glass. To do this we will take some mercury in a watch-glass and use the same glass rod. If we watch closely, as we lower the rod to meet the mercury, we can see that the mercury rises a little around the end of the rod at the instant they come in contact. See Fig. 11. Upon pulling the rod away it is plainly seen that there is adherence. Having performed this experiment we may go into the mineralogy laboratory with a beaker of water and find that any one of a dozen minerals taken at random adheres more or less firmly to water. In some cases, when the mineral is pressed below the surface, we can detect capillary rise and in others a depression.

Then what does our popular term 'wetting' mean? It can mean nothing more than absence of repulsion unless we give it a special definition, as some physicists have done. As for the spreading, Leslie, the sage of more than a century ago, in speaking of adhesion of a liquid to a solid as indicated in Fig. 7, 8, and 11, said: "the result of this pressure, if unopposed, will cause the liquid to spread." When the adhesive force is sufficiently in excess of the cohesive force the liquid will spread indefinitely, regardless of gravity, until the thickness is such that it could only be measured in terms of the diameter of a molecule. If the solid body attracts the liquid strongly enough it will draw every particle of it as near as possible to itself. Thus it is that a liquid spreads over certain clean surfaces. But such perfectly clean surfaces[16] are difficult to obtain and that on account of this very phenomenon. Thus, the least drop of oil touching a glass surface spreads over it quickly and completely changes the effect of adding a drop of

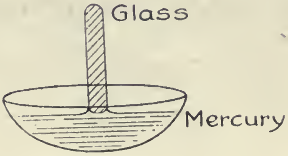

FIG. 11

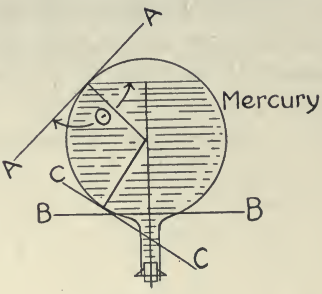

FIG. 13

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[16] 'Mechanics, Molecular Physics, and Heat.' Millikan.

water. Such deportment needs no emphasis to impress those interested in the laws relating to flotation.

The spreading of a group of molecules of water within the radius of molecular activity of the glass is analagous to the spreading of a ball of soft putty while resting on a plane surface. In both cases the distortion is due to attraction; in the first, the attraction is called molecular; in the second, gravitational.

But analogies do not satisfy us; we are seeking the foundations of a new and important science, and there will be opportunities for analogies later. Leslie said "if unopposed." We shall do well to deal with components and not generalities. We are reminded therefore how we stated above that in some cases, when the mineral was pressed below the natural surface of the water, we could detect capillary rise and with other minerals a depression. This statement must be considered with caution lest we let important facts slip our attention.

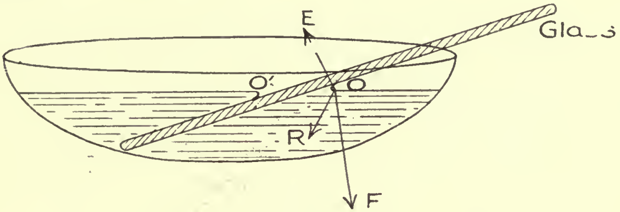

FIG. 12

Look again at Fig. 4 and 5. Shall we agree that in contact with a perfectly clean piece of glass the surface of water always turns up and that of mercury always turns down? You say, Yes; that has been proved. Not so; and here, as has often been our experience, we find that we have to unlearn what we have once learned. Let us place a glass rod in mercury so that it will rest in a position, not vertical as in Fig. 5, but in an inclined position, and draw the components of adhesion and cohesion and their resultant. See Fig. 12.

Now we know that the surface of a liquid tends to adjust itself at right angles to the resultant of the forces acting upon it and that if gravity predominates the surface is horizontal. But let us consider a group of molecules at *O* so small that the molecular forces predominate over gravitational forces. We have the force of adhesion *OE* acting at right angles to the surface of the glass and pulling the molecules to it and the cohesion of the liquid pulling these same particles in the direction of *OF*. The resultant of the two forces, *OR,* is the force to which the surface assumes a position at right angles, and since *OR* lies to the left of a vertical line through *O* it is apparent that the surface of the mercury must turn up to meet the glass. In like manner it can be shown that the mercury turns down to meet the glass at O^1. Since the mercury turns down at *O* in Fig. 3 and up at the same contact in Fig. 12, it is obvious that there is a slope of the glass at which the mercury would stand level. It may seem bold to draw these components so freely when so little is known of their absolute value. It must be said in explanation that they are only diagrammatic and that is all that Milligan and Gale intended. It is a fact, however, subject to a simple ocular demonstration, that mercury does turn up to meet the glass at *O* and down at O^1, Fig. 12. The point to be made is that in both cases the resultant lies in the mercury, even though the mercury turns up to meet the glass as does water against glass where the resultant lies in the solid, and that the slope of the liquid contact must be considered only in connection with the angle at which the mineral meets the original surface of the liquid. The elevation of the mercury at *O* does not mean that the sum-total of all the forces tends to pull the glass down as does water pull the glass in Fig. 4, for we must remember that the film of mercury extends entirely around and under the glass and that it tends to contract and reduce its distorted surface-tension film to a minimum. It will therefore push the glass upward if the downward component due to the weight of the glass is less than the upward component due to the contractile force of the liquid.[17] Briefly stated, an upturned liquid does not always indicate that the resultant turns into the solid as one would conclude from a study of Fig. 2. By the purely theoretical treatment of components adopted in Fig. 12, one can show that the surface of water also may well be approximately horizontal when in contact with glass.

After reaching these conclusions by merely ''reading between the lines'' of a most elementary physics and checking them by laboratory tests, it is interesting to note that a more advanced text-book[18] gives further corroboration in the recitation of a ''test to determine the angle of contact of mercury with glass.''

An inverted spherical flask, as shown in Fig. 13, is used. The quantity of mercury in the flask is adjusted until its surface in contact with the glass is horizontal.

Then $\frac{d}{2} = r \cos\ (\Theta - \frac{\pi}{2})$, where Θ is the angle of contact sought,

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[17] Here the principle of Archimedes, namely, loss of weight due to displaced liquid, is not taken into account.

[18] 'General Physics,' by Edser, p. 306.

d = diameter of circle of contact of mercury and glass, and r = radius of the spherical flask.

Likewise the surface of water would be about as shown by line *BB*. Contamination of the glass or liquid might well give surfaces that lie anywhere between the two mentioned. This might be called a reciprocal method for determining the angle of contact; for in this test the liquid surface is horizontal and the solid surface is inclined, while the angle of contact, as we are accustomed to thinking of it, appears with an inclined liquid surface against a vertical solid surface. The 'direct' position of Fig. 13 appears in Fig. 14 where *AA* and *CC* are vertical. This shows the same angle of contact in a position more familiar to us.

The foregoing shows that it is insufficient to say that the liquid turns up or down. The angle of contact must be given; it is the same regardless of the slope of the solid surface. For example, in Fig. 12 the angle of contact at O must be the same as at O^1 and again the same at O in Fig. 3. Again the actual angle of contact may be distorted by the weight of the mass, as when a drop of mercury rests on glass.

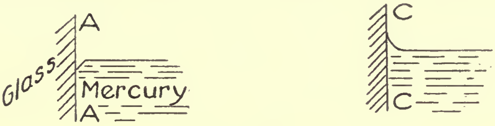

FIG. 14

The question may well be repeated: Is it correct to speak of a surface-tension film of mercury against glass, and if the term is correct, do we need added evidence that it does exist at the mercury-glass interface?

In our first conception of the film we thought only of the upper horizontal surface of a liquid, that is, the liquid-air interface of standing water. We then extended it to include the walls of a submerged air-bubble, and now the only rational application of film or membrane is to include also all interfaces where there is surface-tension. If there is a solid-liquid interface in which the resultant turns into the liquid, the membrane is in the liquid, and if the resultant turns into the solid, the membrance is in the solid. It is of the utmost importance that we add contaminating substances to the mill-water that will cause the membrane surrounding the grains of ore (sulphides) to be in the liquid and simultaneously cause the membrane around the gangue to be in the solid. Since the solid membrane is an intangible sort of a thing because it is solid, it is best to deal with its antithesis: the absence of a liquid membrane. It may well be said therefore that when the flotation metallurgist has contaminated his liquid so that there is a liquid membrane around the ore particles and none around the gangue, he has mastered the first step in his process.

The liquid film must not only surround the ore particles, but it must be of such a nature that it will rupture at the point of contact with an impinging air-bubble and thus cause coalescence; or if coalescence does not take place the films must cohere. This is the second step.

Reference to another simple and familiar physical experiment may be of service here to give added evidence that when mercury is in contact with glass the membrane is in the liquid—a state quite different from water in contact with glass—and aid in further acquainting us with laws second to none in their application to flotation, the laws of molecular cohesion and adhesion.

Take two conical capillary tubes, *a* and *b*, Fig. 15. Place mercury in *a* and water in *b*. The mercury will at once run to the large end and the water as quickly to the small end of the respective tubes. The mercury will travel to the larger end of the tube even though it be slightly elevated. In doing so, it decreases its surface and finally reaches the point where the diameter of the tube is sufficient to allow it to assume the form of a sphere. Such conduct is possible only when a liquid is surrounded by a surface-tension liquid membrane. Here, with the mercury, surface energy in the liquid, after its well-known manner, tends to reduce the amount of surface to a minimum. The same components exist in *b*, but they are of different magnitudes and are such that the liquid membrane is only at the liquid-air surface, and it is obvious that it is reduced by a movement toward the small end. The concave water membranes at the ends are similar to the piston of a hydraulic press, and the liquid is drawn in the direction of the greatest force per unit of area. If we assume that these concave surfaces are hemispherical it is obvious from the formula, $P = \frac{2T}{r}$ that the drawing forces per unit of area toward the ends are inversely as the radii. If the liquid film extended entirely around the water such an increase in total surface could not happen.

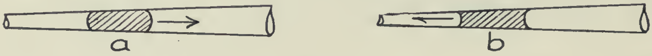

FIG. 15

"At a solid-liquid interface two cases are therefore possible—surface-tension in the same sense as in the case of the gaseous bounding medium may appear or," according to Wilhelm Ostwald, "we may have a surface-tension of the opposite character. In this the (liquid) surface does not tend to become as small as possible, and we say that the solid body is wet by the liquid. Mercury on glass is an example of the first; oil on glass, of the second. When the surface of a solid is wet by a liquid, it (the solid) acts like the surface of a liquid, and therefore seeks to become as small as possible."

At this point an analogy may be of value, not as a proof but as an aid in showing how the deportment of mineral grains in a flotation-cell might well depend on whether they are or are not surrounded by a liquid film.

In this hypothetical case, we grant first that it is a physical fact that glass submerged in mercury is encased in a liquid membrane; that this membrane is squeezing the glass in accordance with the formula $P = \frac{2T}{r}$, in the same manner as if air occupied the hole in the mercury in place of the glass. Second, let us remind ourselves of the great 'affinity' of mercury for gold. This affinity or capillarity[19] is well known and one only needs to be reminded that gold is drawn into mercury[20] in the same manner as glass is drawn into water to see that they are perfectly co-ordinate.

We take a pulp composed of mercury, particles of gold, and crushed glass; we place it in a Callow cell and blow air through it. Can you conceive of the gold entering or even clinging to an air-bubble? No, you would not think of such a thing any more than you would of the gold in the amalgam on the copper plates mysteriously popping to the surface and parting company from the mercury. But, on the other hand, consider the glass. It is surrounded by a liquid membrane of mercury. If this membrane comes into contact with the membrane of an air-bubble and bursts at the junction, the glass will be squeezed out of its little sack into the large one and ride securely to the surface on the wall of the resulting bubble. Thus the cell would produce an overflow of glass and an underflow of mercury with the gold. If we replace mercury with water, glass with galena, and gold with quartz, and adjust the detail by means of a contaminating substance, we af-

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[19] In using 'affinity' and 'capillarity' I am only attempting to use terms that we have all used when discussing amalgamation.

[20] Thomas T. Read, Trans. A. I. M. E., Vol. 37, says that amalgamation is a physical rather than a chemical process; that the surface-tension of mercury draws the gold beneath the surface.

ford a complete and perfect transfer from a hypothetical to an actual operating flotation-cell. Unfortunately, too many of us have concerned ourselves so much with detail—the contaminating substances, etc.—that we have failed to grasp the fundamental idea. Electrolytes, static charges, osmotic pressure, and much of the researches of recent workers in physical and colloid chemistry will all have their places in the science of flotation after the foundation has once been laid.

Archimedes was interested only in the mass per unit of volume, Leslie in the manner in which the molecular forces of substance affected an unlike substance. Since the range of action of molecular forces is so very small it is obvious that only those molecules at the surface could be sufficiently close to another substance to effect it. We are interested, therefore, in the forces at the common surface of two substances. In this, our position is the same as that of the chemist. Bigelow[21] says, "more and more we are realizing that the conditions in contact surfaces often play the decisive rôle in important processes."

I have tried to expose the fallacy that mineral particles adhere to impinging bubbles; as an alternative, I have advanced a theory involving coalescence, this being more in accord with scientific ideas. We are familiar with the coalescence of two soap-bubbles, but have much to learn concerning the coalescence of two films when one of them surrounds a solid. Here I would recommend a study of boiling in the volume on 'Heat' in the 'Text Book of Physics' by Poynting and Thompson. It teaches that the bubbles which carry the steam to the surface of a liquid do not rise from points at random, but from definite points or particles of foreign matter that form a boundary of the liquid. There must be a nucleus in the shape of a minute bubble into which the steam passes. As evaporation proceeds, the bubble grows and finally breaks away, always leaving a small portion behind as a nucleus, just as part of the neck of a drop of water is left when the drop breaks off from a surface. Some substances carry a great many nuclei while others are barren. A beaker, thoroughly cleansed in hydro-fluoric acid, is so barren of nuclei that water can be raised several degrees above the boiling point without boiling taking place. A piece of flint immersed in a liquid was alive with bubbles over its entire face until broken in two, when no steam was given off from the freshly formed surface. The introduction of iron filings caused rapid ebullition. Substances over which water is most reluctant to spread, that is, those solids which show the least adhesion for water, furnish the greatest

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[21] 'Theoretical and Physical Chemistry,' p. 247.

number of nuclei. One paragraph from a paper by Lord Rayleigh,[22] where he discusses 'Liberation of Gas from Super-saturated Solutions,' is sufficient to show the close relation between boiling and flotation. He says: "It seems to me that Tomlinson was substantially correct in attributing the activity of non-porous surfaces to imperfect adhesion. We have to consider in detail the course of events when a surface, for example, of glass, is introduced into the liquid. If the surface be clean, it is wetted by the water advancing over it, whether there be a film of air condensed upon it or not, and no gas is liberated from the liquid. But if the surface be greasy, even in a very slight degree, the behavior is different." In another book[23] we learn that "metal turnings depress the boiling-point because their molecular attraction for water is less than that of glass."

We have ample evidence, therefore, that solids, like fresh quartz over which water spreads freely, do not carry nuclei of air, while solids, like galena over which water does not spread freely on account of adhesion, do have small bubbles attached to them while submerged in water. For an extreme case where air nuclei would be present, we might suppose a glass sphere to be submerged in mercury. As it passes below the surface with its angle of contact of 140°, it would appear as shown in Fig. 16.

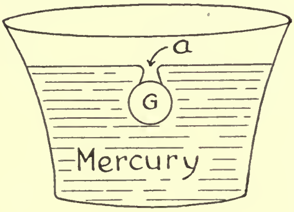

FIG. 16

FIG. 17

With the disappearance of the waist at *a*, the film closes around an air nucleus. A small quantity of air would thus be carried down and if the mercury were transparent, one could see an air-bubble attached to the glass. A fresh piece of glass in water would not do this, for the water would close over it as shown in Fig. 17. But we do not have to go so far afield to account for attached air-bubbles. The surface of all minerals contains depressions and it would be impossible for them to pass from air to water without some of the air residing in the depressions being carried below the surface. Whether or not the air

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[22] *Philosophical Magazine*, Vol. 48, 1899.
[23] 'Theory of Heat.' Preston.

is held in place depends on the adhesion of water and mineral. If adhesion is less than cohesion of the liquid molecules, the surface-tension film will pass around the air nuclei and hold them in place, but if adhesion is great the water will spread over the entire surface of the mineral and ultimately release the air bubbles. The application of these principles to flotation is simple: minerals with the least adhesion for water will retain the greatest number of small bubbles; these bubbles are inflated by gases expelled from the solution and finally an air-bubble in its passage impinges against, and coalesces with, the attached bubbles and the mineral is carried to the surface by the resulting bubble, which is inflated with air and expelled gas. I wish to express my gratitude to Dr. Joel H. Hildebrand for his critical reading of these notes and for his assistance during the seminar in 'Colloids and Surface Tension' at the University of California. Also I wish to thank H. M. Parks and Ira A. Williams of the Oregon School of Mines for their co-operation.

THE NUMBER OF MEN NECESSARY for the operation of large flotation machines is remarkably small. At the Inspiration plant, one operator supervises four sections of flotation machines. Two Mexican helpers assist him in washing the bottoms, thus insuring a free passage of air through the porous medium. At the prevailing high prices of American and Mexican labor, this means an expense of somewhat more than 1.5c. per ton of ore treated. The total expenses representing flotation proper were as follows for the months of March, April, and May, 1916:

	Cents per ton
Labor	1.62
Oils	1.65
Other supplies	0.35
Power	2.14
Total	5.76

The subsequent table treatment of the flotation tailing, the filtering of the concentrate, and other operations connected with the process of concentration, belong more or less to flotation treatment, and their expense should also be considered when the cost of the flotation process is to be calculated. The total milling cost, exclusive of crushing and grinding, has been for the past few months in the neighborhood of 20 cents. When the cost of crushing and grinding is included, the cost is about 40c. per ton of ore. Royalties for the use of the flotation process are not included in any of these cost figures. —Rudolf Gahl, Trans. A. I. M. E.

THE ARMOR IN FLOTATION

By Will H. Coghill

(Written especially for this volume)

As the man of science takes a beam of light and passes it through a crystal prism, and it comes out on the other side of the prism broken up into its components, so we must take each effect in flotation and resolve it into a 'spectrum' to reveal the cause.

It has pleased us, from the start, to speak of a pregnant froth as 'armored.' By this expression we convey the idea of greater stability on account of solid constituents. Are we justified?

At the beginning it is necessary to have in mind the exact physical relation of the film to the mineral grains. In the absence of facts subject to ocular verification I will state what this relation should be when it is the natural effect of causes as I understand them. I believe that a froth gets its load from two sources: first, from grains wholly or partly surrounded while in bulk-water with liquid films which feed the bubbles by coalescence, and second, from mineral grains which become entrapped at the surface of bulk-water, between the ascending bubble and the lower layer of the froth. The chief constituents of the first are sulphides, of the second, gangue or at least minerals on which water spreads freely, and appear as shown in Fig. 1. The first, if wholly non-wetted, ride upon the surface of the froth just as galena rides the surface of bulk-water in a H. E. Wood machine, and further, they are on the outer surface, being the solid residue from perished bubbles. If partly non-wetted (perchance these constitute a great portion of the floatable sulphides), the dry spots would tend to prevent sinking while water would spread on the remaining portion. A hypothesis involving a partly wetted surface is justified by the results of physical measurements. I refer to the work of Dr. Huntington, who found that the angle of contact of dark blende on a principal cleavage face was 53° while on another cleavage of the same specimen it was

Fig. 1. FROTH LADEN WITH QUARTZ

69°.[1] Again, a part of the surface of the mineral might be old while another part is new—formed in a ball-mill, for example.

In a recent article[2] I called attention to the way in which like floating objects are attracted to each other. Let us take the case of two pieces of galena floating on bulk-water to find the numerical value of this force of attraction, that is, the strength of the armor. They appear as shown in Fig. 2.

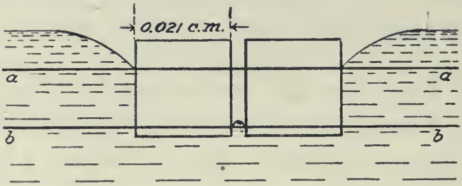

FIG. 2. BULK-WATER LADEN WITH GALENA

The side pressure above the line *aa* is that of the atmosphere and the same at all points. The pressure below *bb* is that of the liquid in equilibrium. The unbalanced force then must lie between *aa* and *bb*. We know that at all points in the free surface of a liquid, where it is plane, the pressure is the same and is that of the atmosphere, increasing at the rate of one gram per square centimetre for every centimetre in depth.

Assume that the pieces of galena have a length of one centimetre with the cross-section shown (about 65-mesh) and that *aa* and *bb* represent traces of horizontal planes containing the contacts of the three phases. The area subjected to the unbalanced force is about 0.01 cm. × 1 cm. = 0.01 sq. cm. The average depth is about 0.02 cm. The total unbalanced hydrostatic pressure is,

$$0.01 \times 0.02 = 0.0002 \text{ gm. or } 0.2 \text{ mg.}$$

It seems apparent then that the unbalanced hydrostatic pressure (0.2 mg.) is such a small part of the tensile strength of the film (70 mg.) that the armor effect from this cause is negligible.[3]

The same method of calculation can not be applied to sulphides on curved liquid films, but I believe that any effect from a similar cause can be ignored. There is, however, an unquestioned armor effect due to the arching of a solid-liquid mixture with the concave (upward)

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[1] Trans. Faraday Society, Vol. 1, 1915.

[2] Colorado School of Mines *Magazine*, January 1917.

[3] The drawing (Fig. 2) is only an approximation of conditions as they exist on bulk-water, but is, I believe, sufficiently correct to justify the conclusion.

surface of the film and the containing walls of the flotation machine for skewbacks. The measure of this effect must be left to conjecture.

Quartz (gangue) in the froth must next be considered to see if it has a stabilizing effect. At first thought it may seem that quartz goes into the froth in opposition to the laws of cause and effect. But this view is wrong, and further, the cause producing this effect is perfectly apparent. Too little thought has been given to this phase of flotation. The pyro-metallurgist gives his chief attention to the slag and lets the metals take care of themselves. In flotation we have given all our thought to the sulphides. Let us consider the gangue for a moment. It is indeed a truism that anything in the category from horse-shoes to diamonds can be collected in a froth, if sufficiently small, so that the force of gravity is negligible as compared with the molecular forces of cohesion and adhesion. Please picture the froth-covered pulp in agitation. A rising bubble about to emerge and pass into the froth is separated from the froth by only a thin stratum of pulp, that is, by water with a uniform mixture (if the gangue is not flocculated) of all the constituents of the ore. In an instant the films come together and a portion of the solids are entrapped. Being thus entrapped, it is contrary to the laws of nature for galena to escape the clutches of the liquid film, and the exit for the quartz is a restricted one, as will be shown later. For galena is repelled from the liquid by the film and obliged to ride upon it and quartz is drawn into the film and made fast between the two surfaces. There is no exception.[4]

It is impossible to practice flotation without entrapping a portion of the solids; these might consist of mineral or gangue in the condition of either galena or quartz, or any of the possible combinations; but whatever the condition, they must conduct themselves as one or the other. It is not at all unlikely that some of the sulphides contributing toward a rich concentrate are entrapped grains in the condition of quartz and therefore held in the film as shown in Fig. 1.

Do such grains add tensile strength to the film? Having proved

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[4] This cannot be over-emphasized. All minerals when classified according to flotative properties (where liquid and air are the fluid phases) come under one of two separate and distinct heads; they either exert an adhesive force greater than a certain minimum so that the liquid spreads upon them with no ultimate increase of surface energy, or, an adhesive force less than this, so that their submergence increases the area of the surface-tension film and therefore the surface energy. In short, a liquid surface-tension film is either absent or present at a solid-liquid interface. Where it is absent the liquid tends to include the mineral. Where it is present the liquid tends to exclude the mineral. I have symbolized the former by 'quartz' and the latter by 'galena.' What I have said applies to vesicles of water inflated with air (a bubble) as well as to bulk-water.

the inefficacy of forces arising from surface configuration in the one case (Fig. 2) it can be dismissed in this; but a scrutiny of Fig. 1 brings to mind the popular demonstration in physics showing the enormous force with which two discs are pulled together by a drop of water. The demonstration runs about as follows:

''It is a matter of common experience that the hairs of a paint-brush cling together when the brush is withdrawn from the water. The reason is obvious; water clings to the hairs, and the free surface of the liquid tends to contract and pull them together. The force is much greater than the force of surface-tension.

''Let Fig. 3 represent the side-view of two plates with a drop of water between them. The water spreads out into a circular disc of considerable area. Let *R* be the radius of the flattened drop; *d* the distance between the plates, equal $2r$; and let *T* equal surface-tension of the liquid. Then the total force *F* urging the plates together is,

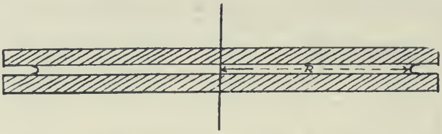

FIG. 3. PARALLEL PLATES WITH A DROP OF WATER BETWEEN THEM

$$F = 2\pi \frac{RT}{1} + \pi R^2 T \left(\frac{2}{d} - \frac{1}{R}\right)$$

''If the surfaces are true planes, the discs will approach each other until *d* becomes exceedingly small, and the force exerted may be sufficient to fracture them.''

This formula cannot be applied to the problem before us because the conditions, so much alike in some respects, are so different in others that the conclusions would be misleading. An acquaintance with the method of derivation is necessary in order to appreciate this. The water between the discs is under a dilational strain due to its tendency to spread. The water between the mineral grains in Fig. 1 is also under a dilational strain, but the strain in this case is due to the weight of the column of water reaching along the films to the surface of bulk-water. It is as if the water-filled opening between them were connected to a water-surface through a suction-pipe. There is an interesting analogy in a discussion of regelation that reads as follows: ''When two blocks of ice are placed loosely together so that the superfluous water which melts from them may drain away, the remaining water draws the block together with a force sufficient to cause the blocks to adhere.'' If the water were drained away from the ice through a draught-tube the analogy would be perfect. Having thus stated the problem, the calculation is simple. Assume that the vertical length of this draught-tube is 25 cm. (about 10 in.) the depth of the froth, using grains of the same dimension as before, and we have as a difference between inside and outside pressure due to the weight of water sustained,

$$0.021 \times 25 = 0.525 \text{ gm., or } 525 \text{ mg.}$$

while as before the tensile strength of the surface-tension film (two surfaces) is about 70 mg. A temporary armor, at least! I say "temporary" because the rough surface presented in Fig. 1 is not one of minimum potential energy. If anything tends to disturb the equilibrium it must be considered. There is one thing. I refer to the weight of the column of water sustained and believe that it would tend to slip the quartz grains along the film to bulk-water. As a result the skew-backs for the arch would be continually dropping back into the water, (see Fig. 4), at a rate depending on viscosity and other factors. The weight of the grains themselves would also tend to produce this slipping. As for viscosity, we know that quartz would drop back faster in a film of low viscosity and that viscosity decreases with rise of temperature. Heat should therefore improve the grade of concentrate. While there might well be causes which would neutralize this effect it is interesting to associate, in this connection, a paragraph from Dr. Gahl's paper[5] that reads as follows: "How can we raise the grade of our concentrates—that is, reduce the percentage of insoluble matter contained in them—without entailing additional copper losses? We know from laboratory experiments that this can be done by expensive methods, for instance, by heating the solutions." Would not heating the froth only, with steam-coils, effect the same advantage at much less cost?

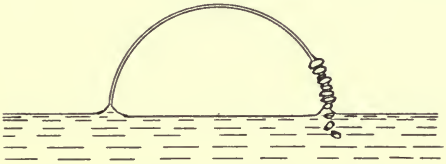

FIG. 4. A BUBBLE SPILLING QUARTZ BACK INTO THE WATER

By the use of fundamental principles of physics I have adduced considerations that are in accord with colloid-chemistry, namely, solids armor a froth. To justify this conclusion, I quote from W. D. Ban-

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[5] Bull. A. I. M. E., Sept. 1916, p. 1675.

croft:[6] "We cannot get a froth with a pure liquid and air. There must be present a third substance in colloid solution." Again, Mr. Bancroft says that we call a phase 'colloidal' when it is sufficiently subdivided, not limiting ourselves definitely as to what degree of subdivision.[7] He states that a sufficiently subdivided phase stabilizes a froth. In so doing he has stated the effect. I have tried to point out the cause.

If the impression given by Fig. 1 is that what I have said about stabilizing causes applies only to coarse mechanical suspensions, that is, where the diameter of the discontinuous phase is greater than the thickness of the film, it should be made clear that suspensions of all degrees of dispersion (diameter of the solid) are included. Wolfgang Ostwald's[8] discussion of internal friction of suspensoids justifies this conclusion. He says: "It may be regarded as typical of suspensoids that their viscosity is but slightly greater than that of their pure dispersion mediums. It must be remembered, however, that this is true only when such systems are dilute. In concentrated form the mass of the disperse solid phase may predominate over that of the dispersing medium, as when powders are merely moistened so as to be coated by a thin but continuous liquid membrane. Such systems may be so viscid that their properties approximate those of solids. We need but recall how moist sand may be cut into slices, and the rigidity of the scales and crusts of dried colloid metals. From this it follows that with increase in concentration the viscosity of a suspensoid rises very slowly at first, but very suddenly and greatly at high concentrations." What I have indicated in Fig. 1 is equivalent to the 'slice' mentioned by Ostwald. It is not necessary for the armor to extend over the whole surface of the froth in order for it to have a stabilizing effect.

When the discontinuous phase has such a high degree of dispersion that the conditions approach those of a molecular solution (soap in water is an example) there is a new set of forces to be considered. This has been described and called 'adsorption.'

One has only to shake finely crushed ore in a test-tube with water to see that the solids lend persistence to the bubbles though in some cases the bubbles taken collectively may not be sufficiently voluminous to constitute what is ordinarily styled a froth. There is nothing new about this. T. K. Rose[9] says: "Losses in amalgamation are also caused

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[6] *Met. & Chem. Eng.*, June 1, 1916, p. 634.
[7] 'The Flotation Process,' by Megraw, p. 28.
[8] 'Handbook of Colloid Chemistry,' by Ostwald, p. 146.
[9] 'Metallurgy of Gold,' by T. K. Rose, p. 207.

by greasy substances contained in some ores, such as the powdered hydrated silicates of magnesia and of alumina, which cause frothing.''

Rose says 'greasy.' This would indicate that the galena type of mineral is the greater stabilizer. On the other hand Gahl[10] thinks that the frothing characteristics follow the tailing-pulp. We must, someday, learn more about this. Taggart and Beach[11] are doubtless justified in their statement that ''the formation of a scum of floated sulphide increases the stability of the float,'' but when they say, in discussing adsorption and surface tension, ''On philosophical grounds it is impossible to consider that a real physical discontinuity occurs at the boundary between two media. In other words there must be a very thin layer of transition in which there is a rapid but continuous change in the concentration of the components,'' they are perpetuating an early conception that has been more befogging to me than anything I have read relating to this subject. After being so perplexed by the frequent recurrence of this statement in the various texts, it was indeed a delight to read from the pen of Irving Langmuir in a paper[12] that impresses me as epoch-making in the studies of surface-tension, as follows: ''The surface of a solid (or liquid), therefore, does not contain, as is usually assumed, a transition layer, consisting of several layers of atoms or 'molecules,' in which the density varies by continuous gradations from that of the solid to that of the surrounding gas or vapor. Instead we find that the change from solid to empty space is most abrupt. In a sense, the re-arrangement of the atoms, in the surface layer, causes this layer to assume the character of a transition layer, but the density of the packing of the atoms in this layer is undoubtedly greater than in the body of the solid, so that there can be no gradual change in density from that of the solid to that of space.'' Mr. Langmuir's conception impresses me as consistent, the other not.

There is yet another thing to be said about a bubble with grains deposited between the films as shown in Fig. 1, to wit, the space between the grains is a repository for water. A wet froth would therefore accompany a low-grade concentrate. Indeed this seems to be in accord with observation. For example, ''Toward the tailing end of the flotation machines,'' says Dr. Gahl, ''most of this dark material has disappeared and the froth is lighter and of a more watery nature.''

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[10] Bull. A. I. M. E., Sept. 1916, p. 1680.

[11] Bull. A. I. M. E., Aug. 1916, p. 1382.

[12] 'Constitution and Fundamental Properties of Solids and Liquids,' Journal of American Chemical Society, Nov. 1916, p. 2249.

ELECTRO-STATICS AND FLOTATION*

By James A. Block

Somewhat over a year ago it was first announced* to the metallurgical world that certain investigators working on flotation were studying the functions of the electro-static charges observed on the surfaces of the mineral particles and of the bubbles. It was suggested that these charges might in themselves account for flotation. In fact one writer, Thos. M. Bains, Jr., excluded all other explanation of flotation phenomena.[1] Much work has been done in that direction during the year past, but since little has been written concerning it, other theorists have recognized, criticized, or trampled upon the so-called electro-static theory to their heart's content. Generally speaking, those working along the lines mentioned have said little, for the reason that they have been attempting to secure practical results rather than popular approval, and they have furthermore wished to avoid the examples others have set in rushing into print without sufficient foundation for their statements. It seems, however, that many metallurgists have refrained from expressing their opinions because of the fact that the 'electro-static theory' has been presented in such form that they have had trouble in understanding just what the theory is. For that reason, I feel justified in attempting to define, so far as is possible at the present time, what I consider to be the function of the electro-static charges observed in flotation.

If we take a large beaker of water, and drop into it some rather finely ground galena, say 80-mesh, it will be seen to entrap considerable air. To avoid confusion, this may be removed by boiling the water, and then allowing it to cool with the galena particles on the bottom. If then, we take a small thistle tube, and attach to the small end a rubber bulb, we may immerse the other end in the water, and by compressing the bulb, make the surface of the air at the lower end convex. We have, then, a bubble on a handle, with which we can study the manner in which particles attach themselves to air-bubbles. See Fig. 1. If we bring this bubble into contact with the galena particles on the bottom, and then slowly withdraw it, the galena will be seen to adhere to the surface of the bubble.[2] This phenomenon, in my opinion,

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*J. M. Callow, Bull. A. I. M. E., Dec. 1915.

[1] M. & S P., Nov. 27 and Dec. 11, 1915.

[2] O. C. Ralston, M. & S. P., April 29, 1916.

represents flotation in its simplest form. Many interesting variations can be made in this experiment, from which considerable information can be obtained. If distilled water is used, quartz particles can also be made to adhere to the bubble, but this adhesion disappears almost completely upon the addition of a little acid or other electrolyte to the water. A most important point to be observed is that, from above, small points of the particles can be seen protruding through the bubble-film, their relationship being somewhat as shown in section in Fig. 2, the surface-films of the particle and the bubble having become continuous. When, on the other hand, quartz is placed in slightly acidulated water, and the bubble brought into contact with it, the surface-films do not coalesce with each other and expose the quartz to the air, as occurred with the galena, but remain unruptured, somewhat as shown by Fig. 3.

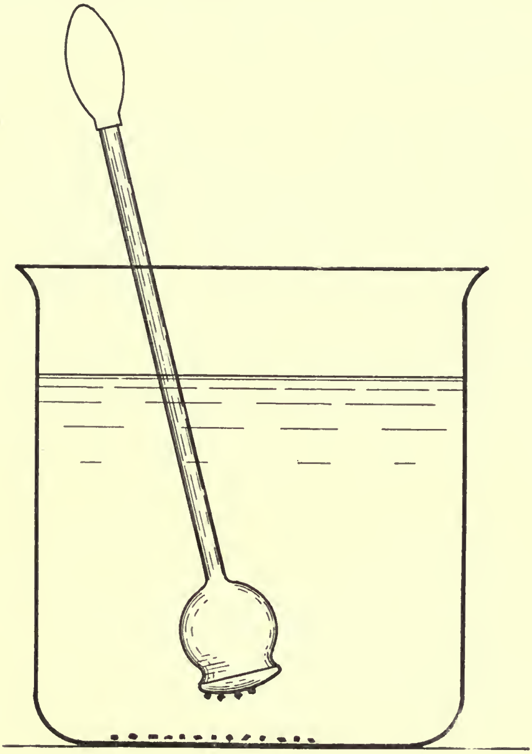

FIG. 1

All these phenomena are manifestly connected with, and dependent upon, the matter of surface-films, surface-tension, and contact-angles. Let us, therefore, consider the molecular forces that underlie these much-discussed properties of liquid surfaces.

In Fig. 4, a molecule of liquid in the interior will be attracted by the molecules adjacent to it in all directions, and the resultant of the cohesive forces acting upon it will therefore be zero. (By 'molecule' we do not refer to chemical molecules, but to physical molecules—extremely small portions of the liquid, which, however, may still be considerably larger than chemical molecules.) A molecule at the surface, on the other hand, will not be equally attracted in all directions. The attractions in the plane of the surface will balance each other, but the attraction of the molecules toward the interior will not be balanced by anything. The resultant of the forces acting upon a molecule at the surface will consequently lie in a line normal to the surface, and toward the interior. In other words, a molecule at the surface will be strongly drawn toward the interior.

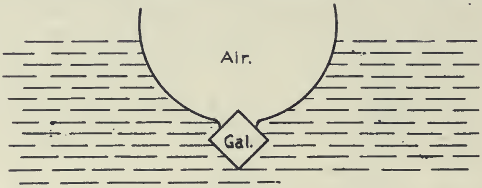

FIG. 2

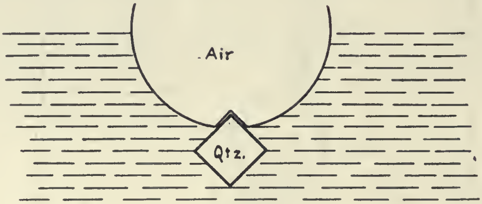

FIG. 3

Now, if a molecule of the liquid responds to this attraction, and leaves the surface, the surface will naturally tend to close in around the space left, giving rise to what we call 'surface-tension.' Conversely, if we desire to extend the surface (as in blowing a soap-bubble larger, or distorting a drop of liquid), we must supply sufficient energy to draw the requisite molecules from the interior to form the new surface. Obviously, there are several means of measuring this surface-tension, and these measurements show that any pure liquid in contact with a given gas will have a constant surface-tension, and that the effect of frothing-agents is to alter this surface-tension (generally to lower it), and to make it variable.

The same effects are observed when two immiscible liquids come into contact. The interfacial tension here can likewise be measured. For these reasons, we are more or less justified in assuming that the same things happen when a liquid comes into contact with a solid. See Fig. 5. Here a molecule at the interface will be attracted by the other molecules of the liquid in the same manner as at a liquid-gas contact, but these forces may be balanced by the adhesive attraction of the molecules of the solid. There is evidence to show that this attraction may be as large as, or larger than, the cohesive attraction of the liquid; and if it more than balances it, the resultant of the molecular forces acting upon a molecule at the interface would lie toward the solid. This would mean that the interfacial tension, if there were any, would be negative, and that the surface in contact, instead of tending to contract, would tend to expand so as to wet as much as possible of the solid. The existence of interfacial tension in such cases, either positive or negative, is more or less a matter of conjecture, but the forces which cause the effect are known to exist beyond any doubt; and, whether we can measure them or not, they also result in other phenomena from which we can, in some degree, estimate their relative magnitudes. From the standpoint of flotation, the most important other phe-

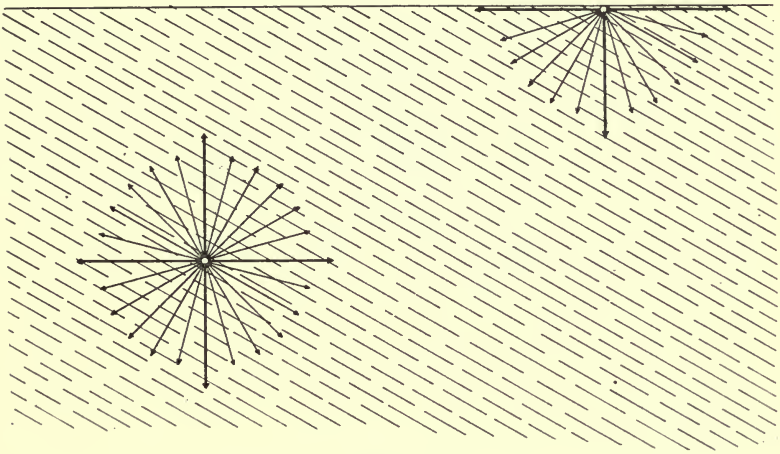

FIG. 4

nomena are the cases where the three phases meet, a solid, a liquid, and a gas. See Fig. 6. Now a molecule at the meeting-point (the toe of the meniscus) will be acted upon by several attractions: the other molecules of the liquid will exert a cohesive attraction upon it, the resultant of which will lie along the bisector of the angle between the gas and solid faces—the line *C* in Fig. 6. The molecules of the solid will exert an adhesive attraction upon it, the resultant of which will lie perpendicular to the face of the solid, and toward it—the line *A* in Fig. 6—and the gas may exert a slight adhesive attraction, probably negligible. In addition to these attractions, the shape of the meniscus will also be affected by the gas-liquid surface-tension, and by gravity.

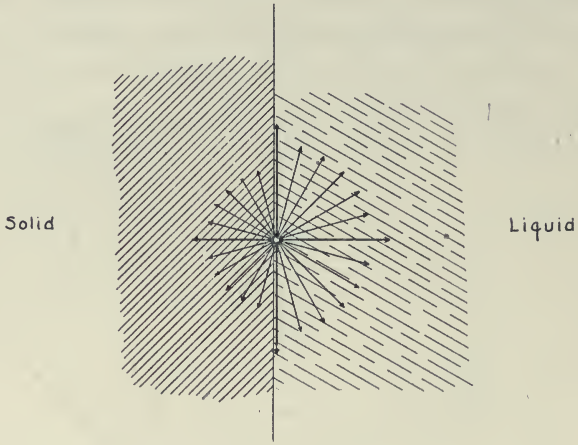

FIG. 5

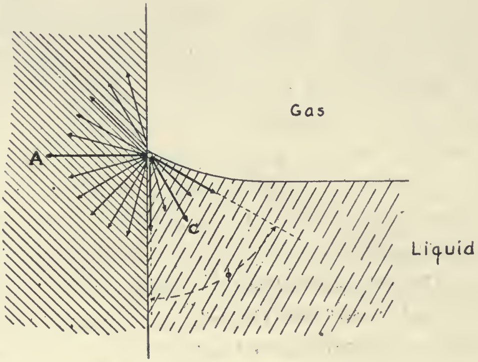

FIG. 6

The resultant of all these forces may lie toward the liquid or toward the solid, but in either case, the toe of the meniscus must lie perpendicular to it in order to be in equilibrium. This resultant, therefore, determines what we call the 'contact-angle' (ϕ in Fig. 6). Since all of the above mentioned forces should be constant for any given combination of gas, liquid, and solid, we should expect that the resulting contact-angle would be constant in value for such given combination. Experimentally, this is found to be true in some cases, but in other cases variations are noticed, which indicates that other forces, of a variable nature, enter into the matter. Such variation in value is called 'hysteresis', and in some cases seems to be due to an attraction between the surface of the solid and the surface of the gas acting across the thin film at the toe of the meniscus.[4] Of course, with solids whose contact-angles exceed 90° (see Fig. 7) there would be no thin film when the solid surface stood perpendicular, but the angles are measured by turning the solid until the liquid apparently 'wets' the solid, and it will be seen by consulting the references that the conditions under which the hysteresis is noticed and measured conform to the explanation. It might easily be assumed from a hasty consideration of the above that all that is necessary for a mineral particle to adhere to an air-bubble is that its contact-angle should be great, as in Fig. 7. This theory is constantly cropping up in technical literature, but it has a serious fault in that it does not conform to experimentally determined facts. The true parallelism has been known for years, and was outlined by T. J. Hoover in his book, 'Concentrating Ores by Flotation.' It is this: that minerals which tend to float are those in which the greatest hysteresis is observed in the value of the contact-angle. Since repeated experiments have proved this to be true, we must look for an explanation of why this hysteresis, or its causes, should also be connected with adhesion to air-bubbles in a froth.

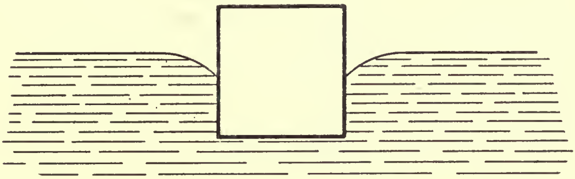

FIG. 7

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[4] H. Hardy Smith, M. & S. P., July 1, 1916. H. Livingstone Sulman, Trans. I. M. & M. Bull. 79 (April 19, 1911).

When a mineral particle under water comes into contact with a bubble of air (see Fig. 8) it might appear that the dense surface-films of liquid surrounding each would keep the air from getting into actual contact with the mineral. C. Terry Durell has gone so far as to say that this contact absolutely cannot take place,[5] but experiments such as were described earlier in this paper cast considerable doubt on the accuracy of his stand. A consideration of the surface-tensions involved, however, will not account for a rupture of the films, since in the parallelogram in Fig. 8, the resultant of *Tg* and *Ts* can never exceed their sum. Since it may be difficult to draw a clear mental picture of what happens when a solid particle and a bubble meet, let us consider what happens when two air-bubbles meet. See Fig. 9.

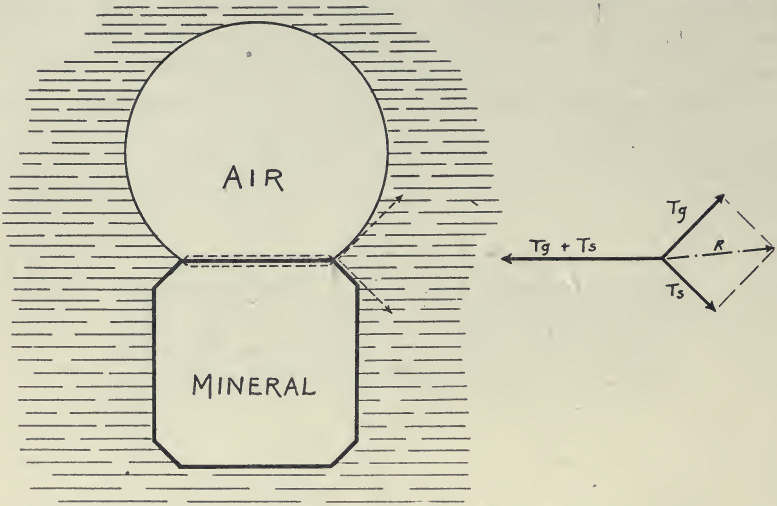

FIG. 8

If two air-bubbles submerged in water impinge against one another, a thin and probably flat film of water will be left separating them—at least momentarily. This film will have typical surface-layers on either side. If the water is pure, this film will not be stable, since the surface-tension will be constant, and the upper part of the film will have to support not only the tension of the lower part, but also its weight. An equilibrium is therefore impossible. If, on the other hand, some frothing-agent, such as soap or oil, were present in the water, the tension would not be constant, but would be greater in a freshly formed

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[5] Durell, M. & S. P., Sept. 18, 1915, and M. & C. E., March 1, 1916.

film than in an older film, and an equilibrium would therefore be possible so long as the separating film contained sufficient bulk-water from which to form new surface to take care of mechanical stresses. From these considerations, we would expect that air-bubbles would unite in pure water, while they would remain separate in water containing soap or other frothing-agent. This is exactly what is observed when a large number of small bubbles are passed into water and into soap solution. It has at various times been pointed out that a frothing-agent is introduced into the pulp in flotation for the express purpose of enabling small bubbles to exist in the presence of each other and of larger bubbles without coalescing. Now, if the surface-film surrounding a sulphide particle is similar to that surrounding an air-bubble, as it very probably is, we would expect that this same frothing-agent would prevent the bubble-film from coalescing with the film surrounding the particle. We know, however, that the films surrounding particles of floatable minerals, those which we previously said were afflicted with "hysteresis of the contact-angle," actually will coalesce with the films of air-bubbles. Let us consider how this may be explained.

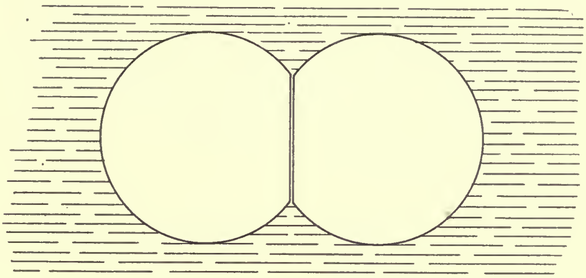

FIG. 9

It has been already mentioned that hysteresis of the contact-angle might be due to some attraction between the surface of the solid and of the gas across the thin film at the toe of the meniscus. If, in Fig. 9, there were some attraction between the surfaces of the right-hand bubble and the left-hand bubble, even in the presence of a frothing-agent, this attraction would tend to squeeze out the intervening film, thus reducing the amount of bulk-water in it, and its stability would be threatened by the lack of liquid from which fresh surface could be formed. The film, in other words, would be pinched out. Now, if the left-hand bubble, instead of being a bubble, were a solid particle, the same thing would happen, and it now begins to appear logical that the same forces which cause hysteresis of the contact-angle should also cause adhesion to air-bubbles in an oiled pulp, since when the films have once ruptured, the contact-angles of most floatable minerals will easily account for the particles being held in the film. These same phenomena have been observed, and the same conclusion arrived at, and stated in various forms by several theorists,[6] and I agree with the statements of most of them concerning this phase of the matter. We can then, if we wish, say that minerals which float are those which have considerable hysteresis in their contact-angles, or that they are not 'wetted' by water, and let the matter drop, but in so doing, we have hardly solved the problem. The reason for desiring a theory of flotation is to give the metallurgist a method of attack for the problems he meets, and in stopping at this point we have given him but little help in the solution of his difficulties. Unless we can determine some of the controlling causes of this hysteresis, unless we can hope to learn how to introduce or remove it to suit our needs, our time has been largely wasted.

I have done a great deal of experimental work during the past year and a half, most of which consisted of a study of the possible causes of hysteresis of the contact-angles. The net result of this work has been to show that there are several possible causes, only one of which has seemed to be noticeably selective in its action. This one is the presence of electro-static charges of different polarities on the surfaces of the floatable particles and of the bubbles. To return to Fig. 9, if we imagine the surface of the left-hand bubble to be covered with a positive charge, and the surface of the right-hand bubble to be similarly covered with a negative charge, it is clear that these charges would give rise to an attraction across the intervening film of the sort previously described as being necessary to cause the film to rupture. If, however, both bubbles were covered with charges of the same polarity, the two sides of the film would repel one another, which would tend to increase the thickness, and consequently the stability of the film. Again, the same results would occur were the left-hand bubble occupied by a particle of mineral. It has been repeatedly observed in the course of my experiments that the conditions best suited for flotation were those under which the valuable minerals bore the highest positive charges and the gangue-minerals and bubbles considerable negative charges. These charges must not be confused with ordinary

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[6] As Hardy Smith and Durell, previously quoted.

frictional electricity, which must be insulated to be preserved. They are due to the greater adsorption by the surface in question of some kinds of ions than of others, resulting in a concentration of ions of one polarity or the other against the surface.[7] To the extent of my knowledge, there is no other cause of hysteresis which will result in selective flotation, all others seeming to affect gangue and sulphide minerals to much the same degree. Methods have been discovered by means of which these charges can be, to some extent, controlled. For instance, when tannine or saponine is added to a properly operating flotation-cell, the positive charges on the sulphide minerals will drop, even to the extent of becoming negative, and the froth, if it carries anything at all, will drop in grade as the potential drops. It has also been possible to secure the reverse of these conditions, the grade of the froth being made to rise as the proper electrical conditions are created. In doing this, it is, of course, necessary to minimize the effects of all other possible causes of hysteresis.

In regard to the effect of tannine, saponine, and similar colloids, it has been suggested once or twice[8] that the disastrous results following the addition of these substances was due to their effect on the condition of the oil. This is by no means impossible, but I wish to state most distinctly that I have never seen these disastrous results occur when an electro-positive colloid was added, nor have I ever tried an electro-negative colloid that did not kill the flotation. Since the science of colloidal chemistry is practically based upon these electro-static charges, this may mean any of several things, but no explanation of the effects of colloids on flotation should overlook these facts.

The reader must be cautioned against assuming from the above that a detailed explantion of flotation can yet be given. Colloidal chemists have yet to agree upon the explanation of many of the phenomena to be observed in connection with surficial and interfacial films, and the experimental possibilities of the work have only been scratched. I believe, however, that work done so far permits of the following conclusions:

1. The tendency displayed by particles of certain minerals to attach themselves, under proper conditions, to air-bubbles in an oiled pulp is due to the presence of considerable hysteresis in the value of their contact-angles with air.

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[7] Powis, Trans. Faraday Society, April 1916, p. 160.

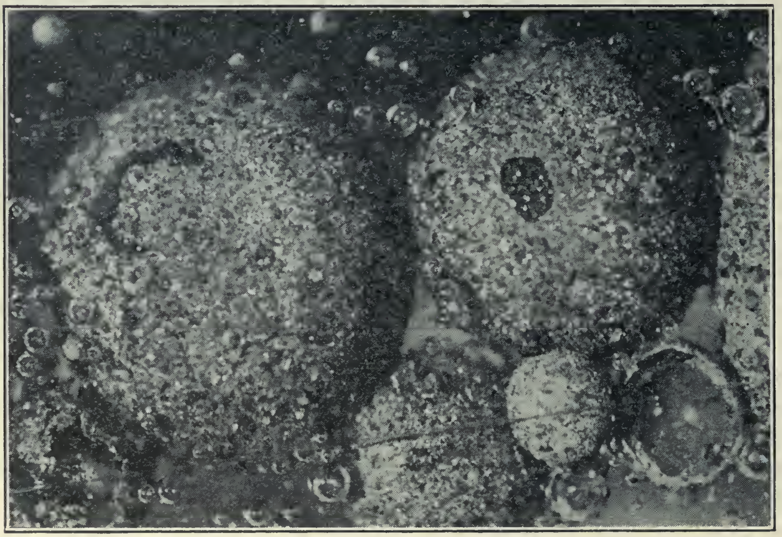
[8] Van Arsdale, Bull. A. I. M. E., May 1916, p. 885; Bancroft, *Met. & Chem. Eng.*, June 1, 1916.

2. This hysteresis may result from any of several causes, some of which are fairly well understood, and some of which are still somewhat puzzling.

3. A great many of these causes do not seem to be selective in their action, but result in the flotation of both gangue and metallic minerals.

4. The cause which seems to result in the selective flotation of sulphide minerals is the possession by these minerals of positively charged contact-films of liquid surrounding them, while the gangue and air-bubbles possess negatively charged films.

I wish to express my thanks to J. M. Callow, at whose instigation this work was taken up, for his kindness in permitting these results to be published, and for his help and advice in the interpretation of the results. I also wish to express my appreciation of the assistance rendered by O. C. Ralston in the collecting of scientific data concerning flotation.



FROTH WITH 0.1% OIL, MAGNIFIED 400 TIMES

THEORY OF ORE FLOTATION

By H. P. CORLISS and C. L. PERKINS

(From the *Mining and Scientific Press* of June 9, 1917)

*The physics and chemistry of ore flotation constitute the subject of extensive literature, but no one contribution presents an explanation of all the physico-chemical factors involved. These articles[1] include collectively considerable information of importance, but have failed to elucidate this very obscure problem.

In this paper is presented an explanation of the actual factors involved in ideal flotation and also of other practical observations incident to the art. The theory presented herein has been substantiated by actual experiment, but only a brief résumé of the experimental results is included.

The greatest success in the art has been obtained in processes in which a gas, usually air, is introduced into the pulp, either by chemical means from carbonate and acid (Potter-Delprat process), assisted by vacuum (Elmore process), by the use of agitation (Minerals Separation process), or by blowing it in through a porous blanket (Callow process), and with or without the use of oil. The explanation offered in this paper is for this type of process especially, although the simple flotation-principles involved in such processes as the Macquisten, the Wood, and the bulk-oil process, are included. In all these processes the material floated must not be wholly wet by the water or solution in the presence of this gas or the material surrounding this gas, for example, an oil-film on the bubble-surface. If the material is completely wet by the water, it will not float, which is the case of the ideal gangue, while the material floated must go to the interface water-air bubble or entirely into the phase other than water, that is, the oil on the air-bubble.

The relations of the forces acting to produce this result were first

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*Jour. Ind. & Eng. Chem., May 1917.

[1] See especially the following: W. D. Bancroft, *Jour. Phys. Chem.*, 19 (1915), 275; Ralston, M. & S. P., Oct. 23, 1915; Callow, Bull. A. I. M. E., Dec. 1915, 2321; Anderson, *Ibid.*, July 1916, 1119; and Taggert and Beach, *Ibid.*, Aug. 1916, 1373. For a very complete bibliography, see School of Mines & Metallurgy, Univ. of Missouri, Bull. 8, No. 1, 1916; also Bull. A. I. M. E., 1916, 1131.

stated by Freundlich[2], and enlarged upon by Hoffman[3] and Reinders.[4] They were first stated for the behavior of a sol, which will be called disperse phase 3 in liquid 1, when shaken with an immiscible liquid 2. Let

$T_{1\ 3}$ = interfacial tension between phase 3 and liquid 1.
$T_{2\ 3}$ = interfacial tension between phase 3 and liquid 2.
$T_{1\ 2}$ = interfacial tension between the two liquids.
If $T_{2\ 3} > T_{1\ 3} + T_{1\ 2}$ the sol will remain unchanged;
If $T_{1\ 3} > T_{2\ 3} + T_{1\ 2}$ the disperse phase 3 will go entirely into liquid 2;
If $T_{1\ 2} > T_{2\ 3} + T_{1\ 3}$ the disperse phase will collect at the liquid-liquid interface and will, if possible, separate the two liquids from each other.

If, however, no one interfacial tension is greater than the sum of the other two, then the disperse phase will collect at the liquid-liquid interface, but the three phases will meet at a certain contact-angle. The application of these principles to flotation may now be stated, for while the greater part of the material floated is much less disperse than that which is considered colloidal, the interfacial tendencies are the same, it simply being a question whether the forces holding the mineral to the interface are sufficient to overcome gravity, if the particle is to float.

Methods of flotation without resort to the use of oil are exemplified in the well-known Potter-Delprat process, in which CO_2 is generated in the acid pulp, but may be carried out successfully on some ores in a Callow cell, using air. Here, if flotation is to result, the mineral must go to the interface water-gas and be carried at this interface to the top of the pulp. The word water will be used mostly to denote the aqueous phase, whether it is pure water or a solution, and the floatable material will be called sulphide, since this is the common case. On the basis of interfacial tensions, where if

$T_{s\ a}$ = interfacial tension sulphide-air (or CO_2),
$T_{s\ w}$ = interfacial tension sulphide-water,
$T_{w\ a}$ = surface-tension water-air (or CO_2),

either (1) $T_{s\ w} > T_{s\ a} + T_{w\ a}$ or (2) no one interfacial tension is greater than the sum of the other two, must be true. It is obviously impossible to have $T_{w\ a} > T_{s\ a} + T_{s\ w}$ as the latter two are very large in comparison with the first, according to theoretical reasoning and

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[2] 'Kapillarchemie,' 1909, 137, 174.
[3] *Zeit. phys. Chem.*, 83 (1913), 384.
[4] *Kolloid Zeit.*, 13 (1913), 235.

measurements.[5] Case 2 is the actual one, as can be seen if a drop of water is placed on a flat sulphide surface. Here the water does not spread over the entire surface, but comes to equilibrium with the three phases, sulphide, air, and water in contact at a certain angle. Case 1 would require that the water should not wet the sulphide at all in the presence of air. In flotation then the sulphide comes to the air-water interface and sticks through the bubble-surface to a certain extent, or is held in such a way that the three phases are in contact. The gangue material is completely wet by water and does not float, that is, $T_{g\ a} > T_{g\ w} + T_{w\ a}$.

Some measurements were made to get an idea of these interfacial tendencies, by a method explained in connection with Fig. 1. Here a flat-ground mineral-surface was placed vertically in water or other solution as shown. By raising and lowering the mineral, a quite constant result was obtained for the rise of the meniscus against the mineral above the general level. Here the meniscus was always upward, showing a greater preference of the mineral for water than for air. In the case of the sulphides, when they were raised, the meniscus would soon draw back to a definite height, leaving the sulphide surface above quite dry. For gangue the water does not draw back quickly, but remains, wetting it for some time. The sulphides are proved interfacial in this way, and the measurements of the height of the point of contact above the general level are interesting. The measurements were made with a cathetometer.

Material	Water, mm.	0.1% H_2SO_4 mm.	0.1% NaOH, mm.
Chalcocite	1.55	2.10	3.07
Chalcopyrite	2.60	2.50	2.90
Gangue (silicate)	3.20	3.25	3.30

The figures for the gangue are not at the point of contact, for there is none, since it is thoroughly wet by water, but are at the point where the meniscus becomes parallel to the face of the mineral surface. The mineral giving the smallest rise should be the most interfacial and the best floating. This was found to be true, for, without oil, chalcocite is a better floating mineral than chalcopyrite, at least for the ores that were tested. The figures above also show that in alkaline solution a very poor float should be made, as the rise is almost as much as for the gangue. This was also found to be true. Differences even among sulphides are clearly shown, hence it is not surprising to find all gradations in floating properties among ores. These measurements, made

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[5] Hulett, *Zeit. phys. Chem.*, 37 (1901), 385. Also the surface-tensions of molten metals and fused salts are high.

on large pieces of mineral, with ground and partly polished surfaces, may not correspond exactly to those for an ore-surface, though in the cases mentioned they were found to give results agreeing with practice.

Another point noticed in these measurements, which is an important one, is how quickly the water is displaced from a mineral-surface when brought in contact with air. If an air-bubble comes in contact with a sulphide particle immersed in water, it must partly displace the water from the sulphide rather quickly if it is to be floated in a pneumatic cell. This was tested for the same minerals, by noting the time taken for the solution to come back to the final point of contact, when the mineral was raised, with the following general results:

(1) Water and acid solutions are removed more quickly in air from chalcocite than from chalcopyrite.

(2) Little difference is noted between acid and neutral solutions.

(3) Alkaline solutions are removed very slowly from all sources.

(4) All solutions adhere strongly to gangue.

These facts also agree with the practical results mentioned above. The success of the Potter-Delprat process may well be due to these facts, since the CO_2 is generated in contact with the sulphide, and time is given for the solution to be partly displaced by the gas or, in other words, for the sulphide to attain the interfacial condition and be floated. When a soluble frothing agent is used, without oil, the same principles apply, the frothing agent simply modifying the water to a certain extent.

The use of oil introduces several new factors which make the problem more complex, but the same principles apply. The sulphides can now be interfacial between water and air as discussed above, but, in addition, may be interfacial between water and oil, or even go into the oil-layer. This oil-layer is on the bubble-surface and the forces holding the sulphides to this surface, if it has an oil-film, are much greater than when no oil is used. This point will be proved a little further on. The oil-layer on the bubble-surface need be only of minimum thickness to act, in contact with water, the same as a layer of oil on water, as far as interfacial tendencies are concerned. Let

$T_{s\ w}$ = interfacial tension sulphide-water,
$T_{s\ o}$ = interfacial tension sulphide-oil,
$T_{o\ w}$ = interfacial tension oil-water.

Then, if (1) $T_{s\ w} > T_{s\ o} + T_{o\ w}$, the sulphide will go into the oil-layer completely; (2) no one interfacial tension is greater than the sum of the other two, the sulphide will go to the oil-water interface, and the three phases will be in contact at a certain contact-angle. The gangue is thoroughly wetted by water, that is, $T_{g\,o} > T_{g\,w} + T_{o\,w}$.

These inequalities have been stated and applied to the flotation process by Ralston.[6]. The second condition given above, where the sulphides are interfacial, seems to be by far the most general, though the first condition may be, and probably is, realized, especially when tarry oils are used, which, in grinding with the ore, coat the sulphides more or less with this tarry material. It is doubtful if the lighter oils or the lighter constituents of a tarry-oil mixture film the sulphide at all in grinding, but rather it is probable that this oil is emulsified in the operation. The condition where the mineral is completely filmed by oil would be the best floating condition, and this could be realized in the flotation cell, where this film would be continuous with the oil-film on the bubble-surface. All gradations of the interfacial conditions are possible, from those that show only a slight tendency to be wet by water in the presence of oil, to those that are thoroughly wet, which is the case of the gangue-material.

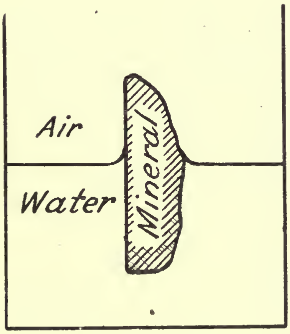

Fig.1.

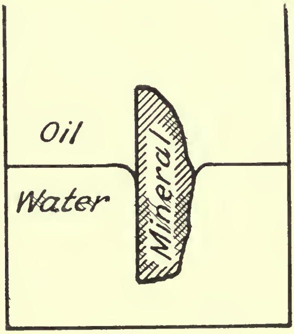

Fig.2.

Experimental determinations of the interfacial tendencies of various minerals were carried out in the same way as described above, except that in this case the interface was oil-water, or aqueous solution. In Fig. 2 is represented the case of a sulphide surface at this interface. The floatable materials were all interfacial, and the sulphides showed a decided preference for the oil. This is an important point in showing that the same sulphides are much more strongly held to an oil-covered air-bubble than to one not so covered. In Fig. 1 the sulphide, while interfacial, shows a preference for water over air, and would easily be displaced in actual flotation from the interface and go

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[6] M. & S. P., Oct. 23, 1915.

back into the water. In Fig. 2 the meniscus is now pushed downward into the water, instead of upward, hence the sulphide is held much more strongly to oil than to air.

The following measurements were made after the meniscus had come to the true point of contact of the three phases, and this point was closely the same, whether the mineral was first wet with the oil or solution. The averages of these two figures are given. Kerosene and a kerosene pine-oil mixture were used mostly, as the interfaces are better defined, especially in acid and alkaline solution, than with many actual flotation oils. These other oils act in the same way, however.

DEPRESSION OF MENISCUS: KEROSENE AND CHALCOPYRITE

Water	0.1% H_2SO_4	1% H_2SO_4	10% H_2SO_4
2.99 mm.	2.02 mm.	1.32 mm.	0.75 mm.

Calcite in contact with neutral, acid, and alkaline solutions and kerosene showed interfacial tendencies in alkaline solution only. Malachite exhibited a small interfacial tendency, except in alkaline solution in which it was thoroughly wet by the solution.

KEROSENE AND PINE-OIL AND AQUEOUS SOLUTION

This was a flotation mixture of 90% kerosene and 10% pine-oil.

	Depression of meniscus	
	Chalcopyrite, mm.	Chalcocite, mm.
Water	3.10	3.42
0.1% NaOH	1.98	2.54
0.1% H_2SO_4	1.45	2.95

Gangue-material in all cases is thoroughly wet by the solution, especially if it is wet by the solution before coming in contact with the oil, as is the case in actual flotation. The case of chalcocite in water, given above, is almost a condition of complete wetting by oil. These experimental results in every way justify the theoretical discussion given, and also show that alkali and acid lower the interfacial tension sulphide-water as the preference for oil is not as great in these solutions as in water, although the sulphide is still distinctly interfacial and hence can be easily floated from acid or alkaline pulps. These results were obtained by the use of a clean sulphide-surface, but in actual flotation this may not be true for all the particles, and since the interfacial properties are a function of the surface only, one may expect many differences from these ideal measurements. In alkaline solution, for example, there may be some of the mineral which, like calcite, is more interfacial in this solution than in water, and hence would float, although it would not do so in a neutral pulp. In tests it has been found with some ores and oil-mixtures that in an alkaline pulp a better recovery was made in the usual length of time than by prolonged flotation in neutral pulp. This might be true also in an acid pulp for some minerals.

It has been noticed that some surfaces have a strong tendency to hold fast to the liquid first wetting them and not to allow it to be easily displaced by another liquid. In the work upon interfacial tension, described above, such a surface would show a great difference in preferential action or angle of contact, dependent upon whether it was wet with oil or water first. It has also been observed that it is principally those substances having smooth or shiny surfaces which float, while those having dull or rough surfaces do not float. These observations and others point to the following explanation of the mechanism of this action: there is first the inherent property of each substance to adhere to oil or to water to a certain degree. When the substance is brought to the interface between water and oil, these forces tend to come to equilibrium with the third force, the interfacial tension between oil and water, at some definite contact-angle. Here is where the physical nature of the solid surface comes into play. If the surface is smooth and shiny, such as that of a polished metal or a freshly fractured sulphide crystal, then the liquid first touching it is easily pushed back to the position of equilibrium. If, however, the substance has a dull, that is, a capillary surface, so that the liquid first wetting it is strongly held in its pores, then, when it is brought to the interface it may exhibit no interfacial properties at all, although, if it were smooth, it might even show a preference for the other liquid. This shows the reason for the difference, or hysteresis, of the contact-angle noted for some surfaces. It also explains why a particle having such a surface, if first wet with water, as is the case in flotation, will be very difficult to float, since it will not easily be brought into contact with oil.

The function of the bubble is to give a large surface to which the sulphide may go and be floated. As already stated, the air-bubble in oil-flotation is covered wholly or in part by an oil-film. For the action of oil on water, see Devaux[7] and Langmuir.[8] It is not necessary that the oil completely cover the bubble, and it probably does not in the greater proportion of the bubbles. The supply of oil for the bubbles will

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[7] Ann. Report Smithsonian Inst., 1913, 261.

[8] *Met. & Chem. Eng.*, 15 (1916), 469.

be discussed under the action of emulsions. If an oil droplet be placed on water or aqueous solution, it will spread over the surface provided the surface-tension of the water is greater than the sum of the surface-tension of the oil plus the interfacial tension oil-water, that is, this inequality must be true:

$$T_{w\ a} > T_{o\ a} + T_{o\ w}$$

For oil-flotation this must be true for all solutions used, as the air in the bubble, surrounded by the pulp, presents this same condition. If to water be added some material which lowers its surface-tension ($T_{w\ a}$), without lowering $T_{w\ a} + T_{o\ a}$ to an equal amount, the inequality is reduced, and finally a point is reached where the oil will not spread on the solution. This is easily realized in the case of soap-solutions, and with many other substances that lower the surface-tension greatly. In this condition a poor float would result. In flotation, in order to produce a froth, material such as the soluble portion of pine-oil is added which lowers the surface-tension of water. Unless this helps in other ways than in producing a froth, it should be used in as small a quantity as possible, and this agrees with many practical observations. The frothing agent added also lowers the interfacial tension oil-water, but here it must be remembered that even if the interfacial tension be lowered in the same proportion as the surface-tension, the inequality is less than before, since the interfacial tension is much smaller than the surface-tension of water. The other factor, the surface-tension of oil ($T_{o\ a}$), is not changed much, for inorganic salts do not dissolve in it. If, however, some substance be added which will not lower the surface-tension of water but will lower the interfacial tension oil-water, then this should produce better oiling of the bubble. This can be done with alkalies and in the case of some oils by acids.

An important point in connection with the use of the pneumatic cell is the time during which the bubble is in contact with the pulp as it passes through, as here it must be attached to the sulphide particles. Any reagent that will give a quicker filming of the bubble-surface by oil, after it comes through the blanket, will be of benefit in the rapidity with which the mineral is attached and raised. Alkalies, as explained, produce a greater inequality between $T_{w\ a}$ and $T_{w\ o} + T_{o\ a}$, and hence the oil will be spread out quicker over the surface than without their use. A large number of surface and interfacial tension measurements were made, a few of which are as follows:

SURFACE TENSION

	Dynes per cm.
Water 25° C	71.8
Kerosene	25.2

	Dynes per cm.
Coke-oven oil	28.0
Pine-oil	30.0
0.1% solution terpineol	68.6
0.1% solution terpenol	49.2
INTERFACIAL TENSIONS	
Kerosene-water	32.8
Kerosene and pine oil-water	11.6
Kerosene and pine oil-0.05% solution NaOH	7.3
Kerosene and pine oil-0.2% solution NaOH	4.5
Kerosene and pine oil-0.2% solution H_2SO_4	13.2
Coke-oven oil-water	14.1
Coke-oven oil-0.05% solution NaOH	5.8
Coke-oven oil-0.2% solution NaOH	2.6
Coke-oven oil-0.1% solution Na_2CO_3	6.6
Coke-oven oil-0.2% solution Na_2CO_3	4.4
Coke-oven oil-0.2% solution $Na_2B_4O_7$.10 Aq	8.0
Coke-oven oil-0.1% solution $Na_4P_2O_7$.10 Aq	9.6
Coke-oven oil-0.2 solution $Na_4P_2O_7$.10 Aq	7.4
Coke-oven oil-0.4% solution H_2SO_4	14.4
Coke-oven oil-0.01% solution saponine	9.3
Coke oven oil-0.01 solution tannic acid	12.7
Coke-oven oil-0.01% solution hemoglobin	8.9

Numerous data of this kind are given by Lewis[9] and Shorter and Ellingsworth[10] on the action of dyes, salts, and soap. The drop-number apparatus used was the same as described by Shorter and Ellingsworth. Their work also shows that soap and alkali together are extremely active in lowering the interfacial tension oil-water. This would be the condition in an alkaline pulp, as there would then be free alkali and some saponified material with many of the oils used.

The results when colloidal material is present are subject to great variation, due to different speeds of formation of drops. The figures given above for these materials approach the dynamic value, as the rate of dropping was fairly rapid. The static values are much smaller, and are interesting in connection with the emulsifying power of these substances. As an example of this the following result on coke-oven oil against 0.005% hemoglobin solution is given. The time is for the total number of drops formed.

Time	Drop No.	Interfacial tension, dynes per cm.
2 min. 40 sec.	22.5	13.2
1 hr. 4 min.	84.0	3.5

It is seen from the table above, that besides NaOH itself, any salt that hydrolyzes to give an alkaline solution lowers the interfacial tension, and all these salts are beneficial to flotation.

The behavior of the oil at the bubble and sulphide surfaces has been

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[9] *Zeit. phys. Chem.*, 74 (1910), 619.

[10] *Proc. Roy. Soc.*, 92 (1916), 231.

given. In the pneumatic cell this oil is supplied by an emulsion or a coarser suspension of oil in water. In the agitator-type machine, the oil may be beaten in at the cell, though it is also customary to grind the oil with the ore. In either case the problem of emulsions comes in. In the pneumatic process this emulsion is formed in the grinding and must be good enough to last throughout the float, yet not so good as to fail to break down with sufficient rapidity to give free oil for the bubble-surface. The subdivision of the oil is such that no doubt almost all degrees of dispersion exist; the larger droplets may be of sufficient size for one to coat a fair area of a bubble-surface, but the better emulsified proportion is of such size that many particles have to unite to give oil enough for the minimum thickness of an oil-film, to spread over even a square centimetre. This can be calculated from the minimum thickness of an oil-film[11] and the size of the particles in an ordinary oil-emulsion.[12]

Experimental evidence on these points is conclusive. If a coarse suspension of oil be made simply by shaking the ore, oil, and water together in a bottle by hand, and then put in a small Callow cell, only a partial float results, and the operation must be repeated several times, adding more oil each time, in order to get a good recovery. If, however, too good an emulsion is had, a poor recovery results. For this purpose a kerosene pine-oil mixture was emulsified with water in a De Laval emulser and allowed to stand over night, and a middle portion of this emulsion was removed for the tests. This emulsion added at the cell gave a small float at first and then stopped. On adding a little acid no further float resulted, but, by allowing the pulp to stand for a few minutes, an additional amount of sulphide was raised, and finally a good recovery was made, though considerable time had to be given for the emulsion to give up its oil. This was also found to be true for another oil that gave an excellent emulsion on simply adding it to water.

It is interesting to note that in these cases it was proved that it was not necessary to grind the oil with the ore, but, by adding it as an emulsion prepared by itself, as good a recovery results. This probably is not true for oils containing tarry matter as explained above. It was also noticed in using the second emulsion, named above, that flocculation of the slime took place in neutral solution, and that these then floated to a large extent, giving a non-preferential float; when, on the other hand, the emulsion was broken by acid and alum, a good prefer-

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[11] Devaux, *Loc. cit.*

[12] Ellis, *Zeit. phys. Chem.*, 80 (1912), 597.

ential float resulted. It was found that this slime in neutral pulp had flocculated with the oil-emulsion so that, on standing, all the oil was carried down, though the emulsion was not appreciably broken.

The value of acid and salts having a polyvalent cation has been demonstrated in some cases, usually in connection with the Minerals Separation type process. In this process there is greater danger of getting too good an emulsion than in the Callow process, and the value of acids and salts of this type consists in their power of breaking down an emulsion, or preventing too good a one being formed. These salts should be used in acid solution, or, otherwise, due to hydrolysis, the insoluble hydroxides formed, for example, $Fe(OH)_3$, and $Al(OH)_3$ have the opposite effect, namely, of preventing the breaking down of the emulsion or promoting its formation.[13] Oil-emulsions in $FeCl_3$ solution, on standing, give a yellow flocculent precipitate, but the emulsion is not broken. The mechanism of this is discussed by Ellis.[14] In a neutral, pneumatic, Callow float, such salts have been found to be harmful. If salts of iron or aluminum are present in the feed-water then acid may be necessary to prevent this action between them and the oil-emulsions.

The value of alkalies has been discussed as giving a better oiling of the bubble-surface. In connection with emulsions, however, a greater effect can be ascribed to the action of alkalies or salts which hydrolyze to give an alkaline reaction, and to those which have a polyvalent anion. If a neutral ore-pulp is shaken with a small quantity of an oil-emulsion it is found that the slime is coagulated with the emulsion and settles out, often leaving the liquid quite free from oil-emulsion. The emulsion is not broken, but simply carried down with the flocculated slime. If alkalies are used, or salts such as last mentioned, then the slime is deflocculated in the great majority of cases. It then settles more slowly, and when it has settled the emulsion is left free and still standing. This is important, for now the emulsion is free to function as it should, that is, to give oil to the bubble-surface. The ore-particles, both sulphide and gangue, are also free to show their own behavior toward the water and the oil. This deflocculation should, and does, result in a higher grade concentrate and a greater and quicker recovery, since now no sulphide-particles are coagulated with, or surrounded by, gangue-particles that prevent their flotation.

The use of lime has not been found to be as beneficial as that of NaOH. This is explained by the fact that this substance, owing to the

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[13] Briggs and Schmidt, *Jour. Phys. Chem.*, 19 (1915), 478.
[14] *Zeit. phys. Chem.*, 89 (1914), 149.

predominating effect of the calcium ion, coagulates instead of deflocculating the slime, and hence part of the emulsion is removed and the individual particles are not free to float as they should. This coagulating action may be more noticeable in a Callow cell than in a cell of the Minerals Separation type, as in the latter the coagulated slime may be broken up considerably, but the tendency is the same in either case.

The principles involved when varying quantities of oil are used, is a question on which there is great difference of opinion. From theory there should be no difference whether a large or small amount of oil be used, provided the oil is properly emulsified. If a large amount, 2% or 3%, be used, and is not emulsified sufficiently, the excess may float and be of disadvantage in several ways. To test this point a float was made with an amount of oil equivalent to 2% of the weight of the ore, emulsified in a De Laval emulser, and added at the cell (Callow), and a float made. It behaved in every way the same as when 0.2% or less of oil was used, and the recovery was better, with as high a grade of concentrate. Of course, economy would settle the minimum amount of oil to use. This was repeated with other oils and ores. The extra amount of oil used gave a greater oiling of the bubble-surface, and in fact these floats were better than when alkali was used to make the smaller amount of oil more efficient.

In the light of the above work the question of flotation 'poisons' was taken up with the idea that any substance which will prevent the breaking down of an emulsion or coalescence of oil droplets, or which gives adsorption of colloidal particles at the oil-water interface, is harmful to flotation. In the first two cases the proper amount of oil will not be freed, and in the other case the oil-surface, if formed, would be covered by an adsorbed layer, so that no oil-surface would be presented for attachment of the mineral. Experimental work, by actual flotation, had shown what substances, including many dyes, were harmful. Solutions of these substances of 0.01% strength were shaken in test-tubes, with about 2 c.c. of oil, for a few minutes, to the same extent and at the same time. The tubes were then placed upright and the amount of emulsification and the rapidity of coalescence of the oil droplets rising to the top noted, with the following results:

(1) Slight or no emulsification and rapid coalescence of droplets when using methylene blue, saffranine, and bismarck-brown. These dull dyes really act like salts, and are not colloidal, nor are they harmful to flotation. In fact, these dyes assist slightly in breaking an emulsion.

(2) Extremely slow coalescence of droplets, the finely divided oil

layer lasting for several hours to days, when using congo-red, bengoazurin, azo-blue, saponine, tannic acid, waste sulphate liquor, hemoglobin, and eosin. These substances are all injurious to flotation. Most of these are negative colloids. Hemoglobin is highly colloidal, and positive, and its adsorption is probably enhanced because it is oppositely charged to the oil-emulsion. Several of this last class of substances, especially saponine, gave marked emulsification, even with the small amount of shaking received. Some of these substances also form quite stable and viscous skins at oil-surfaces. Another experiment consisted in dividing an oil-emulsion into two parts, to one of which tannic acid was added, and then frothing over equal volumes of each in a small cell. The one to which tannic acid had been added contained 3.5 times as much oil in the residue or tail-water as the other. This shows that the oil-emulsion had been kept from breaking down, and the oil being frothed over. Besides the substances given above, the injurious effect of insoluble hydroxides of the heavy metals has been explained under emulsions. Other inorganic colloids have been found to be injurious, for example, when floating with $K_4Fe(CN)_6$, the $Cu_2Fe(CN)_6$ formed from the oxidized and soluble copper hurts the float very noticeably. The experimental evidence proves that the action of these colloids is, without doubt, as stated, though they may also adsorb at the solid surfaces, and in that way cause a poorer result to be obtained. It is easily seen how the water used in flotation and the slime coming from certain ores have a great effect in flotation. This has caused some to say that it is the gangue that determines the success of the process, and if the water-supply be included in this, they are to a certain extent correct.

The froths produced in flotation are useful as a mechanical means of removing the mineral brought up by the bubble. The formation of a froth, and its stability, are due principally to dissolved materials in the water which give to the solution a variable surface-tension. The static surface of a solution has a lower tension than a fresh surface, whether the substance added lowers or raises the surface-tension of the solvent. Since a large lowering may be caused by a small amount of solute and only a small rise may be obtained, the best frothing agents are those that lower the surface-tension. Pine-oil is used to a large extent for this purpose in practice, the soluble portion causing a considerable lowering of the surface-tension of water. In many articles that have appeared on the theory of flotation, it has been stated that oils lower the surface-tension of water. This is not very clearly stated, since, as ordinarily understood, oil is insoluble in water, and only soluble material can affect the surface-tension of water. Besides the soluble portion of pine-oil, a part of many other flotation oil-mixtures is soluble and gives a froth. Terpineol, menthol, and many such substances are powerful frothing agents. The lasting qualities of a froth, as stated above, are due to its variable surface-tension, for if a bubble starts to thin out or to break at a certain point this fresh surface has a greater surface-tension than before, hence is automatically strengthened at this point and resists rupture. In using alkalies it is observed that a more quickly breaking froth results in a pneumatic cell. This can be explained by the fact, as stated before, that a greater extent of bubble-surface is covered with oil, hence there is less surface which contains only the adsorbed frothing agent, and since oils themselves do not produce good froths, the froth breaks more quickly than when alkalies are not used; or, this observation may be used to support the view that the bubbles are better oiled in an alkaline pulp. A froth is also stabilized by the slime present in a pulp, or by other colloidal matter. Colloidal material dissolved in the oils will make an oil-froth more lasting. A mixture of oils, the same as an aqueous solution, gives a better froth than a pure oil.

Considerable weight has been placed by many upon the electrostatic forces that might be present in the flotation process. Some have even considered the attraction that holds the sulphide to the bubble-surface to be of this origin. Air bubbled through water has been found to carry ions,[15] and from this, and the fact that most substances have a contact-difference of potential when in contact with water or solutions, an electrical theory has been built up, though in many cases serious errors have been made regarding the action of these forces. Measurements were made to determine these forces. The small metal Callow cell used was grounded, as this condition prevails in actual practice. The charge carried by the air issuing from the flotation pulp was discharged on a metal screen placed above the cell, and the effect measured by means of a Dolezalek electrometer. The readings in this case are measured in volts per minute. The charge upon the air from several pulps was measured and in no case did it exceed 0.011 v. per minute, and was usually only about half that value. The air was negative in neutral pulps, but slightly positive in one of the alkaline pulps. The charge on the froth was also measured, and this varied from zero to 0.011 v. as the maximum. This was sometimes positive, and under other conditions negative. In two good floating pulps the froth was at

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[15] Lord Kelvin, McLean, and Galt, Proc. Roy. Soc., 1894, 57; Coehn and Mozer, *Ann. Physik*, 43 (1914), 1048.

almost zero potential, though 0.002 v. could easily be determined. It seems, then, that these electro-static effects are far too small to exert any important part in flotation, and cannot possibly be the force that holds the sulphide to the bubble. This, too, would require a dielectric film, such as oil, between the two oppositely charged bodies, the sulphide and the gaseous ions in the bubble; but since flotation results without the use of oil in many cases, and, without doubt, the bubble-surfaces are often not completely covered by oil even when oil is used, it seems that this theory cannot hold. The contact difference of potential of various minerals has been used in some theories. These were also measured by an electro-endosmose method as described by Perrin.[16] To this apparatus a small calibrated tube was sealed at the top of the diaphragm side, so that when dilute electrolytes are used the gas generated can be forced over into this tube, after the experiment is over, and this correction applied to the amount of liquid apparently transferred through the powdered material. The distance between the electrodes was 12 cm. and the potential 110 v. The results obtained give the sign of the charge on the solid in contact with the water or solution, but quantitative results as to the actual potential differences are difficult to obtain in this way. However, some idea can be had by comparing the amount of liquid transferred for the minerals, to that transferred in the case of silica, whose potential difference against water has been found by cataphoresis measurements. This is found to be approximately −0.042 v. For quartz and ferric hydroxide, see Whitney and Blake.[17] The results obtained are as follows:

Mineral	Liquid	Sign of solid	Liquid transferred, cu. mm. per min.
Silica	Water	Negative	30.7
Alumina	*N*/100 HCl	Positive	40.0
Chalcopyrite	Water	?	Approx. 0
Galena	Water	Negative	3.6
Sphalerite	Water	Negative	6.1
Molybdenite	Water	Negative	3.7
Malachite	Water	Positive	4.0
Malachite	*N*/100 HCl	Positive	17.8
Galena	F. W./500 $FeCl_3$	Positive	44.3

Here the sulphides tested are seen to be slightly negative against water, or practically zero in the case of chalcopyrite. This agrees with our ideas concerning the contact-difference of potential of these substances and with cataphoresis experiments on colloidal sulphides, and

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[16] *Jour. Chem. Phys.*, 2 (1904), 601.
[17] *Jour. Am. Chem. Soc.*, 26 (1914), 1339.

the like. Malachite is positive, as would be expected from its basic character. The last result given in the table is probably due to the formation, by hydrolysis, of ferric hydroxide, and its adsorption on the surface of the mineral, so that the action is exactly the same as for ferric hydroxide itself. In this case again, no attraction can exist on the basis of electrical charges between sulphides and oil in emulsions, since they are of the same sign. The charges on oil in emulsions in dilute salt-solutions, etc., are given by Ellis,[18] Powis,[19] and others. This, however, would not determine the charges on a mineral and oil, if the two were in actual contact, as is necessary for flotation. The charges carried by the oil in emulsions are important probably in connection with positively charged colloids which act as poisons, and, of course, the coagulation of slime, and the breaking of an emulsion by electrolytes, is a function of the charge carried by them; but it is not possible to use these charges as an explanation of the primary principles involved in flotation.

The following is a summary of the conclusions arrived at as a result of the experiments made:

(1) For an ore particle to float, it must be interfacial between oil and water, or it must go completely into the oil-phase. If no oil be used, the particle must be interfacial between water and air. The force holding the particle to the bubble is much greater when oil is used.

(2) In addition to its value as a lifting agent, the bubble serves to produce a large air-surface in contact with the pulp. This surface is covered to a greater or less extent by an oil-film, to which the mineral may go, so that a small amount of oil is very efficient.

(3) The oil should not be so well emulsified that it will not be given up to the bubble-surface; and yet should be sufficiently emulsified, in a pneumatic process, to last during the time of floating.

(4) Colloids in general are harmful, owing either to their causing too stable an emulsion, or to their adsorption on the oil-film at the bubble-surface, preventing mineral attachment. This is the action of the so-called 'flotation poisons.'

(5) The froth formed is attributable either to the soluble portion of the flotation mixture, which produces a variable surface-tension, or to finely divided or colloidal materials.

(6) Acids, alkalies, and salts affect all these factors.

(7) The electrical effects, other than the colloidal charges, are not important in flotation.

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[18] *Zeit. phys. Chem.*, 78 (1911), 325.
[19] *Ibid.*, 89 (1914), 91.

(8) The nature of the solid-surface, in relation to its wetting properties, has been discussed and an explanation of the 'hysteresis' of the contact-angle advanced.

In the light of present knowledge it is impossible to measure many of the forces operative in flotation, such, for example, as the interfacial tensions between solids and liquids, or to explain the mechanism of adhesion. Such problems are, however, nearer solution, due to the material advances made recently by Laue[20], and by Bragg and Bragg,[21] by which the actual arrangement of the atoms in a crystal may be determined, and also by Langmuir,[22] whose work on the constitution of solids and liquids, the structure of solid-surfaces, and the mechanism of adsorption, leads toward an understanding of these obscure phenomena.

THE RECOVERY that it is possible to effect in a flotation plant depends largely on the grade of concentrate desired. With a low grade of concentrate, a low tailing can be made, but when a high grade of concentrate is stipulated, increased tailing-losses cannot be avoided. A question that suggests itself in this connection, and which we have tried to answer by laboratory experiments is, "How can we raise the grade of our concentrate—that is, reduce the percentage of insoluble matter contained—without entailing additional copper losses?" We know from laboratory experiments that this can be done by expensive methods—for instance, by heating the solutions—but such a procedure would be undesirable from an economical standpoint. Experience has shown us that concentrate produced in the first compartments of the cleaner-cells is always freer from insoluble matter than the concentrate produced in the last compartments. The problem then resolves itself into finding a suitable cleaning process for the concentrate from the last compartments of the cleaning-cells. By treating this low-grade concentrate hot, with the addition of caustic soda, we have been able to separate it into a high-grade concentrate and a fairly low tailing. This method necessitates only the expense of heating a small fraction of the pulp and may be a commercial possibility.—Rudolf Gahl, Trans. A. I. M. E.

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[20] *Sitz. Akad. Wiss.*, Wein, June 1912.

[21] *Proc. Camb. Phil. Soc.*, 17 (1912), 43; and treatise on 'X-Rays and Crystal Structure.'

[22] *Jour. Am. Chem. Soc.*, 38 (1916), 2221.

FLOTATION AT THE CALAVERAS COPPER—A SIMPLE FLOW-SHEET

By Hallett R. Robbins

(From the *Mining and Scientific Press* of November 25, 1916)

Introduction. The Union mine is situated in the foot-hills of the Sierra Nevada in the extreme southern part of Calaveras county, California. The town of Copperopolis, with a present population of about 600, has grown up around the mine, and is reached by road from Angels Camp, 12 miles; Stockton, 42 miles; or Milton, 17 miles. The mail is carried by automobile-stage daily except Sunday over the last route, and there is also regular auto-stage service from Stockton. Surveys have just been completed, and construction is about to be started, on an extension of the Southern Pacific railroad from Milton to Copperopolis.

This is one of the oldest and most interesting metal mines in California. It was discovered by placer miners in 1859, and soon afterward one portion of the lode was acquired by Frederick Ames of Boston, and another, called the Keystone mine, by Oliver Ames. The Union Copper Mining Co., organized by the former, subsequently absorbed the Keystone property, as well as several smaller holdings on other portions of the lode. Operations were conducted by the Union Copper Mining Co. on a large scale. During each of the years 1865 and 1866 about 23,000 tons of ore, averaging over 20% copper, was shipped to Swansea, by wagon to Stockton, by river-boat to San Francisco bay, and finally by sailing-vessel around the Horn. A stone blast-furnace was erected and operated on second-class ore averaging 10% copper, using charcoal as fuel. The matte was shipped to Swansea. No statistics are available as to the tonnage treated in this smelter.

The fall in the price of copper following the Civil War, as well as the high cost of transportation, caused the mine to be closed-down in 1867, in which condition it remained until 1887, when there was a renewal of activity at the property, culminating in the erection, in 1891, of another blast-furnace smelting-plant, which ran about two years, and produced 150,000 tons of slag.

Operations were again suspended in 1893, the mine remaining idle until 1905, when a gravity-concentration mill and a third smelter were built. The mill did not run longer than a week or two at this period, but the smelter ran about two years on first-class ore. Heap-roasting was practised, the calcine being smelted in a 50 by 7 ft. reverberatory furnace, producing a 50% matte, which was shipped to a refinery at Chicago.

The panic of 1907 caused another suspension of operations, lasting until 1909, when the Calaveras Copper Co. was organized and took over the property on a bond. The smelter was re-built, and two 20-ft. six-hearth McDougall roasters were erected. The plant proved unworkable after two weeks' trial, and then a 40 by 120-in. blast-furnace was built, but it ran for two weeks only. Converting equipment was purchased and delivered, but never installed. The mill was operated intermittently at this time, but did not make over a 50% saving.

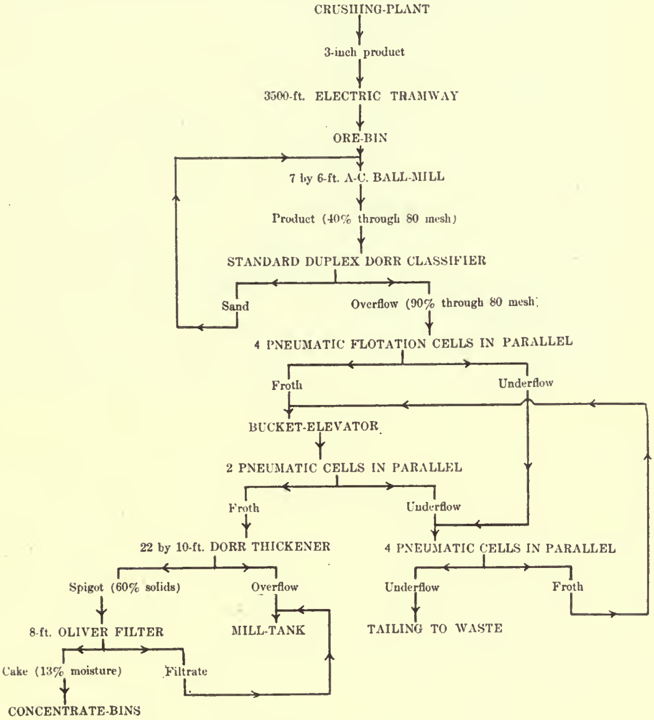

FIG. 1. FLOW-SHEET OF CALAVERAS COPPER MILL

In September 1914 a capable and efficient manager in the person of S. M. Levy, of Salt Lake City, was appointed, under whose guidance, with the assistance of E. C. Trask, mill foreman, D. C. Williams, mine foreman, and Frank W. Royer, consulting engineer, the property has been firmly placed on a paying basis, and has become one of great promise.

THE OREBODY is a replacement in amphibolite schist; it is from 100 to 200 ft. wide, with slate hanging wall and serpentine foot-wall. The valuable minerals are chalcopyrite, containing no gold or silver, and, near the surface, red and black oxides of copper. The lode is free from serious faulting, it strikes north-west, dips 61° north-east, has been fully developed for a length of 1500 ft. and to a depth of 800 ft., and is known to persist over a length of three-quarters of a mile. There is every indication of persistence in depth, as well as to a greater distance along the strike.

The most striking peculiarity of the ore is the association of a large amount of barren pyrite with the chalcopyrite. This is the explanation for the many failures to exploit the mine, for when gravity concentration was attempted, the pyrite was saved, while the chalcopyrite was largely slimed and lost.

THE MINE is opened by two working-shafts, the Union and the Discovery. The former is 800 ft. deep, vertical to the 5th level, and on an incline of 63°, following the lode, from there to the bottom. It was sunk in the 'sixties, and is equipped with a wooden head-frame, 35 ft. high, and with a double-drum hoist with both steam and electric drive.

The Discovery shaft is in the lode, on the hanging-wall side, and is now 400 ft. deep, measured along the 61° incline, but is being connected with the 9th level by raising. It is equipped with an excellent steel head-frame, 80 ft. high, erected in 1902 at a cost of $10,000, and good for four compartments, though the shaft now has but three; and with a steam-driven double-drum hoist, good for 1500 ft., and with a 1500-cu. ft. compressor driven by a 275-hp. motor.

The stopes are 15 to 30 ft. wide; the shrinkage method is followed, at a cost of 50 cents per ton. The total cost of mining, including timbering, hoisting, development, etc., with the present daily production of 200 tons, is $1.50 per ton. It is expected that this will be reduced to $1.25, as soon as the production is increased to 500 tons per day, which is the maximum output expected at present.

The force employed includes 2 shift-bosses at $4; 10 machine-miners at $3.50; 4 timber-men at $3.50; 4 timber-men's helpers at $3.25; and 22 shovelers at $2.75.

Ingersoll-Rand stopers are used for stoping and raising; jack-hammers for sinking and block-holing; and Denver Dreadnought water-drills in the drifts.

The mine is considerably wetter in winter than in summer. In the wet season, one 4½ by 7-in. triplex pump is operated 24 hours daily, raising all the water made by the mine, from the 8th level to the surface. In the summer it is run only six to seven hours per day.

FLOTATION. Experiments began in December 1914; in February 1915, the so-called 'little mill' was started on accumulated tailing from the old gravity-mill, containing about 1.5% copper. The equipment consisted of one Huntington mill, grinding through 50-mesh; a mechanical agitator; a pneumatic flotation-cell, making a final tailing and a rough concentrate; and a Wilfley table, making a final concentrate and a middling that was returned to the Huntington. In May 1915, the treatment of accumulated tailing was discontinued, the 'little mill' after that date handling 25 tons per day of undersize from the 1-in. trommel at the picking-plant. The oversize, after the first-class ore had been picked out, was treated in the 'big mill,' which was the old gravity-mill with some experimental flotation equipment, handling 60 tons per day, with much the same flow-sheet as in the little mill, so that further description is not necessary.

FIG. 2. AIR-PANS OF FLOTATION-CELL

The results of this operation indicated that from a mill-feed assaying 3% copper, 28% iron, 20% sulphur, 20% silica, and 10% alumina, there would be obtained a concentrate assaying about 19% copper, 30% iron, 35% sulphur, and 6% insoluble, with a ratio of concentration of 7:1, and a recovery of 90%.

These operations also indicated that the most efficient oil was

Yaryan steam pine-oil, and that mechanical agitation of the pulp before flotation was necessary for the best results.

The old gravity-mill, which was housed in a well-built and substantial steel-frame building, was then further re-modeled, and in March 1916 operations began according to the flow-sheet shown in Fig. 1. These operations have been remarkably successful.

Present Practice. The extreme simplicity of the plant, and the entire absence of any gravity concentration are very striking. The ball-mill has a normal capacity of about 8 to 9 tons per hour. The reduction in one mill from 3-in. to a product 90% of which passes 80-mesh would not be economical in a large plant, but in a small one the simplicity of the arrangement is commendable. The mill is driven through a counter-shaft, by a 150-hp. motor, at a speed of 23 r.p.m. The normal power consumption when running is 120 hp. Forged steel balls, 5 in. diam., are used, the consumption being 0.5 lb. per ton of ore ground. Of the total product 40% is finished through 80-mesh, the remainder being returned by the classifier. The mill has given reasonable satisfaction, the most serious difficulties being blinding of the difficultly-accessible grating, leakage around lining-bolt holes and dropping-out of lining-bolts, and a peculiar ailment, not as yet fully diagnosed, but probably due in part to the wear of the lining, that at times has caused the capacity of the mill to drop practically to zero. When the mill was opened on such occasions the ore and balls were found in quite separate masses. Increasing the speed from 21 r.p.m., as recommended by the makers, to 23 r.p.m. proved beneficial in minimizing this trouble.

Difficulty has also been encountered in the buckling of the lining-segments, which are the full length of the mill, thicker on one edge than on the other, in order to form steps to lift the balls and cause them to cascade properly through the charge of ore. They are held by three bolts in a line along the centre of each segment. The edges of the segments draw away from the shell, and the lining requires to be discarded and renewed when only about half the metal has been worn away. Similar troubles have been reported at other plants, and it is my belief that they may be overcome by the use of lining in full annular sections, wedged in place, with no bolt-holes whatever through the shell. Such sections may be secured from the Lehigh Car Wheel & Axle Co., and are being tried by the Utah Copper company.

The oil adopted as standard in the present operation, after exhaustive experiments, is the No. 400 crude wood-creosote produced by the Pensacola Tar & Turpentine Co. The No. 350 crude pine-oil produced by the same company was recently tried on a 24-hours run, with a marked increase in the value of the tailing, and a decrease in the grade of the concentrate. A mixture of equal parts of No. 17 hardwood-creosote, and No. 20 coal-tar creosote, furnished by the General Naval Stores Co., has given the best results of any oil other than that regularly used.

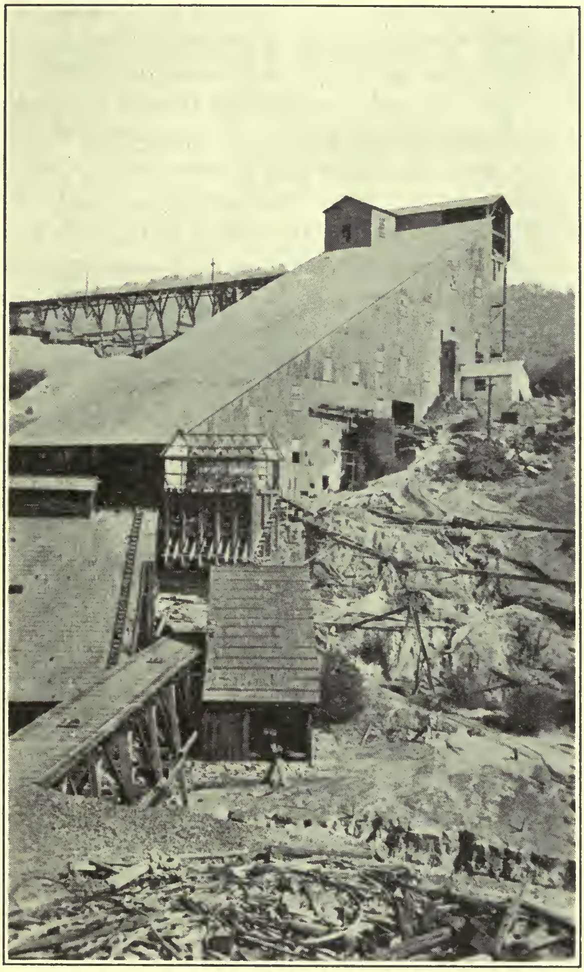

FIG. 3. THE CALAVERAS COPPER MILL

The oil is all fed into the ball-mill feed-box from a 15-gal. zerolene can, fitted with a special bronze stop-cock. The consumption averages

0.3 lb. per ton of ore. It is so well mixed and agitated in the ball-mill that neither mechanical nor pneumatic agitation before flotation is found of any benefit whatever.

The return of the filtrate from the concentrate-filter, and of the overflow from the concentrate-thickener has been found not only to decrease the amount of oil required, but also to effect a closer saving than is possible otherwise, no matter how much oil be used.

The flotation-cells are made locally from Oregon fir, protected with P. & B. paint, at a cost of about $100 each, complete. They are of the type for which J. M. Callow has had process and apparatus patent applications pending in the United States for some time. The porous bottom differs from that used by Mr. Callow in the cells he has built. It is composed of eight separate shallow cast-iron pans, placed side by side along the sloping bottom of the cell, each covered with a multiple-ply canvas, fastened around the edges only. Screens or grids, similar to those used by Mr. Callow, were tried but proved both unnecessary and objectionable.

The outside length of each pan is a trifle less than the inside width of the cell. Two $\frac{3}{4}$-in. pipes are screwed into the bottom of each pan, and pass through holes bored in the wooden floor of the cell. One is connected by means of an easily-removable length of hose, to the air-main manifold, and the other is fitted with a plug-cock, normally closed, but opened periodically to blow out accumulations of water in the pan.

When it is desired to remove a pan, the air-hose is disconnected, and the plug-cock unscrewed, when the pan may easily be lifted from the cell. When the cell is in operation, the holes through which the air and water blow-off pipes pass, are caulked with oakum. This form of air-pan was an original development at Copperopolis, but resembles that developed previously at McGill, Nevada, and used in the pneumatic flotation-cells of the Nevada Consolidated Copper Co. A photograph of two of the Copperopolis air-pans, one right-side up and the other bottom up, is shown in Fig. 2.

A detail drawing of the flotation-cell as a whole, from which one may be built by any competent carpenter, is shown in Fig. 4.

Air is furnished at $5\frac{1}{2}$ lb. pressure by a Connersville blower. The consumption is about 80 cu. ft. free air per min. per cell. Each cell is emptied once per day and the surface of the canvas is washed off with a hose. The canvas lasts several weeks, and when a renewal is necessary, it is effected quickly by removing the pan in the manner described, and replacing it with one already freshly clothed.

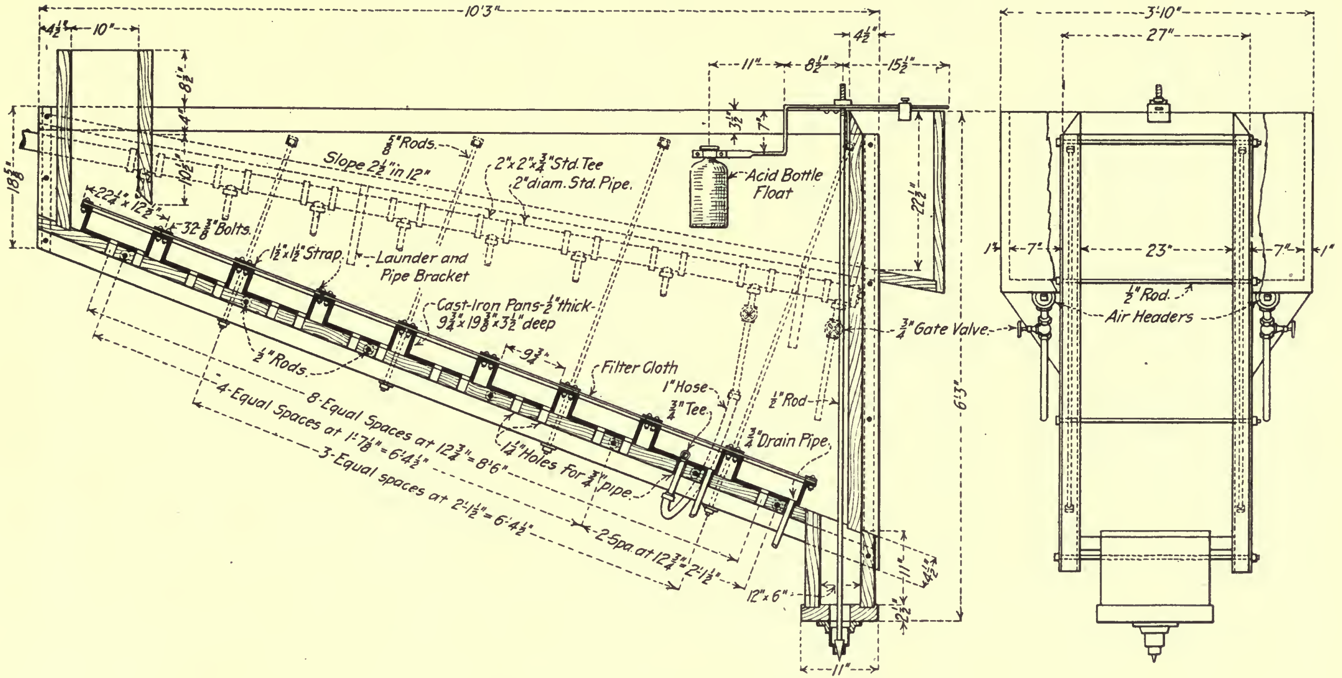

FIG. 4. FLOTATION-CELL IN CALAVERAS COPPER MILL, CALIFORNIA

The air-supply is not filtered, but I believe it is good practice to do so in all cases where porous media are used in flotation-cells. During the past two years I have visited nearly every flotation plant of consequence in the West, and have seen no pneumatic cell frothing so smoothly and evenly as those at Copperopolis.

Some interesting experiments have been made in heating the thickened concentrate in the filter. At some plants where this has been tried, it was found possible to make a cake of double or treble the usual thickness, with no increase in the moisture content. This is probably due to the heat decreasing the viscosity of the oil in the pores of the filter-canvas.

The results of the operation of the plant may be appreciated from the following assays of composite samples for the month of June 1916:

	Copper, %	Iron, %	Insoluble, %
Heading	2.15	20.4	37.0
Concentrate	14.40	29.5	14.9
Tailing	0.09	18.0	43.4
Rough concentrate	8.0	...	...
Cleaner tailing	2.0	...	...

Ratio of concentration, 7:1.
Saving of copper, 96.4%.
Saving of iron, 30.2%.

It will be interesting to compare these results with those obtained in the old gravity-mill, the concentrate from which assayed 5.8% copper, 35.5% iron, 37.4% sulphur, 12.7% silica, and 6.5% alumina. The heading ran 2.4% copper, the tailing 1.5%, the ratio of concentration was 6.6:1, and the percentage of recovery of the copper was 50.

At present the tailing normally assays a 'trace,' which means not over 0.04% copper, a remarkable record, but I believe that any ordinary chalcopyrite ore may be treated by a similar method with similar results. I have myself made a mill-run at this plant with an ore containing 1.38% copper as chalcopyrite, and 22% iron, mostly as pyrrhotite. The grade of the concentrate was 7.32% copper, the tailing 0.07%, the ratio of concentration 5.53:1, and the recovery 95.9%. I have in mind two plants operating under license from Minerals Separation, treating simple chalcopyrite ores, that do not contain nearly so much pyrite as the Calaveras ore and therefore should be much easier to concentrate. Each of these plants uses a more complicated flow-sheet than the Copperopolis plant, and is proud of a tailing containing 0.15% copper. This is eloquent evidence concerning benefits accruing to licensees of Minerals Separation from the superior (?) metallurgical knowledge placed at their disposal by that syndicate.

Operating Costs. These are shown by the following figures taken at random from the company's books, representing actual costs for the week ended July 7, 1916:

Power, 184 hp. per day, at 0.825c. per kw-hr	$191.25
Operating labor, 70 shifts, at $3.25	228.75
Superintendence, repair, and extra labor	137.48
Supplies of all kinds	132.40
	$689.88

On a normal tonnage of 192 per day, this is equivalent to 51.4c. per ton.

Transportation. Incoming supplies and outgoing concentrate are hauled between Milton and Copperopolis by wagon with trailers, drawn by 14 horses, and carrying about 12 tons per load, at a contract price of $3.25 per ton, or about 20c. per ton-mile. The road is very rough, and attempts to use auto-trucks have resulted in failure thus far. During the rainy season the condition of the road is so bad that it is impossible to do any hauling; it has been necessary even to suspend operations during that period. Rail-freight on the concentrate is $1.25 per ton from Milton to the smelter on San Francisco bay, and $6.40 per ton to Tacoma, where this product is now shipped.

Future Operations. There has just been installed an 8-ft. by 30-in. Hardinge ball-mill on trial, under a guarantee by its manufacturer that it will grind 25% more ore, with 25% less power than the 7 by 6-ft. Allis-Chalmers mill. It should be remarked, however, that the price of the Hardinge mill is $1800 more than that of the Allis-Chalmers.

The two ball-mills together, whether operated in series or in parallel, are expected to have a capacity of about 500 tons per day, and 10 additional flotation-cells, with the necessary blower, are being installed to take care of the increased tonnage. The present Oliver filter (8-ft. diam. by 6-ft. face) is to be supplemented by one of the same face but 11½ ft. diameter. This is expected to handle 50 tons per day of thickened concentrate, reducing the moisture to about 12%, with a cake half an inch thick.

It is proposed to convey the concentrate from the thickener to the filter in a 5-in. pipe through the centre of which there will be a 1-in. steam-pipe. This will avoid diluting the thickened concentrate-pulp by condensed steam.

It is estimated that no more labor will be required to operate the plant when treating 500 tons than at present. Assuming the power and supply costs to increase proportionally with the tonnage, an average weekly cost would be approximately as follows:

Power, 479 hp. per day, at 0.825c. per kw-hr.	$497
Labor, as at present	366
Supplies	690
	$1553

This is equivalent to 44.4c. per ton, but it is believed the actual cost will not exceed 40c. On the completion of the railroad, the capacity of the plant may be still further increased by the installation of a third ball-mill, for which room is yet available in the old mill-building.

The total capital expenditure for converting the old gravity-mill into a highly efficient flotation-mill of 500 tons daily capacity will be less than $50,000. A new mill built according to this flow-sheet should not cost much, if any, more, as the figure noted includes the net cost of considerable experimenting, and the dismantling of the entire equipment of the old mill, amounting to as much as a new building would cost under ordinary circumstances.

Without wishing to draw invidious comparisons, it is interesting to note that the National mill in the Coeur d'Alene, built to treat 500 tons per day of a simple chalcopyrite ore, cost $153,000, and has never made so close a saving as the Calaveras plant, and cost about the same to operate as the latter with its present small capacity of less than 200 tons per day. Of course, much less was known about flotation when the National mill was built than today.

Messrs. Levy and Trask are modest as to their achievements, but rumors of the excellent results they have accomplished have traveled widely, and the plant has been a Mecca for metallurgists from all parts of the country. Each visitor has departed with a pleasant impression of the courtesy with which he was received and the freedom with which all desired information was made available.

Collid describes a state and not a form of matter. See Robert J. Anderson in this volume. He also explains the difference between 'adsorption' and 'absorption', questioning the idea that the release of air or other gases occluded by minerals can be a factor in flotation.

THE HORWOOD PROCESS OF FLOTATION

By Allan D. Rain

(From the *Mining and Scientific Press* of October 7, 1916)

*The Horwood process bears the name of its originator, E. J. Horwood, assistant general manager for the Broken Hill Proprietary Company, at Broken Hill, Australia. Briefly, the principle of the process as applied to mixed lead-zinc sulphide ores is that advantage is taken of the different oxidizing temperatures of galena and blende, the galena oxidizing to lead sulphate much quicker, that is, at a much lower temperature than the blende oxidizes to zinc sulphate (given, of course, the ore of a fineness that is necessary for separation of the lead and zinc particles). Such being the case, by judicious roasting of a mixture of these two minerals the lead sulphide can be totally or superficially oxidized to its sulphate under control temperature without affecting the zinc sulphide. By a subsequent flotation operation, the blende may be recovered in the ordinary way and the lead sulphate or the sulphide coated with a film of the sulphate that, not being amenable to flotation, remains as a residue. It may be better, before dealing with the process on a commercial scale, to give a description of the method of making laboratory tests.

Preparation of the Ore. On all ores treated to date, it has been found that the material must be screened through an 80-mesh sieve. Generally speaking, this ought to be considered the maximum of coarseness, and for close recoveries of either zinc or lead, the finer the material the better for the process.

Sulphatization. The success of the process depends on the manner in which this is done, the object being to preferentially sulphatize the galena, leaving the blende unchanged. By keeping the ore at a low temperature for the first portion of the roast, and then raising the heat toward the latter portion (provided the material is kept freely stirred the whole time) no difficulty will be experienced in the laboratory, in changing the galena and leaving the blende unaltered. It is obvious that at no time during the roast must the temperature be raised sufficiently high to oxidize the blende. Should this happen, however, the final object of the process will not be defeated, but the

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*Abstract from *Teniente Topics*, published by the Braden Copper Co., Chile.

resultant zinc loss (due to the solution of any oxidized compounds in the acid used for subsequent flotation) would be increased. The increased quantity of zinc thus lost is directly proportional to the amount of oxidized or sulphatized zinc produced during the roast.

Generally speaking, the temperature to be maintained during the roast should increase from 400° C. at the start to about 500° C. at the end. Some ores require a longer roast than others, the time being dependent on the nature of the sulphides present, and the degree of comminution of the ore. It is not necessary to completely sulphatize the whole of the galena in order to separate it from the blende. The degree to which sulphatization should be carried is to some extent dependent on the size of the ore particles. In order to deaden the galena to flotation it is sufficient to convert the surface of the particles into sulphate, the core of such particles remaining unchanged. The only method of ascertaining definitely when the sulphatization has been carried sufficiently far is to take portions of the roasted ore and make laboratory tests on them, carefully weighing and assaying the products so obtained.

If laboratory tests are made prior to sulphatization on a large scale, and the lead sulphate determined in the sulphatized material, this will afford a simple and rapid method of determining when, in actual practice, the roast has been carried sufficiently far. Then, for example, assuming that in the laboratory the lead sulphide had been sulphatized to the extent of 78%, and that such material gives the desired results, all that is necessary in roasting a bulk lot of ore is to withdraw a sample every quarter of an hour from the furnace and determine its lead sulphate contents, this determination not taking more than a few minutes. For instance, a sample of zinc-lead slime sulphatized in the laboratory over a gas-burner for about two and a half hours was found to contain 73% lead as sulphate; the subsequent separation made on this material yielded approximately an 86% zinc recovery and an 81% lead recovery in zinc and lead concentrates respectively. A small amount of zinc is lost invariably in the subsequent flotation, by reason of the formation of soluble zinc compounds during the roast; but if the roast has been carried out in the correct manner, the quantity of zinc so lost should not amount to more than at most 2 to 3% of the total zinc in the ore.

FLOTATION. Fifty grammes of the sulphatized ore is weighed and placed in a 500-c.c. cylinder, provided with a stopper. Boiling water is admitted to the 250-c.c. mark, then 3 c.c. of 95% sulphuric acid (Sp. Gr. 1.8376) and the mass is agitated for a short time. After this, either 0.1 c.c. or 0.2 c.c. of oleic acid is added, and the whole is then thoroughly shaken by hand. The agitation is continued until the sulphides become thoroughly oiled and float to a large extent. The contents are then transferred to a 16-oz. beaker and the bulk increased with boiling water that has been used to rinse the cylinder. The beaker is then placed on a sand-bath and flotation is produced by heating the bottom of the beaker. A little calcite is added prior to the application of the heat, to prevent the material from lying dead on the bottom and to assist the flotation. During flotation the mass in the beaker is stirred gently with a glass rod in order to hinder the formation of too large clots, which include floured lead sulphate. The concentrate is removed with a spoon from the top of the liquor, the skimming being continued until no more blende floats. The lead remains in the residue as sulphate.

The concentrate resulting from the above first separation is usually dirty; it requires to be re-agitated in a 1% sulphuric acid solution (without the addition of any further oil) and re-floated in a manner similar to the first separation. The float concentrate resulting from this re-agitation is transferred to a tin-can, dried, the oil burned off, and the residue weighed. The residue resulting from the two separations are bulked, transferred to a tin-can, dried, and weighed.

Method of Treatment by Zinc Corporation. After a number of successful laboratory demonstrations, trials more closely approaching commercial treatment were made on large parcels, with encouraging results. Almost the first to become interested in this process, besides the originator, E. J. Horwood, was the management of the Zinc Corporation, which had as a by-product a small proportion (roughly 5 to 6% of total concentrate produced) of a mixed lead and zinc slime, for which it could neither secure sale nor devise any means of successful separation. This process was tried as a probable solution of their metallurgical difficulties, and one by which they could separate into salable products this mixed lead-zinc slime-concentrate. This they were stacking with a view to some successful treatment later. The mixed slime concentrate assayed approximately 35% zinc, 16.5% lead, and 25 oz. silver per ton.

THE DISPOSAL OF FLOTATION PRODUCTS

By Robert S. Lewis

(From the *Mining and Scientific Press* of April 7, 1917)

Introduction. A little over two years ago, I was talking with a mill-man from a certain plant where the flotation process had recently been introduced. To my inquiry regarding the success of the flotation equipment, he replied that, at first, it was impossible to obtain a froth. Then suddenly, due to some reason not understood, froth began to form so rapidly that it soon ran over the machines and piled up in great heaps on the mill-floor. It was of such a tough and lasting nature that it would have been an excellent substitute for sole-leather, and it was practically impossible to handle the concentrate because of its stickiness. These statements may contain some exaggeration, but they indicated that a mill-operator's troubles might not cease as soon as a froth was produced. Despite the improvements that have been made in the technique of the flotation process, the satisfactory handling and disposal of flotation concentrate is still a very important problem. In order to secure the latest data on the practice of handling flotation concentrate, a number of letters of inquiry were sent to companies operating mills or smelters. Nearly all the information given below is the result of this investigation.

Dewatering Flotation-Concentrate. This step is necessary as a preliminary to subsequent handling and metallurgical treatment. The large amount of water present in the froth must be reduced greatly before the concentrate can be transported economically, either in sacks or in bulk, to its destination. If shipped a long distance, the freight charge on the moisture contained may reach a considerable figure. The expense for unloading wet and sticky material from cars is much greater than usual. Then, too, custom-smelters often impose a penalty for moisture in excess of a specified figure. It is interesting to note that steamship companies refuse to carry a flotation concentrate that is very wet. Such materials shift so easily that it is impossible to keep the vessel on an even keel. After one ship had been lost, due to shifting of the cargo, steamship companies refused to transport concentrate in which the moisture ran over a stipulated amount.

When the froth is delicate and breaks easily, as does much of the froth from flotation-machines using only air-agitation, a simple treatment on a concentrating-table of the Wilfley type may give satisfactory results. However, it is generally necessary to employ some additional means to insure disintegration of the froth. Centrifugal pumps have been used with success. Bucket-elevators are fairly efficient, but unless included in the original design of a plant, are hardly to be recommended. At the Utah Apex mill, an elevator 71 ft. high is used to assist froth-breaking. Head-room and floor-space may be saved by employing a jet of water instead. Experience has shown that a single large jet, spreading over the full width of the concentrate-launder, is to be preferred to a number of smaller jets. In the Daly-Judge mill, at Park City, Utah, a patent nozzle, known as the Koerting spray, has been found effective in 'killing' froth. After passing the spray, the concentrate is thickened in Callow cones and is then treated on Wilfley tables to separate the lead from the zinc. The objection to the use of sprays is that the additional dilution of the concentrate means so much more water to be disposed of later. Moreover, where settling-tanks are employed, any appreciable current in the overflow carries out a considerable amount of the finest concentrate. In an endeavor to overcome this objection, Messrs. Cole and Thompson have devised a special nozzle (U. S. patent 1,180,089, Aug. 18, 1916), in which a gaseous liquid, such as compressed air or steam, is mixed with a small amount of water. The resultant jet has a whirling motion. The spray should be directed against the flow of froth and at an angle of from 60 to 90° with the bottom of the concentrate-launder. This retards the progress of the froth and gives the jet more time in which to break it up. The nozzle should be placed at such a distance from the launder as to allow the spray to cover the entire sectional area.

Settling in bins or tanks is a method of dewatering froth that has the merit of simplicity, although it has several disadvantages. Some flotation-concentrate is so fine, all –200 mesh and with a large percentage of – 300 mesh, that the time required for settling is prohibitively long. Where a large tonnage must be handled the size of the equipment becomes serious. This point is well illustrated in the case of one of the big copper concentrators. An estimate showed that a number of concrete tanks 20 ft. wide, 108 ft. long, and from 5 to 6 ft. deep would be required. The proposed method of operation was to run the froth into a tank until the overflow should become contaminated by the fine concentrate carried over. The tank-feed was then to be cut off and the content settled. The clear water was to be decanted and the concentrate allowed to dry for a day or two. However, the tanks were never built, thickeners and filters being finally adopted. Tanks may have either filter or solid bottoms. In the first case, vacuum-pumps can be used to hasten draining. When solid-bottom tanks are used, the water must be decanted from the settled concentrate, and care must be taken not to allow the escape of the froth, which almost invariably accumulates on the surface of the water. Unless of special design, such as those arranged for a Blaisdell excavator, tanks must be unloaded by shoveling. If desired, the tanks may be provided with steam-pipes to assist drying, but their use is hardly to be recommended. Spreading the material out in a thin layer on a drying-platform gives quicker and better results, but, in any case, drying by steam-heat is expensive. Classifiers of the Ovoca and Akins type have been used for dewatering concentrate. These are quite successful on coarse or granular material that drains readily.

The following examples illustrate the practice of settling flotation-concentrate in tanks or bins.

1. The Desloge Consolidated Lead Co., Desloge, Missouri, has been drying its lead concentrate to 6 or 7% moisture in steel drying-tanks, heated by steam, and then loading it by hand into unlined box-cars. The method is expensive, and the company will soon install a thickener and filter.

2. Monitor Belmont Mining Co., Belmont, Nevada. From 3 to 4 tons of a silicious silver-bearing concentrate is produced per day. The concentrate is settled, drained, and dried on floors to 5% moisture. It is then sacked and hauled to the railroad, where it is loaded into box-cars. The cost per ton for draining and drying is $2.20 and $1.22 for sacking. This method is not satisfactory and the present management is arranging for a totally different method of handling.

3. Name not given. About 45 tons of 60% zinc concentrate, all – 65 mesh, is handled daily. The froth, with a water ratio of 6 : 1, is run through a 6-in. pipe into bins. Clear water is drawn off between the settled concentrate and the froth. The bins are of concrete, and each holds 20 tons. They are lined with steam-coils. The dried concentrate, containing about 12% moisture, is dropped through doors in the bottom of the bins into wheelbarrows and is loaded into unlined box-cars. The cost is 40c. per ton for drying and 10c. per ton for loading. Coal costs $2 per ton. The condensation from the pipes is returned to the boilers. A filter will be desirable if a larger tonnage is to be handled.

4. M. W. Atwater, Basin, Montana. About 20 tons of zinc concentrate is produced daily. All of it is – 80 mesh and 70% is – 150 mesh. The froth, with a water ratio of 2 : 1, is run into one of four bins, each 10 by 10 ft. and 13 ft. high. The overflow, carrying a small

proportion of the concentrate, passes into the next bin. When a bin is filled, the upper three feet is discharged into the overflow-bin. The concentrate is then shoveled through the bin-doors directly into box-cars lined with muslin. Two men can load 80 dry tons in 8 hours. The same men prepare the box-cars for loading and attend to the filling of the bins. The concentrate contains from 12 to 13% moisture when loaded, but this drops to 10 or 12% by the time the smelter is reached. As much as 700 tons of concentrate has been handled in the four bins in 30 days. The method is satisfactory, but it is necessary to have deep bins and ample bin-space. Cost of loading is 10c. per ton. The lining of the box-cars costs $2 each.

5. Atlas Mining & Milling Co., Sneffles, Colorado. The concentrate assays 10% silica, 20% iron, 12% zinc, 17% lead, 60 oz. silver, and 0.2 oz. gold. Fifteen tons is produced daily. The froth is treated on tables, and the concentrate sent to 50-ton collecting-tanks, the overflow from which is returned to the mill-circuit. From the tanks the concentrate is shoveled into small cars and trammed to an inclined chute 20 in. wide, 18 in. deep, and 90 ft. long, having three steam-pipes along the bottom. The chute discharges into a bin where the concentrate is sacked. It is then hauled to the railroad and shipped in box-cars lined with paper.

6. Mears & Wilfley, Silverton, Colorado. The 10 tons of concentrate made daily is mostly chalcopyrite, and ranges from 80 to 150-mesh. The froth is run into settling-tanks from which two drag-belts, 15 ft. long and 3 ft. wide, requiring ½ hp., pull the concentrate into a bin, from which it is loaded into canvas-lined box-cars by means of wheelbarrows. The concentrate runs 20% moisture when loaded, but only 13% by the time the smelter is reached. The canvas linings are sent back by return-freight. Linings show no wear after six months' use. Cost of handling is about 35c. per ton.

7. Flotation at Mt. Morgan.[1] The ore contains gold, copper pyrite, iron pyrite, and about 70% silica. At the 100-ton testing-plant of this company, the flotation-concentrate was first run into round vats 20 ft. in diameter, 10 ft. deep, and constructed with filter-bottoms. These proved unsatisfactory, as the wet slime kept to the outside and did not drain well. This difficulty was finally overcome by using a number of rectangular tanks, 9 ft. 10 in. by 10 ft. 9 in. and 3 ft. deep, with cocoa matting on a sand-filter bottom. The froth was run through the tanks in series, three or four always being in operation, and each filled with

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[1] W. Shellshear, Aust. Inst. M. E., June, 1916.

concentrate. The tanks drained to 7 or 8% moisture in 24 hours and the water was perfectly clear.

8. Britannia Mining & Smelting Co.[2] The concentrate, assaying 14% copper, 26.8% iron, and 20.8% silica, is taken from the flotation-machines by a drag-elevator that delivers it to the shipment-bins, where the moisture is reduced from 20 to 8% by draining. The Tacoma smelter draws the line at 10% moisture. The overflow from the bins goes to tanks, from which the sediment is delivered to the flotation-machines, while the overflow goes to Dorr thickeners. The thickeners give an overflow that goes to waste and a spigot product that is treated in the flotation-machines.

At a mill producing 13 tons of concentrate, assaying 5% lead, 5% copper, 28% iron, 18% silica, with some gold and silver, the froth is settled and dried in wooden tanks having steam-coils on the bottom. The concentrate is then shoveled into box-cars that have been lined with paper. Cost is about 18c. for drying, and 23c. for loading, or a total of 41c. per ton. The tanks do not give sufficient settling-area, and the costs are considered high.

At another plant, both a zinc and a lead concentrate are made. The total of concentrates produced is from 3 to 4 tons. The concentrate is settled in shallow tanks, 16 in. and 30 in. deep, the water being decanted. Steam is then turned into pipes on the floor of the tanks. When the moisture is reduced to 11%, the concentrate is shoveled into box-cars lined with resin-sized building paper. The tanks are housed over. Some are provided with fan-induced draft for drawing off the water-vapor and the rest have natural draft. The former are the more satisfactory. The cost of loading is 21c. per ton.

A plant making 24 tons of lead concentrate per day uses a Dorr thickener to remove most of the water from the froth. The concentrate is then dried to the desired point in tanks 16 in. deep with steam-pipes along the bottom and the sides. Steam-pressure is 75 lb. per sq. in. The concentrate is loaded into unlined box-cars. Cost of treating is $1.15 per ton. The method is not satisfactory, and a filter will soon be installed. This use of steam for reducing the moisture-content of flotation-concentrate is expensive.

In the case of a plant producing 10 tons of concentrate per day, part of which is a 50% zinc product and the rest a 65% lead product, this material is settled in flat-bottom tanks, the water is then decanted, and the concentrate shoveled onto draining-platforms, from which it is loaded into box-cars lined with felt. The zinc concentrate contains

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[2] T. A. Rickard, M. & S. P., Nov. 11, 1916.

20% moisture, and the lead concentrate 15% moisture. Cost of treatment is about 20c. per ton. This method is only a temporary expedient; thickeners and filter will soon be installed. Even though it could be done easily, it would not be desirable to dry the concentrate to the point of dusting.

It is said that at the Miami mill, the concentrate from both the flotation-machines and the tables is run into round steel tanks having filter-bottoms, and with a central opening in the tank-bottom. A vacuum-pump accelerates the draining. When drained, a plug is removed and the concentrate is shoveled onto a belt-conveyor passing beneath the tanks. This conveyor discharges onto another or cross-conveyor that loads directly into box-cars.

The most common method of dewatering flotation concentrate is by the use of thickeners and filters. Though this makes an expensive equipment, it gives a rapid and a fairly positive control over the moisture-content of the finished product. There is some accumulation of froth at the top of the thickeners. This is difficult to handle and contaminates the overflow from the tanks. Unique testimony to the apparent solidity of this accumulation is found at one mill where 'near-tragedies' are occasionally enacted because usual canine perspicacity fails to deter inquisitive dogs from attempting to take short cuts across the thickeners. Sprays are sometimes used in an attempt to break up this froth and baffle-boards may be employed, either around the edge of the tanks to protect the overflow, or at the centre and extending below the surface of the water in the tank. In the latter case, the incoming froth discharges into the space within the boards, and is broken up in passing out into the rest of the tank. The Consolidated Arizona Copper Co., at Humboldt, Arizona, has found it profitable to send all the flotation-tailing to thickeners, skim off the froth, and add it to the regular output.

The filters used are generally of the vacuum type, such as the Oliver and Portland, although the Kelly press, a pressure type, has been installed in some mills. The pressure-filter has the advantage that it can reduce the moisture in the concentrate to a very low figure, but it has been considered intermittent in action, costly to operate, and requires close attendance. However, a company that produces a large daily tonnage of concentrate has recently decided to install Kelly filters. These presses, of improved design, were adopted after a competitive test with a filter of the vacuum type. The vacuum-filter has no competitor when treating a concentrate that makes a thick cake and filters easily, but, when the concentrate is exceedingly fine and retains water tenaciously, the capacity of the filter becomes so reduced and the percentage of moisture left in the cake is so high that a filter of the Kelly type is to be preferred. A slight increase in total cost of operation (cost for labor is little, if any, greater than for the vacuum-filter) is more than off-set by the reduced moisture in the product. The positive action of the Kelly press enables it to handle material that cannot be satisfactorily treated on a filter of the vacuum type.

In order to give sufficient capacity together with a low proportion of moisture in the cake, the vacuum-filter must have a feed that is at least 50% solid. At one mill the moisture in the material going to the filter must be held at the low figure of 35% in order to get satisfactory results. Heating the pulp in the filter-tank to about 100° F. or adding slaked lime will often increase the capacity of the filter. At the Inspiration mill Dr. Gahl has plotted the percentage of silica in the concentrate along with the moisture content of the filter-cake. A change in the former due to variations in the ore, or in the operation of the plant, is followed by a closely corresponding change in the latter. This suggests that the percentage of silica present has a marked effect on the dewatering action of the filter. It would be interesting to know whether this holds true in other plants and with different kinds of concentrate.

In a recent bulletin of the American Institute of Mining Engineers, operation (cost for labor is little, if any, greater than for the vacuum-filters. He states: "Our experience has not been satisfactory with the continuous plan, and it is for this reason that in all our recent plants, we have been installing the intermittent system. Until shown to the contrary, we think that this offers the best solution, in that with it you have complete control of the necessary density for the filters, there is no danger from losses in the overflow, and the froth which accumulates during the filling of the tank is completely disposed of at each cycle of the operation, and, therefore, cannot accumulate. The agitator for stirring the contents of the tank during the discharge period is copied from those used at the Goldfield Consolidated mill. It consists of arms secured to a square revolving shaft, suspended by a chain-block, and passing through a square hole in the driving-gear. It is simple, inexpensive, and gives no trouble whatever. It is illustrated in the accompanying figure. The thickened pulp may be drawn off from a central-bottom discharge. More recent practice is to draw off through a valve or molasses gate on the side of the tank, or better still, with a diaphragm-pump." Fig. 1 shows an installation for a 60-ton zinc plant.

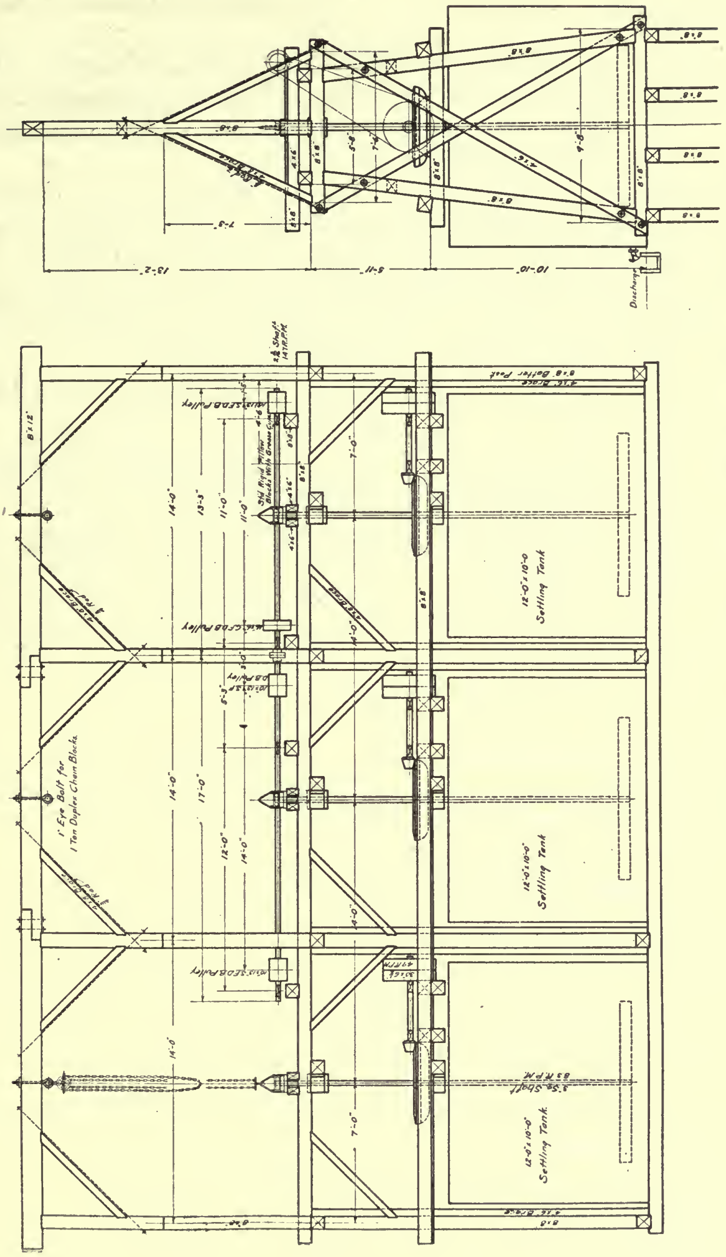

FIG. 1a. AGITATORS FOR 12 BY 10-FT. TANKS, 50-TON ZINC PLANT. MAGMA COPPER CO.

The following examples illustrate the practice of filtering flotation concentrate.

1. Montezuma Mines & Milling Co., Montezuma, Colorado. This plant is producing daily 10 tons of concentrate that assays 42% zinc and 9% iron. The froth is sent to tables and the table-concentrate is filtered. The cake contains only 3% moisture.

2. Portland Gold Mining Co., Victor, Colorado. From 13 to 15 tons of concentrate, assaying 55 to 70% silica and 2 oz. gold, is made daily. The froth goes to Dorr thickeners and Portland filters. The moisture in the filter-cake is 30%. The concentrate is loaded by hand into tight-bottom box-cars. Cost of dewatering and loading is 50c. per ton. The results are not considered satisfactory.

3. Name omitted. Daily production is 10 tons of concentrate, assaying 40% zinc, 7% silica, 14% iron, 30% sulphur, 7% lead, with a little gold, silver, and copper. This is dewatered in Portland filters to 14% moisture, and loaded by hand into unlined box-cars. The cost for dewatering and loading is 15c. per ton.

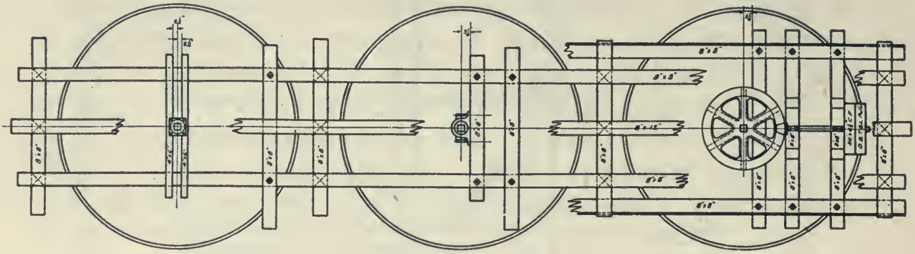

FIG. 1b. PLAN OF AGITATORS IN MAGMA MILL

4. St. Joseph Lead Co., Bonne Terre, Missouri. Forty tons of concentrate is handled per day. The analysis is 50% lead, 2% zinc, 9% lime, 4% iron, and 6% insoluble. The froth, containing 90% moisture, goes to a 38 by 6 ft. Dorr thickener, which gives a spigot-product of 35% moisture. This pulp is sent to one 11 ft. 6 in. by 12 ft. Oliver filter, and the cake, containing 14% moisture, is loaded into gondola cars by means of a rubber-belt conveyor. A Root vacuum-pump, requiring 29½ hp. is used for the filter. The operation of the filter itself required 1½ hp. Cost for dewatering is 26c., for loading 2c., and for maintenance 6c., making a total of 34c. per ton.

5. Engels Copper Mining Co., Taylorsville, California. Between 30 and 40 tons of concentrate is produced in 16 hours. The assay is 35% copper and 30% insoluble. The froth is elevated to two settling-tanks having cone-shaped bottoms. The thickened concentrate then

goes to an 8 by 8-ft. Oliver filter, which gives a cake containing 12% moisture. Steam is used to heat the pulp in the filter-tank. The filter-product is sacked and carried 1½ miles by a tram to auto-trucks, which, in turn, carry the concentrate to the railroad 30 miles away. The cost for dewatering and filtering is $1.50 per ton.

6. Bunker Hill & Sullivan Co., Kellogg, Idaho. Analysis of concentrate is 45.9% lead, 6.6% zinc, 13.2% sulphur, 10.4% insoluble, 9.8% iron, 26.6 oz. silver with a little copper and manganese. Twenty tons is produced per day, all of it – 200 mesh. A 40 by 12-ft. Dorr thickener and a 6 by 8-ft. Oliver filter are used for dewatering. The filtered concentrate contains 11% moisture. It is loaded into box-cars. The cost is 7c. for dewatering and 15c. for loading, making a total of 22c. per dry ton. It is essential that the feed to the filter be as thick as possible, about 35% moisture being a satisfactory figure. It has been found that wiping the oily film that forms on the filter-cake, with a rawhide beater, reduces the moisture nearly one-half.

7. Detroit Copper Mining Co., Morenci, Arizona. All flotation concentrate goes to one Dorr thickener. A 6 by 8-ft. Oliver filter takes as much of the thickened product as it can handle, together with the froth from the top of the thickener, which is removed by paddle-wheels. The slime-overflow from the thickener is sent to a settling-tank, and the spigot-product is shipped as flotation slime. An analysis of a composite sample of the filter-product and slime is 20.32% copper, 22.3% silica, 13.2% iron, 12.6% alumina, 1.4% lime, 1% magnesia, and 19.8% sulphur. The moisture in the filtered concentrate is 34.6%, and the slime carries 80.6% moisture, which necessitates its being shipped in tank-cars. The equipment is inadequate, and a larger plant is required to give satisfactory results.

8. Consolidated Nevada-Utah Corporation, Pioche, Nevada. About half of the total tonnage, 18 tons of concentrate per day, is thickened and filtered. It assays 42% zinc, 10% iron, 1% lead, and 11% insoluble. The flotation concentrate is very slimy and is mixed with the fine concentrate from the tables in order to obtain a product that can be filtered satisfactorily. The coarse concentrate from the roughing-tables is not filtered. Three 16-ft. agitators are used for thickening. One is running and one is filling while the third is being decanted. Each requires 5 hp. The 4 by 8-ft. Portland filter reduces the moisture to between 9 and 10% and consumes 1 hp. for operation. The concentrate is shipped in box-cars with a 12-in. board nailed across the door.

9. Old Dominion Copper Mining & Smelting Co., Globe, Arizona.

Of the 36 dry tons of concentrate handled per day, fully 91% is –200 mesh. An analysis gives 18% copper, 24% iron, 27% sulphur, and 22% insoluble. The froth, containing 8% solid, is pumped by a 3-in. centrifugal pump to a 10 by 28-ft. Dorr thickener, which gives a spigot-product of about 57% solid. This goes to an 8 by 11.5-ft. Oliver filter. The filter-cake contains 19% moisture. The filter discharges into a bin from which the concentrate is loaded into cars by means of wheelbarrows. The power consumption of thickener and filter is 1.24 kw. per hour. The filter operates at a 21-in. vacuum and 18 lb. for blowing-pressure. Cost is 1.6c. for dewatering and filter power, 8c. for repairs to filter and renewal of canvas, and 21c. for loading concentrate, making a total of 30.6c. per ton. The comparatively high cost of loading is due to the necessity of loading into box-cars, which makes it impossible to use a belt-conveyor. Trouble is experienced from the accumulation of froth in the thickener. This robs the thickener of settling and thickening capacity. Sprays of water break up some of the froth but do not prevent a gradual accumulation.

10. Utah Leasing Co., Newhouse, Utah. The froth goes to a 22 by 10-ft. Dorr thickener and then to an 8 by 6-ft. Oliver filter, which gives a product containing 20 to 21% moisture. Great difficulty is experienced in settling and filtering the fine slime. Sodium silicate, soda-ash, and lime have been tried, but without marked success. Allowing 24 hours, or more, of undisturbed settling in tanks seemed to be of little avail. Fifteen tons of concentrate is produced daily. It assays 15 to 16% copper, 33 to 36% silica, and 20 to 22% iron.

11. Gold Hunter Mining & Smelting Co., Mullan, Idaho. A screen-analysis of the 30 tons of concentrate produced per day shows the following results: + 100 mesh, 0.2%; + 150 mesh, 1.8%; + 200 mesh, 6.4%; and –200 mesh, 91.6%. It is a lead concentrate with about 16% silica. The froth is thickened to more than 50% solid in a 30 by 5-ft. Dorr thickener. Froth, running 60% solid, is mechanically skimmed at the top of the tank and unites with the spigot-product, going to an 8 by 6-ft. Oliver filter. A vacuum of from 24 to 25 in. is maintained by a wet-vacuum pump. A receiver with a barometric leg is used for the filtrate, which is clean but is run to settling-tanks. Oakdale No. 3 twill is used for the filter-cover. It lasts six months. The agitator is run at 30 r.p.m., but the air-lifts are not used. The emergency air-agitators are used once daily. The canvas is blown from one to three times per day with compressed air under 20 lb. pressure. Occasionally the canvas is steamed, using a 1-in. pipe per-

forated every inch with $\frac{1}{16}$-in. holes. Steam-pressure is 60 lb. per square inch. A scraper is mounted on a flat rigid casting that holds it just off the wires. The dried product drops into a bin, from which it is loaded into unlined box-cars by means of wheelbarrows. The concentrate contains 10% moisture. The overflow from the thickener is generally clean, but, at times, a little froth escapes. The overflow goes to settling-tanks and ponds. The cost is 4⅓c. for dewatering, of which 3⅓c. is for power and the rest is for repairs and labor. Loading costs 14c. per ton, being based on a wage of $4.50 for 8 hours. The filtered concentrate takes up more space and this adds to the cost, as it has to be shoveled back into cars.

12. Anaconda Copper Mining Co., Anaconda, Montana. From 1800 to 1900 tons of wet concentrate is produced per day. This is about 148 tons per filter-day. The screen analysis shows: + 48 mesh, 0.19%; – 48 and + 200 mesh, 29.7%; – 200 and + 300 mesh, 11.91%; – 300 mesh, 57.18%. The chemical analysis shows 9% copper, 28% silica, 25% iron oxide, 10% alumina, and 27% sulphur. Twenty-one 50 by 12-ft. Dorr thickeners are used. The thickeners for the slime-concentrate require 15 minutes for a revolution and consume 0.6 hp. each. Those for the sand-concentrate revolve once in 9 minutes and consume 1.5 hp. each. The thirteen 11½ by 12-ft. Oliver filters require 1 hp. each for operation, 25 hp. each for wet vacuum, and 15 hp. each for dry vacuum. The filter-feed is thickened to 50% solid and the cake runs 15% moisture. The pulp is heated to 100° F. in the filter-tank. The filtered concentrate is taken directly to the roasters on an 18-in. belt-conveyor, which requires 25 hp. for its operation. The method is satisfactory. The belt-conveyor handles the material without difficulty. The froth, containing from 18 to 20% solid, is delivered to a baffle-box at the centre of each Dorr thickener. The box is about 5 ft. square and extends down to within a few inches of the rakes. Surrounding this is another baffle about 15 ft. square and extending about 18 in. below the surface of the water. The baffles catch a large part of the froth, which is there broken up by a spray of water. The overflow, containing a small amount of fine material that will not settle, is run to a slime-pond.

13. Calaveras Copper Co., Copperopolis, California[3]. The concentrate contains 14.4% copper, 29.5% iron, and 14.9% insoluble. When the remodeling of the plant is completed about 50 tons of concentrate will be produced daily. At present the output is 25 to 28

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[3] H. R. Robbins, M. & S. P., November 25, 1916.

tons. The froth is thickened to 60% solid in a 22 by 10-ft. Dorr thickener and the moisture is reduced to 13% by means of an 8-ft. Oliver filter. In the new plant, it is planned to convey the thickened product to the filters through a 5-in. pipe, which will contain a 1-in. steam-pipe. This will heat the pulp without diluting it with the condensed steam.

14. Braden Copper Co., Chile. Both the table and flotation concentrates are run into concrete settling-tanks at the bottom of the mill. There are eight tanks in all, and four are used together alternately. The settled-table and coarse-flotation concentrates are loaded by a grab-bucket into cars. The tank-overflow, having a water-ratio of 10 or 20 : 1, goes to Dorr thickeners and the thickened product (water-ratio of 1 : 1), is sent to two Kelly and four Oliver filters, only four of which are in operation at the same time. About 50 tons of solid per day is recovered in this manner. The fineness of the material, 98% of which is – 200 mesh, results in low filter-capacity. At this plant supplies constitute 60.4% of the total direct milling-cost. Concentrate-handling makes up 8.33% of the total labor and 1.14% of the total supplies. Filtering concentrate makes up 5.46% of the total labor and 2.61% of the total supplies. About 50 tons is handled per day, of which 98% is – 200 mesh.

15. Inspiration Consolidated Copper Co., Miami, Arizona. Five 60-ft. and three 80-ft. Dorr thickeners are used for handling 651 dry tons per day of mixed table and flotation concentrates. The latter amounts to 75% of total concentrates by weight and carries 90% of the copper. This gives 44.8 sq. ft. settling-area per ton of concentrate. The thickened product, having a water ratio of 1.65 : 1, passes through tunnels to two bucket-elevators, which deliver it to six 11 ft. 6 in. by 12-ft. Oliver filters. The filter-cake contains approximately 17% moisture. In attempting to reduce the moisture in the cake, the pulp in the filter-tanks was heated by steam. This increased the capacity of the filters, but did not affect the moisture in the cake. Adding slaked lime gave the same result. Lime is now used to increase the capacity of the filters. A double ring of high boards is used to prevent the contamination of the thickener-overflow by the froth accumulated on top. A record was kept of the portion of silica in the concentrate and the moisture in the filter-cake. The results are shown in the accompanying chart, Fig. 2 (Sept. 1916 Bull., A. I. M. E.), and would seem to indicate that the amount of moisture remaining in the cake depends upon the silica present in the concentrate. An 18-in. belt-conveyor running at a speed of 150 ft. per min. carries the concentrate to a steel loading-bin, directly above the railroad track. At

the head pulley a rubber scraper is used to assist in removing the concentrate from the belt-conveyor. The bin is round with a cone-shaped bottom. Some difficulty is experienced in discharging the material from the bin. The total power-consumption for thickening, elevating, filtering, and conveying is 5.1 kw-hr. per ton of concentrate. The cost of dewatering and loading is between 20 and 25c. per ton.

A certain plant, producing 15 tons of a 12% copper concentrate per day, uses a Dorr thickener and a 4 by 8-ft. Oliver filter. The cake is shoveled into wagons. Cost for dewatering and loading is given as 50c. per ton. Another plant, making 35 tons of zinc-lead concentrate per day, delivers the froth to a bucket-elevator in order to break it up.

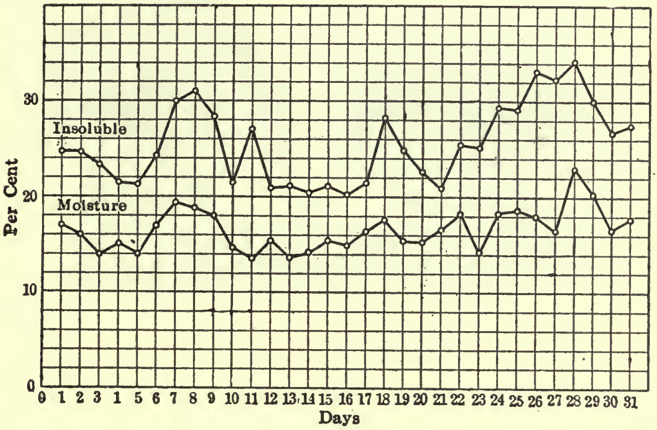

FIG. 2. CHART SHOWING SILICA IN CONCENTRATE AND MOISTURE IN FILTER-CAKE

It then goes, without dewatering, to an Oliver filter, which gives a cake containing 10% moisture. This is loaded into gondola cars lined with canvas. The cost is 10c. per ton.

A copper company, which produces from 15 to 18 tons of concentrate per day, assaying from 14 to 18% copper and 28 to 34% silica, thickens the froth in Callow cones and then sends it to an Oliver filter. The filter-cake drops down a chute lined with 1.5-in. steam-pipes into a bin, which is also lined with steam-pipes. The concentrate is then shoveled from the bin, and shipped in gondola cars patched with sacks and thin boards. In spite of the filtering and drying, the shipping-concentrate runs from 14 to 18% moisture. It is so wet and sticky that it requires a great deal of shoveling. Cost of loading is from 22 to 25c. per ton. The dewatering and drying cost is not known.

Smelting Flotation Concentrate. The concentrate generally comes to smelters so well established in methods of operation that their work is of a routine nature. If this material is put through the regular smelting process, it has been found that the physical condition of the concentrate is such as to require certain modifications in the usual methods of operation.

The actual smelting of a flotation product is quite similar to the smelting of any other concentrate. The objections to it are of a physical rather than of a chemical nature, but they are enough to cause many smelters to impose a penalty of $1 per ton. If the concentrate arrives at the smelter in a wet and sticky condition, it is difficult and expensive to unload. A large moisture-content means extra fuel-consumption in driers and roasters, and in furnaces, when charged directly into them. The great fineness of the material causes a heavy loss from dusting. This is especially true where it is necessary to smelt in blast-furnaces. Briquetting should reduce this loss, but it is often difficult to produce satisfactory briquettes. Unless it can be mixed with a large proportion of coarse material, flotation concentrate is hard to sinter. It chokes the grates, interferes with the draft, and reduces the capacity of the sintering machines. In some cases it may be necessary to pre-roast before a successful sinter can be produced. During the roasting process, there is often a marked tendency toward agglomeration or 'balling up,' and lumps are formed that roast on the outside only. Fig. 3 shows two lumps (natural size) of zinc concentrate that passed through the roaster, but came out with unaltered cores. Often troublesome accretions are formed in the roasters. At one plant it was found that a preliminary drying of the concentrate before roasting prevented 'balling.' However, drying usually makes

FIG. 3. LUMPS OF INCOMPLETELY ROASTED ZINC CONCENTRATE SHOWING UNALTERED CORES OF SULPHIDE

the material lumpy and hard to feed. Where a large amount of flotation concentrate is roasted, special apron-feeders must be provided to handle this material.

The roasted product is of such a light and fluffy nature that it must be handled with great care to keep down the loss from dusting. At one plant, the cars are loaded in a tunnel connected to a dust-chamber and stack. Should a sufficiently large amount of dust be produced, it would pay to add a Cottrell tube-system. At another copper smelter, the side walls of the reverberatory furnaces have slots cut through them just above the slag-line. Inclined iron plates are fastened to the outside of the walls so that the charge can be shoveled onto them and work slowly down into the furnace as the smelting proceeds. This method of gently presenting the charge to the heat at a point where the draft is weakest causes a minimum formation of dust. It is far less than if centre-charging is used.

The foregoing discussion concerns lead and copper smelting, but zinc smelters, as well, have their troubles when treating flotation concentrate. At one plant, the unloading from cars is done by shoveling or by a grab-bucket. The material is then dried in a rotary drier and roasted in muffle-kilns. Because of its fineness, it is considered more difficult to treat than other zinc concentrate. At a second plant, all the unloading is done by shoveling, but it is considered an unsatisfactory method. At a third plant, shoveling is considered expensive, though it is acceptable in other regards. The concentrate is roasted in open-hearth furnaces fired with natural gas. Very little trouble is experienced in roasting. No difficulty is found in smelting, but the dust-loss is higher than for coarser material. At a fourth plant, flotation concentrate makes trouble all through the smelting process. Unloading is done by shoveling into wheelbarrows. The material is frozen in winter and is hard to handle. It is roasted in reverberatory furnaces to 1% sulphur or less (cost of roasting is about $1.70 per ton). The coarse concentrate is first dried to about 4% moisture, but the fine concentrate is not dried. The difficulties found in roasting are high dust-loss, the forming of accretions in the roasters, and the fusing of the fine concentrate. Smelting is done in the usual gas-fired distillation-furnaces. The fine material is more subject to loss through overheating. It slags more easily with consequent loss of retorts. The charge is more likely to cake in the charge-cars, if too wet, and to blow out of the retorts, if too dry. The very fine flotation concentrate is difficult to roast and smelt.

One smelter superintendent forcibly summarizes the situation in the following brief sentence. ''Flotation concentrate is considered a damned nuisance.''

Examples of smelting practice are given below.

1. Consolidated Mining & Smelting Co. of Canada, Trail, B. C. The amount of flotation concentrate smelted is too small to afford reliable data. It is charged directly into blast-furnaces, so that the dust-loss probably is serious. A briquetting plant is being installed.

2. Omaha Plant, American Smelting & Refining Co., Nebraska. The copper concentrate, used incidentally to supply sulphur to the charge, is briquetted with 7% lime, and, after drying for 72 hours, is charged into the blast-furnaces. This material, even after briquetting, produces considerable flue-dust.

3. U. S. Smelting Co., Midvale, Utah. The concentrate is shoveled from the cars and is briquetted with flue or bag-house dust, heavy with lime that had been introduced for the purpose of neutralization. The cost is about $1 per ton. The sintering in Dwight-Lloyd machines is not good, due to a poor mixing. The product is smelted in lead blast-furnaces. Flotation concentrate is considered a great nuisance.

4. Garfield Smelting Co., Garfield, Utah. The flotation concentrate is mixed with table and vanner products. It is then bedded with fluxing ores and later fed to McDougall and Herreshoff roasters. While the quantity of flotation concentrate treated is too small to cause any serious difficulty or to require special treatment, close observation shows that it has a tendency to form lumps that do not break up easily in the roasters. In fact, some lumps roast only on the outside. A large increase in the amount of flotation concentrate handled would probably necessitate a special feeding device.

5. Selby Smelting Co., California. The flotation concentrate is unloaded by shoveling and is spread out to dry. Cost for spreading is about 30c. per ton. It is then sintered and smelted in lead blast-furnaces. No trouble is experienced, other than the production of a large amount of flue-dust.

6. Anaconda Copper Mining Co., Montana. About 20% of fine table and jig concentrate is mixed with the flotation product. This is delivered to Wedge roasters by belt-conveyors. Each furnace-bin holds 25 tons. A large steel apron-feeder is used for supplying the material to the furnace. The roasted product is extremely fine and difficult to handle. It is loaded into covered cars in a tunnel that is entirely closed except for a stack at one end, which produces a slight draft. The amount of dust issuing from the stack is small. If sufficiently valuable, the dust could be recovered by a Cottrell precipitator.

The smelting in coal-fired reverberatory furnaces presents no difficulties.

7. Murray Plant, American Smelting & Refining Co., Utah. The flotation concentrate arriving at this plant is wet and sticky, and bad to handle. It is mixed with sulphide ores and roasted or sintered and then smelted in lead blast-furnaces. It is considered to have an adverse effect on the smelting process. It chokes the roasters and tends to give a poorly-roasted product. The dust-loss is heavy. The fine powdery product is objectionable from a lead-smelting standpoint.

8. Ohio & Colorado Smelting & Refining Co. All flotation concentrate is either pre-roasted and sintered or sintered directly. The pre-roasting is done, after mixing with coarser material, in Godfrey and Wedge furnaces. The flue-dust and mechanical dust-loss is increased. Dwight-Lloyd machines are used for sintering. Even though coarser material is added, the capacity of the sintering-machines is decreased.

9. Bartlesville Zinc Co., Bartlesville, Oklahoma. The zinc concentrate from filter-presses is unloaded by shoveling. It must be dried in a machine of special design to avoid excessive dust-loss. It is then roasted in ordinary kilns. Allowance for excessive dust-losses met with at every step in its treatment should be provided for when purchasing flotation concentrate.

10. Braden Copper Co., Chile.[4] The first flotation concentrate produced at the plant was so wet that it could not be briquetted, and so fine that it was hard to filter and dry. When charged directly into the blast-furnaces, the amount of coke required was increased from 12 to 16%. The drained concentrate from the bins contained 50% moisture and the filtered concentrate ran 30% moisture. After much experimenting, it was found that nodulizing in rotating kilns gave a product that was a first-class smelting material.

11. International Smelting Co., Miami, Arizona. The concentrate is unloaded from steel cars, having removable bottoms, onto belt-conveyors that deliver it to bedding-bins, where the necessary fluxes are added. The beds contain about 4000 tons, 80% of which is flotation concentrate, and are made in V-shaped steel bins that have removable-slat bottoms. Beginning at one end, the mixture is fed from an approximately vertical face onto a belt-conveyor, which discharges into Wedge roasters, used as driers only. The material is sticky and hard to handle. It is dried to about 14% moisture, and is then fed to

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[4] R. E. Douglass and B. T. Colley, *Eng. & Min. Jour.*, February 12, 1916.

oil-fired reverberatory furnaces. The difficulties in smelting are practically of a mechanical nature, due to the handling of this extremely fine charge, 50% of which is – 200 mesh. The plant was designed for smelting flotation concentrate, and every precaution was taken to avoid dust-losses.

12. At Mt. Morgan, Queensland, Australia,[5] an ore containing about 2% copper and from $5 to $7 in gold is treated by flotation. Nearly 70% of the gold is free. It was found that by grinding the ore very fine, much of the gold was caught in the thick froth of the flotation-machine. The ore was ground to 80-mesh. There was no increase in the saving of copper, but the extra gold recovered paid for the cost of grinding. As long as only a small tonnage was treated, the concentrate was mixed with blast-furnace flue-dust, in the proportion of 1 : 3, and sintered in a Dwight-Lloyd machine with excellent results. But when the percentage of concentrate was increased, the sulphur content rose to such a figure that the machine did not give a good product, and its capacity was reduced, owing to the choking of the bed by fine concentrate. Pre-roasting followed by pot-roasting was then tried. An Edwards furnace was first used, but the roasted product was so fine that it could not be handled in the Dwight-Lloyd machine or in the pots. Tests made by pre-roasting in a Godfrey furnace and sintering in pots proved satisfactory, and such a plant was installed. It was found that the product from the Godfrey furnace was coarser than the concentrate, some agglomeration evidently taking place. A sketch of one of the sintering-pots is shown in the accompanying figure.

13. Tacoma Smelting Co., Tacoma, Washington. The flotation-concentrate arriving at this plant is unloaded from ships in tubs that are filled by hand-shoveling. Owing to the sticky character of the material, this work is disagreeable and costly. Roasting is done in Herreshoff furnaces, the upper floors of which are used for drying only. It is necessary to clean the roasters frequently. Reverberatory furnaces are used for smelting. Elaborate machinery must be used in order to keep dust-losses from becoming excessive.

14. Helena (Montana) plant of A. S. & R. Co. Unless filtering or drying has been done at the mill, the flotation-concentrate sent to this plant carries from 20 to 25% moisture. In summer this material has the consistence of liquid mud, and could almost be unloaded from cars by means of a pump. In practice, men wearing high rubber boots shovel the concentrate from the cars into bins. The cars can be washed

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[5] B. Magnus, 'Sintering Flotation Concentrates.' *Eng. & Min. Jour.*, June 10, 1916.

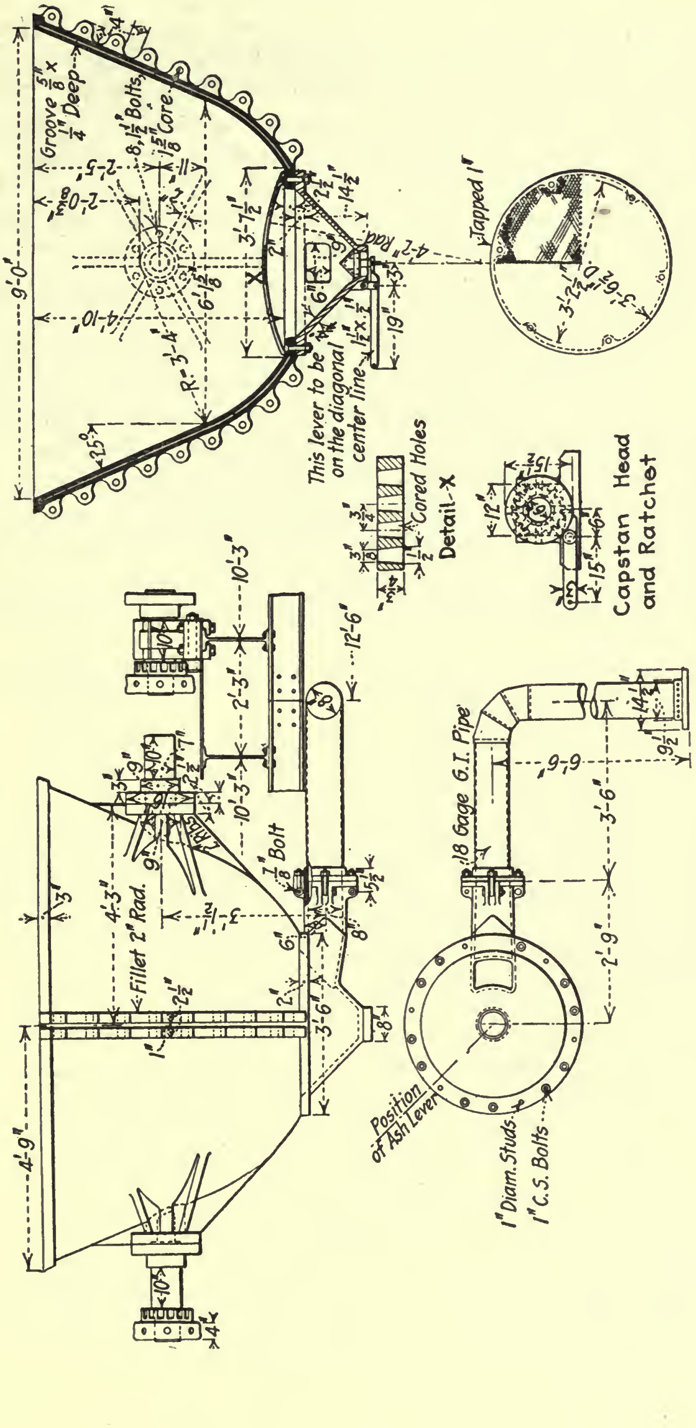


FIG. 4. SINTERING-POT USED AT MOUNT MORGAN.

out, but the material sticks to the sides of the bins, dries, and causes loss from dusting. In winter the concentrate will freeze solid in the car, and has to be thawed or else mined with gads and picks. The cost of unloading is then excessive. No particular difficulty is presented when the concentrate has been dried or filtered before shipping. The lead concentrate is first sintered in Dwight-Lloyd machines. From 10 to 15% of flotation-concentrate is mixed with miscellaneous sulphide ores, including a small quantity of matte and from 5 to 10% of crushed limestone. With this mixture a fairly good sinter can be obtained. This material is then transferred to H. & H. pots, where it is converted into a slagged and fairly porous product containing less than 2% sulphur. Smelting in lead blast-furnaces presents no difficulties. Owing to its extreme fineness, smelters must necessarily suffer considerable loss from dusting when handling flotation-concentrate. This loss is undoubtedly higher than in the case of ordinary ores or coarse concentrate; therefore it justifies a higher charge for treatment.

SUMMARY. The various methods of handling froth may be classified as follows:

1. Breaking by means of centrifugal pumps, bucket-elevators, jets, or on tables.
2. Dewatering in tanks, with or without filter-bottoms. Steam may be used to assist drying.
3. Dewatering in classifiers of the Ovoca and Akins type.
4. Continuous thickening, followed by filtering.
5. Intermittent thickening, followed by filtering.

The use of tanks for dewatering concentrate necessitates unloading by shoveling, unless the tonnage to be handled is sufficiently great to warrant the installation of a crane and grab-bucket. The cost of loading varies from 10c. per ton, where the concentrate can be shoveled directly into cars, to 25c. and more per ton, when wheelbarrows must be used. In case gondola cars are to be loaded, a belt-conveyor will reduce the cost to 2 or 3c. per ton. The employment of steam for drying can hardly be recommended, especially where pipes are placed in tanks. The concentrate should be spread out in a thin layer on a uniformly heated surface. In a tank the concentrate in contact with the steam-pipes is quickly dried, but the moisture is driven out only to condense in the main body of the concentrate, which dries very slowly. Such a method of dewatering is necessarily expensive. Filter-bottoms for tanks may be advisable where the concentrate drains fairly well, and, in such instances, the trouble from accumulated froth is eliminated. Where the water must be decanted from settled concentrate, the decanting apparatus should be so designed that it can work in the clear water between the unbroken floating froth and the top of the settled concentrate.

Continuous thickening, followed by filtering, is a method commonly employed, but the troubles arising from the accumulation of floating froth in the thickener and the difficulty, at times experienced, in getting a spigot product low enough in moisture for satisfactory filtering should be considered when making such an installation. One large company gives the cost of thickening in Dorr thickeners, dewatering on a continuous filter and loading by gravity at 65c. per ton. Another company states that thickening and filtering (continuous type) costs 10c. per ton. Intermittent thickening, followed by filtering, seems to offer the most positive control over the moisture in flotation concentrate. Filters of the pressure type will give good results on material that cannot be satisfactorily treated on vacuum-filters.

A preliminary treatment, before smelting, is nearly always given flotation concentrate. Such treatment would come under one of the following heads, although two or more may be combined:

1. Drying.
2. Briquetting.
3. Nodulizing.
4. Sintering.
5. Roasting.

The difficulties in the smelting of flotation concentrate are caused by the extreme fineness of this material. Briquetting should be a good method of preparing the concentrate for direct smelting in blast-furnaces, but it is not easy to make a strong briquette that will not break up and produce much flue-dust before it is smelted. Nodulizing gives an excellent smelting product, besides driving off some sulphur, but the loss in dust may be considerable. Roasting presents such troubles as the necessity of specially designed feeders for furnaces, the formation of accretions, and the non-roasting of the interior of lumps, heavy dust-losses, and the production of a light fluffy product that is not easy to handle. The cake from sintering or pre-roasting and sintering is quite suitable for feeding to blast-furnaces, but it is necessary to mix coarse material with the flotation concentrate in order to get a well-sintered product and to prevent too great a falling off in the capacity of the machines.

At the present time flotation concentrate, being a new and unusual material, is difficult to handle. Unless specially designed for the purpose, smelters cannot be expected to treat this product in the smooth manner of their regular work. However, metallurgists are keenly interested in solving the problems thus presented, and, as the tonnage of ores that are being concentrated by the flotation process increases, plants smelting only such concentrate will soon experience no serious hindrance to satisfactory operation.

SUMMARY OF RESULTS WHEN TREATING SLIME AT ANACONDA

1. The economic capacity of the M. S. No. 1 machine when treating slime, as produced from the mill at present, is approximately 80 tons per 24 hours. We have found that the tonnage treated by the experimental machine, which had agitator boxes 2 ft. square, is to that treated by the full-size machine, with boxes 3 ft. square, as the cross-sectional area.

2. The best combination of reagents for the treatment of slime seems to be sulphuric acid, kerosene acid-sludge, wood-creosote, and stove-oil. There is some question as to the real value of stove-oil—its principal function being to make a more compact froth.

3. It would not be economical to retain the round tables, as the recovery by treating the slime directly by flotation is just as high as by retaining the round tables and treating the round-table tailing by flotation. The heating of the round-table tailing pulp, on account of its low density, would increase the cost of flotation.

4. In treating the round-table feed directly by flotation, the resulting tailing should assay 0.30% copper, or less, with a concentrate carrying not over 40% insoluble. Possibly the concentrate can be made much cleaner with no sacrifice in the recovery.

5. It is thought that the best circuit-density for the slime-pulp in flotation treatment is about 12% solid.

6. It is thought that about 70° F. will be found to be the most economical temperature at which to keep the pulp.

7. Acid seems to be absolutely essential to the successful treatment by flotation of our slime.

8. The addition of air in the last spitzkasten is of no advantage.

9. Any considerable increase in speed of the agitators above a peripheral speed of about 1300 ft. per min. seems to be disadvantageous.— F. Laist and A. E. Wiggin, Trans. A. I. M. E.

MECHANICAL DEVELOPMENT IN FLOTATION

By O. C. Ralston

(Written especially for this volume)

The greater number of inventions that have appeared in connection with flotation during recent years have been of a mechanical nature. Many of them have been mistaken by the uninitiated as belonging to new processes but usually they are only old ideas in a slightly changed form. The more ordinary types of such machines have often been described in the technical press and so will be omitted from this discussion or only briefly mentioned. Many of them are true improvements in the art and many are crude modifications of a good fundamental type designed to avoid infringement.

Mechanical Froth-Making Machines. In froth-flotation there are many ways of introducing gas into the pulp; one of the oldest and best is to beat air into the pulp by the use of rapidly revolving propellers.

Hoover's book gives drawings of many of the earlier types of machines. These have been used so often in later papers by different writers that they need not be described here. Only the present standard single-level M. S. machine need be shown. See Fig. 1 and 2. This also has been described often. The only thing to be mentioned here is that the gears on the drive-shaft are so set that alternate ones drive the impeller-shafts in opposite directions in order that the thrust on the drive-shaft will be zero—an important point in design. The drive-motors are usually placed at the head of the machine unless hot pulp is being used or acids are being added, in which case the motors are placed at the other end of the machine, so as to avoid steam and corrosive vapors. Fig. 1 shows two standard machines placed back to back in order to economize floor-space. The result of this method of placing the machines and the method of conducting away the concentrate in launders is indicated in Fig. 3, which shows the longitudinal section of the slime-flotation plant at Anaconda.

By making the impeller-shaft horizontal and turning the blades in a vertical plane, G. B. Eberenz and J. I. Brown, of Cripple Creek, claim a new invention. Their machine is shown in Fig. 4, which is taken from their patent (U. S. 1,187,822 of June 20, 1916). The patentees make the following claims: The blades revolving in a vertical plane can beat air into the pulp more effectively. The pulp is driven down into the bottom of the spitzkasten instead of into the side, as is

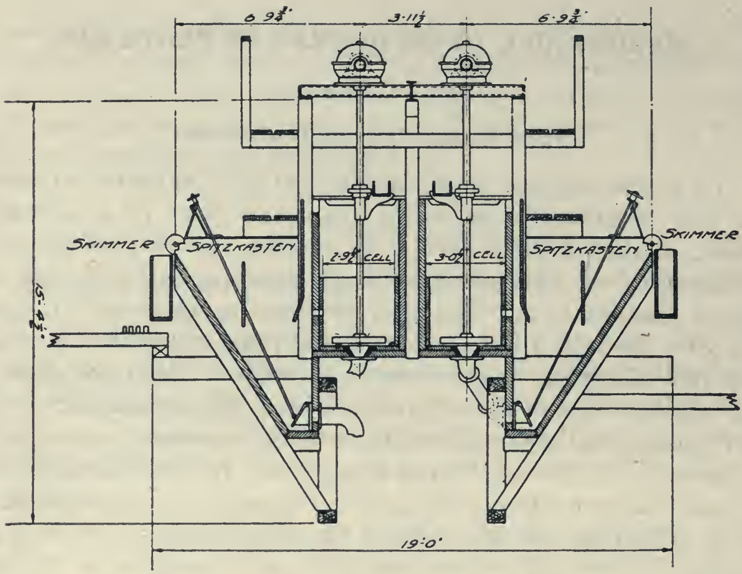


FIG. 1. STANDARD M. S. MACHINES PLACED BACK TO BACK

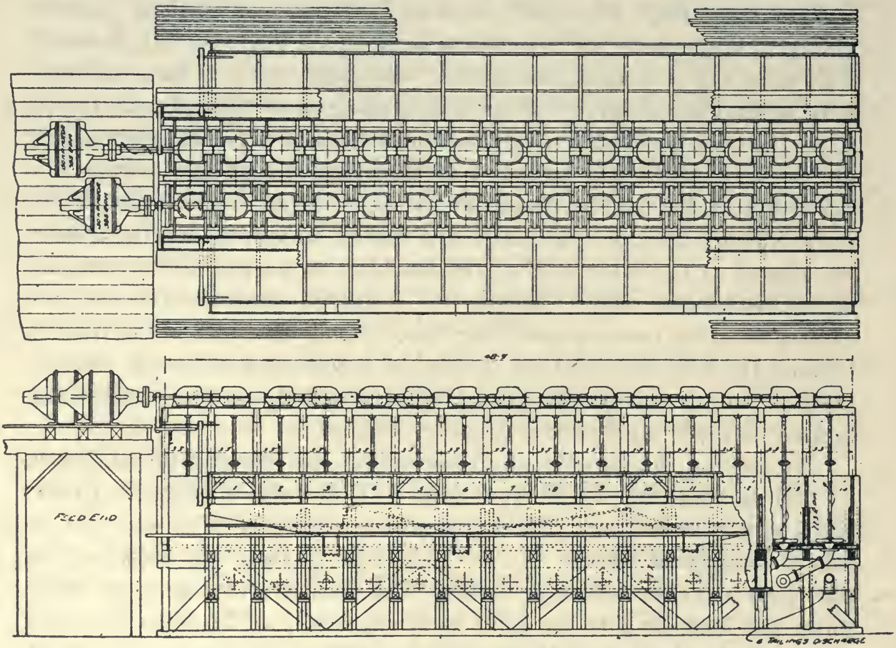


FIG. 2. STANDARD SINGLE-LEVEL M. S. MACHINES

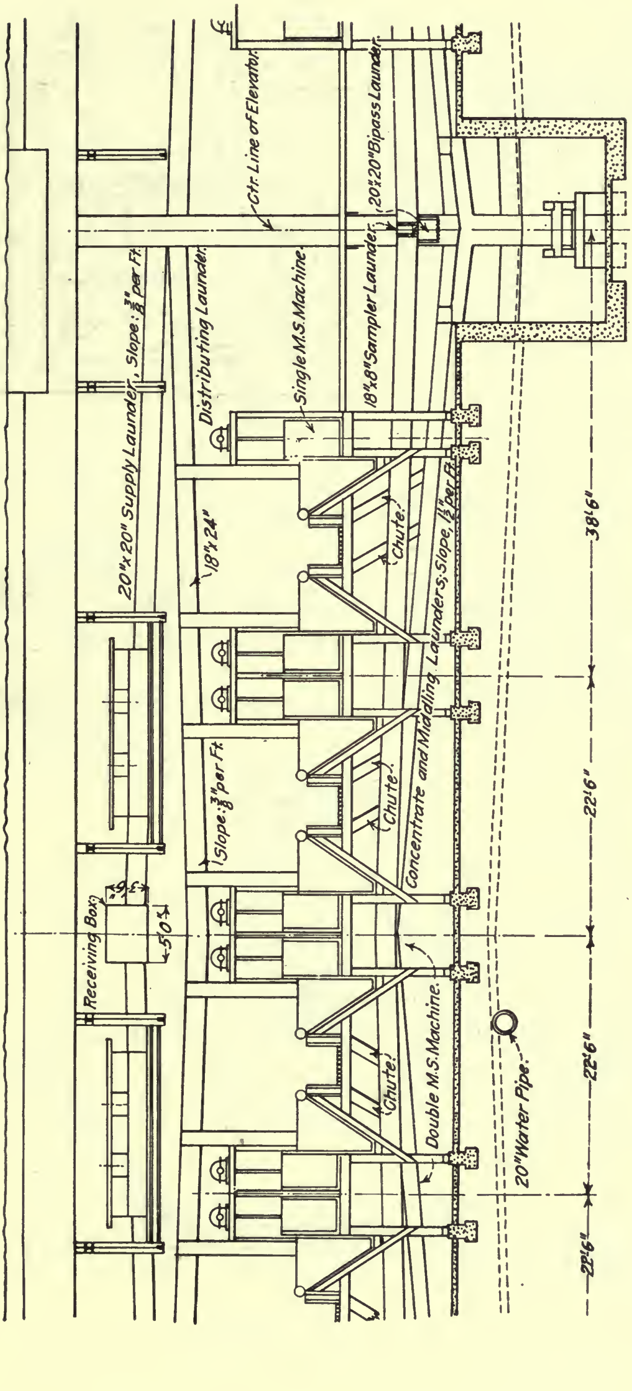


FIG. 3. LONGITUDINAL SECTION OF SLIME-FLOTATION PLANT AT ANACONDA

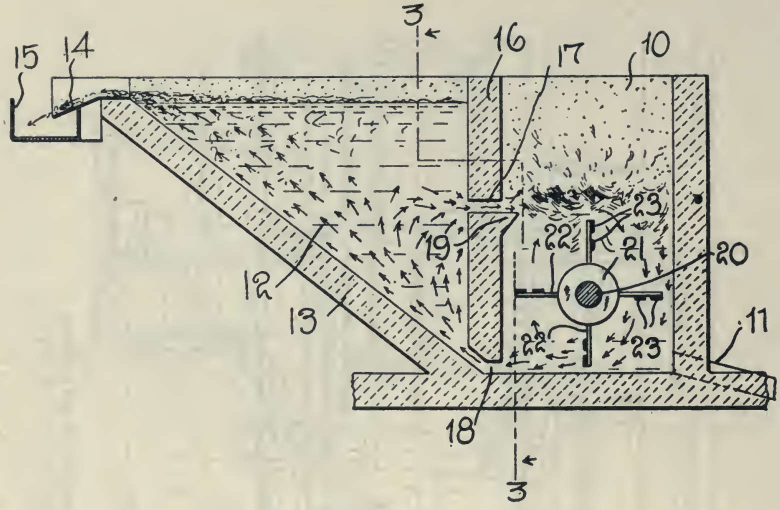


FIG. 4. EBERENZ & BROWN MACHINE

usual in the Minerals Separation machine. A better churning-in of the oil and air is claimed and it is stated that in practical operation the machine makes so much froth through the action of the agitators that no frothing-oil is necessary.

Charles E. Rork, of Douglas, Arizona, invented a machine that

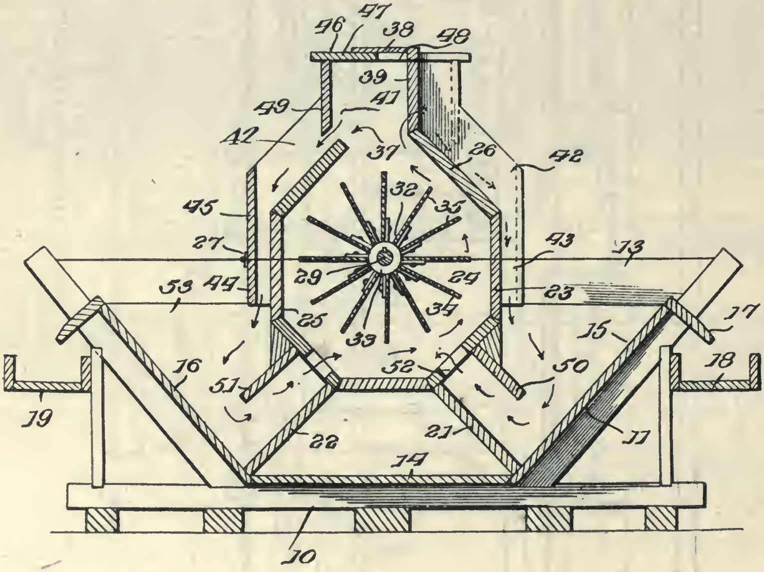
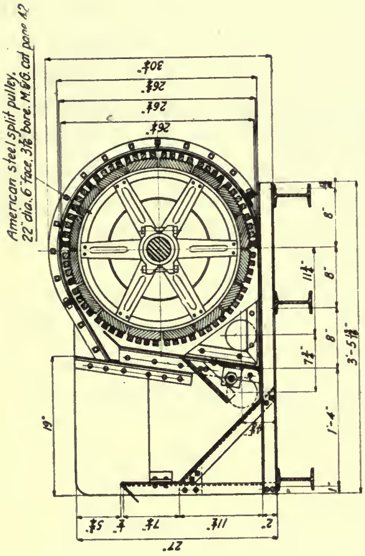


FIG. 5. RORK MACHINE



K. & K. MACHINE. CROSS-SECTION

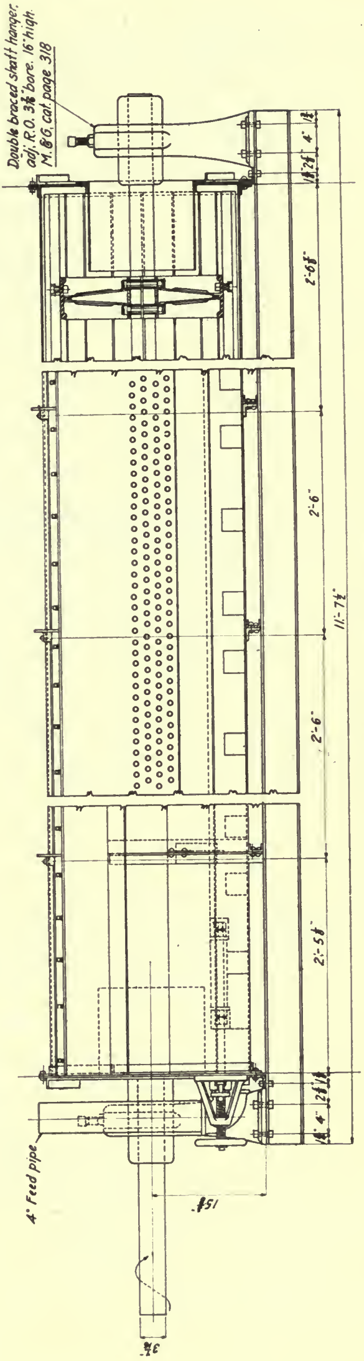


FIG. 6. K. & K. MACHINE. LONGITUDINAL SECTION

was tested in several of the mills of the Phelps-Dodge company, notably the Burro Mountain plant at Tyrone, New Mexico. It was patented on April 20, 1915, and the patent drawings are shown in Fig. 5, as taken from U. S. 1,136,485. By comparing the figures it can be seen that in the machine of Eberenz & Brown the shaft passes through the end wall of the machine beneath the level of the pulp while in Rork's machine the shaft is above the level of the pulp and hence not subject to continual abrasion, leakage, etc. The paddles merely dip into the pulp and throw it into the top of the beating-chamber. The advantages of having only one rotating shaft are obvious, and if there were no other advantages over an M. S. machine one might expect this machine to have lower maintenance costs. However, a disadvantage has been discovered in having such a long shaft supporting beating-blades in three or four successive compartments. This shaft is likely to whip unless it is of rather large diameter. Thus the length of the machine is limited. In the tests at Tyrone, Rork's machine was found to use more power than had been expected. On that account modifications of the machine were made until it finally resulted in the form shown below. This is now known and sold as the K. & K. machine, named after the inventors, Max Kraut and F. B. Kollberg, both of Douglas, Arizona.

By expanding Rork's shaft and beaters into a cylindrical drum with a riffled surface, as seen in Fig. 6, considerable longitudinal strength was gained and it was found that the power-consumption was considerably lowered. The whirling cylinder dips into the pulp and the air is trapped between the riffles. The moving part is almost perfectly balanced and the weight of entrained pulp is relatively small. The low consumption of power is a natural consequence of this design and raises the question whether other machines do not whirl all of the pulp to their disadvantage. While the pulp is passing around with the cylinder of the K. & K. machine the centrifugal force is tending to drive it out, so that it receives a considerable aeration in a single revolution of the cylinder and is thrown through the air at the top, to drop into the frothing-spitzkastens. These are four in number.

This machine retains all of the advantages and eliminates some of the troubles of the Rork. The claim is made that it requires no blowers, no compressed air, and no pre-agitators. As far as pre-agitators are concerned, I believe that any machine can do better and faster work if the oil is already well disseminated in the pulp when it reaches the flotation-machine. Otherwise, the machine is extremely simple

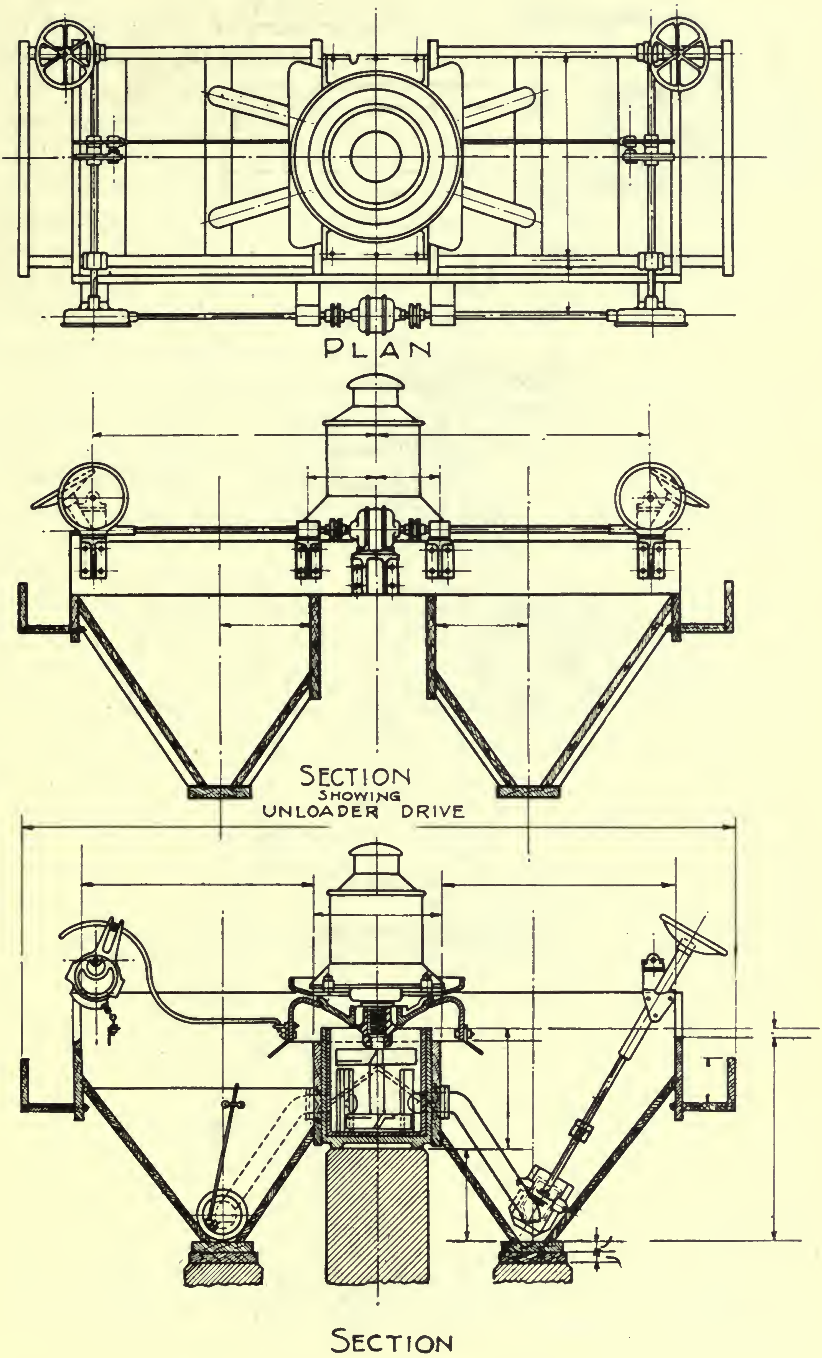


FIG. 7. JANNEY MACHINE

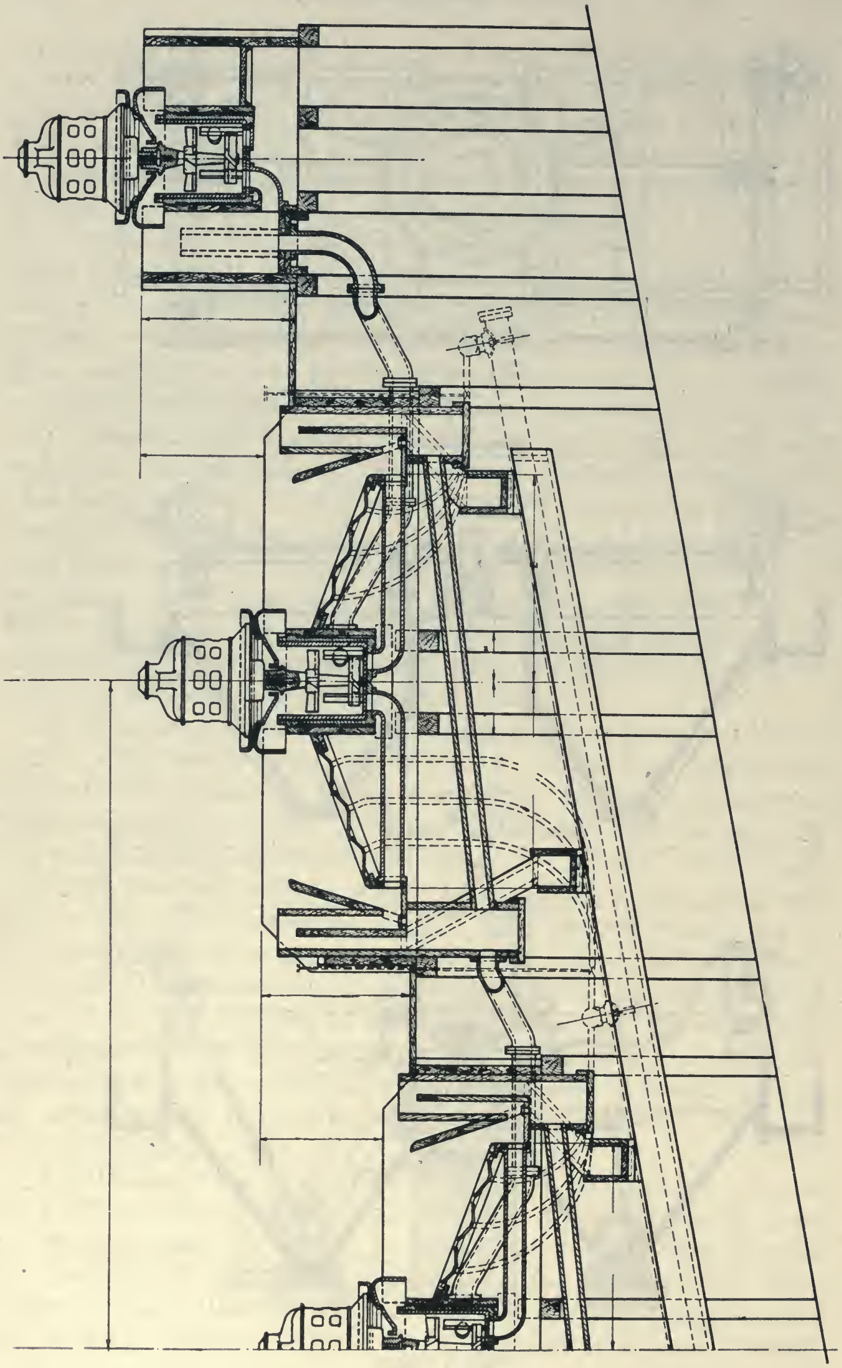


FIG. 8. JANNEY AIR-MACHINE

and requires only a single belt-and-pulley connection to a source of power. The inventors claim a capacity of 80 to 150 tons per 24 hours with 10 to 15 horse-power. These figures seem low and have caused many engineers to doubt their reliability. The fact that these machines are used in nearly all of the mills of the Phelps-Dodge companies would indicate that they must have decided merit. The lively appearance of the froth is very attractive. I am inclined to suspect that with low-grade ores these machines would not give as low a tailing as other machines, although they are known to make a high-grade concentrate; therefore it seems advisable to supplement them by pneumatic machines, to glean the tailing.

The Janney machines are of two types; the mechanical and the mechanical-air cells. Both are used in large numbers in some of the largest copper-concentrating mills. They are the invention of T. A. Janney, mill-superintendent of the Utah Copper Company.

The 'mechanical' machine is shown in Fig. 7. This shows that two impellers are used on the same shaft and that the pulp is agitated violently against baffles, which are part of a cast-iron liner. The whirling of the pulp over the top of the liner allows it to flow into the spitzkasten, of which there are two for each agitation-chamber. The agitator-shaft is a continuation of the motor-shaft, being screwed into it, and revolves with the motor at about 570 r. p. m. The first machines were made of one main casting into which fitted replaceable liners, but at the present time concrete is being used for the main portion of the machine and cast liners are used to protect all portions subjected to wear. The drawing shows two circulating-pipes, used in each 'spitz,' up which the pulp passes to the agitation-chamber, the head of pulp in the 'spitz' being such that the pulp enters by these pipes to replace the pulp thrown out of the agitation-compartment. Adjustable gates between the adjacent spitzkasten allow the pulp to pass from one cell to the next by gravity. However, the circulating-pipes permit the repeated treatment of most of the pulp in each cell before it passes to the next one. The drawing also shows a good design of a froth-remover which allows any depth or length of stroke.

Since these cells are separately constructed they can be installed in a variety of ways to suit the convenience of the designer. Fig. 8 shows part of an equipment of two mixers and 15 cells in a row. The feed is split between the first five cells. These make clean froth. The tailing then passes in series through the remaining cells, which make middling. This is called the 'multiple-series' arrangement. The machine is especially adapted to the flotation of coarse material such

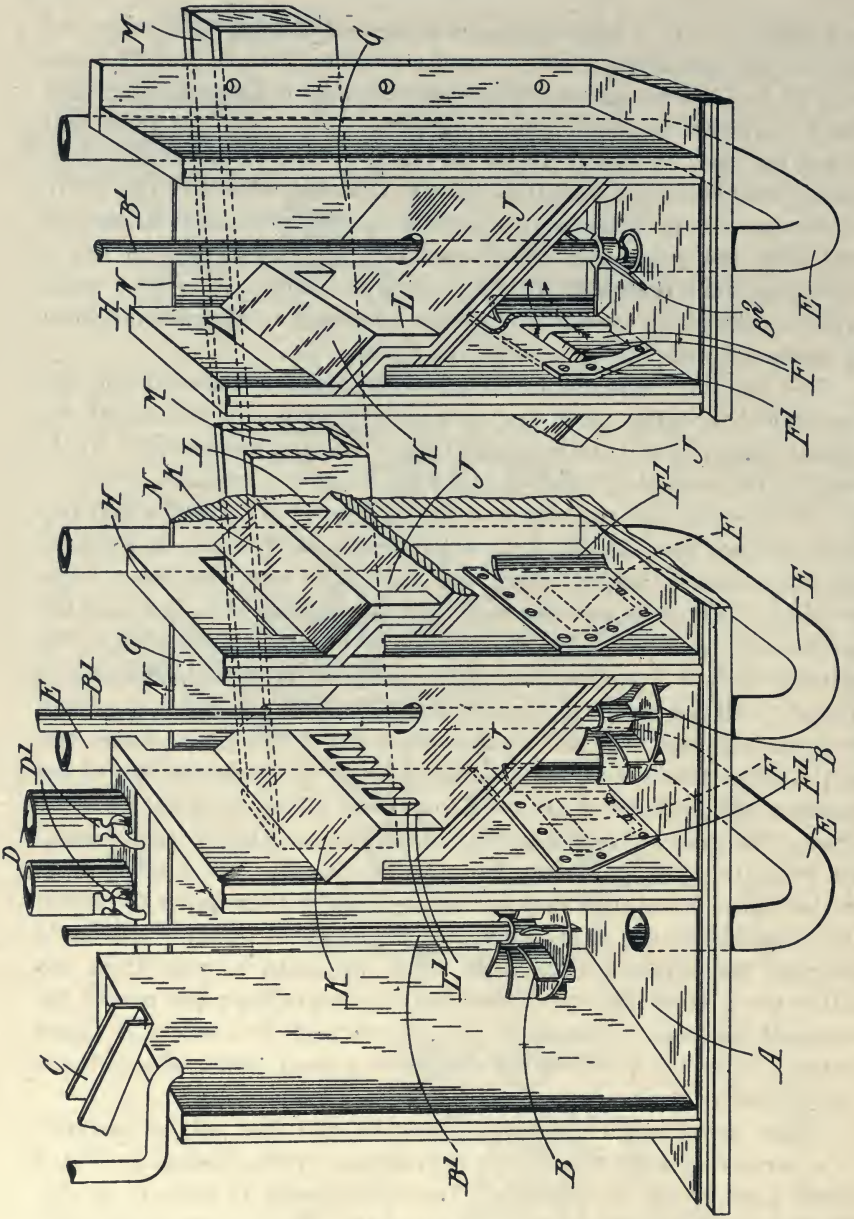


FIG. 10. HIGGINS & STENNING SUB-AERATION MACHINE

as low-grade concentrate produced by vanners and the like. The percentage of solid in such feed should range between 20 and 23. The motors use about 10 hp. each, consequently an installation of this type of machine requires more power than almost any other standard device

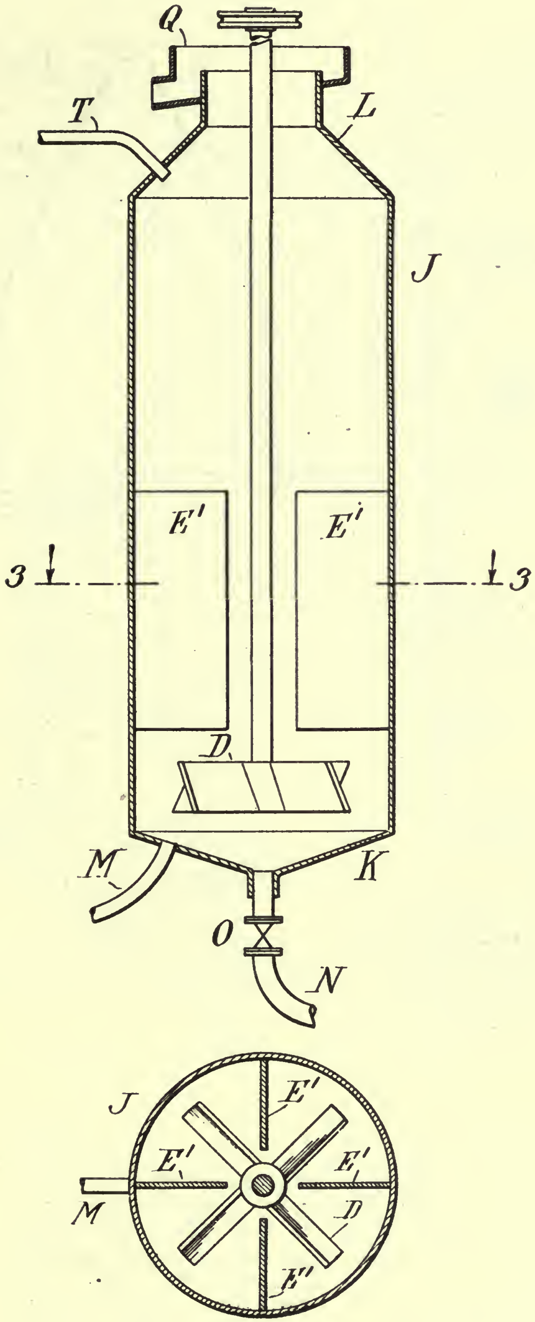


FIG. 11. THE OWEN MACHINE

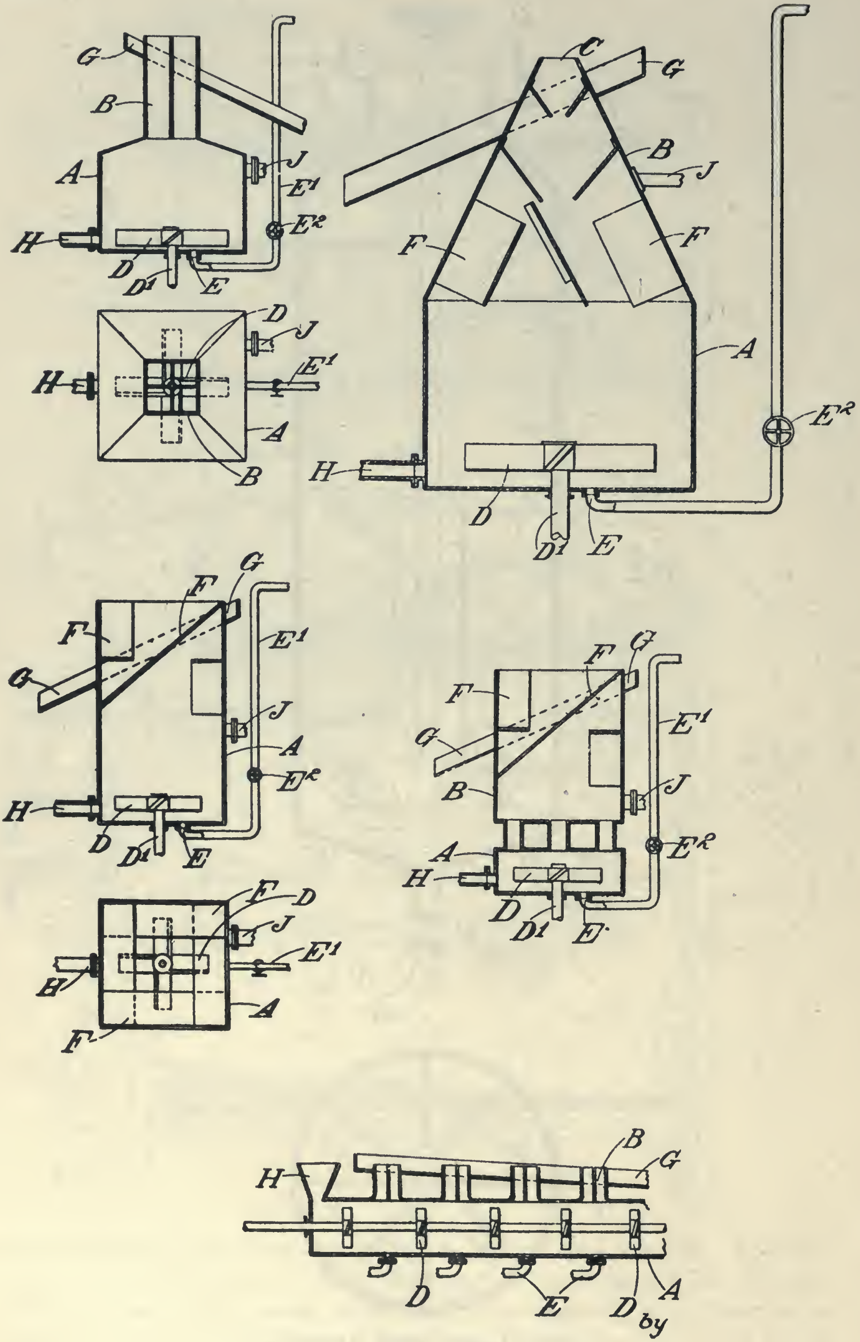


FIG 12. THE HIGGINS MACHINE

used for flotation. On that account, the later 'mechanical-air' cell has displaced it to a great extent.

The mechanical-air cell, as shown in Fig. 8, likewise utilizes a vertical-shaft motor set directly over the agitation-compartment. The impeller-shaft is a continuation of the motor-shaft. The bottoms of the spitzkasten are covered with a slanting air-mat, similar in construction to that in Callow cells. A pneumatic froth is produced, which flows over the discharge-lip of each 'spitz' without the necessity of a skimmer. The tailing drops into a box-like arrangement at the foot of the air-mat and thence passes up over a weir of adjustable height (not shown). The adjustment of the height of this weir regulates the depth of pulp in the spitz. Usually, the weirs require little manipulation after once being set to give proper depth of froth.

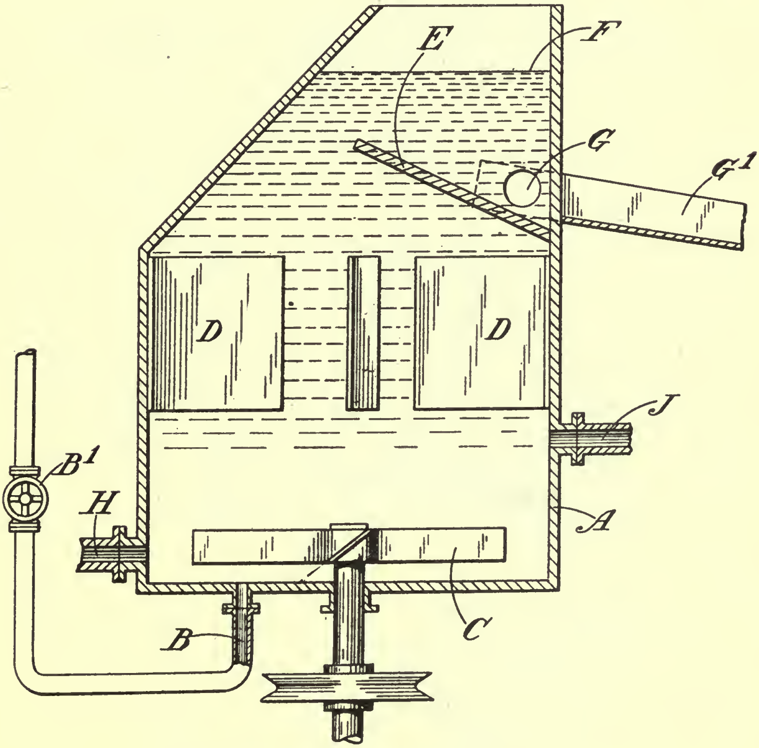


FIG. 13. WOOD SUB-AERATION MACHINE

The motor uses less power than that of the mechanical machine, averaging 7 hp. per cell. About 150 cu. ft. of air per minute at four to five pounds pressure per square inch is needed for each machine. Two operators can easily serve a unit of 3000 tons and have to adjust only the amount of air in the wind-boxes and occasionally the oil-feed.

These machines are placed either side by side or end to end, according to the preference of the designer. About five of them in series are used for roughing and two for cleaning. Such an equipment, together with an emulsifier, treats 150 to 200 tons per 24 hours. By decreasing the amount of air it is possible to raise the grade of the concentrate, but the tonnage is lowered.

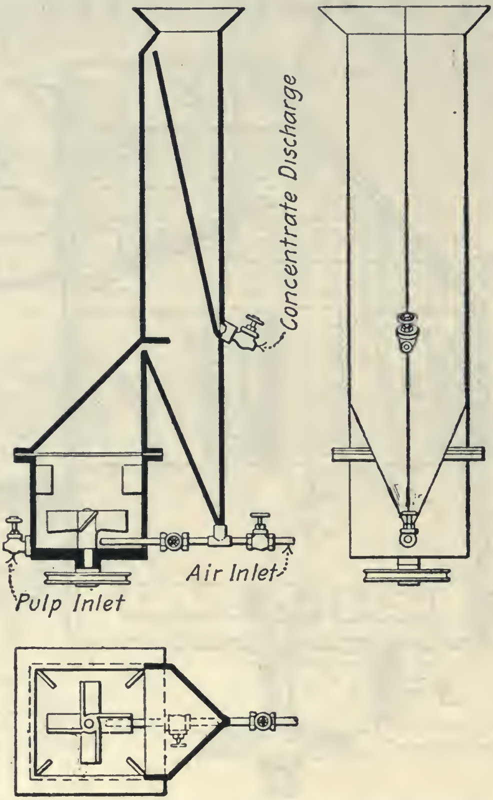


FIG. 14. ANOTHER DESIGN OF WOOD MACHINE

The main wearing-parts are the impellers and the liners. A liner will last from three to five months and the impellers two to three months. A single cell can be shut-down for repairs without disturbing the operation of the others since there is a drop of three feet between them. The motor is lifted off with a small crane, exposing the

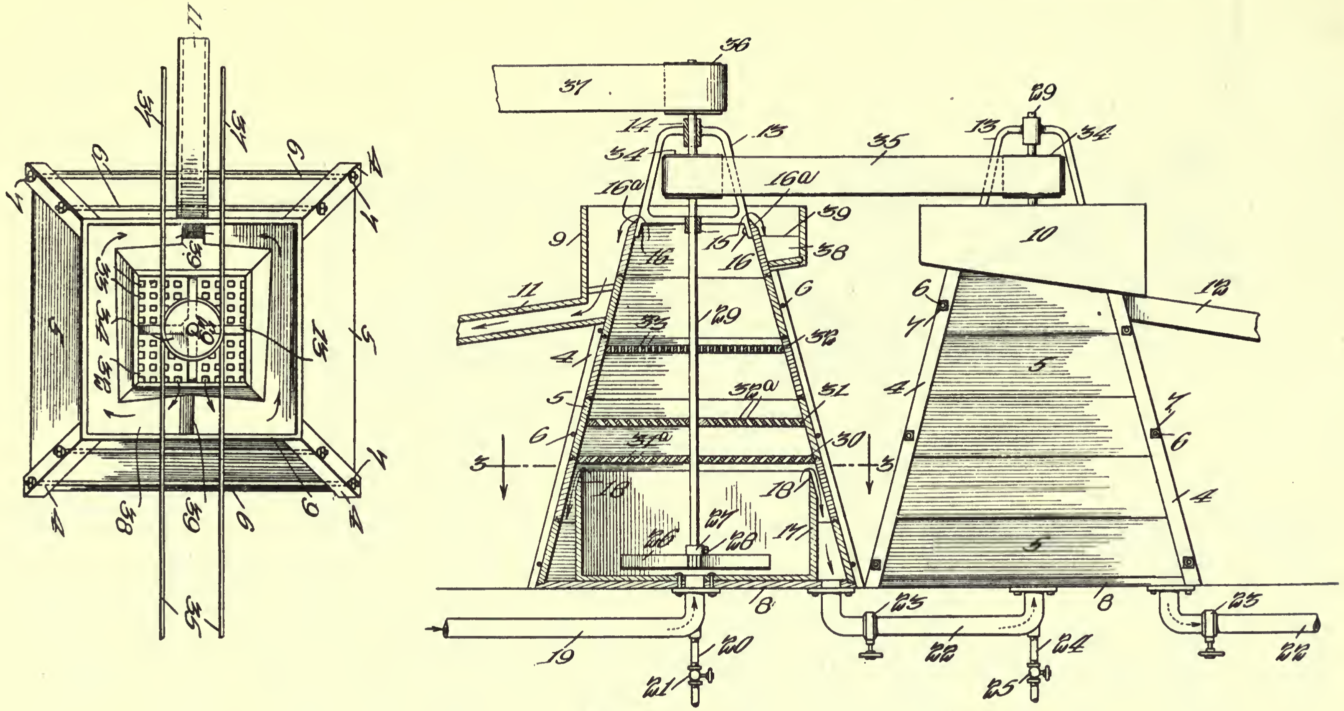


FIG. 15. FAGERGREN & GREEN MACHINE

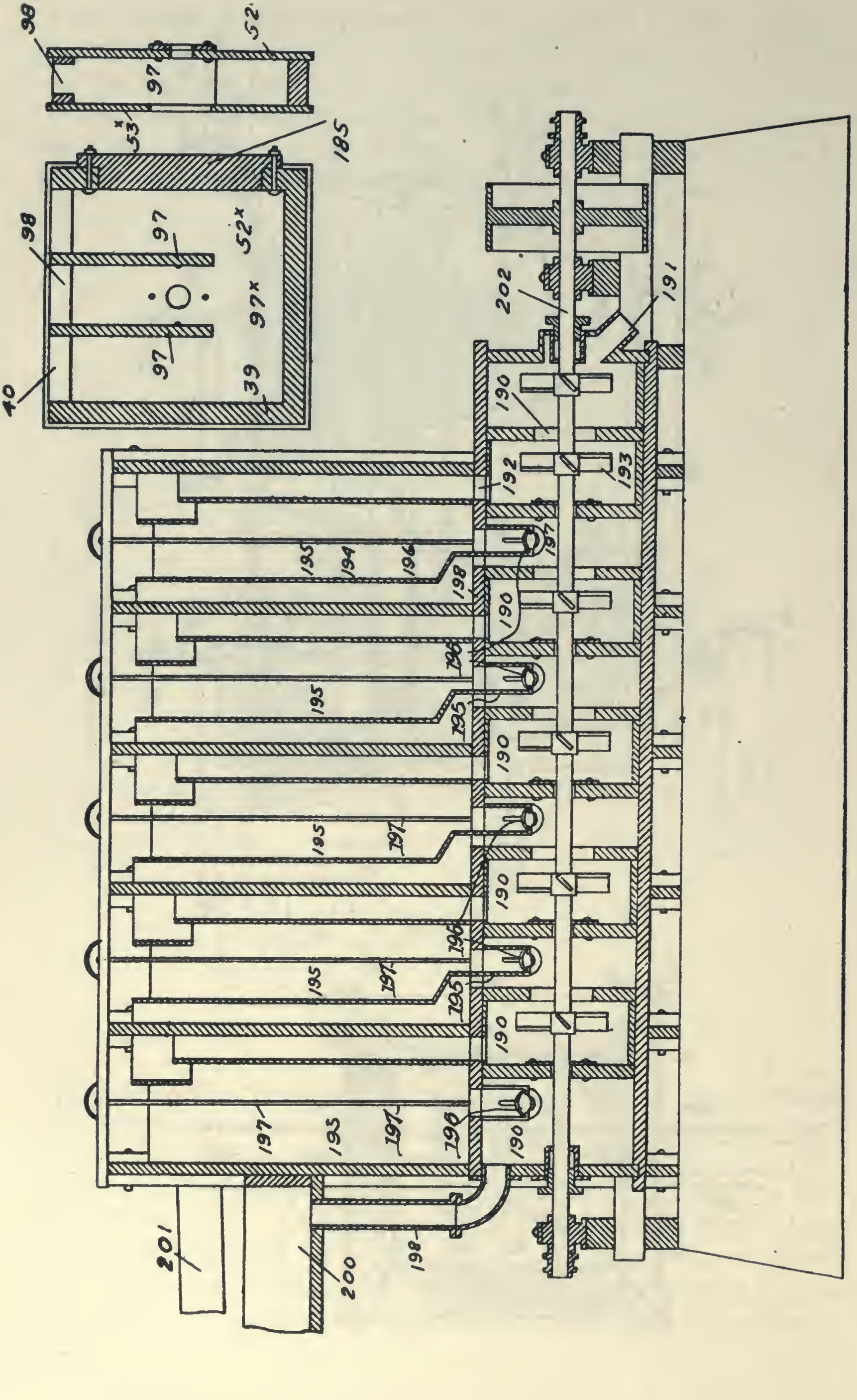


FIG. 16. THE MISCHLER MACHINE

inside of the agitator-chamber. Replacing a liner or screwing on a new shaft with new impellers occupies only about 20 minutes. Hence practically continuous operation is possible.

Since each cell has an agitating-compartment oil may be added at any step in the series.

The use of individual motor-drive for flotation cells is parallel with the tendency to do the same with grinding and concentrating machinery. The designers claim that the first cost is not excessive when compared with the cost of belting, shafting, and super-structure necessary for a group-drive. When shafting is used in a group-drive the settling of buildings and other causes bring about friction in the bearings that support the shafting. Stopping to true-up requires a shutdown of the mill, and this is generally not done. The individual-motor drive eliminates all such difficulties and removes a great deal of superstructure, so that a small crane can have proper access to the cells.

The great disadvantage of the Janney machine is its excessive use of power. Where power is cheap the cost is low but in other localities this item is very important. I also question the advisibility of using agitators after dissemination of the oil in the pulp has been accomplished. The porous blanket cells will then froth out all the mineral without the necessity of using more power for agitation. I am indebted to E. Shores of the Stimpson Equipment Co., which makes these machines, for much of my information and for the drawings.

Sub-aeration Machines. The mention of the use of air-baskets in spitzkastens of the Janney machine suggests the many devices that call for the use of moving blades in the pulp and the introduction of air. After all, the thing desired is to so attach air or gas bubbles to valuable mineral particles that they will be floated in a froth. Whether atmospheric air be beaten into the pulp by mechanical swirling or whether compressed air be introduced into the pulp close to the swirling blades, the result is that bubbles of air are caught in the pulp in front of the impellers and are disseminated through the pulp.

A. H. Higgins and W. W. Stenning invented one of the first sub-aeration machines used in the United States by the Minerals Separation, Ltd. It was protected by U. S. 1,155,815 of October 5, 1915, from which is taken Fig. 10. The reason for the designing of such a machine is given in the words of the patentees:

"One object of this invention is to provide an apparatus in which agitation, aeration, froth formation, and froth separation are effected in one box or series of boxes without requiring the use of spitzkasten. A further object is to remove the froths immediately they are formed so that a mineral-bearing froth ready for flotation shall not be subjected to further agitation with the pulp. An incidental object is to effect the efficient recovery of so-called 'tender' froths from which the mineral has a tendency to shower.''

These objects are attained by introducing air beneath the impellers through the pipes *E*. The impellers beat the stream of air-bubbles into a fine froth, which immediately rises and strikes the inclined baffle *J*, which directs it to the left into the box *K*. The pulp issues into the upper half of this box from the box *K* through the openings *L* and the froth rises to the surface, while the pulp in this relatively quiet zone sinks to the top of the baffle *J* and is deflected to the right, passing through opening *F* into the bottom of the next compartment. The drawing shows the compartment farthest to the left as a mixing-compartment without any froth-overflow. Two different shapes of impeller-blades are also shown. The first of these machines was made with the air-pipes *E* open to the air, with the expectation that the violent rotation of the impellers would create enough suction to pull air into these pipes. This expectation was never justified and compressed air was found necessary. Further, the glands where the impeller-shaft passed through the inclined baffles wore out fast and admitted too much air. The impeller-blades and liners of the beating-boxes wear out soon and are inaccessible, and the machine must be

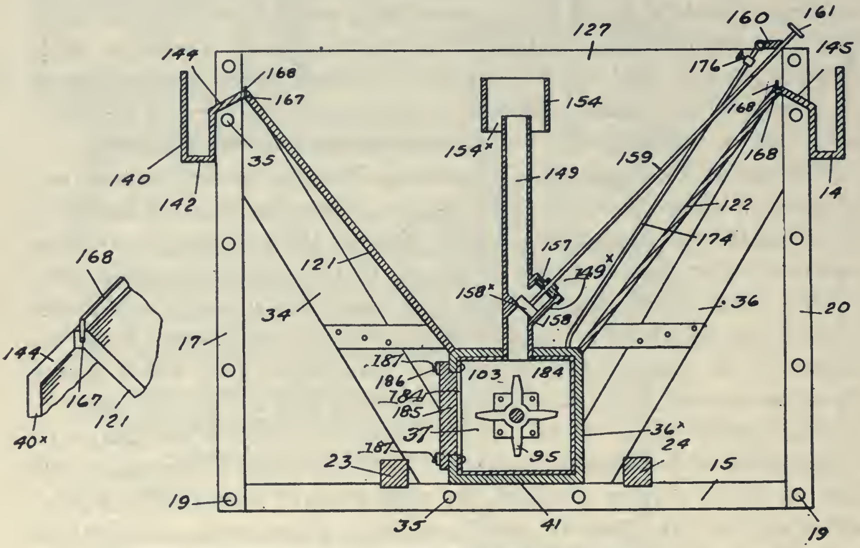


FIG. 17. SECTION OF MISCHLER MACHINE

taken apart in order to replace them. On that account this particular type of sub-aeration cell is not now being used, although a machine of this pattern was employed for a while at Anaconda.

T. M. Owen has invented a much more practical machine which is protected by U. S. 1,155,836 of October 5, 1915. Air is admitted beneath the impeller through the valve *O* and the pulp is fed into the machine through the pipe *M*. The froth rises as soon as it is formed, as can be seen in Fig. 11. The zone below the baffles E^1 is violently agitated, but the baffles prevent the disturbance reaching the upper portion of the cell and the froth has a chance to separate quietly from the pulp. It overflows into the lander *Q* and the tailing passes out of pipe *T*. This machine is accessible for repairs, as can be seen by looking at the section taken through the line 3-3. Moreover, the construction is simple, being especially adapted to steel-work. The constricted top is characteristic of machinery often used in differential flotation, in which a minimum amount of oil is added in order to cause flotation of only one mineral, and excessive aeration is necessary to build up any depth of froth whatever, on account of its tendency to break.

A. H. Higgins gives alternative designs of many similar sub-aeration machines in U. S. patent 1,155,816 of October 5, 1915. These are shown in Fig. 12. In each case the air-inlet is lettered *E*, the pulp-inlet *D*, and the tailing-discharge *J*.

The patentee claims the following advantages for this kind of machine: It is possible to regulate the amount of gas employed for gaseous selection and flotation. It is also possible to regulate the degree of division of the air by the form and speed of the agitator. These are of great importance, as Higgins claims that different ores and different characters of suspended particles are considerably affected by the total amount of air or its degree of division. Further, the amount of frothing-agent to be used with this apparatus may be considerably reduced from that necessary in the usual apparatus for the agitation-froth process. It is characteristic of this apparatus that it has a continuous admission of air at the bottom and continuous feed and overflow above, so that the upper part of the pulp is in a state of comparative quiet although reinforced constantly by a stream of rising bubbles, so that it overflows continuously.

The Hebbard sub-aeration machine is an even simpler type of construction. A long series of compartments like the standard mechanical type of M. S. machine is used, except that large openings are cut in the walls between the adjacent agitation compartments and the spitzkastens have been omitted. A deep heavy grid is placed in each agitation compartment above the impellers and air is introduced under each impeller. The froth overflows from each compartment into a launder. This machine is in fairly common use on account of its simple construction.

The Hebbard-Harvey sub-aeration machine is an improvement on the Hebbard machine made by R. J. Harvey of the Central mine at Broken Hill. The impellers are driven by shafts passing up through the bottom of the machine instead of coming down from above. This removes the unsightly structure above the machine and allows free access to the top but necessitates the maintenance of a packed gland for each impeller-shaft.

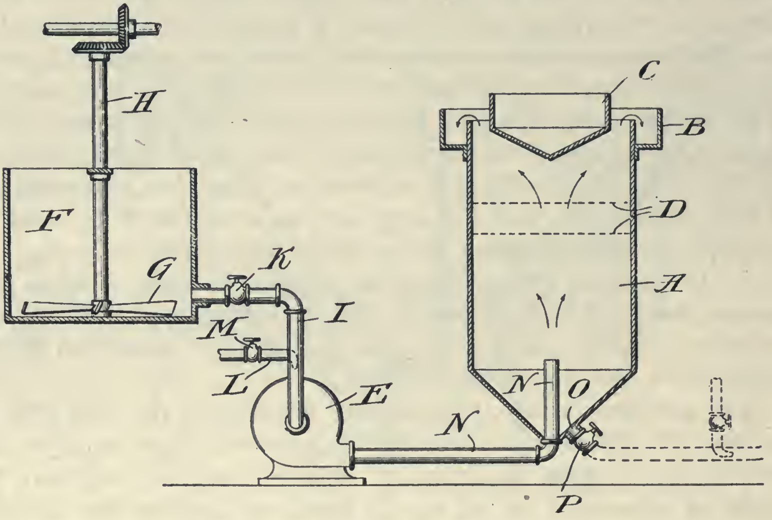


FIG. 18. SECTION OF OWEN MACHINE

The L. A. Wood sub-aeration machine is a somewhat different design, said to be adapted to floating sulphides and other minerals by use of air and without the addition of a frothing-agent or an oil. This is shown in Fig. 13, which is taken from the patent specification, U. S. 1,155,861 of October 5, 1915. The air-bubbles with their associated mineral break; hence a baffle *E* is necessary to catch them. The pulp-inlet is at *H* and the outlet at *J*. Fig. 14 is another design, covered by British patent 10,312 of 1914, also granted to Wood. The process is described as being applicable to the flotation of sulphide ores of copper in neutral pulp at ordinary temperatures; but it has been applied to Broken Hill tailing with the addition of 1% sulphuric acid, and heating to 60° C. is recommended. Differential flotation is also claimed by varying the aeration according to the nature of the ore and the degree of crushing. These patents are assigned to Minerals Separation.

W. Fagergren and W. D. Green, under U. S. 1,195,453 of August 22, 1916, have shown still another design of sub-aeration machine. Its chief claim is simplicity of construction, being made of plain lumber, as can be seen in Fig. 15.

R. T. Mischler, metallurgist for the El Tigre mine, in Sonora, Mexico, has patented a machine in which the agitation-shaft is horizontal and submerged. Fig. 16 and 17 give a general idea of the construction. The pulp-inlet is at 191 and the air-inlet is through pipe 160 and valve 176. The construction seems to be involved and inaccessible although the bolted plate 185, shown in the cross-section, can be taken off for inspection and replacement of the agitators or agitator-chamber lining. The patentee states that the objects of the invention are, "First: To separate the concentrate from the gangue during a repeated agitation of the pulp, in the presence of air or other gas, such agitation being followed by a period of quiescence or separation, when the concentrate rises to the surface, and overflowing, while the gangue settles to the bottom and is subjected to agitation and separation during successive alternating periods, in order to remove the remaining traces of the concentrate. Second: In an apparatus of the character described, to provide a series of alternating agitation and separation chambers. Third: To maintain a minimum power consumption, by simultaneous agitation of the gangue in the agitation chambers. Fourth: To obtain maximum extraction and grade of concentrate by agitation of the gangue, in the presence of air or other gas, and under the pressure of a considerable height of pulp, thereby obtaining the advantage of the expansion of the gas bubbles, as they rise to the surface, carrying the concentrate. Fifth: To obtain from the impulses imparted to the pulp by the agitation in all of the separation chambers, an approximately uniform overflow level for the concentrate. Sixth: To prevent resettling of the concentrate, by minimizing agitation in the separation chambers. Seventh: To prevent the settlement of sand, and the consequent clogging of the apparatus; and Eighth: To transfer the pulp from one chamber to another within zones of intense pulp agitation."

Mischler's machine is covered by U. S. 1,197,843 of September 12, 1916. He claims that the novel principle of his invention consists in the agitation of the pulp, while submerged, with introduction of gas at a considerable distance below the surface and under a considerable pressure of pulp. This means a greater volume of air per unit-volume of pulp than is possible when air is merely being churned into the pulp at the surface. He also claims that a cleaner concentrate is produced by the rupture at the surface of a portion of the sulphide-bearing bubbles, the concentrate thus liberated attaching itself to the underlying bubbles, while the liberated gangue slides from their surfaces.

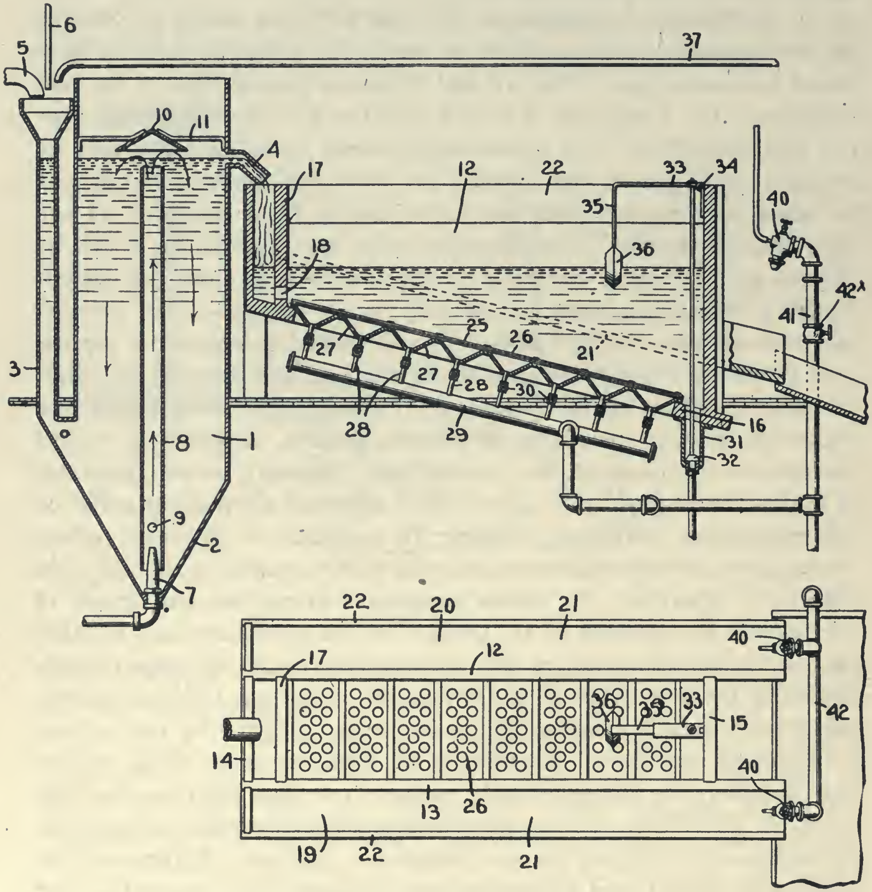


FIG. 19. CALLOW PNEUMATIC MACHINE

The introduction of air into the suction of a centrifugal pump through which the pulp is passing constitutes another method of subaeration. One way of carrying this into effect in a continuous plant is shown in the patent of T. M. Owen (U. S. 1,157,176 of October 19, 1915). The pulp is mixed with the oil and other addition-agents in tank *F* (See Fig. 18) and the air enters the pulp-stream through the pipe *L*. The pump discharges into a frothing-box and the tailing passes out at *O* into the suction of the next pump. Any number of flotation-cells of this construction can be used in series. A crowding cone *C* can be used when the froth is brittle or thin. In this way a close control of the aeration is possible. Owen recommends this apparatus for differential flotation.

The centrifugal pump is also used in the Bunker Hill & Sullivan mill in a machine similar to that of Owen, but this machine, the invention of R. S. Handy, is of more simple construction. The froth-boxes are built into one long box with partitions in which spaces are left for the gravitation of the pulp from one compartment into another. A centrifugal pump, into whose suction a compressed-air pipe is led, draws the pulp from the bottom of each pair of froth-boxes and returns it about half-way up the side. The froth rises and is removed by an endless belt with attached rakes. Where pneumatic machines gave a concentrate of 40% lead this machine gives a concentrate of nearly 60% lead, the restricted agitation causing a clean froth to form. Turning the air-valve slightly in either direction is often enough to spoil the froth.

Sub-aeration machines are now much more popular than the older standard mechanical machines, because the use of them decreases the consumption of power and also of oil. Higher recoveries likewise are obtained. Undoubtedly the introduction of compressed air in flotation-cells usually benefits the operation. Only with an ore or a frothing-agent that gives too much froth is sub-aeration a disadvantage.

Pneumatic Flotation Machines. The use of air for flotation, without mechanical methods for breaking up the bubbles, has undergone notable development during the last two years. At first, the machines were provided with porous media for introducing the air into the pulp, but later this was not always found necessary. On that account pneumatic machines may be divided into two classes, one in which a porous medium is used and the other in which the air is introduced through jets or under pressure.

The standard Callow machine is the invention of J. M. Callow, one of the pioneers in pneumatic flotation. One fairly common design of this machine is shown in Fig. 19 together with the Pachuca in which the oil is mixed into the pulp previous to flotation. The eight air-distributing boxes at the bottom are usually cast in one block and the bottom is unbolted and removed when the canvas needs replacement. Punched-iron plates are shown supporting the canvas rigidly. Sometimes the canvas is overlaid by wire-screen instead of the punched-iron plates to prevent its bulging out or breaking under the air-pressure, or the canvas is stretched tightly and is not otherwise supported. The construction of the bottom also varies in the manner of holding the canvas in place. In the drawing it is clamped between punched-iron plates. It may be clamped with a special frame that goes over each wind-box; or a groove is cut into the frame all the way around each wind-box and the canvas is driven into this groove and held tightly by pounding in a solid rope slightly greater in diameter than the groove. For removal the rope is merely pulled out and a new canvas can then be placed and roped in.

The round type of Callow cell, Fig. 20, was one of the earlier forms tested by him and was protected by U. S. 1,141,377 of June 1, 1915. A carborundum stone was used as the porous bottom; it was satis-

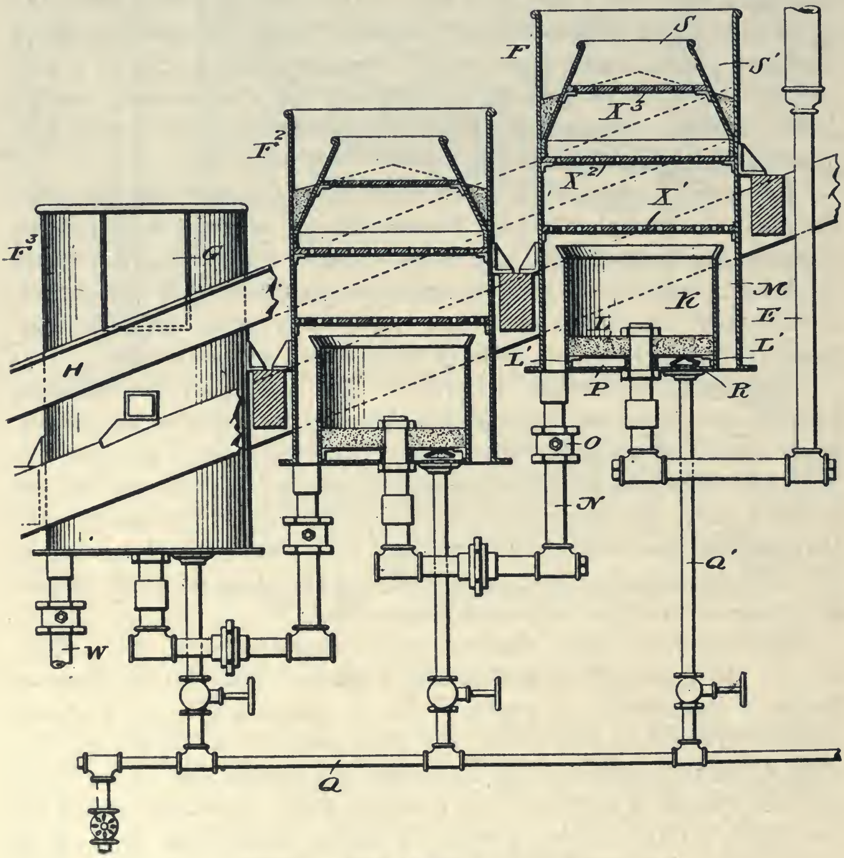


FIG. 20. ROUND TYPE OF CALLOW CELL

factory except that the continued use tended to cause the pores to choke with dirt and grit. 'Filtros' blocks suffered the same fate. Canvas was found best for this work and was later used in all the standard machines. Hence there was no more necessity for building the machine round, to accommodate the use of a carborundum wheel.

The canvas is usually discarded after about six months, for by that time it has become clogged with ore-particles, by grease from the blower, or by dust from the air. In the Chino and Utah Copper mills the air is filtered through cloth by encasing the blower in a room with walls of muslin. Trouble is caused if the air is turned off while a pneumatic machine is full of pulp and the machine is allowed to stand for a number of hours. In this case the fine slime has an opportunity to settle upon the canvas and cake in its pores. Canvas, being pliable, clears itself of such obstruction much more easily than rigid carborundum or 'filtros' blocks.

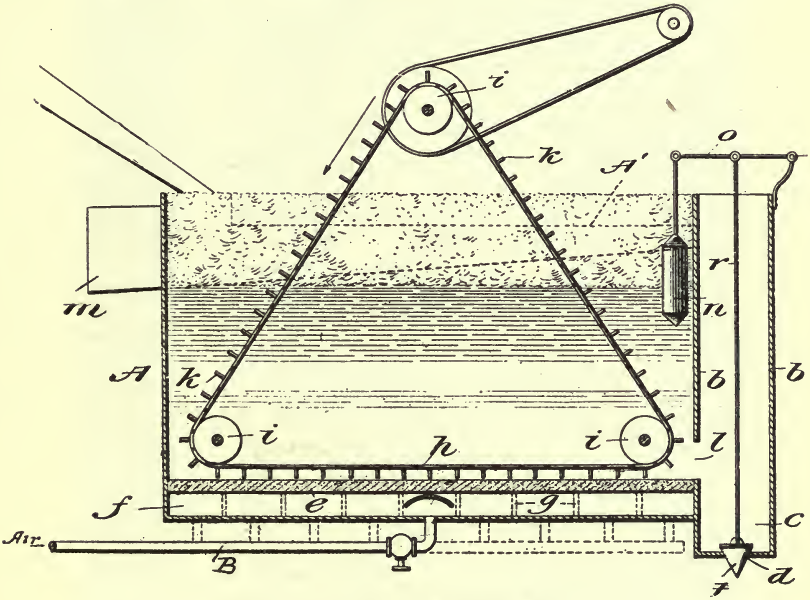


FIG. 21. CALLOW FLAT-BOTTOM CELL

The Callow flat-bottom cell, U. S. 1,182,748 of May 9, 1916, is shown in Fig. 21. The sand is advanced over the bottom by the use of a drag-belt. It is not certain that this is necessary, for the Inspiration machine, described elsewhere, has a flat bottom and the sand slides gradually across the canvas. I have seen such a flat-bottomed cell in use without a drag-belt.

The tripple-length Callow cell has more recently been devised for treatment of the finely divided slime of the Cobalt district. It is 29 ft. long and is made from castings intended for three of the standard-length cells. Only pulps containing small percentages of sand can be used, as the slope of the machine is much reduced.

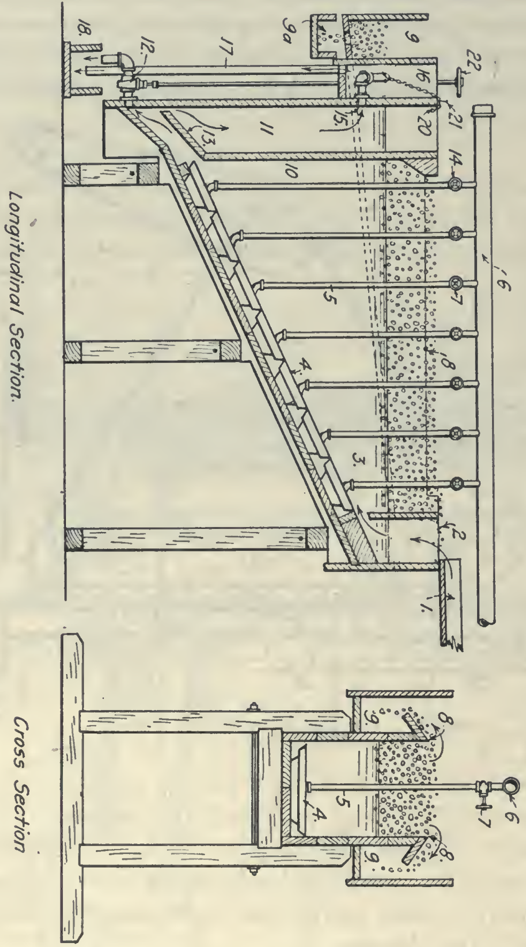


FIG. 22. SECTION OF THE HYDE FLOTATION MACHINE

James M. Hyde has described a pneumatic flotation machine in the *Mining and Scientific Press* of August 5, 1916. The individual wind-boxes can be removed without disturbing the others so that the machine can be run continuously while any one of them is removed for replacement of the canvas. The essentials of this machine are shown in Fig. 22 and 23. By having the air-inlet valves directly above the

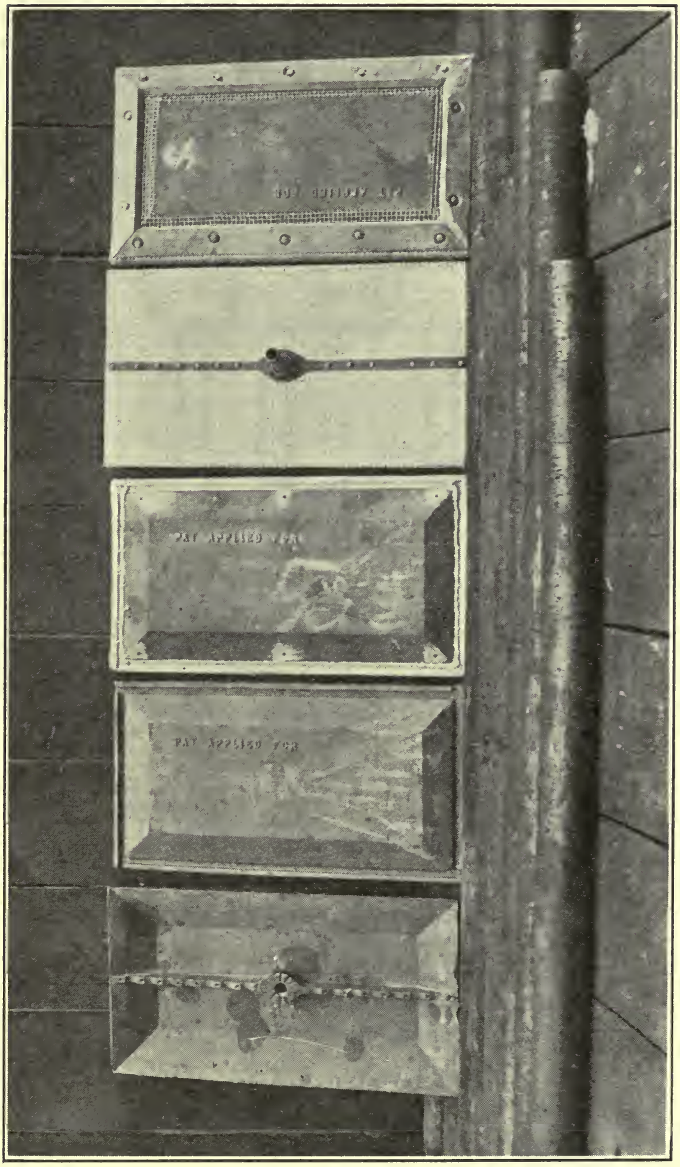


FIG. 23. SHOWING METHOD OF DRESSING INDIVIDUAL AIR-CELLS

froth in the cell there can be no excuse for operators allowing the distribution of air to become uneven.

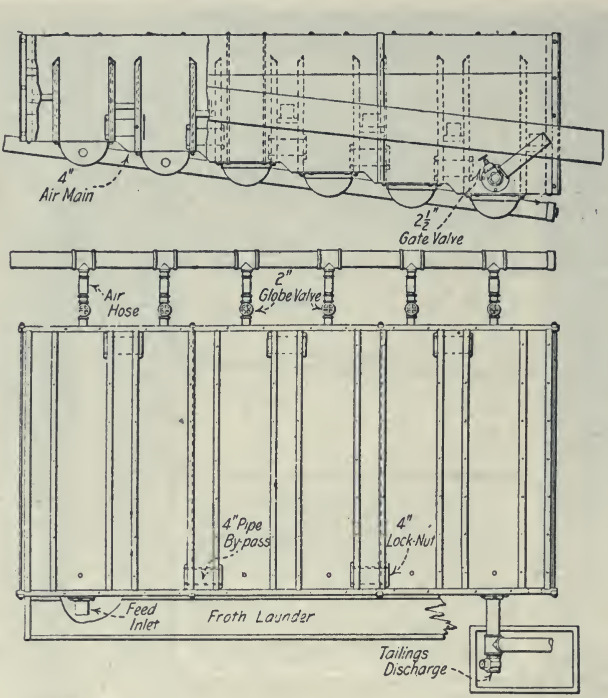


FIG. 24. LAUNDER OR CRERAR MACHINE

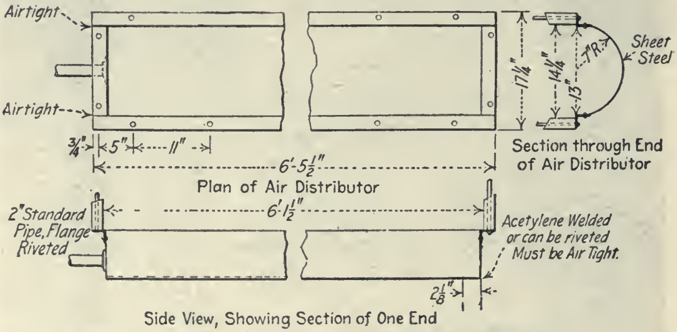


FIG. 25. SHEET-STEEL BOTTOMS OF WIND-BOXES

A similar machine, used in the Inspiration mill, was likewise developed from the fundamental conception of using a launder with a porous bottom. Its evolution is graphically illustrated by Fig. 26, which is taken from the paper by Rudolf Gahl presented at the September meeting of the American Institute of Mining Engineers in 1916. The details of the machine are given in Fig. 27. It consists of a series of boxes with false bottoms of canvas in which frothing is produced by compressed air introduced beneath the canvas. The pulp goes from one cell to the next by passing underneath the partition between the two boxes. This arrangement has the advantage of giving a treatment in series, forming a rougher-froth, which is retreated in a similar set of cells. The sand tends to settle in this machine and at present is stirred occasionally by the introduction of a pipe on the end of a hose, injecting water under 80-lb. pressure. The machine has the advantage of great compactness and is easily repaired. The bottom of each cell can be removed without stopping, as the air-line is led down to each individual air-box in a manner similar to the Hyde machine, above described.

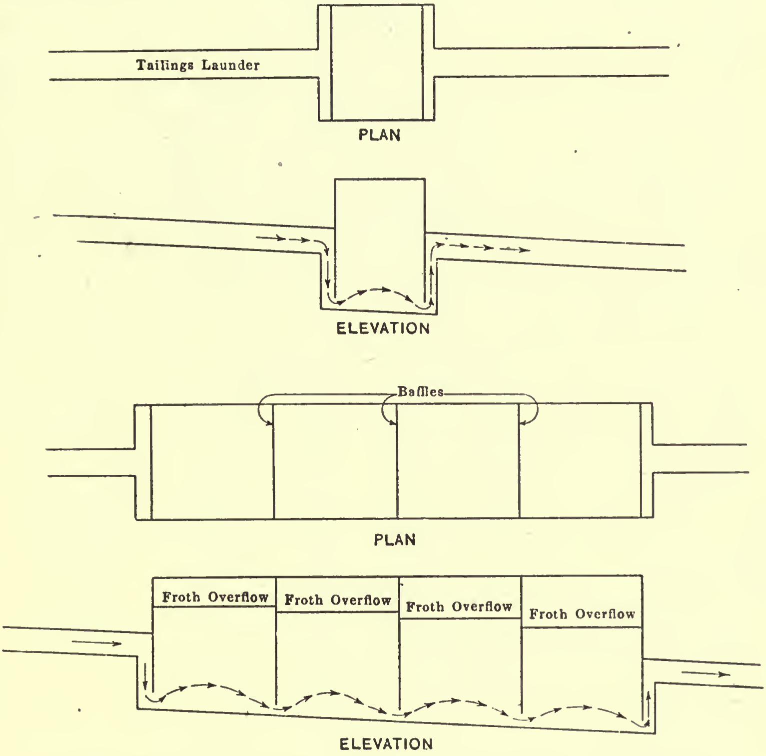


FIG. 26. DIAGRAM SHOWING ORIGIN AND DEVELOPMENT OF INSPIRATION FLOTATION MACHINE

It is believed that the principal advantage of the Inspiration machine is the large tonnage that can be treated on a given floor-space. Being almost flat-bottomed the sand tends to collect on the canvas and two or three laborers on each shift are kept busy passing a small pipe with high-pressure water-jets over the surfaces of the canvas bottoms in each compartment in order to stir the sand and cause it to pass on. For a plant of the size of that at Inspiration the increased cost per ton due to this extra labor is small. The individual air-baskets make possible the removal and replacement of the canvas squares without stopping the machine, one compartment merely running empty and overflowing no froth.

The Launder, or Crerar, machine is one in which the pulp passes through a considerable length of launder. It is adapted, as can be inferred, to making a low tailing owing to the length of time that the pulp is in the machine. The speed of advance of the pulp through the machine, however, is faster than in the Callow type in order to obtain the same tonnage. The description of this machine is taken from the *Engineering and Mining Journal*, of December 16, 1916, where it was described by B. M. Snyder. See Fig. 24. It consists of a series of six launders 6 ft. long by 14 in. wide, placed side by side, connected in series with sufficient space between to allow for removal of froth. These are also successively deeper in order to induce a flow of pulp. Fig. 25 shows the construction of the sheet-steel bottoms of the wind-boxes, which are easily made at the workshop of an ordinary mill. The total cost of construction of such a machine is estimated at $458. The air required is 10 cu. ft. per minute per square foot of frothing-area at 3 to 5 lb. per sq. in. This gives an average of about 60 tons daily capacity.

The Fynn-Towne or bubble-column machine was one of those used during the period of competitive testing at Inspiration. It consists of a deep column for pulp with a porous carborundum stone at the bottom for the admittance of atomized air. The machine did not do as well as did the Callow machine during the Inspiration testing so it was discarded by that company.

The C-B frothing-classifier, invented by David Cole and Julius Bergman, of El Paso, is shown in Fig. 28 and 29. Compressed air is introduced into the cell through perforated pipes which are wrapped with canvas to further break up the streams of air. A series of these pipes is used near the bottom of the cell, as seen in Fig. 28, but enough space is left for the sand to drop between the pipes and pass out of the cell. Hence this type of machine is not troubled by the sand in

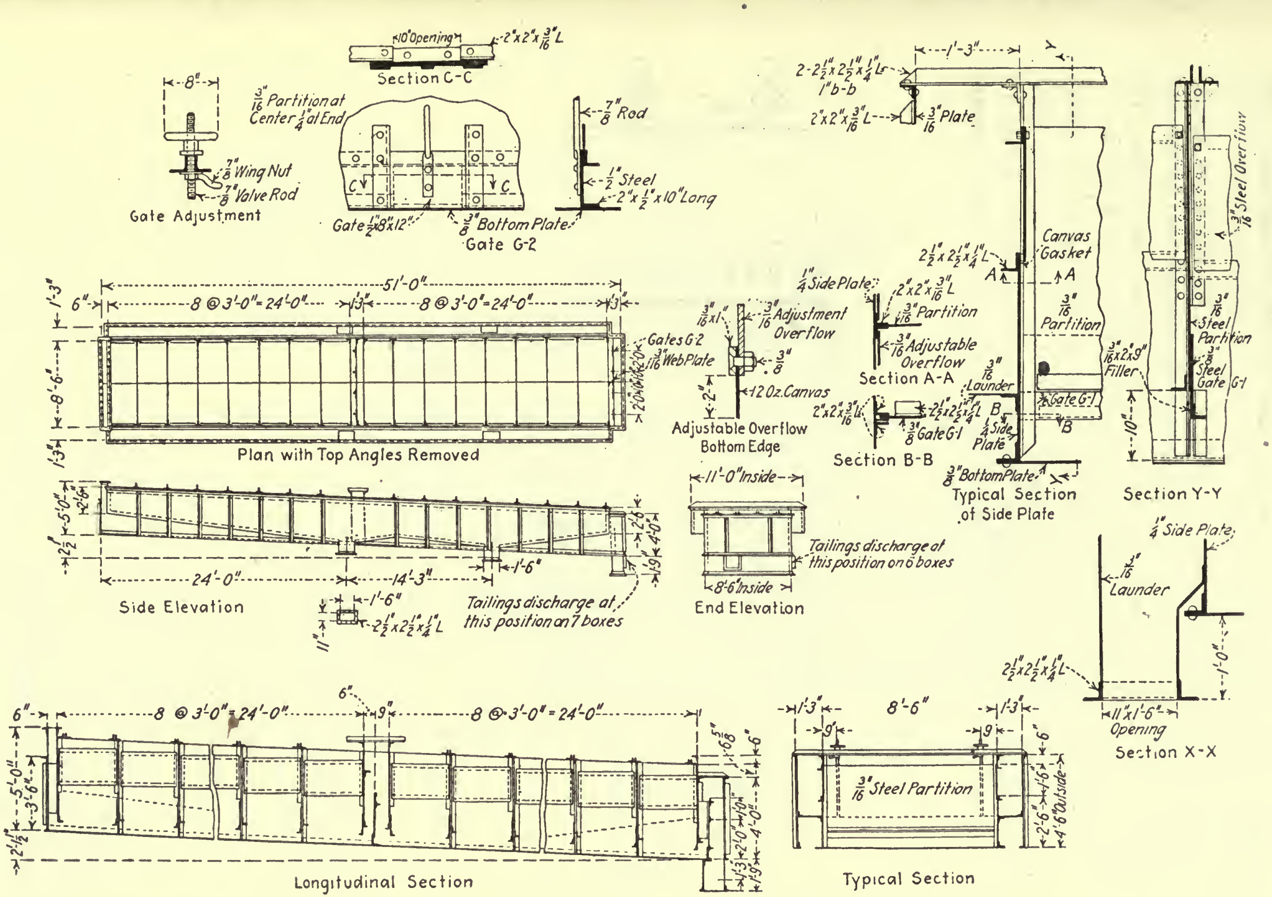


FIG. 27. INSPIRATION FLOTATION ROUGHER-CELLS OF STEEL CONSTRUCTION

the pulp. The coarse mineral in the sand is table-concentrated after the slime has been floated.

In U. S. patent 1,201,934 of October 17, 1916, Callow gives a modification of his standard cell in which sand is spigoted out at 21 (see Fig. 30) and the slime passes out of a separate pipe, marked 24. The sand can then be tabled and the slime treated further by flotation.

It was soon found that the size of the bubbles produced by porous media depended more on the composition of the solution into which they were blown than on the size of the holes in the medium. A rapidly moving jet of air or gas was found to be fairly well emulsified if water containing a frothing-agent was used. A number of machines have been designed to utilize this principle.

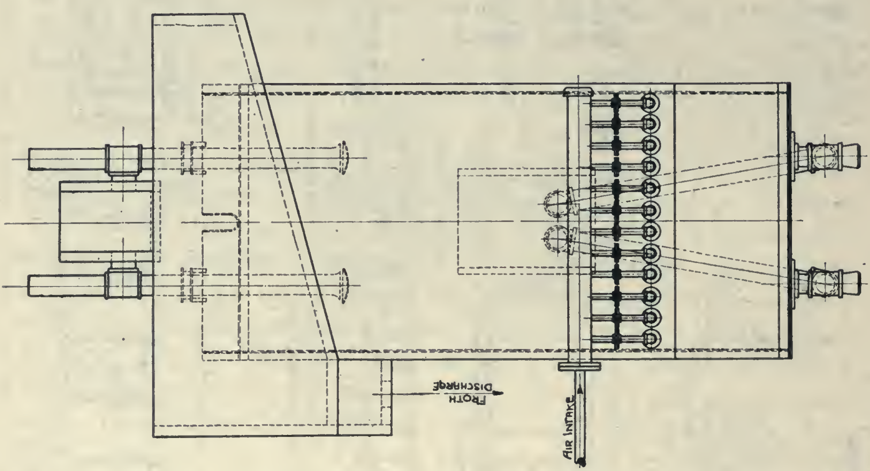


Fig. 28. CROSS-SECTION OF C-B TUBE-GRATE FLOTATION-CELL

Dudley H. Norris invented the 'pressure' machine shown in Fig. 31, taken from U. S. 1,167,835 of January 11, 1916. Water is fed into an injector-tube 7 and air is entrained from tube 8, so that water with an excess of air is allowed to collect under pressure in 4. When this water with an excess of dissolved air is released in the flotation-tank the released pressure allows the dissolved air to appear in the form of bubbles in a fine state of division. Mr. Norris states that he first had the idea when noticing the water in the wash-room of a Pullman car made milky by dissolved air. As is well known, the water-tank of a Pullman car is underneath and air from the brake-system is used to force it into the faucets. As far as I can learn this machine is not now used in any mill, but it is suggestive and very much like some machines now in use.

G. E. Ohrn has invented a machine shown in Fig. 32 taken from his patent U. S. 1,187,772 of June 20, 1916. A jet of steam is fed by the pipe *D* and the oil is allowed to enter through the small inner pipe *E*. The jet plunges into the pulp and air is entrained around the steam-jet. The resulting froth must pass a jet of water *L* arranged to wash out any gangue that tends to stick in the mineral froth. *J* is the

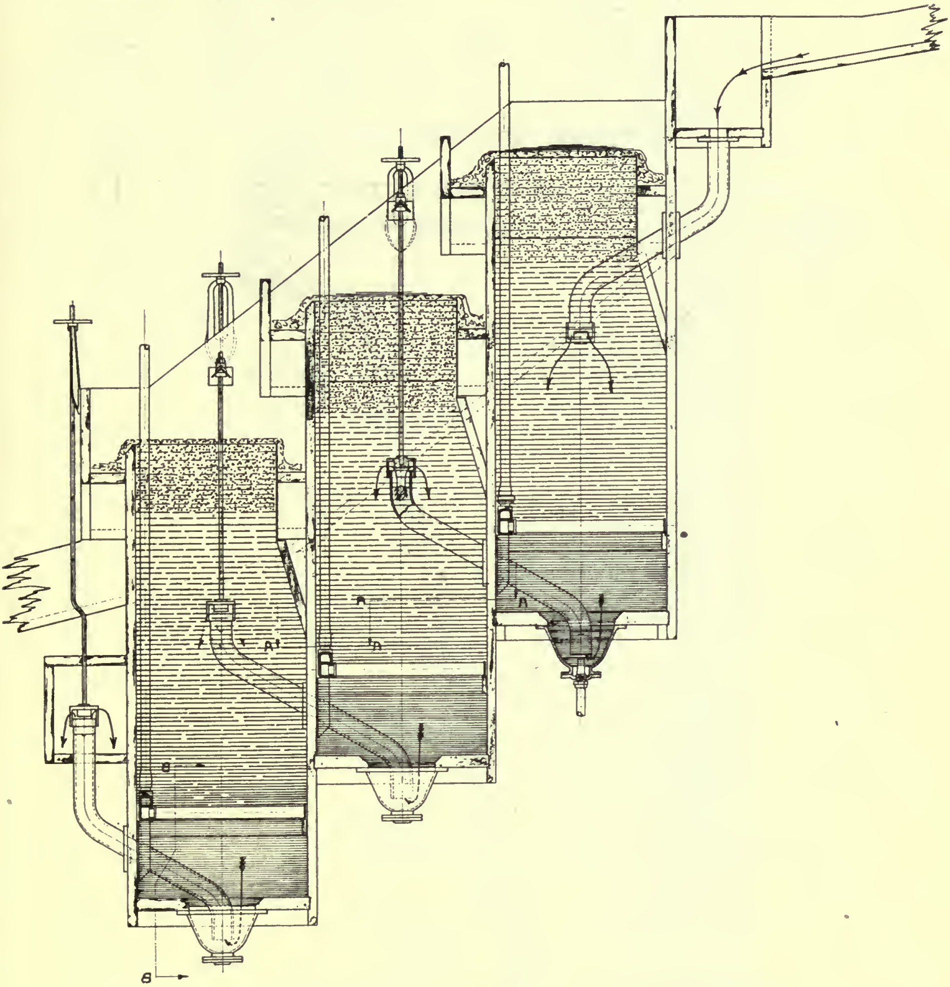


FIG. 29. LONGITUDINAL SECTION OF C-B FLOTATION MACHINE THREE CELLS IN SERIES

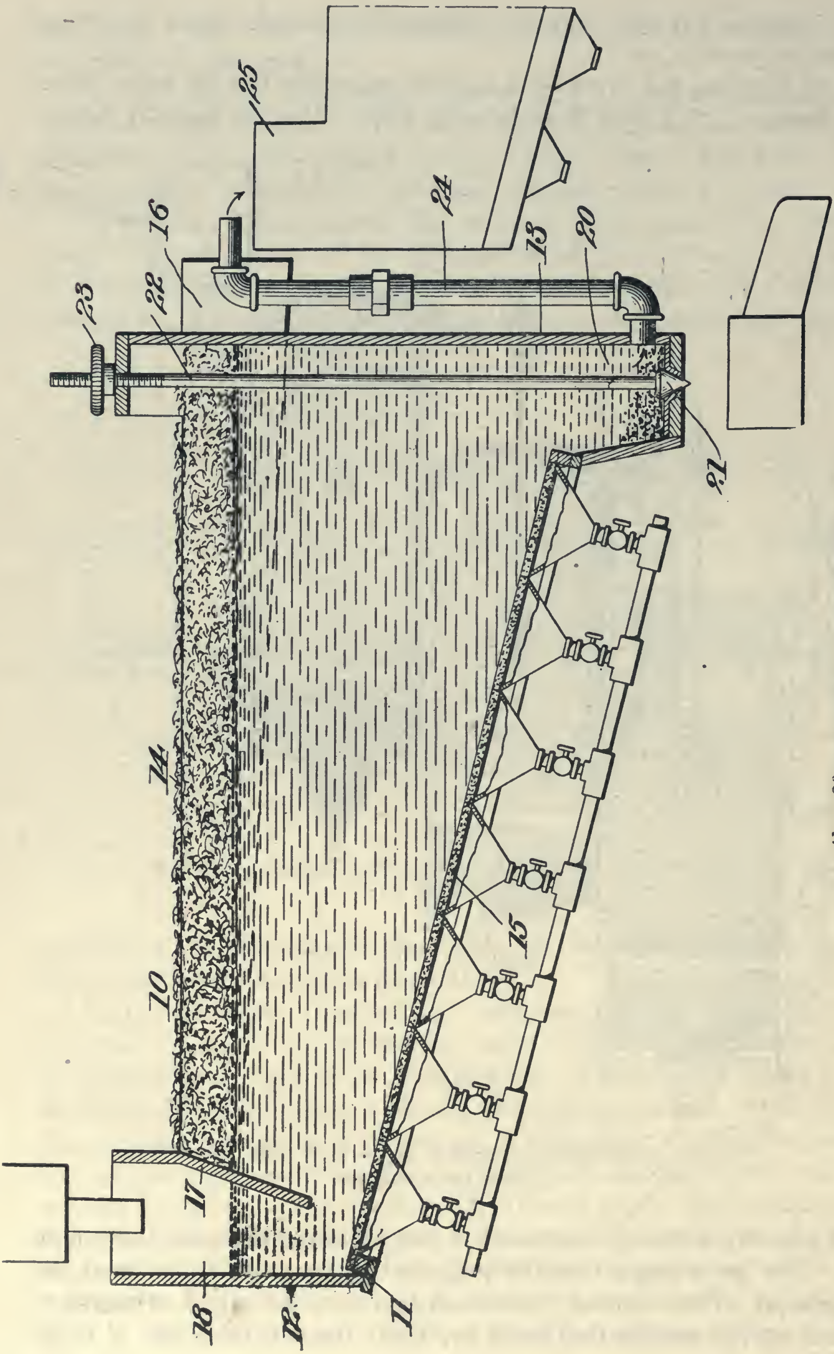


FIG. 30. MODIFIED CALLOW CELL.

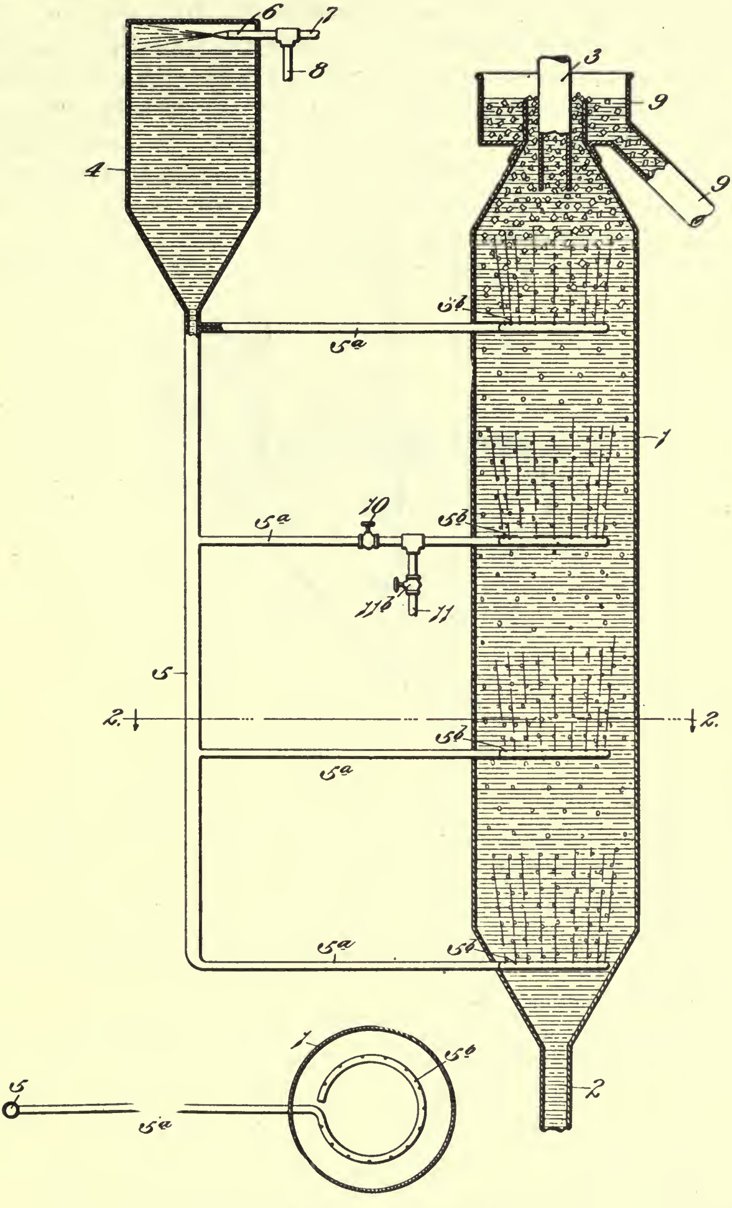


FIG. 31. NORRIS PRESSURE MACHINE

froth-overflow launder and *K* is the tailing-discharge. A central baffle can be used to allow slime to overflow separately from the sand. The feed, if desired, can be led into hopper *B*. The steam tends to vaporize some of the oil and spread it over a greater amount of pulp. This machine was assigned by the Swedish inventor to Minerals Separation as was also his British patent. So far as can be learned the machine is not in use on this side of the Atlantic but the figures on its operation in Sweden, given out by local promoters, look most interesting. However, steam is a rather expensive medium to use for mixing pulp.

Another steam-jet machine has been patented by Gustaf Gröndal, another Swede, under U. S. 1,202,512 of October 24, 1916. The drawing in Fig. 33 is taken from the patent specification. *I* is a small pipe conveying the frothing-agent; *C* is a steam-pipe; *b* is a Körting steam-jet, which allows the entrainment of a great quantity of air, and *d* is a distributer to allow the air, steam, and oil-vapor to be dissipated through the pulp. The feed-pipe is at *g*. The froth-overflow is at *k* and the tailing-discharge at *m*.

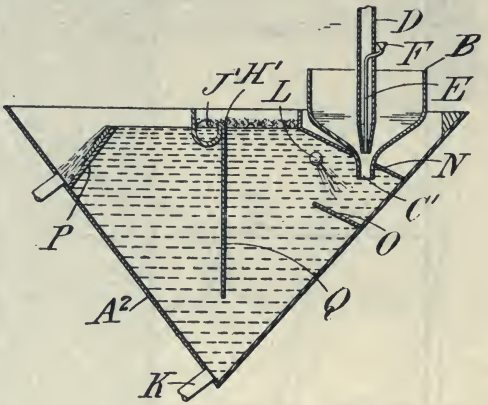


Fig. 32. THE OHRN MACHINE

In the case of an ore that requires heating, like some sphalerite ores. this machine might be useful, because the steam used for heating could also be made to produce the aeration. This patent is assigned to Beer, Sondheimer & Co., formerly agents for Minerals Separation.

J. D. Fields and G. H. Wyman have invented two machines of similar construction. They consist of a series of flotation cells, each of which has a spitzkasten like the M. S. standard machine, but in place of an impeller in an agitation compartment a jet of air is used in an air-lift for aerating and transferring the pulp. Wyman's machine was invented several years ago and was used in several localities in the North-West. The Fields machine grew out of an 'electrolytic' flotation-cell that proved a failure. After Fields abandoned the use of electricity in his pulp and came down to the use of air for flotation he obtained better results. The Keystone Consolidated Mining Co., in Arizona, has used one of these machines. The box, which is divided into small individual cells, is 30 ft. long, 3 ft. wide, and 8 ft. deep.

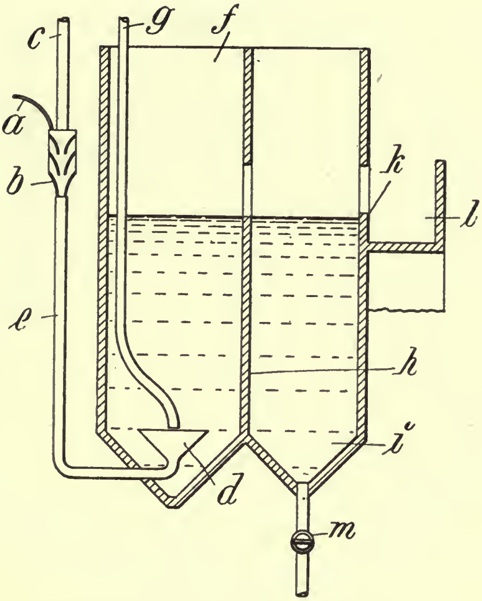


FIG. 33. GRONDAL STEAM-JET MACHINE

This is divided into 15 cells each 2 ft. wide and an air-hose leads down into the bottom of each air-lift. This machine constitutes the 'rougher' unit; a 'cleaner' unit of similar construction, but smaller size, is also used. Nothing is known as to the consumption of power, but it is probable that many of the larger air-bubbles escape without doing any useful work. If this be true, this type of machine could not operate as efficiently as a cell using a porous diaphragm.

FILM-FLOTATION MACHINES. During recent years not many surface-tension machines have been developed. The Wood machine and the Macquisten tube are well known and need not be described. The engineers of the New Jersey Zinc Co.—G. C. Stone, A. R. Livingston, and L. G. Rowand in particular—have invented various machines of this type.

Stone's machine is not shown here because it does not seem adapted to large-scale work. It consists of a scoop or series of scoops fed with dry crushed ore in a thin layer. The movement of the scoop cuts off the ore-supply and it is lowered at a slight angle into acidified water in a trough. The sulphides float and the gangue sinks. The scoop reverses its motion and passes back beneath the ore-hopper, opening the ore-gate at the bottom by properly arranged catches. The reversal of the motion of the scoop closes the ore-gate and the scoop tilts and descends into the water again. The machine therefore is intermittent in action and of complicated design. It is covered by U. S. 1,156,041 of October 5, 1915.

Livingston's machine is covered by U. S. patent 1,147,633 of July 20, 1915. Fig. 34 shows that it is a much enlarged Macquisten tube, being six feet in diameter and about ten feet long. The ore is fed through launder *D*. The rotation of the drum carries the pulp up to the left and tacks or brads are used to entrain more ore so that it will be lifted out of the water into the drum. A row of water-jets sprays the wall of the tube above the rising layer of ore, washing it down and floating the sulphides as a skin concentrate that overflows the side of *E*, a launder, which discharges the concentrate outside the machine while the tailing advances by motion of the drum until it falls into the box *C*. The advancing of the pulp from the back end of the drum to the front is accomplished by slanting plows placed on the under-side of the concentrate-discharge launder. The machine was said not to have been successful until the tacks were introduced for retaining the main body of ore while the surface was being washed by the descending jets of water. The descending particles of ore enter the water at so slight an angle and so quietly that the sulphides are easily floated. Aeration of the incoming water is recommended and this is accomplished by the use of the aspirator h^3, which sucks the air in at h^4. Relatively coarse material, 16 to 20-mesh, is said to be best adapted for treatment in this machine and the patent specifications state that some cheap oil and acid improve the operation. Data for tonnage, power, acid, oil, and labor are not available but it can be seen that it is a considerable improvement over the Macquisten tube, being a machine of much larger capacity.

Rowand's machine is covered by U. S. 1,159,713 of November 9, 1915. A sketch of the machine, taken from the patent specifications, is given in Fig. 35. *B* is the chute through which powdered ore, not coarser than 16-mesh, is dropped in a thin layer on a moving belt *e* covered with a film of oil. The oil is stored in compartment *D*, into which the belt dips before the ore is fed onto it. The ore meets the water at *f* and the skin of concentrate is discharged over the lip, *d*, into the launder *c*. Water is fed through the valve *b* and the tailing discharges at *a*. Like Wood's machine, the speed of the belt determines the movement of the laden film on the surface of the water. No data have been issued on the speed of the belt or the tonnage.

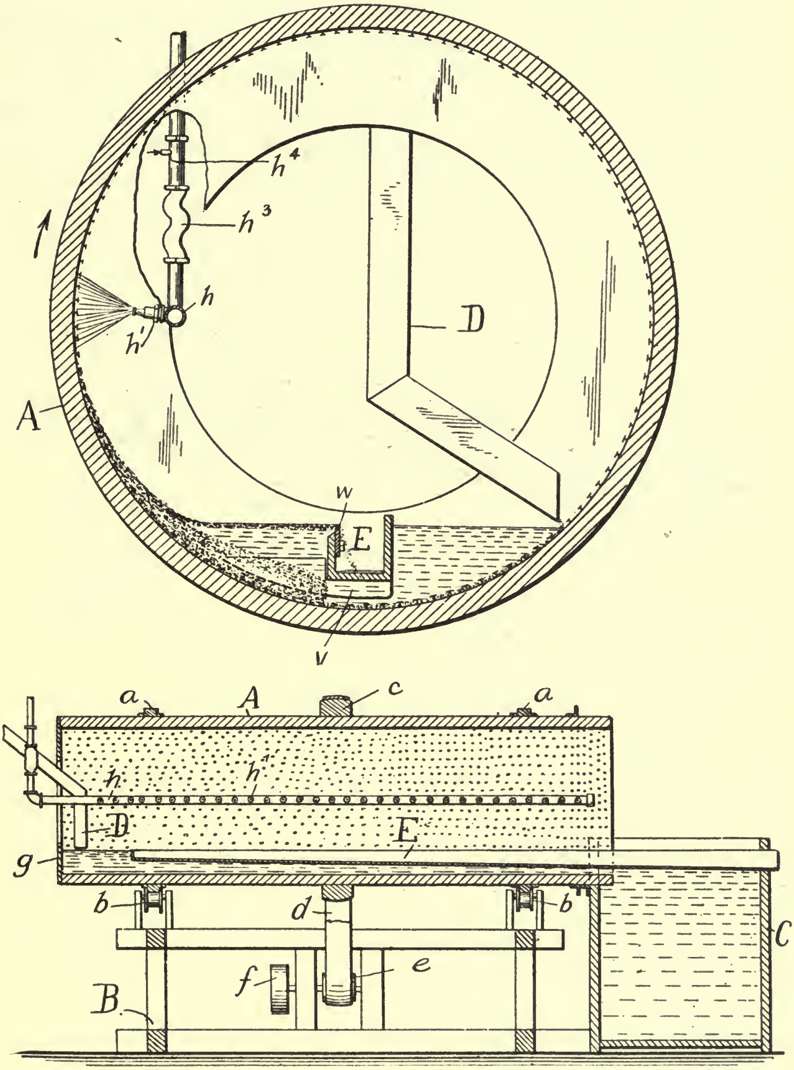


FIG. 34. THE LIVINGSTON MACHINE

It is possible that, as in most skin-flotation machines, slime cannot be treated, only fine sand. The oiling of the sulphide particles before entering the water probably is done most neatly by this arrangement.

Such machines are not widely applicable because they do not separate slime cleanly. They are best adapted to the treatment of table-middlings that consist of minerals of nearly the same specific gravity, such as sphalerite, barite, siderite, fluorite, and pyrite.

General Considerations. Mechanical, pneumatic, and skin-flotation machines have been considered separately. In many cases it has been found advantageous to use both mechanical and pneumatic machines in series on the same pulp for the reason that one may do good work on the sand while the other does good work on the slime constituent of the pulp. Experience has shown that it is inadvisable to compare mechanical with pneumatic machines but that they supplement each other well. In the order of decreasing coarseness of the pulp that they will treat successfully we have skin, mechanical, and pneumatic machines. There is an apparent exception to this rule if the flotation machine is made to disperse the oil, as a very 'colloidal' slime can then be treated best by a mechanical machine that gives intense agitation. If the oil is fed into the tube-mill or other grinding machinery before the pulp reaches the flotation machines, no further dispersion is necessary and a pneumatic machine will show an advantage.

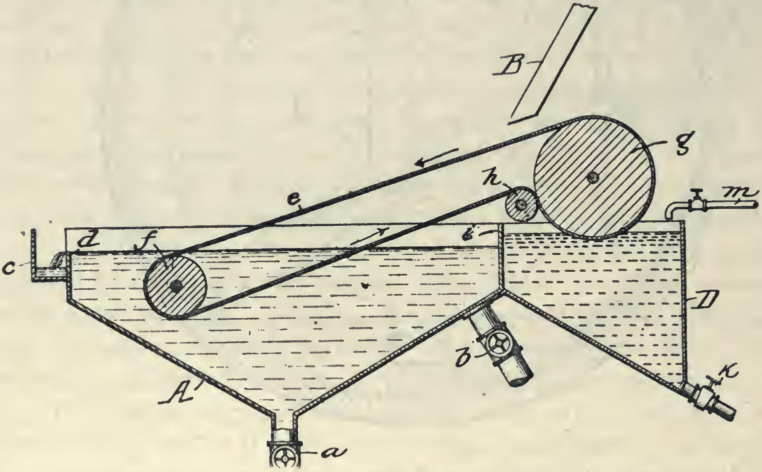


Fig. 35. THE ROWAND MACHINE

COLLOIDS

By E. E. Free

The following article is made up of portions of a series of articles on 'Colloids in Ore-dressing,' which appeared in the *Engineering and Mining Journal* during 1916.[1] It is a pleasure to express my thanks to the editor of that journal for permission to use the material in this place. The alterations from the original text are almost entirely by way of condensation.

The conceptions of colloids to be found in the current literature of ore-dressing are surprisingly hazy. With increasing interest in the flotation processes the catchwords of two years ago have given way to a new set of phrases involving 'surface forces,' 'interfacial tensions,' and the like. The relief to the overworked 'colloids' is considerable and one is grateful for the lessened tendency to 'explain' obscure phenomena by reference to mysterious 'colloidal substances' that, themselves remaining unknown, leave the problem precisely where it was before. This lessened misuse of colloidal concepts appears to be accompanied—one may hope that it is caused—by a more definite appreciation of the physical and chemical nature of colloidal bodies, an appreciation that may be expected to bring important returns in actual experimentation, advancing our knowledge of these bodies and of their metallurgical significance.

In the original text of these papers considerable attention was devoted to the loose use of colloidal terminology caused by a comparison between the kinds of colloids present in ore-slimes and the glue-like bodies, also called 'colloids,' of which gelatine and albumen are typical. It was pointed out that there are important differences between these glue-like bodies and the materials encountered in metallurgical practice and that the examination of the latter is best approached by abandoning all preconceptions concerning the gelatinous colloids and by confining attention, in the beginning at least, to the properties of simple rock-powders. So far as is actually known ore-slimes consist merely of fine mineral particles suspended in water that usually contains dissolved traces of the minerals present in the ore. It was asserted that the determinable properties of such a simple suspension of rock-particles in water would explain

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[1] *Eng. & Min. Jour.*, Vol. 101, pp. 249-254, 429-432, 509-513, 681-686, 1068-1070, 1105-1108 (February to June, 1916).

the behavior of slimes, even the most colloidal ones, without need of assuming the presence of gelatinous substances or other intangible mysteries. It is obvious that the physical properties of simple suspensions become of much importance to the inquiry.

Fortunately, suspensions have been studied thoroughly by geologists, soil-physicists, and the specialists in colloids. The most weighty result of this study is the conception of the possible existence of suspensions of smaller and smaller particles.[2] It is possible to prepare suspensions of clay or other minerals the particles of which are so fine that they remain permanently suspended, though still distinguishable by microscopic examination. It is a small step from this to the typical colloidal solutions that appear free of particles ("optically empty") before the microscope. The investigations of colloidal solutions made possible by the ultramicroscope,[3] during the past decade, have established firmly the conclusion that the typical colloidal solution, as, for instance, that of colloidal gold, is simply a suspension in which the particles are extraordinarily small.

The important concept here is the perfect continuity of the suspension series. There is no natural break or division of any kind between a suspension of coarse gold fragments in water and a colloidal solution of gold particles so fine as to remain permanently suspended and be microscopically invisible. It is possible to prepare a suspension of any intermediate degree of fineness. Indeed, if one regards ordinary solutions as composed of single molecules or ions distributed through the mass of the solvent, these 'true' solutions appear simply as the limiting case of the suspension series—suspensions in which the particles have become so small as to reach the dimensions of the molecule or the ion.

The immediately obvious objection to this concept of the unity of the suspension series from the coarse visible suspension at one end to the true solution at the other, is that the properties of the systems differ markedly in different parts of the series. A mixture of coarse gold particles and water is very different physically from a colloidal gold solution, and both differ in properties from a solution of, say, gold chloride containing the gold ion. This is quite true, but close examination of the series shows that all differences are of degree

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[2] For details see Ashley, U. S. Geological Survey, Bull. 388 (1909) and Bureau of Standards, Technologic Paper 23 (1911), and the general works cited in the appended bibliography.

[3] Siedentopf & Zsigmondy, *Ann. Physik*, Ser. 4, Vol. 10, pp. 1-39 (1903). In English see Zsigmondy, 'Colloids and the Ultramicroscope,' translated by Alexander, 1909.

only. Thus, in a coarse-sand suspension, the most evident controlling factor is gravity. Nothing but the continuous expenditure of energy (for example by shaking) will keep the sand suspended. As we consider suspensions of finer particles, gravity grows less and less important, while simultaneously the surficial forces between the particles and the aqueous medium grow more and more important until gravity yields control to these other forces and the particles remain in permanent suspension without external assistance. This is typical. The changes are always gradual as one passes up or down the series; they always result from continuous increases or decreases in the intensity of the affecting factors. They are never abrupt. From the practical viewpoint, however, it is precisely these gradual changes of degree that are important. The fact that the properties of the finer-grained suspensions do differ from those of the coarser is what has attracted attention. It is important theoretically to know that the differences are of degree rather than kind, but that does not dispose of the differences.

The most troublesome properties of colloidal ores are two, namely, the slow settling of slime, which also means the imperfect separation between fine and coarse particles, and the low permeability of settled masses of slime, filter-cakes, and the like. The latter is usually accompanied by a high retention of water in the thickened slimes. Both of these are comparative rather than absolute. The colloidal slime settles slowly and packs imperviously by comparison with slime that is less colloidal. It is easy to demonstrate by experiment with suspensions of known character that slowness of settling and the other troublesome properties increase gradually and continuously with decrease of the particle, and it is an obvious inference that an unusually small size of particle is the cause of all the trouble with colloidal slimes. The mechanisms may be pictured by recalling that in dilute suspensions gravity becomes less important and surficial forces more important as the particles decrease in size, and that in thickened masses of slime, if the particles are very small, the spaces between the particles are similarly tiny and offer tremendous frictional resistance to the percolation of water.

These effects of minute particles are so manifest and so manifestly sufficient to explain the behavior of slime that I suspect no other explanation would have been suggested were it not for the anomalous fact that the degree of colloidality of a slime has no constant or determinable relation to the fineness of grinding of the ore or to the amount of very fine material in the slime as determined by screen-tests, by elutriation, or by other methods. There is much more likely to be a relation to the original character of the ore. For instance, oxidized and 'rotten' ores are especially prone to yield colloidal slimes. These anomalies are to be explained by two things: the variable disintegration of ores and the variable flocculation of the slimes. The ease of disintegration is essentially a matter of mineral composition. Mechanical grinding by itself cannot reduce ore-particles beyond a certain size, which is probably considerably above the size necessary for high colloidality. If disintegration occurs beyond this limit of mechanical grinding, it is because the ore or some of its constituents are of such physical nature as to disintegrate spontaneously when shaken with water, as, for instance, clay will disintegrate. Natural processes of weathering in the oxidation zone tend to produce materials that will so disintegrate, as, for instance, when feldspar is altered to kaolin. By the second factor, flocculation, is meant the aggregation of several smaller particles into more or less persistent groups or floccules, which then behave much like single larger particles. This will be discussed in detail below.

The most important result of the study of colloids and suspensions during the past decade is the conception of colloids simply as suspensions the particles of which are very small.[4] It is unnecessary to make any sharp distinction between suspensions and colloidal solutions. The emphasis, indeed, is reversed and is on the unity of this series rather than on any possible severalty; but for the purposes of purer science it is convenient to have distinctions, so that a greater precision of definition becomes necessary. For these purposes there has come to be nearly general agreement on a set of size-limits given in the following table:[5]

CLASSIFICATION BY SIZE OF PARTICLES

Suspensions....................	Particles over 0.1 micron in mean diameter
Colloidal solutions...	Particles between 0.1 and 0.001 micron in mean diameter
True solutions................	Particles under 0.001 micron in mean diameter

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[4] The detailed experimental evidence supporting this conclusion is ample and beyond question, but its discussion would require too much space. It will be found in detail in the works of Freundlich, Ostwald, and Zsigmondy, cited in the appended bibliography. It is excellently summarized by John Johnstone in his introduction to Ashley's monograph on the 'Technical Control of the Colloidal Matter of Clays,' U. S. Bureau of Standards, Technologic Paper 23 (1913).

[5] Zsigmondy, 'Erkenntniss der Kolloide,' p. 22 (1905). A micron is one-thousandth of a millimetre, or approximately one twenty-thousandth of an inch.

While these limits are purely arbitrary, the use of them is convenient as indicating the range of size within which the typical colloidal properties are best developed. It is not implied that these properties cease entirely to be exhibited by suspensions the particles of which lie outside these limits. In metallurgy especially it is necessary to consider many important extensions of colloidal properties into the field of the coarser suspensions. Nearly all slimes, even the most colloidal, belong to the field of suspensions rather than to that of colloidal solutions, as these fields are defined by the size-limits given.

This conception of colloids points immediately at the chief characteristic of these bodies and the one that is at the bottom of most of their properties, namely, their great internal surface. It is manifest that if a colloid is composed of very fine particles of one substance suspended in another, the total surface of contact between the two substances will be very great. This mutual surface is called the internal surface. It has been found that a number of peculiar properties, of which surface-tension is the best-known, characterize all surfaces where two substances come into contact, and the great extent of such surface in suspensions and colloids gives these surficial properties and forces an unusual importance in controlling the salient characteristics of the entire system. For instance, the phenomena of adsorption or the concentration of dissolved substances at surfaces are exhibited in a high degree by suspensions and colloids and are of much technical importance in dyeing, the clarification of wines, the manufacture of contact sulphuric acid, and in many other industrial processes.

In speaking of the large internal surface of colloids one means, of course, that the surface is relatively extensive with respect to the masses involved. The criterion is a large ratio of internal surface to mass. Formal definitions are of small value, but it is possible to define a colloid from this viewpoint as a mixture of at least two substances the internal surface of which is very large relative to the mass of at least one of the substances. It may be pointed out again that the definition is purely relative. What ratio of surface to mass is to be considered 'very large' will depend upon circumstances.

In the foregoing paragraphs there has been much mention of colloidal properties, but the only ones that have been discussed specifically are the slow settling of colloidal slimes and their imperviousness when settled. From the standpoint of ore-dressing these two are the most important of all colloidal properties, and the emphasis is not unjustified. However, several other properties are of interest. Most important scientically are the similiarities to, and differences from, the true or ordinary solutions the particles of which are supposed to be of molecular or ionic dimensions. The typical colloidal solution resembles a true solution in being persistent so long as conditions remain unchanged. That is, the particles remain in suspension and the colloidal solution retains an unchanged chemical composition. The colloids differ in (1) failure to show a true and constant solubility; (2) an optical heterogeneity shown by translucence or turbidity; (3) the causing of no change, or a very small change, in the freezing-point and boiling-point of the solvent; (4) the production of no osmotic pressure; (5) slow diffusion and failure to dialyze or pass through a parchment membrane. The causes of all these differences will be evident on consideration of the difference in particle-size that distinguishes the colloids from the true solutions. Details need not be pursued further than to say that the differences, as before, are of degree only. Colloids do not fail entirely to show the typical solution properties, but they show them to so slight a degree as to escape all but the most painstaking researches.

Of the other properties of colloids, flocculation and adsorption have been mentioned and will be discussed further below. Another, of much technical importance, is the tendency of the colloidal particles to wander in the electric field and accumulate at one or the other of the poles. This forms the basis of the well-known Cottrell process for the collection of acid and smelter-fume, the removal of dust from stack-gases, the separation of oil-globules from condenser-water, and the like.

In what precedes, the reader has probably detected a tacit assumption that all colloids consist of solid particles suspended in a liquid medium. It is easiest to attain an initial concept of the nature of colloids by regarding them in this way, but the concept is incomplete. Common experience furnishes numerous examples outside this simple case. For instance, the usual medicinal emulsions of cod-liver oil, or, to use an illustration with pleasanter associations, the ordinary oil-vinegar salad dressing, consists of globules of oil suspended in an aqueous liquid. Obviously both particle and medium are liquid, yet the properties of the mixture are (with some exceptions in detail) the typical colloidal properties. As a matter of fact it is possible to prepare suspensions and colloidal mixtures the particles of which are solid, liquid, or gaseous, and which are suspended either in solid, liquid, or gaseous media. In 1907 Ostwald[6] published a classification on this basis, which classification is given below in tabular form and supplied, so far as possible, with metallurgical examples. In selecting the examples no attempt has been made to distinguish between colloidal solutions and the coarser suspensions. It is obvious also that examples of all of these classes exist among the true solutions.

A CLASSIFICATION OF COLLOIDS

	Solid medium	Liquid medium	Gaseous medium
Solid particle.	Many cryptocrystalline ores, especially those containing finely divided metals. Most solidified slags. Glazes, glasses, etc.	Ordinary suspensions and colloidal solutions of solid particles. Slimes, thickened or not. Wet plastic clays. Turbidity in water.	Fume and smoke. Flue-dust. Dust of mines, flour-mills, factories, etc. Systems involved in processes of air separation.
Liquid particle.	Liquid inclusions in crystals. Much occluded water and water of crystallization. Some filter-cakes, etc., while wet.	Emulsions. Oil in condenser-water and water in fuel-oil. The glue-like organic colloids.	Fog, cloud, and wet steam. Acid-fume. Collection of acid from smelters, fertilizer-works, etc. Oil-sprays.
Gaseous particle.	Dry filter-cakes. Silica-brick and many other refractories. Mineral-wool and metal-sponge. Gas-inclusions in crystals.	Foams and froths. Wet steam (phenomena of foaming in boilers). Systems used in gas and foam processes of ore-separation.	No tangible examples.

Of course, the limit of colloidal complexity is not reached by the examples in the table. Only two substances are there considered, the particle and the medium. The medium is regarded as homogeneous, and all particles are assumed to be of the same substance. It is obviously possible to have more than one kind of particle or a medium that is itself complex, and it is not necessary for all of the particles to be solid, or liquid, or of any single state.

The particulate theory of colloids and the classification according to the respective physical states of the phases is reflected in the terminology developed for the subject. Thus a useful concept regards the size of particle as due to the 'degree of dispersion' of the particulate substance. A decreased size of particle is spoken of as a greater 'dispersion,' or the substance as more highly 'dispersed.' By extension all suspensions and colloids are 'disperse' (or 'dispersed') systems or 'dispersoids;' the particles compose the 'disperse' phase and the medium is the 'dispersion medium.' A true solution pos-

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[6] Grundriss der Kolloidchemie,' first edition, pp. 94-7 (1907). English edition, pp. 42-43.

sesses a molecular or ionic degree of dispersion and is a 'mol' or 'ion-dispersoid.'[7] These terms include all colloidal systems, regardless of the solid, liquid, or gaseous state of particle or medium. Colloidal solutions with a liquid medium are referred to as 'sols.' If the medium is water, the colloid is a 'hydrosol;' if alcohol, an 'alcoholsol,' or 'alcosol,' etc. By analogy with the systems of coarser particles the solid-particle sols are frequently called 'suspensoids;' those of liquid particles, 'emulsoids.' The terms 'sol,' 'suspensoid,' and 'emulsoid,' with their compounds, are properly applied only to systems within the assigned colloidal range of particle size.

The distinction between emulsoids and suspensoids on the basis of the liquid or solid character of suspended particles has been generally accepted, but recent evidence indicates that this is not precisely the ground of difference between typical members of the two classes. The typical emulsoids are gelatine and the related glue-like colloids. The typical suspensoids are the colloidal solutions of metals. These classes differ markedly in many properties; for instance, the metal sols are much more easily precipitated by electrolytes. However, a suspension of small droplets of mineral-oil in water behaves much more like the metal sols than like the typical emulsoids such as gelatine. It is probable that the explanation lies in two facts. First, the globules of oil are so small that they are practically rigid and behave like solid particles. Second, the materials of the typical glue-like emulsoids are miscible with water. Thus the gelatine sol has been shown to consist of two phases both of which are solutions of gelatine in water.[8] The globules are composed of a concentrated solution of gelatine and are in a medium that is a dilute solution of gelatine. Under proper circumstances water can pass from globule to medium or the reverse, resulting in changes of the gelatine concentrations in the two phases and in shrinkage or swelling of the globule phase. It is believed that this behavior is responsible for the peculiar properties of the glue-like colloids and it is probable that we must recognize two classes of emulsoids, as that term is above defined. One class will consist of those liquid-particle colloids the particles of which cannot absorb the medium, like, for instance, mineral-oil in water. The other class

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[7] This terminology is due to Wo. Ostwald, *Koll. Zeits.*, Vol. I. pp. 291-300, 331-41 (1907); 'Grundriss der Kolloidchemie,' 1st ed., p. 83 (1909); English ed., p. 24.

[8] Hatschek, 'Introduction to the Physics and Chemistry of Colloids,' p. 46 (1913).

will contain those in which water can be absorbed by the particle. These will include gelatine and its analogues.

It is the emulsoids of this second class that form the 'gels;' jellies of the sort typified by the ordinary table jellies made from gelatine or the pectin of fruit-juices. The discussion of the structure and properties of gels would take us far afield. It may be noted, however, that the only inorganic gel of common occurrence is that of silicic acid or hydrated silica. The effect of the gel-forming emulsoids on the flocculation of suspensions will be noted below and we shall then return briefly to the possiblity of their occurrence in ores and slimes.

From the practical point of view, in ore-dressing at least, the most important properties of colloids and other suspensions are those that are concerned with the rate of subsidence of the particles through the medium. This is what controls the rate of settling of slimes and the many practical matters depending thereon. When a single mineral particle falls freely through water or any fluid medium it soon attains (if it be not too large) a constant velocity, which is maintained thereafter regardless of the distance it falls. This constant velocity is expressed mathematically by a formula due to Stokes,[9] as follows:

$$v = \frac{2}{9k} r^2 (d - d^1) g$$

in which v is the velocity, r is the radius of the particle, d and d^1 are the densities of the particle and medium respectively, g is the acceleration of gravity, and k is a constant depending upon the viscosity of the solution.

Ignoring the self-evident effects of gravity and of the difference in densities, it is apparent that the velocity of fall of a particle will vary directly with the square of its radius and inversely with the viscosity of the medium through which it falls. The chief departures from this formula that are encountered in experiment occur with the smaller particles, these falling more slowly than is required by the theory. It is probable that such deviations are due to several forces, active only in the case of the finer particles and not taken into account in the formula, of which forces the chief appear to be molecular bombardment and electric charges on the particles. The possible efficacy of repulsive electric charges in modifying the rate

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[9] Trans. Camb. Phil. Soc., Vol. 9, Part 2, pp. 51-2 (1850). For more recent treatments see Cunningham, Proc. Roy. Soc. (London), Ser. A, Vol. 83, pp. 357-65 (1910) and Lamb, *Phil. Mag.*, Ser. 6, Vol. 21, pp. 112-21 (1911).

of fall is obvious. Knowledge of the importance of molecular bombardment is due to recent work demonstrating that the vibratory movement of suspended particles known as the Brownian movement is really due to bombardment of the particles by the moving molecules of, or in, the medium.[10] It follows that small suspended particles have in some degree a tendency to become distributed throughout the medium, a tendency similar in kind to the diffusiveness of a gas or of a dissolved substance, but much less intense. In actual experiment, furthermore, we seldom deal with a medium entirely free from convection currents and even less often with particles that are perfect spheres. Any such disturbances in the medium or irregularities in shape of the particle will retard settling, and it is obvious that the rates of fall actually found may be importantly below those expected on the basis of the formula. All of these disturbing factors lead to decreases rather than increases in the rate of settling required by the formula, which it is possible to regard as an expression of the limiting maximum velocity that a given particle can attain in a given medium. The actual velocity will be always smaller than the theoretical.

From the presence in the formula of the square of the radius of the particle it follows that the velocity of fall decreases rapidly with decrease in size. In this and in the fact that all deviations are toward lesser rather than greater rates lies the cause of the extremely slow rates of subsidence exhibited by fine clays, slimes, and the like. Indeed, with ordinary mineral particles in an aqueous medium and under the usual conditions of experiment or of metallurgical practice, single particles entirely cease to subside, although large enough to be microscopically visible and considerably larger than the diameter established by the Zsigmondy table as the upper limit of truly colloidal particles. This means that suspensions that are not fine-grained enough to be colloids at all, in the technical sense of the word, are capable of persistent suspension and that much of the material of many slimes would not settle at all were it controlled only by the factors mentioned. The fact that slimes do settle and that the situation is not so bad as would be inferred from the theory outlined brings us to the matter of flocculation.

Flocculation is the technical term for the gathering of suspended particles into aggregates. An aggregate composed of many parti-

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[10] For a review of this subject, with citations of literature see Wo. Ostwald, 'Grundriss der Kolloidchemie,' 2nd ed., pp. 231-61 (1911); English ed. pp. 186-210.

cles will behave to some degree like a single larger particle, although one of very irregular surface. It follows that flocculation changes the suspension from one of a multitude of tiny particles into one that behaves as though it were composed of a relatively small number of larger particles. The average effective radius of particle is increased, and the Stokes formula indicates the increase to be expected in the rate of settling, it being remembered that this increase will correspond to the squares of the respective radii. Experiment is fully confirmatory. A flocculated clay-suspension will subside in a few minutes whereas the same material, unflocculated, may remain suspended indefinitely. The rate of settling may be largely increased, even multiplied by hundreds or thousands, by flocculation, and in this lies the explanation of much of the anomalous behavior of colloidal slimes. Slimes settle faster or more slowly not only in response to the actual size of the ultimate mineral particles, but also in response to the more or less complete flocculation of these ultimate particles into larger or smaller aggregates. These floccules are not fixed enough to persist through screen-testing or elutriation even when it can be carried to their dimensions, and the reason for the failure of such tests to agree with the degree of colloidality encountered in practice is clear.

It should be noted that flocculation and its opposite, deflocculation, are purely relative terms like, for instance, 'high' and 'low' or 'smoothness' and 'roughness.' A suspension is more or less flocculated merely with reference to some other suspension. For this reason it is preferable to use the concept of 'degree of flocculation' rather than to refer to suspensions as 'flocculated' or 'deflocculated.' Precision in the determination of this degree of flocculation is not yet possible. No method is known for the accurate measurement of floccules or the counting of their constituent particles, and even if there were, it is probable that the individual floccules of a single suspension would vary widely and irregularly among themselves.

The degree of flocculation of a suspension is extremely sensitive to surrounding conditions; so sensitive, indeed, that changes of flocculation in the true colloidal solutions are among the most delicate of analytical reactions. These changes and similar ones in the coarser suspensions may be caused by many kinds of influences. Temperature, light, the radiations from radium, electro-static charges, and many other variations in energy relations all appear to have perceptible effects. However, these effects of direct energy are less important than the effects of added substances, and it is these latter alone that require consideration here. A large amount of observation and incidental experiment going back for centuries has established three general classes of substances that effect the degree of flocculation or, as it is generally conceived, the rate of settling of suspensions. First are the neutral inorganic salts and the inorganic acids, all of which increase the degree of flocculation and promote settling. Second are the alkalies which (in certain concentrations) have the reverse effect; they decrease the degree of flocculation and hinder settling. These are known as 'deflocculators.' Third are the gel-forming emulsoids, such as gelatin and the like. The effect of these is somewhat complex, but in general they also decrease the degree of flocculation, or at least prevent its increase.

A convenient illustration of the effect of a flocculating agent is furnished by a series of measurements of the flocculating effect of sodium chloride upon kaolin suspensions recently made by Herbert F. McCall under my direction. The data are shown graphically in Fig. 1, the degree of flocculation being expressed upon the vertical axis, the concentration of sodium chloride upon the horizontal. For convenience the scale of the horizontal axis is cubed. The degree of flocculation cannot be set down in any absolute or standard units. The curve expresses no more than the relative degree of flocculation of suspensions in solutions of different concentration and has, so far as its vertical dimension is concerned, only a roughly quantitative value. From this curve it is apparent that in extremely dilute solutions there is no perceptible effect on the degree of floc-

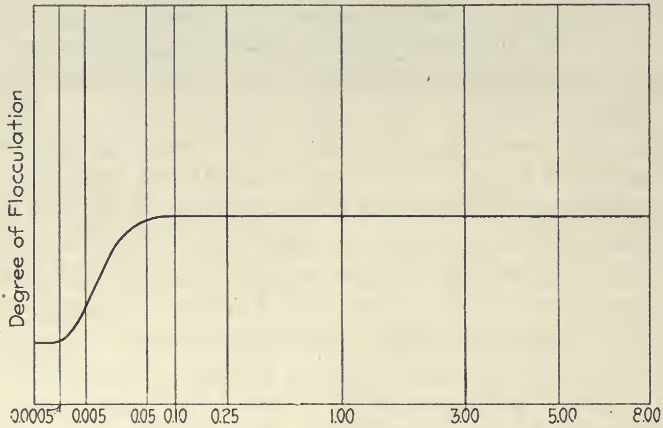

FIG. 1

culation. At a concentration of about 0.0005 gramme per litre an increased flocculation begins to be perceptible; this increases rather rapidly at first and then more slowly to a maximum at about 0.07 gm. per litre, beyond which increases of concentration produce no further perceptible effect on the degree of flocculation. The experiments were extended to saturation (250 gm. per litre), but the corresponding portion of the curve is not shown in the figure.

This behavior is characteristic of nearly all soluble salts and acids acting on most suspended substances. The initial concentration at which an effect begins to be apparent is known as the 'threshhold concentration,' and varies considerably in suspensions of different materials and with different salts or acids. It is worth noting that, contrary to the current conception of the matter, this threshhold concentration is not a sharp point at which the flocculation begins suddenly—like, for instance, the beginning of boiling at a definite temperature—but is rather a range of concentrations inside which the flocculating effect begins and rises more or less gradually to its maximum.

The different acids and salts vary greatly in flocculating power, but these variations have not been investigated with precision. Among typical colloids such as colloidal metals there are many cases in which the flocculating action of added salts appears to increase rapidly with rise in the valence of the flocculating ion. The salts of univalent elements are least active, those of bivalent elements somewhat more active, those of the trivalent elements still more active, and so on. However, there are many exceptions, and general application of the rule is not possible. Doubtless further investigation will supply principles for the prediction of the flocculating powers of various salts, but at present these powers must be regarded as individual and specific.

In solutions of the alkalies the relations are more complex. Fig. 2 gives the effect of potassium hydroxide on the degree of flocculation of kaolin suspensions as determined by F. K. Cameron and me.[11] It is apparent that the degree of flocculation in pure water is not zero, but is importantly greater than in some of the alkaline solutions.

There is again the phenomenon of the threshhold concentration, but when the threshhold is passed, the effect is a decrease rather than an increase in the degree of flocculation and there is a zone of

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[11] Cameron and Free, *Science* (n.s.), Vol. 32, p. 482 (1910); Free, Jour. Frank. Inst., Vol. 169, pp. 430-4 (1910).

deflocculation reaching to a concentration of nearly 1 gramme per litre. As concentration increases beyond this, there is an increased flocculation, surpassing at about 4 gm. per litre the degree of flocculation attained in pure water and rising thenceforth to a maximum of flocculation at about 30 gm. per litre. In greater concentrations there is a decrease, which, however, may be in part merely apparent and due to increasing viscosity and density of the solutions. The characteristic deflocculating effect of alkali appears to be an effect over a certain concentration range only. At higher concentrations there is a flocculating effect not unlike that of the acids and neutral salts.

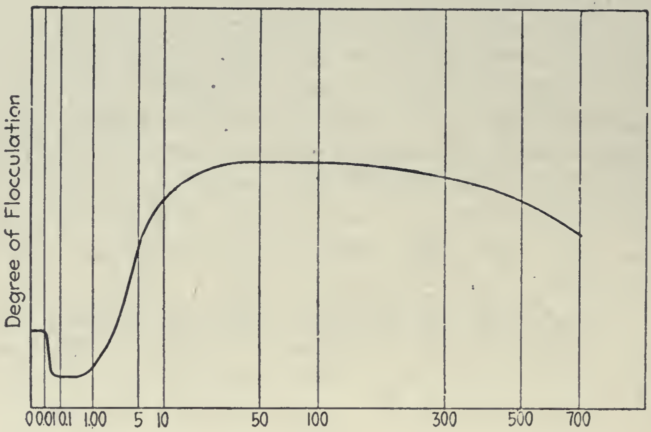

FIG. 2

Concerning the effect of the remaining class of deflocculators, the organic colloids, there is, paradoxically, rather less of precise experimentation but more of theoretical understanding. Substances of this class tend to prevent the flocculation that normally exists or that would otherwise occur on the addition of flocculating agents. It is matter of common knowledge that glue, gelatin, and the like will prevent the subsidence of suspensions, and the similar effects on plastic clays have long found commercial employment. It is significant that these deflocculating effects are exhibited only by colloids composed of liquid particles. It has been suggested that the protective action is due to the coalescence of the liquid droplets of the colloid with the particles of the suspension that it is stabilizing. In this manner liquid films of the protective colloid are formed about the particles of the suspension, and the resultant change in surficial properties is supposed to be responsible for the failure of these particles to flocculate and subside. There is much evidence favorable to this conception of the mechanism and it is generally accepted.

It is important to note that most mineral powders, including all ordinary slimes, exhibit a considerable degree of flocculation when they are suspended in water even when no flocculating agent has been added. It does not matter whether this normal flocculation be regarded as a property of the pure mineral in pure water or considered an effect of the traces of flocculating substances (for instance, carbon di-oxide) present in ordinary waters. The significant fact is that normal slime is always more or less flocculated. Excessive colloidality is usually due to the presence of some substance or circumstance that acts as a deflocculator and destroys or prevents such flocculation as would otherwise occur. It becomes important, therefore, to search out the cause or causes responsible for this deflocculation. It is natural to think of alkalies or of organic colloids, both of which are known to be deflocculators. Traces of alkali in ores are not impossible, especially in highly weathered ores, which are most subject to colloidal difficulties. That the alkali can reach ordinarily a concentration sufficient to develop the deflocculating effect is less probable. The glue-like colloids are not to be expected in slimes except in those rare cases in which slime or mill-water has become contaminated with decaying vegetation or other organic material. If excessive colloidality in general is due in any degree to the deflocculating action of emulsoid colloids it must be because of the presence of some inorganic emulsoid and the only such emulsoid now known and at all probable in rock-powders is colloidal silicic acid. This substance has never been identified in slime but it is possible that it is produced superficially on particles of silicate minerals by the action of water or water containing dissolved carbon di-oxide. Cushman[12] has observed surface alterations of silicate fragments after long grinding with water, and these alterations may correspond to something of this kind. It is difficult to see how any such alterations could occur on sulphide particles or any minerals other than silicates, but the entire matter of deflocculation in slime is so little known that speculation is of small value. Detailed experimentation is essential to a better understanding of the matter and this experimentation may disclose active causes now entirely unsuspected.

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[12] U. S. Department of Agriculture, Bureau of Chemistry, Bull. 92, 24 pp (1905).

Aside from the matter of removing the cause of excessive deflocculation, if that cause can be discovered, there is a possiblity of increasing the degree of flocculation by the addition of flocculating salts or acids, as suggested especially by Ashley.[13] From the curve of Fig. 1 it is apparent that the minimum active concentration (the threshhold concentration) of sodium chloride is not high, and this is true of most of the flocculating salts. There is nothing inherently impracticable in the use of such flocculating agents in ore-dressing; this is already done in several industries and is a common procedure in slime-testing, and in the analytical laboratory generally. An important series of experiments on the action of flocculating agents on slimes has recently been reported by Ralston.[14] Other experiments (with common salt and with ferrous sulphate) have been reported by Laist and Wiggin,[15] whereas Caldecott[16] has observed in practice the reverse, or deflocculating, effect of caustic soda. In this connection it should be noted that the acid or other solutions used in the several leaching processes, and probably also the usual cyanide solutions, have a flocculating action that is not unimportant, although the employment of these solutions is for other ends.

A word must be devoted to the use of lime as a flocculating agent, this material having been used by a number of engineers.[17] At first sight it would appear improbable that lime could have a purely physical flocculating action, lime being an alkali and the characteristic effect of small concentrations of alkali appearing to be a deflocculation rather than the reverse. There is nevertheless a certain flocculating action exhibited by lime, even under laboratory conditions, and it appears that the hydroxides of calcium, and probably of magnesium, do not behave exactly like potassium and sodium hydroxides. It appears probable, also, that certain purely chemical factors enter as well and that the efficacy of lime as a clarifier is due in part to chemical reactions of the same sort as those that control, for instance, the action of aluminum salts in clarifying water. These clarifying actions apparently depend upon the formation by chemical reaction of some flocculent precipitate that entangles and sweeps down the suspended particles. Probably the occasional cases of clarification by organic colloids[18] belong to the same class.

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[13] Trans. A. I. M. E., Vol. 41, pp. 380-95 (1910).

[14] *Eng. & Min. Jour.*, Vol. 101, pp. 763-769, 890-894, 990-994 (1916).

[15] Bull. A. I. M. E., No. 92, pp. 2201-16 (1914).

[16] Proc. Chem. Met. Soc., S. A., Vol. 2, pp. 381-29 (1898).

[17] See, for instance, Richards, 'Ore Dressing,' Vol. 2, p. 1149, and Vol. 3. pp. 1416-17 (1903 and 1909).

[18] See Ralston, *loc. cit.*

The preceding discussion of the causes of excessive colloidality of slime may be summarized as follows. The necessary conditions for the production of a colloidal slime are two: (1) great fineness of particle of at least a part of the slime; (2) a low degree of flocculation of this finely-divided material. Both conditions are necessary. Neither is sufficient alone. It is useless to enter here into the question of fineness of particle or its possible control. Usually such a degree of control as might entirely prevent the production of a very fine material is not practicable, and no less degree of control will be of much assistance against colloidal troubles. The degree of flocculation will be increased by dissolved salts and acids in practically all concentrations and by alkalies in certain concentrations, mostly high. It will be decreased by low concentrations of some alkalies and by the presence of organic gelatinous coatings, in the rare cases when these are present. It is possible that surface alteration of silicate particles, or some other cause, may produce colloidal silicic acid, which may then act as an emulsoid deflocculator. If this is due to surface alteration of the particles it will probably be favored by long-continued grinding or by storage in contact with water, especially in the presence of carbon di-oxide, as, for instance, under long exposure to the atmosphere. High temperatures also favor this alteration. There are probably many other factors affecting the degree of flocculation but they remain unknown.

Ignoring minor uncertainties and assuming a slime of constant fineness, rules for practical procedure may be stated thus: colloidality will be increased by (1) the presence of small amounts of free alkali (except lime), (2) prolonged grinding or long exposure to water or the atmosphere, (3) grinding or storage at high temperatures, (4) the presence of organic materials such as would be supplied by decaying animal or vegetal matter. Colloidality will be decreased by the avoidance of the four conditions just cited and also by (1) the presence in solution of acids or of neutral salts or of certain alkalies in certain concentrations and (2) rapid grinding and handling. The relative quantitative importance of the various factors mentioned and the decision as to which should be selected as a means of practical improvement will depend upon local conditions different in each case. In general, the presence of organic matter has the most effect, but is rarely encountered. Next in quantitative importance is the presence of dissolved acids, salts, or alkalies. Of much less effect is the time of grinding, or storage unless it runs into years, and of still less effect are changes, between usual limits, in the temperature of grinding or storage.

With the recent remarkable development of flotation processes much interest has been focused on the fact that these processes work much less successfully on 'very fine' slime than on material of larger particles. The failure is frequently ascribed to colloidal difficulties in slimes. It is difficult to discuss this matter usefully. The basic theory of the flotation process is not known and no theory has proved generally satisfactory. Accordingly the following suggestions are offered tentatively and merely as a contribution to the current discussion. Only from the slow progress of experimentation can one expect a dependable theory of the flotation processes or of the relations of colloidal theory to them.

Regardless of ultimate theory it seems evident that the essential thing in the flotation process is the tendency of certain minerals to attach themselves to films or globules of oil or to complexes consisting of oil-globules and air (or gas)-bubbles. This tendency of attachment or adhesion varies with different minerals (as well as with different oils) and thus provides a possibility of mineralogical separations. The various matters of froth production, gravitational separation, generation or incorporation of the air or gas, and the like, are all secondary, from my viewpoint, to the fundamental matter of the differential attachment of minerals to the oil or the oil-gas complex. And so far as the size or mineral nature of the particles are concerned interest may be confined to the attachment between the mineral and the oil. The attachment of gas-bubble and oil-film or the maintenance of whatever kind of oil-gas complex is desired may be important to the success of the process but it will depend upon the mutual properties of oil and gas and not upon the properties of the mineral particles. These matters can have no direct effect on the attachment between the mineral and the oil. It seems probable, therefore, that answers to questions concerning the inapplicability of flotation to slimes are to be sought in the peculiarities of the forces controling the oil-mineral attachment.

It is customary to refer to these forces as interfacial tensions. This is merely a matter of words. The fact seems to be that surfaces of contact between dissimilar substances have peculiar properties, which properties are instanced by adsorption and the surface-tension of liquids and which have been referred to above as important among the characteristics of colloids. It appears that the surficial layer of atoms in any mass of matter has properties somewhat different from those of atoms within the mass. When two masses of different kinds of atoms are in contact the one kind of atoms may affect the other kind across the surface, and hence the differences in behavior of surficial atoms, which differences constitute the 'properties of the surface,' may depend upon the natures of *both* the substances in contact. The fundamental theory of these differences in the surficial layers of atoms is unknown but the recent papers of Langmuir[19] are most suggestive.

The special characteristics of surfaces are exhibited, in the main, by two things: adsorption and the surface-tension of liquids. Adsorption has been referred to above as the tendency of dissolved substances to concentrate at the surface of the liquid, either a free surface exposed to the atmosphere or a surface in contact with solids. The best instances are furnished by finely divided solids, which have the great ratio of internal surface to mass mentioned above. Thus, powdered charcoal will remove nearly all of certain dyes from their aqueous solutions by adsorption alone, without chemical reaction or destruction of the dye. Surface-tension is shown in the tendency of liquid globules to take spherical form and, in general, the tendency of all liquid surfaces to contract whenever not prevented by external force. The liquid may be supposed to draw itself together into the most compact shape possible. Among other peculiarities, both adsorption and surface-tension have the characteristic of varying with the curvature of the surface, especially when the radius of curvature is very small. Thus substances in very fine fragments or droplets have properties significantly different from the properties of the same substances in mass. For instance, the solubilities and vapor-pressures are greater. Here again the mechanism is imperfectly understood, but it is not necessary to the present argument.

Returning to the conditions present in the flotation process, if the essential matter is the establishment and persistence of the attachment between mineral and oil and if the tendency to this attachment varies, as do adsorption and surface-tension, with the curvature of the active surface, it is evident that the tendency to attachment may vary markedly with the size of the mineral particle. As a particle decreases in size the average radius of curvature becomes very short. Attachment to the oil might be rendered more easy or less easy—one could not decide which, *a priori*—but it would be likely to be affected in some way. A further complication is introduced by the matter of

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[19] *Metall. & Chem. Eng.*, Vol. 15, pp. 468-470 (1916); Jour. Amer. Chem. Soc., Vol. 38, pp. 2221-2295 (1916).

adsorbed films on the mineral particles. These particles do not present to the oil-globules mineral faces fresh from cleavage and therefore clean. The surface actually presented has been in contact with water or air or both, and the water has probably contained many dissolved substances. It follows that the oil must not only attach itself to the mineral surface but, in order to do so, must displace from that surface a film of water, air, or some dissolved material or materials adsorbed from the water with which the particle was previously in contact. It is probable, though I do not think it is certain, that such attached films of water, air, or other adsorbed substances are held more tenaciously when the particles are small than when they are large. If so, it is possible that such adsorbed films might prevent the necessary oil-attachment in slime but not in larger particles.

It is not necessary, of course, that the disturbing effects of small particle-size should operate always or merely to prevent oil-attachment. The flotational separation would be equally impaired if the tendency to oil-attachment were increased, provided that this increase affected the non-metallic minerals as well as the metallic. All that is necessary to destroy the efficacy of the flotation process is that something should impair the differential character of the attachment of oil to different minerals. The argument outlined above will indicate that this is quite to be expected when the mineral particles become unduly small. As particle-size decreases the properties of the surface become more important, those of the mass (for instance, specific gravity) become less so. Small particles tend to behave more and more alike the smaller they are, regardless of the minerals (or other substances) of which they happen to be composed. Much significant and suggestive work indicates, in general, that surfaces of different substances are much more nearly alike in essential physical properties than are masses of the same substances.

It is not particularly encouraging to come out of the argument merely with the conclusion that the inefficacy of the flotation process with slimes is to be expected. One hoped for suggestion as to how the disability might be removed. It does not seem probable that such suggestions will be forthcoming until the nature of the surface properties of substances shall have been elucidated by further investigation. Improvements made in the meantime in the application of the flotation process to slimes are likely to be purely empirical and largely accidental. Such improvements have been made and undoubtedly will be repeated but it is to be hoped that detailed investigation of the properties of surfaces will furnish before long a surer ground of progress.

SELECTED WORKS ON COLLOIDS

ASHLEY, H. E., 'The Chemical Control of Slimes.' Trans. A. I. M. E., Vol. 41, pp. 380-395 (1910).

BURTON, E. F., 'The Physical Properties of Colloidal Solutions.' London and New York, 1916, 194 pp.

CASSUTO, L., 'Der Kolloide Zustand der Materie.' Leipzig, 1913, 252 pp.

FREUNDLICH, HERBERT, 'Kapillarchemie.' Leipzig, 1909, 565 pp.

HATSCHEK, EMIL, 'An Introduction to the Physics and Chemistry of Colloids.' 2nd ed., London and Philadelphia, 1916, 102 pp.

OSTWALD, WOLFGANG, 'Grundriss der Kolloidchemie.' Dresden. 1909, 509 pp. The first half of a second revised edition has been issued (1911, 329 pp.) and re-printed without change (1913) as the first half of a third edition. The second half has not been issued either in the second or third editions. The second-third German edition has been translated into English by Martin H. Fischer under the title 'A Handbook of Colloid-Chemistry,' Philadelphia, 1915, 266 pp.

TAYLOR, W. W., 'The Chemistry of Colloids,' London, 1915, 328 pp.

ZSIGMONDY, RICHARD, 'Zür Erkenntniss der Kolloide,' Jena, 1905, 185 pp. Translated and revised edition in English by J. Alexander, New York, 1909, 245 pp.

ZSIGMONDY, RICHARD, 'Kolloidchemie,' Leipzig, 1912, 281 pp.

FLOTATION TRIBULATIONS

By Jackson A. Pearce

(From the *Mining and Scientific Press* of September 16, 1916)

Idaho Springs lies within a heavily mineralized district covering the better part of two counties, Clear Creek and Gilpin, in Colorado. Gold, silver, lead, copper, zinc, molybdenum, tungsten, and uranium in most of their manifold mineralogical forms, occur in commercial quantities. In the ores they occur individually and collectively, offering an excellent field for metallurgical research. Within easy reach of Denver with its milling machinery and of Golden, the seat of the Colorado School of Mines, this district is utilized as a testing yard for processes and machinery, falling intermediate between the laboratory and the modern plant. Thus it has become a museum of the world's metallurgical processes. One can find here almost anything from a long-tom to an electrolytic refinery.

Flotation, the most recent process to be placed on exhibition, had been in operation in a couple of local plants a few months before any decision had been made to install a machine at the Argo mill. Much laboratory work had been done on flotation, but as concentration and cyanidation had been running smoothly the desire to change was not burning. However, tests showed that it might be useful on certain low-grade silver ores not particularly well adapted to cyanidation. With this end in view a machine was installed.

Having dedicated the better part of my life to cyanidation, and having contributed largely to the adaptation of cyanidation to these ores, I entered upon flotation with many misgivings, and these few notes may be taken as a confession of a cyanider—not that of a flotation expert.

The preliminary tests were made in a home-made single-cell machine. Especial attention was given to an ore assaying 0.12 to 0.40 oz. gold, 8 to 20 oz. silver, and a strong trace each of copper, lead, and zinc. On account of its relatively high silver-value this ore is not particularly amenable to cyanidation. Although the gold in these ores yields readily to cyanidation the silver is backward, 60% being the average extraction. These tests were carried out with a view to establishing the best conditions as to speed of impellers, consistence of pulp, combination of oils, temperature, and fineness of ore. No critical condition was established in any of these lines, a satisfactory extraction, 85 to 90%, resulting from within wide limits of each. Other gold ores yielded a good extraction by flotation, but not sufficiently to enthuse one as to its preference over cyanidation.

A flotation machine of 100 tons capacity was installed to handle silver ores only, giving us two distinct flow-sheets within the mill. The flotation system comprised stamping to 16-mesh, classifying in Dorr machines, concentrating on Card tables, re-grinding in a tube-mill, re-concentrating on slime-tables, and thickening the combined slime and re-ground sand for flotation. With this arrangement we expected to get 55 to 65% extraction on the tables, and 50 to 60% on the flotation machine, or a mill extraction of 75 to 85%, which, considering the laboratory extraction of 85 to 90%, was a conservative estimate.

In the first three weeks of operation the extraction on the primary tables was 50%, but, contrary to expectation, the extraction in the flotation machine was nothing. Before table concentration this ore carried a trace each of galena, chalcopyrite, and blende, with sufficient pyrite to give a concentration ratio of 4:1. The exceedingly small amount of flotation-concentrate was composed of galena, chalcopyrite, and blende, with an abundance of silica but very litle pyrite. The amount of this product was not sufficient to make an appreciable difference in the assays of feed and discharge. I may add that the assays covering this test averaged a shade higher for the discharge than for the feed. This was disconcerting, to put it mildly. Three weeks is not a long time in which to perfect a process, but it's a mighty long time to watch half the value of the ore going into the creek.

During this time we gave particular attention to oils. According to information gathered from reports, and from personal conversation with flotation metallurgists and salesmen, it seemed that the oil was the most important consideration in flotation. It is generally believed that different ores require different oils. Adjoining properties on the same ore deposit seem unable to use the same combination of oils. In this respect the outlook for flotation here was painful to consider, since this is a custom-mill fed by a multitude of mines in a district producing a great variety of ores. During the three weeks we made exhaustive tests, covering a wide range of oils, trying one after another, individually and in combinations. Operators seem to have favorite places in the system for feeding oils, some favoring the batteries, others the tube-mill, and so on, down to the last cell in the machine. We covered everything from the coarse crusher to the tail-race. Special mixers or emulsifiers are in common use, and we installed one. It seemed to make little difference what oil, how much, or where fed; the froth was always the same—abundant and barren. At times it was excellent to the view, according to one metallurgist, "a most beautiful froth," three to six inches deep, bluish black, and covering the entire froth-cell. At other times it was over-abundant, rolling over both ends, back and front of the machine, developing so rapidly that it required the best efforts of two men to sluice it to the creek. We ran it in this manner for 24 hours—not that we wanted the froth, but to ascertain the ratio of extraction to quantity of froth. Although the total amount of material floated was appreciable, there was no difference in assays of heading and tailing, clearly indicating non-selective action.

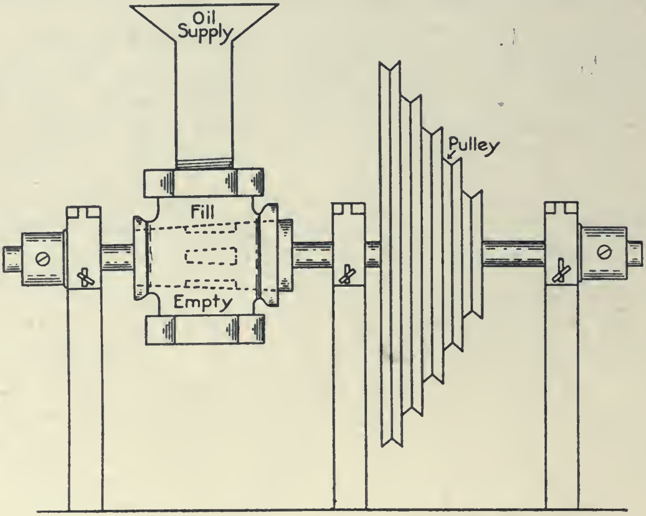

FIG. 1

We used oils furnished by several companies, including crude wood-oils, pine-tar oils, tar, wood-creosote, crude and refined turpentine, asphalt, coal-tar, gasoline, coal-oil, gas-oil, and coal-tar creosote.

Regular examination of the tailing showed pyrite in great plenty, every particle of which was thoroughly oiled, and easily floated from the gangue by simple panning. Was there some condition in the machine to disengage these oiled particles from the froth? Or, were they ever attached to the froth? Or to the bubbles preceding the froth? The machine was built with an intricate set of baffles following the agitation, through the tortuous course of which the bubbles might have dropped their burden. We simplified the baffles, trying a dozen different kinds, one after another, terminating a heart-breaking task with no baffles at all. The machine worked as well without as with baffles; so why baffles?

The mineral particles were well oiled, but lacked the balloon arrangement necessary to conduct them to the surface. Perhaps the agitators were not fast enough to churn the air into the oil. Most people emphasize the importance of peripheral speed, some giving 1500 ft. per minute as the best, extraction and power considered. We were operating at this speed, but increased it by stages to 2100 ft. The motor would not carry this load for more than a few hours at a time; besides, the results were no better than at 1500. We decreased the speed to 1200, and, finding it more economical in power and just as efficient in extraction, left it at that. Later on it was reduced to 1100. Turning our attention to ore-fineness we found a wide range of recommendations, some operators recommending –40, some –60, others –100, and yet others close to –200, nearly all contending that the finer the ore the better was the flotation. My own laboratory experiments on this particular ore gave good extractions on a 12-mesh product. We tried everything from a 16-mesh product direct from the stamps to a product 95% of which would pass a 200-mesh screen. While there were no encouraging signs within this range, the advantage, though small, lay with the coarser product.

During these tests (from January to March this year) the temperature hovered around zero, at times reaching 12 to 15° below. Mill-water was close to the freezing-point, and great care had to be exercised to prevent pipes and launders freezing. Although many consider higher temperatures, say 70° F., essential to good work, we were unable to attain this economically, for lack of facilities for returning the mill-water. Nevertheless, to satisfy ourselves on this point, we turned the full capacity of a boiler into the feed, thereby raising the temperature to 60° F. After six hours at this temperature the difference in effect was in no way sufficiently marked to justify heating.

Next we turned our attention to consistence, the general report favoring 6 : 1 for very fine pulp down to 3 : 1 for sand. We covered a range from 20 : 1 to 2½ : 1, coming to the conclusion that we were nosing the wrong scent.

It might be assumed that inexperience in, or prejudice against, the process, to the one or the other of which most failures are due, was at the bottom of our troubles. While I have spent most of my life at cyanidation, and greatly value the process, and perhaps have a soft spot in my heart for it, the fear of failure in any undertaking greatly exceeds any prejudices I may have against it. Also, it may be said, we had the personal services of several distinguishel flotation metallurgists, no one of whom was able to suggest any change leading to decided improvement.

It was the firm conviction of one engineer that the machine was over-loaded. Although it was carrying $\frac{1}{4}$ its rated load, I reduced the feed to 1/40 its rated capacity, not that we could expect to operate on that basis, but to get a clue if possible to the trouble. There was no improvement.

At last we did what at first we would have done with any other process: we investigated the theories. But with flotation, where everybody has gratifying success and nobody has a gratifying theory, it seemed unreasonable that we alone should need a theory. Theories of flotation are now running the gauntlet of thoughtful criticism so essential to the survival of the fittest. ''Fittest'' in this instance is not amiss, for almost all theories are limited to certain facts, and that theory survives or is accepted which is fittest, that is, which fits the greatest number or widest range of facts. The ionic theory of chemical reactions superseded the affinity theory by virtue of its being more inclusive. No sooner is a flotation theory advanced than there arises a brilliant array of facts tending to disprove it, or, in other words, to limiting its fitness, so that in the present state of the subject it ill becomes us dogmatically to assert that any one is the correct theory, exclusive of all others.

The early efforts to establish a theory involving adhesion, which is only a begging of the question, and one involving the angle of contact or angular hysteresis, have given way to those of more apparent merit involving occluded gases, electro-statics, and interfacial tension. Whether any one of these, or any combination of them, survives is problematical.

Regarding the application of the theory of angular hysteresis, we assumed that the pyrite was not making the desired angle of contact, and, knowing of no way to cause it to do so, we dismissed the subject.

THEORY OF OCCLUDED GAS. The theory of occluded gas so ably advanced by Durell appealed to me in its tangibility. All substances occlude gases, the tenacity of retention being more pronounced in some than in others, but in all cases capable of expulsion by osmotic pressure, increased temperature, or vacuum. Only by virtue of this occluded gas can a bubble of gas be attached to the substance. The sulphides of metals, iron, lead, zinc, etc., constituting the economic portion of the ore, are more tenacious in the retention of the occluded gas than silica, lime, feldspar, etc., constituting the waste portion of the ore. Therefore by regulating the osmotic pressure, temperature, or vacuum the occluded gases of the gangue-material can be expelled entirely, at the same time leaving sufficient gas in the sulphide to act as a nucleus in the formation of adhesive gas-bubbles, thereby giving us 'selective' flotation. Silica was coming over with the froth in preference to sulphides. The evident procedure was to expel the gas from the silica, taking care not to expel it from the sulphides.

We had already tried heat with no success; we were not prepared for trying vacuum; so we tried osmotic pressure. To increase the osmotic pressure, we increased the number of ions by the addition of some easily dissociated solute, say, sulphuric acid. Acid has the advantage over salts in its power to reduce the surface-tension, or the 'surten,'* permitting the formation of bubbles. Starting with a very small amount of acid we increased it gradually to 20 lb. per ton. The more we added the more disheartened we became.

Interfacial Tension. Roughly stated, water and oil (if insoluble) in contact maintain their individual faces, the oil facing the water, the water facing the oil. This is the interface of the two. Now, introducing a solid, say, a small particle of ore, it is found to have three tendencies: it tends to enter the water only; it tends to enter the oil only; it tends to enter both oil and water. If the tendency to enter both water and oil is sufficiently marked for each liquid, it remains between the two, or on the interface, a phenomenon on which is based the theory of interfacial tension. This was wonderfully exemplified in our machine, the only drawback being that it was the silica that displayed a preference for the interface.

Electro-static Theory. Gas and oil films are negatively charged irrespective of the electrolyte in which they are formed. Silica, and perhaps silicious gangue, is negatively charged in the presence of the hydrogen ion, reversing its polarity in the presence of the hydroxyl ion. Sulphides are perhaps positively charged. The mutual attraction of oppositely-charged bodies together with the mutual repulsion of similarly-charged bodies operate to produce selective flotation.

On this assumption we examined the electrolyte: mill-water plus the soluble constituents of the ore. It carried copper and some iron and, among other things, a weak trace of acid. It would seem logical to acidify it more strongly to ensure a negatively-charged silica. But in acidifying to increase the osmotic pressure we observed that it improved neither the osmotic nor electro-static effect. Evidently the

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*M. & S. P., July 29, 1916.

pyrite particles were not electrified, or else were unsuitably charged. We induced electrification, or tried it. By the hit or miss method we attempted to get an electrolyte that would make a more desirable distribution of the electric charges. We tried a long list of salts, acids, and bases, organic and inorganic. Nothing especially noteworthy resulted from these experiments.

By this time we had been operating or experimenting nearly three months, all the time at high tension. I had exhausted myself of ideas, likewise the entire mill-crew, and every visitor to the mill. I pressed everybody for suggestions, talked bubbles all day and dreamed bubbles all night. It certainly seemed that we had left nothing undone that should have been done. I must admit that the extraction had been improving gradually. The froth was making a better selection of material, but was still high in silica, voluminous and difficult to handle. Our endeavor was to produce less froth with more mineral, intensive as well as selective flotation. Exhausted of ideas, we drifted along a few days, when to our great surprise and for no apparent reason whatever, the froth so long sought appeared. The voluminous tough and silicious froth had given way to a thin heavily-laden froth with a greenish-yellow cast of the pyrite. Simultaneous with it the extraction went up and the silica down.

When the recovery increased to 92%, which exceeded our expectations, we felt more kindly toward flotation, even to the extent of trying it on ores that were being cyanided. For seven days we ran flotation and cyanidation side by side on the same ore with a recovery of 96.2% for cyanidation and 96.5% for flotation. This was a surprise from which we have not yet fully recovered.

Suspending cyanidation, we applied flotation to all the different ores we could muster to the mill. The results were so gratifying, cost and recovery considered, that cyanidation was abandoned.

For the four months ending July 31, the recovery by months has been 95.01, 95.06, 95.5, and 95.6%. Recovery by metals: gold, 97.35%; silver, 82.2%; copper, 93.4%; lead, the few assays would indicate about 95%; zinc, no assays. The recovery of the silver, though considerably higher than in cyanidation, is still unsatisfactorily low. This is contrary to the impression so general that because a mineral floats off the table it is amenable to flotation. Silver floats off the table to a greater extent than copper, yet the flotation machine removes a greater percentage of the copper than of the silver. Figures from four months operation show a recovery on table, copper 64.3%, silver 63.9%; on the flotation machine, copper 81.1%, silver 50.7%.

This recovery by concentration and flotation compares agreeably with the best cyanide practice under the most favorable conditions, and when viewed in the light of the wide range of ores treated it is surprising. I am including a table made from assays of lots sampled giving a general idea of the range covered.

I have had a keen desire to know what was at the bottom of our three months' troubles, and to this end have carried on the operation under different conditions as to oil, temperature, consistence, etc. In practice we are using crude wood-creosote, 15%, and a Wyoming gas-oil, 85%, this being one of the best two combinations found in the laboratory tests. We ran 10 days on wood-tar oil and gas-oil; ten days on crude turpentine mixed wtih coal-tar creosote; 2 days on pine-tar and creosote with gas-oil; 2 days on pine-oil with gas-oil; and 3 days on wood-creosote with coal-oil, in all cases getting the same high extraction. During our early efforts to find the right combination of oils we would make a mixture of this, that, and the other oil, try it for 12, 15, or 24 hours as indications suggested, and that not used in the trial was thrown into a slop-barrel. In this way we accumulated a barrel or so containing every conceivable oil on which we could lay hold, organic and mineral, with some organic acids, such as oleic. Running short of other oils one day, we had recourse to this slop, which proved as efficient, entirely so, as any other oil used.

	Gold, Oz.	Silver, Oz.	Copper, %	Lead, %	Gangue	Concentration ratio about	Remarks
1..........	0.14	1.84	..	2.0	quartz	10:1	
2..........	0.18	11.60	trace	trace	feldspar	4:1	
3..........	2.50	7.50	2.0	1.5	quartz	3:1	Gray copper
4..........	1.72	6.88	3.0	..	feldspar	2:1	
5..........	0.74	0.58	..	..	quartz	40:1	Free milling
6..........	0.40	12.20	1.4	..	feldspar	12:1	20 years on dump
7..........	0.62	4.40	..	..	talc	10:1	40% saved on tables
8..........	2.06	0.40	none	none	quartz	2:1	
9..........	1.96	1.30	1.0	0.5	feldspar	5:1	Mostly free milling
10..........	1.05	20.50	1.9	8.0	quartz	3:1	Chalcopyrite

As to temperature, one day during a particularly cold snap, we had occasion to stop the machine for a short time, during which ice of considerable thickness formed over the entire machine. When we started again it was necessary to break the ice to remove the froth, yet the froth was never more heavily laden with mineral than at that time.

To test the influence of consistence, we allowed the entire mill-flow, battery-water, table-wash, and all to run through the machine for three days. The consumption of oil might have been heavier, but the recovery was not impaired.

Many other changes were made involving submergence, speed, baffle, though regularly we use no baffles, none of which interfered with the extraction, that is, noticeably so. The problem of going backward we found as difficult as previously it was to go forward, though beset with much less worry.

I believe that oil, temperature, speed, etc., each has its own influence on the recovery, but within wide limits this can be measured in fractions of 1%. I believe our greatest trouble was due to accumulated slime—colloidal slime, if you like. Tests not yet complete seem to show that not the absolute amount of slime, but the proportion of slime, is the disturbing element.

At present the salient features of the process are:

Ore: Pyritic, containing gold and silver, with small amounts each of copper, lead, and zinc, concentrating anywhere from 50:1 to 2:1.

Oil: Wood creosote 15%, Wyoming gas-oil 85%. Much trouble was experienced in feeding the oil, due to the separation of tar, closing the openings of the vessels. To obviate this I devised a feeder with a rotating cylinder with impressed cups. One can be made easily by filling the central part of a plug-valve with metal and fixing with shaft as shown in sketch. This has been working quite satisfactorily.

Consistence: 4 or 6:1.

Temperature: That of the mill.

Screen test: *minus* 60. The grinding is more for the purpose of liberating the sulphides from the gangue than for preparing the liberated sulphides for flotation. The machine will handle a surprisingly coarse product if it follows good table-concentration.

Speed: 1100 r.p.m.

No acids or other reagents are used.

The froth is small in volume, about ½ in. thick, covering but one-third of the froth-cell. It is removed by revolving scrapers made of 20-mesh battery-screen. The screen-openings are small enough to prevent the froth passing back, but large enough to pass the slime, thus reducing the silica in the concentrate.

COST DATA

By O. C. Ralston

(Written especially for this volume)

The First Cost of installing flotation machinery is low, much lower, in fact, than the other machinery that is necessary to prepare the ore for flotation and to treat the resulting concentrate. The average unit-costs of a number of plants have been summarized in the following tables, which will indicate the probable cost of a complete equipment of flotation machinery.

First Cost of Minerals Separation Machines

Tons per day	Cost per ton
30	$30 to $50
50	25 " 45
100	20 " 40
250	15 " 35
1000	12 " 25

First Cost of Pneumatic Machines

Tons per day	Cost per ton
30	$12 to $20
200	8 " 12
1100	6 " 8
5000	4 " 6

First Cost of K. & K. Machines

Tons per day	Cost per ton
80	$10 to $15
150	5 " 8

In these tables a 24-hour day is assumed. The differences in the cost of machines of the same capacity are due to the fact that a given machine has a much greater capacity for sand than for slime, and it is self-evident that the lowest cost of flotation will be obtained with the easily floated granular material rather than with colloidal slime, which requires high dilution. Other variations in the above data are due to differences in materials of construction and the care with which the machines are built.

Mill-units of more than 1000 tons daily capacity are rare, consequently the first cost of the larger plants is not much smaller than that of the 1000-ton mills. Usually the increase in capacity brings no saving. So the above figures will have to be used with caution, as they represent the averages of a great many plants. It is also to be noted that the above figures cover only the flotation machinery and accessories, not the housing, the crushing and thickening machinery, or the filters. Considerable differences in the cost items are found according to the materials from which the plants are built and it is possible to put up a flotation unit that will have a reasonable life and cost much less than the lowest figure quoted.

The costs of a few equipments are as follows:

In a 50-ton unit in which a single M. S. machine was used, making concentrate from the first few cells and middling from the remainder, the cost ready to run was $2000, while the factory cost of the machine was estimated to be $1500. In case such a machine is to be used with sub-aeration the blower will cost an additional $250.

A 250-ton M. S. machine will cost about $4300 at San Francisco. In one plant in California the total cost of the mill was $115,000 and the flotation machine of the above capacity was only a small part of the total. Where a mill is already running and flotation is added the addition is usually inexpensive whereas a new mill will cost a great deal more. The grinding and crushing machinery alone usually costs many times the amount that is necessary to build flotation machines.

An 1100-ton installation was made in a copper-mill at the following costs. Three 14-box M. S. rougher machines cost about $7000 each and a smaller cleaner unit cost $6000, set up.

Turning to the pneumatic type of machine, the standard Callow cell, 2 ft. by 8 ft., has cost as low as $100 in wooden construction and $200 in iron construction. Usually the iron construction will cost $400 when set up and ready for shipment. Such a cell will have a capacity of from 25 to 50 tons per day. The total cost of a 500-ton plant with grinding machinery and filters, as given by H. R. Robbins for the Calaveras plant, was about $50,000, the machinery being placed in an old mill-building. The National plant, at Mullan. Idaho, built to handle the same tonnage and constructed during the winter, with a fine building to cover it, and with grinding machinery sufficient to treat extremely hard quartzite, cost $153,000. These figures show how hard it is to draw comparisons between two plants designed to concentrate the same tonnage of ore but of different hardness and physical condition. It also shows how unreliable are cost-data when conditions are not specified. The individual machines in these two cases probably cost about the same, but the difficulties of construction and the amount of new construction made the difference.

The Southwestern Engineering Co. advertises the cost of the K. & K. machine as $800 for wooden construction and $1100 for steel construction. Such a cell will have 80 to 150 tons daily capacity.

Janney machines, both of the 'straight agitation' and the 'agitation and pneumatic' types, cost about $850 per cell, which includes the cost of the individual motors. An emulsifier, five roughers, and two cleaners form an equipment capable of treating at least 250 tons daily.

THE OPERATING COST has varied a great deal according to the excellence of the work attained in the individual plants. For instance, a flotation equipment treating 30 to 50 tons of slime per day in a small mill might require the constant attention of one man per shift, while the great plant at the Inspiration mine calls for only one man to each four 800-ton sections (two Mexican helpers are also occasionally used). This is a big difference in labor cost. One of the things to be done in the near future is to develop flotation machines of small capacity for small concentration mills and so designed that they will require only occasional attendance from the table-man.

The tabulated averages of operating costs at a number of plants are given herewith:

OPERATING COSTS OF M. S. MACHINES

Tons per day	Flotation, per ton	Total milling
25	21–75c.	$2.50
100	35	1.30
250	28	0.53
500	23	1.03
800	..	0.58
1100	17	...
2000	..	0.30
4000	20	0.30

OPERATING COST OF PNEUMATIC MACHINES

Tons per day	Flotation, per ton	Total milling
60	15–75c.	$1.50–2.50
90	11–50	...
200	10–35	...
500	9	...
1,000	7	...
2,000	6.75	...
5,000	5.30	...
15,000	5.176	0.40–0.55

It was hard to bring all of the above figures together and in many cases they are scarcely comparable. This applies especially to the total cost, as the data have been collected from all kinds of mills some of which were treating complex ores that required complicated flow-sheets, while others required only grinding and flotation. However, the flotation operations in the different mills do not differ so greatly and the figures for cost on the flotation alone are much more nearly comparable.

At the Mount Morgan test-plant, in October, 1913, the flotation costs were as follows, covering a plant in which 83 tons daily was treated by an M. S. machine:

	Per ton, cents
Supervision	1.83
Wages, operating	3.69
Power	2.96
Supplies, general	0.20
Oil, eucalyptus, petroleum	10.20
Maintenance	5.77
Plant and general	1.25
Sampling, assaying	9.02
Total	34.81

A 250-ton mill operating an M. S. machine in a Western American mill, gives the following figures:

	Per ton, cents
Power and supplies	21.6
Labor	19.3
Flotation royalty	12.0
Total	52.9

The Consolidated Arizona Smelting Co. has given out particularly valuable figures of cost at various times. The mill concentrates a copper ore and the total cost on the 500-ton plant is $1.03, including coarse crushing and flotation royalty. The following are the items over a period of six months, from July to December, 1915.

	Per ton, cents
Wages	5.07
Repairs	0.42
Supplies	0.34
Flotation-oil	3.90
Water	0.62
Power	5.04
Lubricants	0.28
Miscellaneous	0.18
Total	15.85
Overhead, royalty, etc.	18.31
	34.16

Itemized according to operations the costs in this mill as given in another estimate are:

	Per ton, cents
Crushing	25.07
Grinding	32.95
Tabling	19.92
Flotation	34.16
Total on 42,696 tons	$1.1210

A management that allows the publication of such data deserves the thanks of the profession.

A fourth copper-mill to give costs is the Britannia Mining & Smelting Co., which operates its 2000-ton M. S. plant at a cost of 56c. per ton of ore, including royalty, but expects to reduce it to 30 cents.

Another M. S. plant is that of the Timber Butte Milling Co., at Butte, Mont., where a complex zinc-lead ore is treated. This mill requires the addition of acid and heat to obtain good flotation of the sphalerite. This increases the cost, and the complicated flow-sheet causes a total milling cost of $2 to $2.25 per ton of ore in a 500-ton mill. The flotation items, exclusive of royalty, are as follows:

	Per ton, cents
Heat	15
Acid	08
Power	03
Oil	04
Labor	10
Total	40

Another large copper concentrating plant, which originally found it necesesary to heat the pulp and add acid, but which has discontinued the use of heat, incurred the following costs on an 1100-ton scale:

	Per ton, cents
Power at 10c. per hp.-day	3.0
Oil and acid	4.7
Attendance	1.7
Repairs	1.5
Miscellaneous	1.0
Heating	5.0
Total	17.0

The discontinuance of heating lowers the cost to 12c. per ton, exclusive of royalty.

In the Missouri lead-mills 30c. per ton of slime is allowed for pulp-thickening, flotation, and filtering of the concentrate, in units of 500 to 1000 tons daily capacity. Most of these mills are using M. S. machines.

Turning to pneumatic machines, the Calaveras Copper Co., as mentioned in the paper by Robbins (re-printed elsewhere in this book) gives the following costs on a 192-ton plant for crushing, grinding, flotation, and filtering:

	Per ton, cents
Power, 184 hp. at 0.825c. per kw-hr	14.20
Operating labor, 10 shifts at $3.25	17.00
Superintendence, repairs, extra labor	10.20
Supplies	9.86
Total	51.40

With an increased capacity of 500 tons daily, the company expects to lower the cost to 44.4c. per ton.

At the sulphide plant of the Magma Copper Co., at Superior, Arizona, the cost of flotation by Callow machines is said to average about 33c. per ton on 200 tons mill-feed daily. The total milling cost is about $1.11 per ton, of which 22c. per ton is used for ore-sorting before entering the grinding system and 19c. per ton is used in the table department.

At one small mill, in the Coeur d'Alene region, treating 90 tons daily of a galena ore in a home-made pneumatic machine, flotation costs 11c. out of a total milling cost of 35c. per ton.

At a mill in the North-west treating a complex zinc-lead sulphide, differential flotation, calling for careful operation and the use of sulphuric acid, is costing as follows in a 62-ton plant:

	Per ton, cents
Labor	24.25
Flotation-oil	10.23
Acid	3.44
Thickening, filtering, blowers, etc	33.96
Loading concentrate	3.71
Total	76.59

This plant uses pneumatic cells, but the rigid requirements of differential flotation make necessary the use of excessive power and air, and considerable acid and oil. Besides this the need of close attention makes the labor cost rather high for such a small unit.

In the same district another plant is treating a simple galena ore. About 190 tons of slime was treated per day by pneumatic flotation, which has since been displaced by a mechanical agitation equipment which gives a higher-grade concentrate. While in operation the costs were as follows:

	Per ton, cents
Oil	0.83
Power	2.94
Lime	0.56
Labor	1.67
Total	6.00

The lime was used for settling the concentrate. The flotation machines were tended by the table-man who gave them about a third of his time. The simple ore allowed of continuous operation without much attention, and as the operation was not a delicate one the cost of labor was quite low.

At one large copper-concentrating plant containing a unit of 1100 tons the estimated cost of flotation is higher owing to the use of considerable oil and acid, as well as the heating of the solutions. The itemized costs, when the oil is fed into the tube-mill and the Pachuca mixer is left out of the circuit, are as follows:

	Cents
Power	1.5
Oil, acid	4.7
Labor	1.7
Repairs	1.0
Miscellaneous	1.0
Heating	5.0
Total	15.0

At the Miami mill, in Arizona, the total cost of operation for flotation in a 5000-ton plant is 5.3c. per ton. Neither acid nor heat is used and the difference would make about the same relative costs as the set last given.

Royalties. It was to avoid the payment of royalties that the Butte & Superior Copper Co. took up Hyde's method. At the time they commenced operations the royalty asked was about 25c. per ton of ore. Since then Minerals Separation has modified its method of asking royalties and has eliminated the flat rate. In such a district as Joplin or Flat River, in Missouri, the total cost of milling is rarely over 25c. per ton and to pay a royalty as great as the total cost of milling seems prohibitive. The contract between Minerals Separation and the Anaconda-Inspiration companies was published in the *Mining and Scientific Press* of September 16, 1916.[1] It disclcses a sliding scale of royalty ranging from 12 cents on 4000 tons to 4 cents on 30,000 tons or more. A royalty of $\frac{1}{3}$ cent per pound of copper, but not less than 12c. per ton of ore, has been exacted from other mining companies. On zinc ores the royalty is based on the old smelter penalty, being at the rate of 2c. per unit, or percentage, above 8% zinc in the concentrate, so that on a 50% concentrate it is 84c. per ton. On this basis the Elm Orlu company, at Butte, pays about 35c. per ton of crude ore. The lead schedule is the same as that for zinc. On precious-metal ores the royalty is 25c. per ounce of gold and 2½% of the silver value. However, all these royalties are dependent on circumstances, such as the tonnage, the strength of the licensee, and the ups and downs of the patent litigation, which one day appears to have established the M. S. people where they can do what they like and the next appears to divest them of the power of exacting any tribute.

Power. As an example of the importance of the power question I would cite the instance of one 'porphyry-copper' company which reports that the use of flotation in its re-arranged mill will call for 150% of the former power used.

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[1] See also editorial on 'Flotation Royalties' in the same issue.

The power requirements of various Minerals Separation machines have been determined in many instances. At Inspiration a 10-compartment rougher machine takes 100 hp. for 840 tons of ore and two 6-compartment cleaners use 75 hp. This totals 5.1 kw.-hr. per ton of solid passing through the machine. In the same mill the pneumatic machines use only 3.06 kw.-hr. per ton of solid. The M. S. machines are of the Hebbard type, which injects air under the beaters (sub-aeration) and hence is comparable with the pneumatic machines. The comparison is evidently not in favor of the M. S. machines. However, as Laist points out,[2] the oil can be added in the tube-mills at Inspiration and hence the pneumatic cells do not require Pachuca or other mixers. The M. S. cells are good mixers and the difference in power consumption between the pneumatic and mechanical systems is small when power has to be expended on emulsification of the flotation-oil before passing to flotation. At Anaconda, where the acid-oil cannot be added to the tube-mills, the power for flotation is 0.24 hp. per ton of daily capacity while the Inspiration pneumatic machines call for only 0.15 hp. The point is, then, that by adding the oil in the tube-mills the power can be cut down as much as 40% if pneumatic machines are used.

Another Hebbard sub-aeration machine on which some data are available is that of the Utah Leasing Co., at Newhouse. In this plant there are six cells without sub-aeration and six cells of the Hebbard type. The capacity is rated at 500 tons daily and the power used is 75 hp., or 0.15 hp. per ton. Actually this capacity and this figure are not attained, although the oiling in the tube-mill seems to result in some benefit. The air required for the six Hebbard cells of 24 by 24 in. section is 800 cu. ft. per minute at 5-lb. pressure.

At the Daly West mill, at Park City, Utah, a 16-compartment M. S. machine consumes 0.20 hp. per ton, or 3.58 kw-hr. per ton of solid.

At Anaconda, some good data have been collected. On the Anaconda slime a 14-cell M. S. machine with 3 by 3 ft. agitation-compartments and 8-in. impellers requires 75 hp. and has an economic capacity of 130 tons per 24 hours. This corresponds to the use of 0.577 hp. per ton, or 10.32 kw-hr. per ton of solid. The Anaconda sand is much more easily treated and the same size of machine can treat 400 tons per 24 hours with an expenditure of 85 hp., or 0.212 hp. per ton or 3.81 kw-hr. per ton of solid. The total power con-

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[2] Bull. 119, Am. Inst. M. E., Nov., 1916, p. 1880.

sumed in milling at Anaconda is 0.96 hp. per ton capacity or 17.2 kw-hr. per ton of solid.

At the Consolidated Arizona mill, at Humboldt, an 11-cell M. S. machine is said to be operating with 2.61 kw-hr. per ton of solid. This is much lower than the power consumption of other M. S. machines.

At the Old Dominion mill, at Globe, Arizona, the power consumption in a 16-cell M. S. machine is given as 8.6 kw-hr. per ton of solid, the slime being a difficult one to treat by flotation. This is 23.5% of the total mill-power.

As intimated above, the power consumption of a pneumatic equipment is usually smaller than in a mechanical agitator. The Inspiration mill contains largely pneumatic machines and the power consumption, as stated above, is 3.06 kw-hr. per ton of solid. The total mill-power is 16.07 kw-hr. per ton. Hence flotation consumes 19% of the total.

At Miami the power used in Callow cells amounts to 2.88 kw-hr. per ton of solid and the total mill-power is only 11.36 to 12.53 kw-hr. per ton of solid, depending upon which season's reports are used in making the calculation. It is of interest to note that the air is used under 5-lb. pressure and that about 8.9 cu. ft. per minute passes through every square foot of canvas bottom. There are sixty 2 by 9 ft. cells in this plant.

At the Silver King Coalition mill, at Park City, Utah, 5 hp. is needed to supply air for each standard 8 by 2 ft. Callow cell. The pressure is 5 lb. and the air consumption per square foot of canvas is 7.45 cu. ft. per minute.

At the Hunter mill at Mullan, Idaho, 5.6 hp. per Callow cell is needed.

At the Calaveras plant at Copperopolis, California, the air is used at 5.5 lb. per sq. in. and the consumption is 8.2 cu. ft. per square foot of canvas, per minute. The total mill uses 184 hp. on 192 tons of ore per 24 hours, or 0.96 hp. per ton, or 17.2 kw-hr. per ton of solid milled.

The pneumatic plant in the Magma mill at Superior, Arizona, uses 80 hp. for the flotation of 200 tons of ore, or 7.15 kw-hr. per ton of solid—a rather high figure for a pneumatic plant. The total power consumed in this plant amounts to 22.8 kw-hr. per ton of solid, the power used on the concentrating machinery amounting to as much as that used for flotation and the power for grinding amounting to 165% of that used for flotation.

The power consumption by Janney machines is usually not given out by those using them, as it is rather high owing to the intense stirring effects obtained by their peculiar design and their high rate of speed. I am informed that in one plant where five cells in series receive 200 tons of feed daily, the total power consumed is about 75 hp., or 6.26 kw-hr. per ton of solid. This is known to be somewhat high and it is believed that the figure can easily be lowered to 5 or 6 kw-hr.

The K. & K. machine has made some remarkable records in power consumption and is at present being sold on the statement that it uses 8 to 10 hp. per 80-150 tons of feed. This means 1.2 to 1.6 kw-hr. per ton of solid.

Summing up, it would seem that other things being equal, the power consumption of mechanical and of pneumatic machines is about the same when mixing of the oil does not take place previously in a tube-mill or similar grinding-machine. In case it is possible to add the oil to tube-mills the pneumatic system presents a saving of power. For ores that require an extreme degree of agitation, the Janney machine has probably proved better than any others, although it has a rather high power-consumption. The dark horse in flotation machinery, as far as low power-consumption is concerned, is the K. & K., for which very low power-consumption is claimed.

Tabulating what I believe to be the best work demonstrated by the various types of machines in use, the following table of power-consumption has been prepared:

	Per ton of solid kw-hr.
Janney machines (with air-baskets)	5.0 to 6.0
Mechanical Minerals Separation	4.0 " 5.0
Sub-aeration Minerals Separation	3.5
Pneumatic (Callow, Inspiration)	3.0
K. & K.	2.0

THE CONTROL OF ORE-SLIME

By Oliver C. Ralston

(From the *Engineering and Mining Journal* of April 29, 1916)

Not so many years ago it was an accepted axiom among mill-men that "you must not make slime in your mill if you wish to save the mineral." But, sadly, whenever men put ore through crushing machinery some 'rock flour' was inevitably formed, and slime soon came to be considered a necessary evil. For years the slimes were run to waste from concentrating mills for the simple reason that there was no known way of concentrating the valuable minerals in them. If the slimes were rich enough to be smelted as a whole, they were so treated, but this was rarely the case, and even then much of the fine material went into the flue-dust. Those were the days when we knew little more about handling flue-dust than we did about concentrating slime.

Some of the first slimes to yield to any treatment were those from free-milling ores in which some of the gold could be amalgamated, although 'flour-gold' was soon recognized as a source of loss. The ancient buddle recovered galena to some extent from slime containing it, and occasionally it did fair work on the recovery of other slimed sulphides. The savings were rarely large, and it was a case of grab all you can. The development of the Wilfley table brought about the invention of slime-tables, on which recoveries were better, but still left much to be desired. Vanners, likewise, have never made recoveries as high as desired.

For a time after the introduction of slime-tables we were prone to pat ourselves on the back and say that we now had machinery for the treatment of all sizes of ore. At one end of the line we had bull-jigs, and at the other end were vanners and tables. After such pompous talk it is little wonder that many mill-men became timid about publishing tailing-assays. Every mill-man knew that in spite of the best work that he was able to get out of his slime-handling machinery, he was getting lower extractions than were desirable. It was only too well-known that we were still afraid to make slime in a mill and that a classification of crushing machinery was made according to whether

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*Communicated by D. A. Lyons, metallurgist in charge of Salt Lake station in co-operation with the Metallurgical Research Department of the University of Utah. O. C. Ralston, metallurgist, United States Bureau of Mines.

any particular machine in question made slime or not. Further, stage-crushing was developed in order that a minimum of slime might be produced.

Imagine the distrust with which the proposals of the cyanide-men were received when it was found that some ores would have to be slimed in order that their gold might be liberated for cyanidation. As cyaniding developed into the stage of all-sliming, it broke every supposed rule of the art. The procedure seemed suicidal when the experiences of concentrating mills were considered. Thanks to the fact that gold had a fixed price and could always be sold, no matter in what amount it was produced, the cyanide-men went ahead undaunted and developed new machinery. We have seen settling, classifying, decanting, thickening, agitating, filtering, and grinding machinery develop to a stage where slime can be made and treated cheaply.

These were all mechanical methods and were absolutely necessary before we could turn to the chemical or semi-chemical methods of controlling slime. We have seen cyanide-men use lime as a flocculating agent for making slime settle faster, and flotation has recently been added to the methods by which we can control slime. We have found that we can separate sulphide minerals from most slimes by flotation and with recoveries much more nearly perfect than by any of the older machinery. In spite of all the appreciation of this new process, we have not taken sufficient stock of its potentialities.

But the old fear of slime has been slow to die, and there have been doubters that have said that like all other new methods the promise of flotation will be greater than its fulfillment. This verdict must be withheld for a time, as we have seen flotation expand its field wonderfully in the past two years. We find that it is not only possible to float sulphide minerals, but also metals such as gold, silver, and copper, while it is easy to alter oxidized minerals into such a condition that they will float. Further than this, it seems possible to float one sulphide mineral in preference to another—differential flotation.

The significance of these facts is beginning to force itself home, and people all over the mining world are beginning to take stock of the ores that have resisted treatment by ordinary methods. Low-grade and complex ores are becoming popular, for we are beginning to feel confident that we can grind any ore until the particles of the individual minerals are liberated mechanically from one another, and after that we can separate them by flotation or some other slime-process. The War has stimulated mining in the United States to such an extent that some of these new methods have been put directly into practice. A movement of some magnitude has been made toward the dumps and stope-fillings of past generations. This is as good as the opening of new mines, except that the metallurgist reaps the reward.

It is the purpose of this paper to point out a few other methods that seem to promise well in the treatment of slimes and to present the results of some experiments in settling such mill-products. The object of these experiments was to gain control of the settling of slimes in such a manner that they could be caused to settle faster, slower, not at all, or else to make one particular set of minerals settle out of a suspension while another set would remain suspended. This work met with notable success except in differential settling, where only incomplete separation was attained with one ore.

All of this work has been based more or less on colloid chemistry, and it had been my original purpose to discuss thoroughly the principles of colloid chemistry involved. The publication of the series of articles on 'Colloids in Ore Dressing' by E. E. Free makes this unnecessary and allows this paper to be shortened. I am obliged to Mr. Free for the privilege of perusing his papers in advance and for the opportunity to publish my paper coincidently with his. Most of his ideas have my hearty endorsement, and this paper may be looked upon as a verification of many of the principles he has explained. I have already discussed the theory of flotation from the colloid-chemical standpoint[1] as well as a colloid-chemical[2] explanation of the adsorption of gold from cyanide solutions by charcoal and other carbonaceous materials.

My recent work has shown that suspensions of fairly coarse material will react like those colloidal sols known as suspensoids, even though they settle completely in a short time. It is possible to greatly affect the rate of settling of ore-slimes by the addition of relatively small amounts of the proper substances, which are also known to affect recognized colloids in a like manner. Confirmation of the effects produced can be found in current literature, especially in recent patents.

As an example we may take certain patents of B. Schwerin[3], in which a method of separating magnetic particles from slime is set forth. Schwerin depends upon suspending the slime in water and deflocculating it with the proper deflocculating agent in order to break up the little groups of material into individual particles so that the

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[1] 'Why Do Minerals Float?' O. C. Ralston, M. & S. P., Vol. CXI, p. 623 (1915).

[2] 'Precipitating Action of Carbon in Cyanide Solutions,' M. & S. P., Vol. CXI, p. 77 (1915).

[3] U. S. Pat. No. 1,063,893 of 1913 and British Pat. No. 19,313 of 1914.

introduction of a magnet will remove only the magnetic particles. He speaks of the deflocculated ore as being in a sol condition, this being a colloidal term that assumes that a colloid is in such a condition that it will not settle out of the suspending liquid. For my purposes the term 'deflocculated' (also accepted by colloid chemists) is better, as the only assumption in the word is that the floccules usually present in ore-slime are caused to separate into their individual constituents, even though these individual particles are still heavy enough to settle out of the water on standing. Deflocculation leaves the magnetic particles individually suspended so that they can be removed by means of magnets with a minimum of entrainment of non-magnetic particles. Deflocculation is obtained by use of electrolytes of basic nature (containing an excess of hydroxyl ions) when the slime is made up mostly of particles carrying a negative electric charge. Electrolytes of an acid nature (containing excess of hydrogen ions) will likewise deflocculate a slime whose particles are positively charged. Most ore-minerals are negatively charged, and hence the effect of alkaline electrolytes like sodium hydroxide in making many slimes settle more slowly, by deflocculating them, is a well-known observation.

The reality of the electric charges on suspended particles of matter in liquids can be demonstrated by trapping some of the slime between two microscope slides and applying a direct current of 110 volts to the two ends of the arrangement, taking care that space is afforded for the gases evolved by electrolysis in such a manner that the movement of the particles will not be affected by these bubbles of gas. By observing the particles with the microscope, they will be seen to move as the potential is applied, and their motion reverses when the current is reversed. Knowing the polarity of the current applied, we find that the particles moving toward the positive electrode must be negative and the negative electrode is the distinction of the positively charged particles. An improved miniature electric cell of this type has been used in my laboratory for a study of the charges on the particles of material that were tested for flotation in a testing-machine.

The colloid chemists explain deflocculation somewhat as follows: Suspended colloids have been found to possess the power of adsorbing dissolved substances and ions from solution in amounts that vary with the different substances involved. Water is somewhat ionized, and substances that are negatively charged when suspended in water, or even in contact with it, have adsorbed more hydroxyl ions than hydrogen ions, and as the hydroxyl ions are negatively charged, the particles show a negative charge. The amount of the electro-static charge has been measured to be as low as the charge on a single monovalent ion and as large as that on at least a thousand ions, for several typical colloids. If an alkali is added to the water, the excess of hydroxyl ions due to the alkali can be further adsorbed by such a negatively charged particle, and it will repel other similarly charged particles with greater force; or in case they are adhering together in floccules, they become so highly charged that they break apart and the result is deflocculation. Varying dilutions of alkali cause various numbers of ions to be adsorbed onto the surfaces of the suspended particles, giving them greater or less electric charges and causing higher or lower degrees of flocculation. The laws of adsorption are obscure, and we do not know why suspended particles adsorb ions or dissolved substances onto their surfaces and hold them so tightly. It is equally hard to explain why some particular ions are adsorbed more than others. However, the phenomena have been well-enough classified for us to use these various effects intelligently.

Returning now to Schwerin's patents, he describes an experiment in which 1950 grammes of raw ore containing 23.5% iron was pulverized in the wet state until all the particles would pass a screen with ¼ mm. opening, and reduced to a slime by water. To this was added 20 gm. of a normal solution of caustic soda, which deflocculated the components. Part of the ore remained in suspension, and the other part settled out. This latter part was led to a magnetic separator (of the Gröndal wet type) in which the magnetic portion was separated from the non-magnetic. There resulted 175 gm. of magnetic material containing 49.6% iron and 15.6% sludge. The non-magnetic product amounted to 775 gm. with 9% iron and 87% sludge. In the suspension, which was not taken to the magnetic separator and whose largest grains were less than $^1/_{15}$ mm. diameter, a further settlement occurred after some time, amounting to 520 gm. containing 37.9% iron and 29% sludge, while 480 gm. of clay material remained in suspension. The 175 gm. of magnetic concentrate, together with the 520 gm. of settled material, form concentrate weighing 695 gm. of 40.6% iron and 25.6% sludge. This amounts to an extraction of 61.4%. While the work is not particularly good, it indicates possibilities. Further investigation of this process is certainly warranted.

Another magnetic process that works with suspended slimes is the Murex, owned by the Murex Magnetic Co., of London, and protected by U. S. Pat. No. 933,717 of 1909, 959,239 of 1910, and 996,491 of 1911, as well as British Pat. No. 25,369 of 1911 and 174 of 1915. These patents were taken out by A. A. Lockwood and assigned to the

Murex Magnetic Co. The process depends upon the fact that certain oils adhere to particles of sulphide minerals when suspended in water, in preference to adhering to the gangue-particles. The flotation process depends upon the same fact, though utilized in a different way. In this case a finely ground magnetic material, such as iron filings or ground magnetite or pyrrhotite, is mixed into the oil before it is mixed with the ore, and when the oil adheres only to the sulphide minerals we find that these are receiving a coat of 'magnetic paint.' By using a magnetic separator adapted to slime separation, such as the Gröndal machine, the sulphide particles are lifted out of the pulp, away from the non-magnetic gangue. Material of sizes hardly regarded as slime, such as particles 2 or 3 mm. diameter, can also be treated in this way.

The process has been tested at the Bergwerks-Wohlfahrt, near Clausthal, in the Harz mountains of Germany, as well as at the Whimwell mine in Australia. Fairly satisfactory results have been obtained, though occasionally baffling difficulties were encountered. The magnetic paint, which is made up of oil-gas tar mixed with twice its weight of finely ground cast-iron (any animal, mineral, or vegetal oil can be used, or even a fatty acid, soap, or other such material), is applied in a horizontal rotating cylinder resembling a tube-mill except that it is lined with blocks of wood set on end. The mill contains iron or lead shot and pebbles, and the discharge is preferably at the periphery of the end. The metal balls, which are about $\frac{1}{4}$ in. diameter, become coated with the paint, which they, in turn, rub onto the surfaces of the ore-particles. The function of the pebbles is to prevent formation of granules of oiled minerals or any other lumps or agglomerations, and to prevent the shot from sticking together. It is best to give the pebbles a coating of paint before they are put into the mill. The shot are inspected from time to time, and it has been found that so long as they are well-coated, the process works satisfactorily. In case the ore requires grinding, the operation can be carried on in an ordinary tube-mill.

Some difficulty was caused by the tendency of the ground magnetite or other material to leave the oil and go into the water. One of the patents already mentioned covers a method of preventing this loss of the magnetite by using additional agents with the oil when the magnetic paint is made up. When using saponifiable oils, all that is necessary is the use of any sulphate, chloride, sulphide, hydrate, or other salt soluble in the oil or which forms insoluble soaps with the oil. In case the oil used is a mineral-oil that will not saponify, it will require, in addition to the salt, a small amount of soap or saponifiable oil. A small amount of a solution containing 1 to 5% of alum, mixed with the oil, has been found to do good work.

With some ores it is found that an acid solution works best and with others, alkaline solutions. As a mineral froth does not have to be formed, this process can work through a wider range of solutions than can the flotation process. The plant at Wohlfahrt used a neutral solution and treated a galena ore containing 10% lead, while the Whimwell plant used an alkaline solution and treated a copper ore containing sulphides and carbonates.

The Wohlfahrt plant was discussed by James M. Hyde.[4] The plant is a 10-ton experimental one and is said to have done such satisfactory work that other operators have been considering the introduction of the process. A mixture of paraffine oil, pitch, resin, and finely ground magnetite is used. A feed of 9000 kg. of ore per day requires 20 kg. of paraffine oil, 40 kg. of brown pitch, and 0.2 kg. of resin, mixed with 72 kg. of finely ground magnetite. The total cost of running this process is about 59c. per ton of ore. The feed averages 6 to 8% lead and the concentrate 62% lead and 1.13% silver. The tailing averages 1.1% lead. Mr. Hyde asserts that the American equivalents of the oily materials used will cost less in America than they do in Germany.

The Whimwell plant was forced to do a great deal of experimental work and always seemed to have good chances of success, although there were unknown adverse conditions that were never completely mastered. The addition of caustic soda to the pulp seemed to be the best general corrective whenever anything went wrong, but so far as I have been able to learn, the plant left many things to be desired. I do not know what has been the fate of this and of the Wohlfahrt plant since the War started.

The underlying theory of the process is undoubtedly much the same as that of the flotation process, wherein certain minerals are coated with oils while others remain uncoated. In fact, it has not been proved that the Murex process will treat any ore that the flotation process cannot treat unless we except Hyde's statement that under proper conditions it is possible to treat lead carbonate by this process.

In this connection Hyde probably had in mind U. S. Pat. No. 996,491, taken out by Lockwood and assigned to the Murex Magnetic Co., in which is given a method of applying the process to the concentration of oxides and carbonates. This consists of the use of a soluble alkaline sulphide in solution to form a film of metallic sulphide

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[4] 'The Murex Process in a German Works,' James M. Hyde, M. & S. P., June 6, 1914.

over the surface of the carbonate particle by reaction with the same. Thus the reaction with the lead carbonate of an ore is as follows:

$$PbCO_3 + Na_2S = PbS + Na_2CO_3$$

Lockwood gives two examples of the method of working. A 100-lb. lot of ore containing carbonate, phosphate, and chloride of lead was crushed to pass a 24-mesh screen and then suspended in 80 lb. of water. To this was added 4 lb. of finely ground magnetite in 2 lb. of Texas residuum-oil. After agitation for about 10 minutes, a solution containing about 3 oz. of potassium sulphide was added. A film of lead sulphide was formed on the oxidized lead minerals, and they were successfully coated with magnetic paint ready for separation in a magnetic separator. The second example is of the sulphide-filming of a carbonate ore of copper—likewise successful.

As the sulphide-filming of carbonate ores of lead and copper is now meeting with considerable success in the flotation process, it cannot be said that the Murex process has any field that is particularly its own. In fact, there does not seem to be anything the Murex process can do which the flotation process will not do. The greater uncertainty of successful operation of the Murex process, as well as the greater amounts of oils and chemicals used, seems to make it less desirable.

Lockwood[5] has also presented a method of treating the fine of mixed materials in order to avoid having to grind it further. Middlings of galena and sphalerite can be treated with a solution of a caustic alkali and silicate of soda, with the result that the galena and sphalerite separate along cleavage-lines without the need of further crushing. Supposedly this is due to the tendency of sodium hydrate and silicate to disperse a suspension of negatively charged particles. The increase in degree of dispersion of clays by the use of these chemicals is fairly well known. After freeing the galena and sphalerite in this way, they can be separated on a table or on a vanner. He proposes the same method for the tabling of mixed zinc-lead flotation concentrates.

SEPARATION BY USE OF SODIUM HYDROXIDE

Size	Concentrate Lb.	Pb, %	Zn, %	Middling Lb.
On 60	103.5	76.8	3.9	43.5
On 80	172.0			36.5

COMPARISON BY USING PURE WATER

Size	Lb.	Pb, %	Zn, %	Lb.
On 60	88	72	6.5	130
On 80	134			68

Lockwood quotes two tests that were run on two tons of ore from

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[5] U. S. Pat. No. 956,381 of April 26, 1910.

the Broken Hill Proprietary mine. The ore was crushed to about 40-mesh and divided into two lots. One lot of 2240 lb. was treated with 500 lb. of a solution containing 5% of caustic soda and 1% of sodium silicate. After agitating for 30 minutes, the pulp was fed onto shaking screens, and the material remaining on the 60 and the 80-mesh screens was run over vanners. The results are shown above. With the other lot of 2240 lb. the same conditions were observed except that pure water was used on the ore instead of the dispersing agents. The results are tabulated for comparison.

Lockwood examined the middlings in each instance and found that in the case of the dispersed pulp they seemed to be made up of free crystals of galena and sphalerite, while the middling from the test in water seemed to be a true middling, containing composite particles of the two sulphides that required further grinding. Just how he did this is not mentioned, and I am inclined to doubt that true middlings were actually broken up by the sodium compounds. It is thoroughly possible that floccules containing both sulphides could be dispersed by the sodium salts and that it was hence easier to get a good clean tabling test on this account. The idea certainly merits further investigation.

One particularly interesting method of controlling slimes of all descriptions has been described by Count Botho Schwerin, a citizen of Germany, in a number of patents[6]. Schwerin has been instrumental in the application of colloid chemistry to many problems, among which are the dehydration of peat and other organic materials, the purification of clay, the production of special ceramics, and the concentration of various ores. It has been found that many suspensions of clays with their impurities can be purified by utilizing the fact that particles of colloids, when suspended in water, will migrate toward one or the other of two electrodes introduced into the suspension, depending upon the sign of the electric charge carried by the particles. Direct current is used, and since most ordinary particles found in ores will be found to be negatively charged, they migrate toward the anode. As mentioned earlier in this paper, we are able to control these charges by the use of the proper electrolytes added to the suspensions and thereby control the direction in which they migrate and the speed at which they migrate. The water migrates in the opposite direction, and

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[6] No. 670,351, 720,186, 894,070, 993,888, 1,027,004, 1,029,579, 1,053,303, 1,098,176, 1,120,551, 1,121,408, 1,121,409, 1,133,967, and 1,156,715; British Pat. No. 24,670 of 1904, 3364 of 1911, 2379 of 1911, 11,626 of 1911, 27,930 of 1911, 27,931 of 1911, 28,185 of 1911, 23,545 of 1912, 24,666 of 1912, 14,369 of 1912, and 11,823 of 1914; German Pat. No. 239,649, 249,983, 251,098, 252,370, 253,429, 253,931, 265,628, 266,825, and 272,383.

if the particles are congealed into a gel or into a porous diaphragm, the water can still migrate when the electric current is passed. This travel of the water is known as electro-endosmosis, or electro-osmosis. It was first noticed in electrolytic cells containing porous diaphragms, such as have been used in the electrolysis of brine solutions for the formation of chloride and sodium hydrate. The motion of the particle through the liquid is known as electro-phoresis. When a particle migrates toward the anode, the phenomenon has been called cataphoresis and when it migrates toward the cathode, the phenomenon is anaphoresis. The word cataphoresis is often used in place of electrophoresis for the reason that the commonest particles met usually have a negative charge.

One special application of this migration of particles and water is in the purification of clays. This process has been described by Ormondy[7] in the purification of English clays, and by Bleininger[8] for American clays. The impure clay is made up into a 'slip' of the consistence of thick cream, by the use of water, and is preferably deflocculated by the use of a little sodium hydrate. The coarse particles, as well as some of the iron minerals present, separate out by sedimentation. The suspension is run into a metal trough into which dips a revolving horizontal cylinder made of lead or type-metal. The cylinder is made the anode and the trough the cathode for the passage of an electric current under 110 to 220 volts. Bleininger[9] gives a photograph of a laboratory machine of this type, and Schwerin[10] gives a sketch of a larger machine.

Under the influence of the current the clay is deposited on the type-metal cylinder, which rotates slowly, and the deposited blanket of pure clay (this deposit is about $\frac{1}{4}$ in. deep) is scraped off at the top by a scraper. This clay contains about 17% moisture, which is less than that remaining after filter-pressing with a pressure of 2 tons per square inch, and the clay is whiter and more plastic than the impure original clay. The velocity of migration of the particles is about $43 \text{x} 10^5$ cm./sec./volt/cm., which is about the same rate as that of many ordinary ions in solutions. Hence the clay slip requires stirring to bring the particles in contact with the cathode in large enough numbers to prevent water being electrolyzed by the current instead of the particles being deposited. The cost of current in England for the

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[7] Trans. Eng. Ceramic Soc., Vol. XII, pp. 36-64 (1912-13).
[8] Trans. Am. Ceramic Soc., Vol. XV, p. 335 (1913).
[9] Technologic papers of the Bureau of Standards, No. 51
[10] U. S. Pat. No. 1,333,967.

depositing of a ton of clay is from 10 to 64c., and a plant capable of producing 40 tons per week of finished product will cost $25,000.

Bleininger is of the opinion that the greatest use of this machine will be as a substitute for the filter-press. Recent experiments seem to bear out that opinion. Most of the impurities of the clays are removed during the period of sedimentation preceding the electrophoresis, and the only function of the electrical operation is to remove the clay-particles from the suspension in a fairly dry state. When very colloidal ore-slimes resist all attempts at filtration, this method of collecting may prove useful. Experiments with ordinary free-settling slime by this method have been carried on in my laboratory and have shown that most of the particles are too large to be handled effectively by the method. With a clayey ore capable of a high degree of dispersion, better results can be obtained, although they are still far from what can be done with the true clays.

In passing it might be well to call attention to the fact that Schwerin's patents contain a wealth of information on the properties of various suspended particles and on methods of controlling them. He finds, for instance, that a particle more or less indifferent toward the electric current can often be electrified into life by the addition of some colloid body, such as colloidal silicic acid, and a deflocculating agent, like sodium hydrate. The colloidal silicic acid is adsorbed on the surfaces of the indifferent suspended particles, and the resulting composite particles are more active. Sodium silicate will hydrolize into silicic acid and sodium hydrate; hence it is at once a combined activating and deflocculating agent. In another place he mentions the fact that with a well-deflocculated suspension the consumption of electric energy is less and the speed of the particles greater.

The importance of the investigation of all these colloidal phenomena in their bearing on the control of ore-slimes need not be magnified. They are mentioned in the hope that further research will be instigated by parties who can profit by the results of such investigation.

Most of the original work to be reported in this paper deals with the subject of slime-settling, my original object having been to control the rate of settling of ore-slimes by the application of the principles of colloid chemistry. As previously mentioned, it has been possible to make almost any slime settle faster or slower, and some success has been attained in differential settling.

The use of lime for the flocculation of low-settling slimes has been common practice among cyanide operators, and many a cyanide plant would not be able to work without the use of lime. Slow-settling slimes in which the individual particles can hardly be distinguished, can often be caused to gather into large floccules by the addition of small percentages of caustic lime. These large flocks settle with much greater speed than do the small individual particles. Nicolai[11] gives the results of recent work in Germany on the clarification of muddy mill-water by the use of magnesium chloride, a waste-product from the potash works. Magnesium chloride is an effective coagulant.

The idea of deliberately causing a slime to settle more slowly does not seem to have been applied by anyone. There are, however, conditions under which such deflocculation could be utilized, aside from those already mentioned. For instance, the work reported here shows that it is possible to deflocculate the so-called true slimes so that the coarser material can settle out of the suspension separately. This would be the ideal separation of non-leachable material from leachable sand, which the Dorr and similar classifiers approximate. Under these conditions the sand that settles will not be coated with entrained slime. In fact, the Dorr classifier could be used to make the improved separation.

Another application of deflocculation could be made in the transfer of slime through launders over considerable distances on level ground. When deflocculated, the slime does not tend to settle out so badly, and on arriving at its destination it could be flocculated and deposited by the use of the proper agent. Ditches that have become clogged with clay ought to be opened up by occasional flushing with water containing a deflocculating agent, while the settled material can be loosened by drags. The use of lye to open clogged drain-pipes is a familiar example. Deflocculated clay slips have much less viscosity than ordinary clay slips, and a piece of damp clay will almost liquefy upon the addition of small amounts of the proper alkalies. With these points in view, there seemed to be a sufficient encouragement for the following series of systematic investigations.

Owing to the fact that the chief interest of the mill-man lies in the rate at which he can draw off clear water from a thickening-tank and what will be the percentage of solids in the thickened pulp, the following method was used in the study of the rate of settling:

A series of 200-c.c. graduates of approximately the same size was obtained, and weighed quantities of ore were introduced into the graduates, which first were partly filled with water. The rise of the water-surface on the introduction of the ore allowed a measure of the volume of the ore, and knowing its weight and volume, the density of

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[11] *Metall und Erz*, Vol. III, pp. 135 and 155 (1915).

the dry ore could be calculated. The graduate was then filled to the 200-c.c. mark. By placing the hand over the mouth of the graduate and inverting and shaking several times, it was possible to suspend the ore homogeneously in the water before the graduate was put down and settling allowed to begin. The rate of subsidence of the surface of the settling slime was then noted. As the particles in the suspension have zero velocity at the beginning, the rate of subsidence of the slime-surface increases to a maximum and then diminishes as the density of the thickened pulp increases, causing the particles to get more and more in one another's way. In Free's series of papers we find that he observed the position of the surface of the consolidated slime in the bottom of the graduate, instead of the surface of the sinking column of thickening slime. Either method gives us an idea of the average rate of settling of the slime-particles.

With dilute suspensions, the larger particles tend to drop out first and the smaller particles gradually thin out of the upper layers of the water so that no definite upper surface of the thickening slime is formed. However, with most ore-slimes this is only a tendency, as the smaller particles sink with a measurable velocity and the surface of the thickening slime will be indistinct and hazy, owing to these slowly-settling particles tending to cloud the clarified water above. Later this hazy surface of the thickened slime, at a perfectly definite position and at a perfectly definite time, will suddenly change to a sharp line of separation between the settling slime and the clarified water. Shortly after this the rate of settling of this surface will fall off greatly. With slimes containing more and more solids at the beginning of settling, the position at which this line appears is higher and higher up in the tube, although it takes a measurable length of time for any previously agitated slime to consolidate to a condition such that a definite line of demarcation can form. With thick slimes and when well flocculated, the line appears in a few seconds and practically at the surface of the water.

This difference in behavior between dilute and concentrated suspensions is undoubtedly due to the fact that in the dilute suspensions the particles fall individually, while in the concentrated suspensions they seem to settle collectively. The particles, when falling individually, exhibit the greatest speed of settling. In Free's papers I find much the same observation. He has termed the two types of settling 'subsidence' and 'consolidation.' In order to avoid confusion of nomenclature, I have adopted his terms in the following discussion. Nearly all the dilute suspensions of slimes that I have studied begin to settle by subsidence until at a definite concentration of solids the line appears and consolidation settling begins. With most commercial pulp-densities subsidence-settling takes place only to a limited extent unless the slime is deflocculated. It is rare that the mill-man deals with as slow-settling a slime as Free's kaolin suspensions.

In addition to the two types of settling already mentioned, I have observed a third, for which I propose the name 'compacting.' With most freely-settling ore-slimes, this type of settling sets in at about 40% solids, illustrated in Fig. 1 and 2. During this phase of settling,

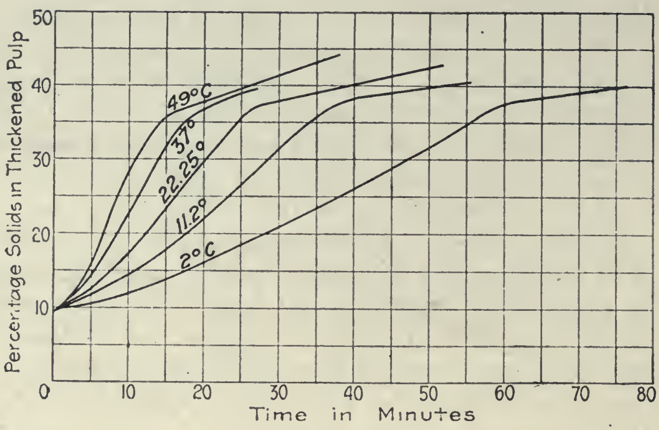

FIG. 1

the thick material in the bottom of the graduates seems to be slowly re-arranging itself into closer packing. The rate of settling is always considerably slower than during consolidation. When long settling tubes are used, the material that has settled onto the bottom first is well compacted by the time the column of slime above it has reached the consolidation stage, and hence consolidation shades imperceptibly into compacting. Only short tubes showed this particular phenomenon, and as Free's work was with long tubes, his results do not show the compacting stage. In my own work the compacting was very evident in the 200-c.c. graduates, which were about 10 in. deep. It was not observed in a tube giving a column of 36 inches.

Roughly speaking, most ordinary dilute slimes will settle by subsidence until the thickened material reaches about 10-20% solid, at which point the surface of the settling material suddenly becomes clear-cut and the settling enters the consolidation phase, which it pursues until the pulp contains an average of about 40% solid, where it enters the compacting phase. Some decrease in velocity is noticed on passing from the subsidence to the consolidation phase, but a great decrease in velocity often takes place on passing into the compacting phase. As will be seen later, the effect of the addition of electrolytes and of colloids is to shift the critical, or transition, points (where the settling changes from one phase to another).

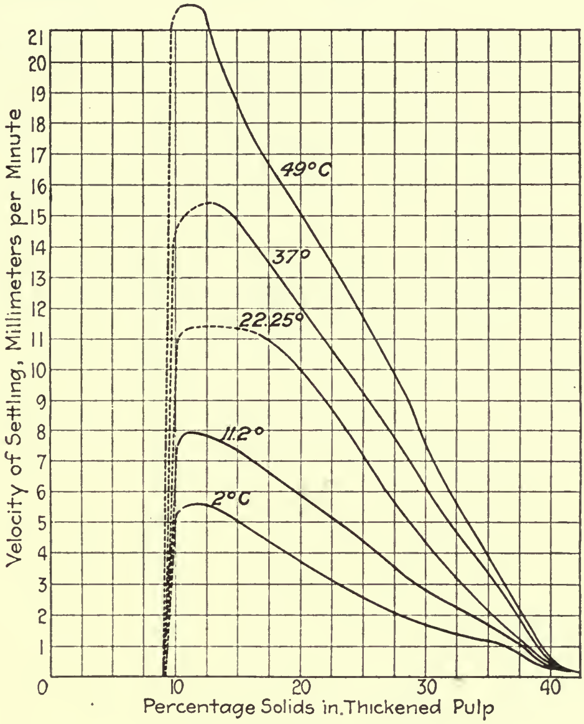

FIG. 2

The only feasible explanation of the difference between subsidence and consolidation would appear to be the following: In dilute suspensions the larger particles of the slime would tend to settle relatively faster than the others, and in dilute suspensions they can go down without entraining smaller particles; so the latter are left behind to settle more slowly. Hence the water above the subsiding slime is always somewhat cloudy. With more concentrated suspensions it is possible to reach a consistence in which the distance between the larger particles is so small that the particles of smaller size are trapped and carried down. This suspension of the larger particles might be regarded as a filter for the suspension of the smaller particles.

THE FLOTATION OF OXIDIZED ORES

By Glenn L. Allen and Oliver C. Ralston

(Written especially for this volume)

Introduction. *Concentration of sulphide ores by flotation has met with such success that attempts have recently been made to apply the process to the flotation of ores other than natural sulphides. Most of the experimental work in our laboratory at the Utah station has been done on the oxidized ores of lead. Only minor attention has been given to the oxidized ores of zinc and of copper, for the following reasons: little success has been had with the zinc ores; many others are engaged in testing copper ores, so that there was no pressing necessity for experimentation with copper ores by the Bureau, although an attempt has been made to co-ordinate the work of those who are willing to join in solving the problem. Flotation of oxidized minerals depends upon a preliminary 'sulphidizing' by any method that will convert at least the surface of the mineral particles to a sulphide of the metal. This step is followed by flotation of the artificial sulphide.

Patents. The first method for the flotation of oxidized ores to appear in patent literature was that of F. B. Dick. It is contained in British patent 16,667 of 1908. This method calls for the reduction of the oxide to metal in a furnace with a reducing atmosphere, followed by the flotation of the 'prills' of metal formed. As lead and copper are the only two common metals easily reduced to the metallic form, it is probable that Dick had no others in mind. He mentions the oxidized ores of copper in silicious gangue from the Benguella and Katanga districts of Central Africa as being amenable to this kind of treatment. From the coarse grinding recommended by him (20-mesh) it is probable that he had in mind either the film or the bulk-oil types of flotation.

In British patent No. 8650 of 1910, Sulman & Picard, of Minerals Separation, Ltd., have patented a like idea, evidently with froth-flota-

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*This review of the subject is based mainly on a paper, by the same writers, issued by the U. S. Bureau of Mines in July 1916. There has been added a discussion of the patent literature dealing with the subject. The text also is altered somewhat to include more recent information. Most of the portion concerning flotation of lead-carbonate ores has been revised by Mr. Allen, who has continued his work while in the employ of the Shattuck-Arizona Copper Co., in whose Bisbee mine a large tonnage of lead-carbonate ore has been disclosed while mining copper ore. N. C. Christensen and R. W. Johnson have assisted in collecting some of the evidence on which the conclusions of this paper are based.

tion in mind. They claim the application to metals in "easily reducible oxides." Such metals as lead and copper are mentioned. One specific application is the treatment of mixed zinc and lead oxidized ores. The lead can be reduced easily in a reducing atmosphere at 600° C. while the oxidized zinc compounds are unaffected at this temperature. After cooling the reduced product out of contact with the atmosphere the lead could be floated away from the zinc. We have not tested this process thoroughly but we are inclined to believe that oxidized forms of copper are more likely to be reduced to an easily separable form than oxidized forms of lead. However, in the examination of the reduced product of copper prepared by others for proposed gravity-separation small shots of metallic copper could be seen attached to the gangue. After the reduction it would be necessary to grind the product to liberate the 'prills' and 'leaves' of metal from the gangue.

Treatment of complex sulphides by this process assumes that the ore is first roasted to oxides before reduction. In case part of the metallic sulphides is roasted only to sulphates these would tend to be reduced to sulphides again during the reduction period. In the case of mixed lead and zinc sulphide ores it would be all right to allow the lead to roast to sulphate (which is easily accomplished), but any sulphate or basic sulphate of zinc would be undersirable, because the sulphide of zinc formed would tend to float.

The first American patent covering sulphidizing and flotation is that of Alfred Schwarz (U. S. 807,501 of December 19, 1905). It was taken out coincidently with other patents covering methods of bulk-oil flotation, for froth-flotation was only then being started. He claims the use of any 'soluble sulphide' and states that he generally uses an excess of sulphur over that theoretically necessary to convert the oxide, carbonate, or chloride of the metal in question completely to the sulphide. A poly-sulphide of sodium made by boiling sulphur and caustic soda is mentioned.

The next mention of sulphidizing and flotation of oxidized minerals was in British patent 26,019 of 1909 by Sulman & Picard. This patent shows familiarity with the sulphidizing and flotation of ores. While oxidized copper ores are given a prominent place, the sulphidizing of oxidized ores of lead is also mentioned. Hydrogen sulphide, as well as other soluble sulphides, is said to be suitable, and it is here that the use of sulphur vapor is first mentioned in patent literature. One variation of this method is to heat the powdered ore with pyrite in a neutral or reducing atmosphere. Such treatment distills the feeble atom of sulphur from the pyrite, so that the sulphur combines with the oxidized lead.

Joseph T. Terry, in U. S. 1,094,760 of April 28, 1914, describes the use of hydrogen-sulphide gas in a flowing pulp of an oxidized ore of copper (other metals also are claimed) with a suitable apparatus for the recovery of any excess gas after sulphidizing the pulp. The use of sodium sulphate is also described and the addition of copper sulphate to help in the formation of nuclei of copper sulphide around which the formation of sulphide granules and coagulations can take place.

H. B. Hoveland and G. B. Frankforter entered the sulphidizing field with U. S. patent 1,098,668 of June 2, 1914. This claims the application of hydrogen-sulphide gas to dry ore for the sulphidizing of oxidized minerals previous to flotation. It claims advantage in the greater rapidity of the sulphidizing reactions, 10 to 20 minutes in an atmosphere of hydrogen-sulphide gas being said to be sufficient. From the known great velocity of diffusion of gas molecules as compared to the velocity of the diffusion of the same molecules when in aqueous solution, such a claim seems justifiable. Our own experience on lead ores does not verify this statement, as will be seen later. However, Hoveland and Frankforter mention the carbonate ores of copper in illustrating their process while our work has been confined largely to the carbonates of lead. A surprising claim is made for the sulphidizing of an oxidized capping in place. The patentees state that the gas molecules finally penetrate to the centres of the masses of ore, sulphidizing the oxidized minerals of copper and disintegrating the rock so that it can be more easily mined.

Raymond F. Bacon, in U. S. 1,140,865, of May 25, 1915, discloses the use of hydrogen sulphide and sulphur di-oxide in a pulp to effect flotation by means of the colloidal sulphur resulting from the reaction of these two chemicals. The colloidal sulphur is said to serve as a substitute for flotation-oil. By introducing hydrogen sulphide first the oxidized minerals can receive a sulphide coating before the excess of hydrogen sulphide is neutralized by the introduction of sulphur dioxide. This feature is embodied in another of Bacon's patents, No. 1,140,866 of May 25, 1915, and is described in connection with some tests of an oxidized copper ore. ''One ton of oxidized copper ore containing 2% of copper, and crushed to pass a 60-mesh screen, is placed in a Pachuca tank with three tons of water. The air is turned on and the water agitated for a few minutes, just enough to obtain a good mixture of the ore and water. Immediately after the violent agitation has ceased and while considerable of the ore is still in suspension hydrogen sulphide is forced into the body of ore and water through suitable inlet-pipes in the bottom of the Pachuca tank. With the ore used in this experiment 60 cu. ft. of hydrogen sulphide was admitted. This amount of hydrogen sulphide is not sufficient to convert all the oxidized copper present into the sulphide, but for purposes of flotation this is not necessary. It is only necessary to form a surface-film of copper sulphide surrounding each oxidized particle. The mixture of ore and water is allowed to stand a few minutes with the hydrogen sulphide, then a slight excess of sulphur di-oxide is run in through the inlet in the bottom of the tank. The sulphur di-oxide gas used for this purpose may be the pure gas or dilute impure gases such as smelter fumes. In case the latter are used they may be introduced in place of air to effect the agitation of the mixture. A short time after the introduction of the sulphur di-oxide the mixture of ore, water, etc., is tested with lead-acetate paper and when the hydrogen sulphide has disappeared the mixture is allowed to flow into a flotation-tank, where the sulphide-coated copper oxide, carbonate, and silicate particles are floated off and thus separated from the gangue. With the particular ore cited, a recovery of 83% of the copper was thus effected, the concentrate containing 21% copper.''

Our own tests show that it is very difficult to obtain flotation after the pulp has been treated with sulphur di-oxide. Sulphur di-oxide and the sulphites are known as inhibitors of flotation, and yet Bacon makes the claim that better flotation is obtained in the presence of a slight acidity due to sulphur di-oxide. Bacon's process is not as simple as it sounds.

In U. S. patent 1,197,589 of September 12, 1916, he has still further broadened his claims, and states that this patent is an improvement over his former method. This patent is well written. He has reversed the order of application of the two gases. Sulphur di-oxide is applied first in order to convert all of the copper to sulphite and the subsequent treatment with hydrogen sulphide precipitates the copper as sulphide. He states that it is not necessary to obtain complete solution of all the copper before precipitation although it may be best with some ores. Colloidal sulphur, from the reaction of sulphur dioxide on hydrogen sulphide, is also produced and the claim is made that this acts as a substitute for flotation-oil in whole or in part, resulting in better flotation. In case an ore contains lead, copper, and zinc the copper and zinc go into solution. The hydrogen sulphide precipitates only the copper from solution and it is then floated out. A subsequent precipitation of the zinc with an alkaline sulphide renders it amenable to subsequent flotation. We regard this as a most extravagant claim.

A few months later Hoveland took out another patent for the sulphidizing of minerals, U. S. 1,159,942 of November 9, 1915. It is claimed that in the application of calcium sulphide for the sulphidizing of minerals the action is greatly accelerated by the presence in the solution of some ferric sulphate. Sulphuric acid, or sulphur di-oxide and oxygen, is first applied to the ore-slime to form copper sulphate. On addition of calcium poly-sulphide and ferric sulphate to the pulp copper sulphide is formed and can be removed by flotation. The function of ferric sulphate is to oxidize any excess sulphurous acid. We fail to see the advisability of getting copper into solution and then reprecipitating it as sulphide, except that flotation serves as a substitute for filtration. Since lead carbonate does not go into solution, the same advantages are not obtained and this method offers no apparent advantage when applied to lead ores.

Later Hoveland obtained two more patents; these covered the use of apparatus for carrying his invention into effect. These patents were 1,164,188 and 1,164,189 of December 14, 1915. The idea that seems uppermost in his mind is that of sulphating the ore by treatment with sulphur di-oxide and oxygen under pressure in a specially constructed agitating-apparatus, arranged for continuous operation. He claims that the sulphating under pressure of minerals like copper carbonate in such an apparatus is much quicker and more complete than at ordinary atmospheric pressure. Here he explains that in order to sulphidize the sulphated material well with calcium poly-sulphide the excess of sulphur di-oxide can be oxidized by the presence of ferric sulphate. In fact, we believe that Hoveland could not conduct flotation well if sulphur di-oxide or sulphites were present in his pulp in any considerable quantity. His apparatus is also adapted for flotation in a closed vessel, so that the same air could be used over and over again for flotation, and if necessary some other gas than air could be employed, in order to prevent re-oxidation of the precipitated copper sulphide.

Bacon was the next patentee (U. S. patent 1,180,816 of April 25, 1916). His patent covered the use of hydrogen sulphide under pressure during sulphidizing. One of the most recent ideas is contained in his patent No. 1,197,590 of September 12, 1916. This deals with both oxidized ores and those that can be wholly or partly roasted. The application to the mixed sulphide ores is discussed in this volume under ''Differential Flotation.'' Occasionally an oxidized ore containing lead and zinc carbonates is so intimately intergrown that on applying a sulphidizing agent it is possible to film the lead carbonate with lead sulphide, but so much zinc is entrained with the lead that flotation fails to separate them. As will be seen later, zinc carbonate does not appear to sulphidize under these conditions and occasionally the lead carbonate can be separated from a free ore. But when it is not freed by crushing, Bacon proposes to treat the ore with an acid, such as sulphuric, converting the lead to the insoluble sulphate and the zinc to a solution of zinc sulphate. On treating the pulp with hydrogen sulphide the lead is converted to sulphide and any silver or copper are likewise converted to sulphides, while the solution of zinc sulphate, being acid, is unaffected. Flotation is then supposed to remove the lead, silver, and copper. After this has been accomplished, the acid in the pulp is neutralized and the zinc sulphate converted to sulphide by addition of an alkaline sulphide. The zinc sulphide is then likewise removed by flotation. By these methods metals like copper, lead, silver, mercury, cadmium, and bismuth can be separated from metals like iron, zinc, and nickel in oxidized ores. The flotation is merely a substitute for filtration.

As mentioned elsewhere, the chemistry involved in this patent is good, being that underlying qualitative analysis, but owing to the practical difficulty of obtaining satisfactory flotation in the presence of such soluble compounds as iron sulphate and copper sulphate we doubt whether this process, as patented by Bacon, can be made to work. If the patent is valid, it is probably broad enough in its claims to cover many truly meritorious ideas that may be developed and that will not be subject to the same difficulties.

Lead Carbonate. The necessity of a process for the recovery of lead from its low-grade carbonate ores has never been emphasized, yet it is a common thing to find old mill-dumps containing from 5 to 10% of lead as carbonate in a finely divided form incapable of satisfactory recovery by gravity methods and too 'dry' to smelt. The tendency of lead carbonate is to form flakes; that is why the artificially manufactured basic lead-carbonate, used as a paint under the name of 'white lead,' is efficient in covering a surface.

As the flotation process is applied successfully to finely divided material, the extension of the process to slime containing lead carbonate is immediately suggested. So far the most promising method is a preliminary treatment by 'sulphidizing,' whereby the particles of lead carbonate are first converted, superficially at least, into the sulphide of lead, which is amenable to ordinary flotation.

Several ways of doing this have been proposed:

1. Sulphidizing by means of hydrogen sulphide gas applied to either the dry crushed ore or to the wet pulp.

2. Sulphidizing by means of a solution of sulphide of sodium or other sulphur-compounds of sodium.

3. Sulphidizing by means of a solution of calcium poly-sulphide or other sulphur compounds of calcium.

4. Sulphidizing by means of sulphur vapor applied to dry crushed ore.

5. Sulphidizing by means of a flotation-oil containing loosely combined sulphur and capable of giving up the sulphur to the oxidized ore.

6. Sulphidizing by the use of a solution of colloidal sulphur.

Not all of these ideas are new; in fact, patent claims have been made that are probably broad enough to cover them all. However, exact data as to the effectiveness of the various methods of sulphidizing oxidized ores are lacking.

Hydrogen Sulphide is the sulphide most naturally suggested as a reagent for the sulphidizing of ores. This was the first reagent tested by us, because Hoveland's patent for dry sulphidizing looked so tempting. Some of the best results with dry hydrogen sulphide are given in Table I. The ore tested came from the May Day mine in the Tintic district of Utah. Practically all of the tests were performed in a Janney machine. At first we thought that the low extraction of lead following a short time of sulphidizing of this ore in the dry state was due to the rubbing off of the sulphide film, so the more gentle treatment possible in a Callow cell was tried. Practically identical results were obtained. It was found that with longer treatment with hydrogen sulphide the extractions increased on both silver and lead. Hence the trouble with the early tests must have been due to insufficient time of gas treatment. It was surprising to see the way in which the gas would react with the ore. When placed in a bottle on a rolling agitator the

Table I

Sulphidizing with dry hydrogen sulphide.
Ore from May Day mine, Utah. 4.2% lead, 2.36 oz. silver, 4.6% iron, 84% insoluble.
500 gm. per test, Janney machine. Oil, 0.9 lb. per ton. (Sunny South pine-oil No 5)

No.	Sulphidized Minutes	H_2SO_4 added during flotation	Weight Gm.	Froth, Analysis, and Recovery.							
				Lead		Silver		Iron		Insoluble	
				Assay %	Recovery %	Assay oz.	Recovery %	Assay %	Recovery %	Assay %	Recovery %
1	15	none	31·3	13·3	20·1			11·7	15·9	60·0	4·5
2	30	″	22·5	9·6	10·1			17·1	16·7	59·1	3·2
3	60	″	40·5	13·7	26·4	5·74	19·7	10·4	18·3	60·6	5·8
4	120	″	54·0	8·7	22·3	5·28	24·2	16·9	39·7	60·7	7·8
5	480	″	93·0	9·5	42·0	4·24	33·4	14·7	59·5	58·6	13·0
6	15	95·7 lbs. per ton	23·5	22·9	25·6	16·00	31·9	20·1	20·5	30·2	1·7
7	30	″	36·5	21·6	37·5			17·5	27·8	33·2	2·9
8	60	″	39·5	21·3	40·1	13·50	45·2	16·1	27·7	35·0	3·3
9	120	″	52·0	25·3	62·7	11·70	51·6	11·3	25·6	38·6	4·8
10	480	″	68·0	24·6	79·7	9·60	55·3	10·4	30·7	37·4	6·0

ore would be showered through the atmosphere of hydrogen sulphide like the material in the old Bruckner furnace. The ore would begin to blacken almost immediately and absorbed the hydrogen sulphide with such avidity that a considerable amount of heat was generated. Even after eight hours treatment with the gas it took only a few minutes for the ore to use up all of the hydrogen sulphide remaining in the bottle so that no smell of hydrogen sulphide remained.

The second group of experiments in Table I shows plainly that the use of acid in the flotation of the sulphidized pulp is absolutely essential both for getting higher recovery of the lead and silver from the suphidized ore and for giving a suitable grade of concentrate. It was found that this ore used less acid than many of the other ores treated and that most of them called for amounts of acid nearer to 300 lb. per ton of dry ore before a clean concentrate and a higher recovery could be obtained. Such quantities of chemicals are, of course, prohibitive unless they can be obtained very cheaply.

A noticeable concentration of iron appears in the flotation concentrate. The iron present in this ore was largely limonite. It was determined by visual examination that the iron was blackened by the hydrogen sulphide, thus accounting for its presence in the concentrate.

Application of the hydrogen sulphide to the ground ore suspended in water gave similar recoveries and grades of concentrate, the only difference being that the amount of gas used was much smaller and it was occasionally possible to get fair work done in a neutral solution—a great advantage. On the whole, we think it improbable that hydrogen sulphide will be used on dry ore on account of the amount of chemicals required. Large lumps of the ore when exposed to the hydrogen sulphide in a bottle reacted vigorously, and on breaking them open it could be seen that the gas had penetrated deeply. Hence, we feel justified in stating that when sulphidizing the dry ore enough gas must be applied to convert all of the lead in the ore, together with some of the oxidized iron, into sulphides. On flotation, the application of acid will break up the iron sulphide with evolution of hydrogen sulphide (this was observed), while lead sulphide is fairly stable in acidified solutions. As the hydrogen sulphide is liberated in the body of the ore by the action of the acid, it is possible that the gas sulphidizes some of the lead and silver that may have escaped reaction previously. Further, after the iron is dissolved by the acid there is probably more of the lead sulphide exposed to the action of the flotation-oil; hence higher recoveries and better grades of concentrate were obtained in the tests where sulphuric acid was added during flotation.

All of the above shows that the particles are not merely 'filmed' but are entirely converted to sulphide of lead. In the wet pulp it was possible to use much less than the theoretical amounts of hydrogen sulphide and to get better recoveries, so that only a 'film' on the lead carbonate particles could have been transformed. However, sulphuric acid was still necessary in order to get clean flotation after sulphidizing in the wet pulp. As most of the lead-carbonate ores contain considerable amounts of acid-soluble material, the consumption of acid was always high. This caused us to turn to the alkaline sulphides as a method of sulphidizing.

Much of the old literature has insisted that the presence of hydrogen sulphide in the pulp during flotation is deleterious, so we were much surprised that some of our best work was obtained when a sulphidized pulp was acidified, giving a noticeable odor of hydrogen sulphide. Therefore, we conclude that for the artificial lead sulphides, at least, the former belief does not hold.

Commercial methods of making hydrogen sulphide are available if a demand for the gas should be created; in fact, it is being used on the Magma ore at Superior, Arizona, with marked success. The simplest method of making the gas, and one with which practically every engineer is familiar is the treatment of iron matte with sulphuric acid. Iron matte can be made at a cost of from \$5 to \$10 per ton by distilling the feeble atom of sulphur from pyrite and melting the residue. Sulphuric acid is available at from \$5 to \$20 per ton in many mining districts. This will make the hydrogen sulphide cost from \$30 to \$60 per ton. Hydrogen sulphide can also be made from calcium sulphide by treatment with carbonic acid gas—known as the Chance or Claus-Chance process:

$$CaS+H_2O+CO_2=CaCO_3+H_2S.$$

Calcium sulphide can be prepared by the reduction of gypsum. Another method of preparing hydrogen sulphide consists of passing sulphur vapor, mixed with excess hydrogen or a hydrocarbon gas, through a heated zone.

The greatest objection to hydrogen sulphide, outside of the cost of chemicals, is its bad effect on workmen. It is not only poisonous but small amounts seriously affect the nerves.

SODIUM SULPHIDE was chosen as a more promising reagent for commercial sulphidizing. The results contained in Table II will show that it is much better adapted to the purpose.

The ore from the Shattuck-Arizona mine, at Bisbee, has given the best results. As can be seen from the analysis of the head sample, this ore contains lead, silver, and gold. It is possible to get good recoveries of the metals in a high-grade concentrate by the application of only a few pounds of sodium sulphide per ton of ore. In test No. 4 the ore (crushed to pass 80-mesh) was treated for 2.66 hours with an equal weight of 1% solution of sodium sulphide or 20 lb. Na_2S per ton of ore. The concentrate collected practically all of the lead in a 50.75% lead product containing almost all of the silver and gold. Theoretically, an ore containing 15.42% lead will require 116 lb. sodium sulphide to convert all of the lead into the sulphide form. As this ore contains no sulphur and only 20 lb. of sodium sulphide per ton was used on it, we have good proof that the lead carbonate particles are being converted only superficially into the sulphide of lead by the solution of sodium sulphide. In other words, we have true 'sulphide filming.' Since making the tests in Table II a mill-run has given equally successful results with the use of as low as two pounds of sodium sulphide per ton and a time of contact with the ore of only a few minutes.

Table II

Sodium Sulphide solutions for sulphidizing.

Ore from Shattuck-Arizona mine. 500 gm. per test. 15·42% lead, 12·88 oz. silver, and 0·05 oz. gold per ton

No.	Sodium Sulphide	Hours	Flotation oil lb. per ton	Froth, Analyses, and Recoveries.						
				Lead		Silver		Gold	Insoluble	Iron
				Assay %	Recovery %	Assay oz.	Recovery %	Assay oz.	%	%
1	5 lbs. per ton in 0·25% sol.	2·0	Refined turpentine, 0·4 lb. Hardwood-creosote, 1·2 " Eucalyptus, 0·2 "	34·5	36·9	43·10	51·8	0·14	44·6	3·1
2	10 " " " 0·5% "	2·0	Same	37·3	93·2	32·70	88·9	0·10	43·8	3·3
3	15 " " " 0·75% "	2·0	Same	39·1	84·8	32·26	86·3	0·10	44·0	3·6
4	20 " " " 1·00% "	2·66	Refined turpentine, 0·3 lb. Hardwood-creosote, 0·9 "	50·75	97·75	39·82	88·8	0·14	29·6	3·5
5	40 " " " 2·00% "	1·5	Creosote, 1·40 lb. Turpentine, 0·24 " Pine-oil, 0·08 "	70·1	96·25	58·34	93·5	0·22	6·4	1·27

In Table III are two similar series of tests on ore from the Scranton mine in the North Tintic district of Utah, and from the Wilbert mine, in the Dome district of Idaho. While the Scranton ore gives excellent black froth of good grade and a high recovery, it is difficult to do anything with the Wilbert. The reason for this was never quite apparent.

In Table IV is shown the effect of time of contact when sulphidizing with sodium sulphide. A short period seems satisfactory. Further time decreases the recovery, leaving the grade of the concentrate unaffected. In test No. 8, an oil that had been boiled with sulphur, until its smell became noticeably bad, gave little better results than in other tests in which it was not used.

In another test the ore was agitated with sodium sulphide in a Pachuca. This test proved that the air oxidized the sodium sulphide to sodium sulphate with but little sulphidizing of the ore, and on further treatment the sulphidized ore re-oxidized. Hence it seems imperative that the treatment with sodium sulphide solution must be without any admixture of air. The simplest machine in which agitation of the relatively coarsely ground ore with sodium sulphide solution could take place without having an excess of air beaten into pulp, would be a long rotating cylinder like a cement-kiln, rotated only fast enough to turn over the charge gently without entraining air.

Table III

Sulphidizing with Sodium Sulphide.
Scranton Ore. (No. 1, 2, 3, & 4.)
Wilbert mill-dump. (No. 5. 6. 7. & 8.)

No.	Sodium Sulphide	Hours	Oil; pounds per ton.	Lead	
				Assay %	Recovery %
1	12 lbs. per ton in 0.6% Sol.	½	Mixture of refined turpentine 0.2 lb., and coal-tar creosote 1.0 lb.	65.5	89.7
2	20 " " " " 1.0% "	1½	Coal-creosote, 0.36 lb. Cedar-oil, 0.36 lb.	29.5	90.4
3	40 " 2.0% "	2	Mixture of coal-tar creosote 1.2 lbs; and refined turpentine, 0.2 lb.	53.7	91.2
4	40 " " " 2.0% "	1	Mixture of cedar-oil, refined turpentine coal-tar creosote, and rosin; 2 lbs.	66.6	84.3
5	5 " " " ¼%	18	Mixture of crude coal-tar, 1.5 lbs. No. 1580 special pine-oil, 0.6 lb.	16.5	52.4
6	10 " " " " ½% "	18	Special pine-tar oil, 0.6 lb.	27.3	31.3
7	10 " " ½% "	3½	Mixture of refined turpentine, 0.2 lb.; and crude coal-tar creosote 1.0 lb.	33.15	79.4
8	20 " " " 1.0% "	2	Mixture of turpentine and S_2Cl_2, 0.8 lb; and crude coal-tar creosote, 0.8 lb.	27.2	57.2

Table IV

Sodium Sulphide Sulphidizing
Bullion Beck slime-dump, 5.5% lead, 7.2 oz. Silver, 0.02 oz. Gold.

No.	Sodium sulphide	Hours	Oil: pounds per ton	Froth, Analyses and Recoveries.					
				Lead		Silver		Gold	
				Assay %	Recovery %	Assay oz.	Recovery %	Assay oz.	Recovery %
1	20 lbs. per ton in 1% Sol.	0.5	Turpentine, 1.0	34.2	74.7	21.8	36.4		
2	" " " " " " "	1.0	" "	35.0	44.5	28.1	27.3		
3	" " " " " " "	1.5	" "	30.8	41.4	35.9	36.9		
4	" " " " " " "	2.0	" "	36.4	46.3	29.5	38.7		
5	" " " " " " "	4.0	" "	34.6	37.7	28.2	23.5		
6	" " " " " " "	16.5	" "	33.0	59.4	26.2	36.0		
7	" " " " " " "	17.0	Creosote, 1.6	19.4	62.4	18.7	46.0		
8	40 " " " " 2% "	17.0	Pine-needle oil saturated with sulphur, 1.2	27.0	68.7	27.8	54.2		
9	100 " " " " 5% "	88.0	Creosote, 1.6	20.0	63.0	19.4	46.6	0.07	60.6
10	20 " " " " 1% "	24.0	Turpentine, 1.2	13.1	70.0	13.4	54.5	0.05	73.0
11	" " " " " "	17.0	Creosote., 1.6	19.4	62.4	18.7	46.0		

Table V contains the average results obtained in testing various other ores. It can be seen that some ores are not adapted to the process of sulphidizing with sodium sulphide, followed by flotation. The ores that give a poor recovery contain notable amounts of acid-soluble alumina, which makes them clay-like. A number of ores failed to give any results at all—notably the slime from the test-mill of the Copper Queen Consolidated, whose ore has a different geologic association from that of the Shattuck-Arizona. A highly colloidal slime from the mill of the Mine La Motte, in Missouri, is also difficult to treat. Most of these refractory ores will not even turn black with amounts of sodium sulphide that have been successful on other ores. Whether alumina reacts with sodium sulphide to form aluminates, leaving the sulphur in the elemental condition, is not known, but this might afford a reasonable explanation. Ores containing manganese di-oxide or basic sulphates of iron also consume sodium sulphide without allowing blackening of the lead carbonate.

Sodium sulphide normally costs $30 to $40 per ton at Chicago. With a consumption of 5 to 20 lb. per ton of ore it can be seen that the cost of such sulphidizing is not prohibitive. In fact, it is necessary to decant some of the solution before flotation and we have often found that not all of the sodium sulphide applied to the ore has been consumed, although the tables of results give the sulphide applied to the ore. Hence the figures given in the tables are probably the maximum possible consumptions and might be considerably reduced in practice by decanting the excess of unused solution before flotation, or by using less sodium sulphide in sulphidizing. This suggests a method of sulphidizing by use of some such device as a thickener where the overflow solution containing sodium sulphide can be returned to the feed of the thickener, together with a small amount of a strong solution of new sodium sulphide. We have determined that if over 0.3% of alkalinity due to Na_2S is left in the water in which the sulphidized ore is suspended, the froth is too tough or else it is entirely killed. Hence, the desirability of decanting the excess of sodium sulphide solution, and re-pulping with fresh water. We have tested the overflow solution of sodium sulphide for sulphidizing new ore and often find it efficient.

Table V

Sodium Sulphide Sulphidizing

Miscellaneous ores. Average results.

Ore				Concentrates			Recovery			Sodium Sulphide	Time
Mine	Analysis										
	Pb.	Ag.	Au.	Pb.	Ag.	Au.	Pb.	Ag.	Au.		
	%	oz.	oz.	%	oz.	oz.	%	%	%	lbs. per ton	Hours
Chief Consolidated, Utah.	2·8	8·0		8·7	31·9		68	45		10	3·5
Eureka Hill dump, Utah.	2·0	4·7	0·02	14·0	16·9	0·07	40	20	30	20	28·0
American Flag, Utah.	4·2	18·12	0·19	27·1	216·0	1·33	43	48	40	12	3·0
Bullionville dump, Nevada.	9·87	11·12	0·10	35·9	14·8	0·16	63	46	40	6	2·0
Dry Valley dump, Nevada.	7·12	10·04	0·10	57·8	23·2	0·10	76	27	34	20	5·0
Yellow Pine, Nevada.	15·04	11·92		48·3	29·64		89·2	51·7		20	1·25
Ontario dump, Utah.	4·92	9·44	0·04	32·5	35·78	0·22	62	45	29	20	2·0
Daly West dump, Utah.	5·25	21·8	0·02	9·27	58·70	0·02	15	44		20	2·0

Sodium sulphide may be prepared for large-scale use by the reduction of sodium sulphate with carbon. This is the usual commercial method. The largest use of sodium sulphide at the present time is probably in the tanning industry. When prepared for shipment it is usually in crystals containing a considerable amount of water of crystallization to prevent spontaneous combustion. Hence the market brands of '60%' and '30%' usually consist of only 60% or 30% Na_2S and the remainder is mostly water.

The poly-sulphides of sodium did not prove as efficient for sulphidizing, whereas the sulph-hydrate of sodium, NaSH, seemed to be somewhat more efficient. The normal sulphide of sodium hydrolyses to sodium sulph-hydrate and sodium hydroxide, and the activity of sodium sulphide is, for that reason, probably exactly the same as that of the sulph-hydrate, although the presence of the sodium hydroxide from hydrolysis might have some effect on the efficiency of sulphidizing. The poly-sulphides of sodium can be prepared commercially by boiling caustic soda with powdered sulphur and probably consist of mixtures of Na_2S_4 and Na_2S_5. We hazard the guess that only one of the sulphur atoms in these complex molecules is acting as a sulphide sulphur, the others being liberated as free sulphur, for the reason that some of the tests showed white colloidal sulphur lining the bubbles of froth.

In consequence of the above mentioned test-work, carried on at the University of Utah, the Prince Consolidated Mining Company, of Pioche, Nevada, tested the process further in its application of two old pan-amalgamation tailing-dumps at Bullionville and Dry Valley. It was found that practically all of the finely powdered lead carbonate in the ore could be extracted, together with a portion of the silver and gold present. This resulted in the erection of a 300-ton mill. The ore contained about 8.2% lead and 11 oz. silver per ton, together with about $1.40 worth of gold per ton. The finely ground tailing is excavated from the old marsh where it has lain for about 20 years and is then passed through a tube-mill to break up the lumps. It is sulphidized in a round wooden tank with about 7 lb. of sodium sulphide per ton. The agitator in this sulphidizing-tank is the regular square-shaft square-arm agitator used in a number of Nevada cyanide-mills and was introduced by the engineer, C. F. Sherwood, who designed the mill. This was installed after the regular Trent agitator (minus the air, not wishing to oxidize sodium sulphide and the ore with air before flotation) had failed to give satisfactory sulphidizing. About one half-hour in the sulphidizer is the minimum time. The ore is then treated for flotation in Callow cells, making a concentrate containing 55% lead.

The recoveries are: lead over 90%, gold 45%, silver 35%. The tailing from the six Callow roughing-cells is separated in a Dorr classifier into sand and slime. The sand is treated on four Deister tables and the slime is mixed with more oil and more sodium sulphide and then passed through two Callow cells, which make a middling concentrate and a finished tailing. The middling is re-treated with the original feed.

After a short time the feed of the mill began to contain many weeds from the old roots that had accumulated from the growth of vegetation during the 20 years. The froth was spoiled and not until some sulphuric acid was added and the pulp warmed did it return. The present practice is to add sodium sulphide and sulphuric acid together in the agitator, and the mill is at the present time just commencing to operate after the correction of these various unforseen difficulties. The concentrate contains only about 15 to 20% of insoluble but on being thickened in a Dorr tank and filtered in an Oliver filter it still contains about 26% of moisture. A part of this moisture is removed in a dryer before shipment.

The Shattuck-Arizona Copper Co. is now preparing to build a similar mill for treatment of its ores.

The work at the Shattuck caused a company at Kellogg, Idaho, to take up similar work on a local lead-carbonate ore. It was found that it could be treated successfully and a 40-ton plant is now in operation. The consumption of sodium sulphide is occasionally as low as 2 to 3 lb. per ton. R. S. Handy is responsible for the success of this work.

Calcium Sulphides are more sluggish in their action than the corresponding sulphides of sodium. Again we find the sulph-hydrate of calcium more active than the sulphide, which in turn is more active than the poly-sulphide. But for ease of preparation at the mill the poly-sulphide takes precedence. It is obtained by boiling slaked lime with powdered sulphur for two to five hours and is extremely soluble, while the normal sulphide of calcium is only slightly soluble. The normal sulphide can be obtained by reducing gypsum with carbon at high temperature.

The results of a few tests with the poly-sulphide on the May Day ore (Tintic district) are contained in Table VI. The work done with sodium sulphide is superior to that done with calcium sulphide. There are places where the use of calcium poly-sulphide might be advantageous or even necessary, either alone or in combination with sodium sulphide. Some slimes are deflocculated by sodium sulphide so that it is difficult to make them settle. The use of calcium poly-sulphide will have the opposite effect and the proper mixture of the two might be used to control the settling of the sulphidized slime.

The other methods of sulphidizing, such as the use of sulphur vapor on heated ore, colloidal sulphur solutions, and sulphuretted flotation-oil, have not proved technically successful or adaptable, according to our experiments with lead-carbonate ores.

Table VI.

Sulphidizing with solutions of Calcium Poly-sulphide.
May Day ore. 4·5% lead, and 2·8 oz. silver per ton.
Oils: coal-creosote, 1·2 lbs. per ton; turpentine, 0·4 lb. per ton.

No.	Calcium Poly-sulphide (pounds per ton)	Hours	Froth			
			Lead		Silver	
			Assay %	Recovery %	Assay oz.	Recovery %
1	1·6	6	12·5	32·2		
2	8·0	1·5	18·4	20·7		
3	16·0	3·6	26·1	73·0	11·56	48

Oxidized Copper Ores. Many attempts have been made, both by large operating companies and by other experimenters, to float the carbonate and other oxidized minerals of copper. For that reason the testing of such ores by us has been limited.

Hydrogen sulphide seems to be by far the best medium for sulphidizing oxidized copper ores previous to flotation. When applied to the dry ores we found the same conditions as those mentioned for lead; the particles are sulphidized to the centre, which requires an excesssive amount of hydrogen sulphide. Applied to the wet pulp, the hydrogen sulphide seems to cause true filming. Our work has yielded a black concentrate, but we are informed by J. M. Callow, of the General Engineering Co., that the company has been able to reduce the amount of sulphur used to a point where the froth is green with slightly coated malachite. He states that as little as half a pound of sulphur per ton of ore is giving good extractions in the plant of the Magma Copper Co., at Magma, Arizona, where his company has put in the first successful installation of this kind.

Sodium sulphide has been tested by a number of the larger companies that have oxidized copper minerals in their sulphide ores. The amount of oxidized copper in such ores is usually a fraction of 1%, so that only two or three pounds of sodium sulphide per ton of ore is necessary. This is usually added to the machines during flotation, or to the mixing-tanks before flotation. Our experience is that if some little time of preliminary contact is allowed before flotation is attempted, better sulphidizing of the material will result.

Calcium poly-sulphide has been used for some time in a number of the large copper-concentrating mills with indifferent success, and seems to be detrimental in some instances. On the ores tested by us fair results were obtained if the calcium poly-sulphide was allowed to act until the ore had become well blackened.

It is stated that sulphur vapor was tested at one of the large plants for flotation of oxidized forms of copper and gave better results than any other methods of sulphidizing. Of course this method has the disadvantage of having to be applied to dried, heated, and finely divided ore.

Sulphuretted oils are being used at a number of plants to supplement other methods of sulphidizing and considerable secrecy is observed as to the technical details of this work. During a recent visit of the Utah section of the American Institute of Mining Engineers to the Arthur mill of the Utah Copper Co., the strong smell in the air elicited the information that the flotation unit of 1000 tons daily capacity was receiving a flotation-oil that had been previously distilled with sulphur.

So far as we are aware colloidal sulphur does not assist in the flotation of oxidized forms of copper. Neither has the silicate of copper been successfully floated by sulphidizing flotation. It will blacken when sulphidized, but it resists flotation. Possibly it still presents a silicate surface rather than a sulphide surface. For this reason, most of the large copper companies in Arizona have been considering the leaching of oxidized copper from their tailing rather than lose the silicate copper that may be present.

Another difficulty has arisen from attempts to recover both the oxidized and sulphide copper simultaneously from partly oxidized ores. Throughout Arizona and New Mexico the larger companies have attempted sulphidizing of the oxidized copper followed by flotation of the natural and the artificial sulphides together. In almost every case they have failed because the flotation of the natural sulphides seems to be spoiled by the conditions that are best for the artificial sulphides. A similar experience is recorded by the Anaconda Copper Co. Only at Chino has this difficulty been mastered, through the efforts of O. Wiser. The product being treated is the vanner-concentrate, which contains considerable oxidized copper. It is, of course, desirable to clean the vanner-concentrate in order to put the iron and silica into a selffluxing ratio for the smelter. This could not be done if the oxidized copper could not be floated. At first, the sulphidizing reagents caused the natural sulphides to drop out of the froth in this plant, as in many others, and for a time the natural sulphides were floated out first before the sulphidizing reagents were added, but finally the proper mixture of chemical and oil was found to float them simultaneously. One of the principal ingredients is a solution of sodium resinate prepared by dissolving resin in a solution of caustic soda. This stiffens the froth. The froth is red with magnetite and hematite, which float with the copper minerals. The sodium resinate solution is used at several mills.

The plant at Chino is further along in the successful treatment of semi-oxidized copper ores than any of the other mills in the Southwest. Sulphidizing of the whole mill-feed is not yet allowable on account of the large quantities of sulphidizers necessary. Only the vanner-concentrate is being sulphidized with sodium sulphide. However, an experimental unit of one to two tons capacity is also used. The crushed ore for this testing-plant is tube-milled and then tabled to remove the coarse concentrate; after that it is treated in an agitator with sulphuric acid amounting to 3 lb. per pound of oxidized copper present. This dissolves all the copper, including the silicate. On passing the pulp through a ball-mill filled with scrap-iron the copper in solution is cemented and issues with the pulp from the tube-mill. The greater portion of the copper is now ready for flotation without any oiling. The smell of hydrogen is strong and it is the opinion of the metallurgist in charge that the reaction of the acid on the iron liberates hydrogen and hydro-carbons from the cast-iron used and that these hydro-carbons are partly oiling the cement copper formed. However, on passing to the flotation machine some tar and coal-creosote are necessary in order to get a high extraction of the natural sulphides and the cement copper together. It is said that trouble was experienced in getting a good froth with this material.

This process is being considered by others, notably the Miami and the Inspiration companies. It has been patented by Dr. Rudolf Gahl in U. S. 1,217,437.

One question to be considered in the use of such a process is whether or not substances like iron sulphate will accumulate in the solution to a point where they will injure flotation. It is known that a small amount of ferrous sulphate or of copper sulphate in solution is deleterious. As most of the Arizona mills find it necessary to operate in closed circuit this question of contamination of mill-water is important. It is not impossible that the addition of a little lime to the tailing, as it flows from the mill, would throw out most of the iron and other metals so that the water returned from the tailing-pond would not be contaminated.

The Detroit Copper Co. is known to be experimenting with sulphide-filming of copper carbonate ores. A visit to the test-mill at Bisbee showed an acid-tower used for the preparation of a solution of hydrogen sulphide, which was generated from iron matte and sulphuric acid. The copper ore was being treated with this solution, in round tanks with mechanical agitators, for a number of hours before passing to the flotation-machines of the Rork-Kraut-Kohlberg type. Laboratory work had previously shown an excellent recovery and the details of larger-scale practice were being worked out at the time of the visit (September 20, 1916).

An interesting paper by M. H. Thornberry was published in the Bulletin of the Rolla School of Mines, Vol. 3, No 1. A soap, called Naphtha Powder, manufactured by Peet Bros., was used at the rate of two pounds per ton of ore, with a 6.5:1 water: solid ratio. A minute amount of oleic acid was added. The ore contained both sulphides and oxidized minerals of copper and assayed 2.95% total copper, of which 2.34% was oxidized.

A number of Thornberry's tests, re-calculated to eliminate losses of weight, show the following recoveries when treated by flotation under the above conditions:

	Percentages of recovery		
Test	Oxidized	Sulphide	Total copper
4	61.0	92.1	72.1
5	63.8	93.0	75.1
6	68.7	89.6	76.6

He offered the following conclusions:

(1) With rain or distilled water this process can be used to advantage.

(2) Water containing sulphates will prevent carbonates from floating.

(3) Water containing chlorides will prevent the carbonates from floating, but this difficulty can be overcome by the addition of sodium carbonate.

Thornberry is the only person who has reported much success with the use of soaps in the flotation of sulphide ores. It is possible that different effects are involved when oxidized ores are considered. Evidence is accumulating to show that it is possible to make certain organic acids form combinations with heavy metals present as carbonates in the ore. The soap is known to hydrolyze in dilute solutions and it is entirely possible that the liberated fatty acids have combined superficially with the copper-carbonate particles sufficiently to 'oil' them for flotation. The use of sodium resinate in the flotation of copper carbonates at Chino has already been mentioned. Sodium resinate is nothing but a resin-soap. The resin acids are not so well known to metallurgists as are oleic, palmitic, stearic, and other acids, whose sodium salts form the principal ingredients of soap. A study of the action of these organic acids on minerals is desirable.

Some excellent data on use of hydrogen sulphide for sulphide-filming of copper carbonate have been published by J. M. Callow in a paper abstracted elsewhere in this book.

OXIDIZED ZINC MINERALS. So far as we know no one is successful in the flotation of oxidized ores of zinc. Our results are absolutely negative. We are informed that some headway was made with the problem by F. W. Traphagen and one of his students, at the Colorado School of Mines, but the sulphide film seemed to come off easily. Poor results were obtained, whatever the cause. Only Bacon claims any success in this line and his method is to get the zinc into solution in, say, the sulphate form, followed by precipitation of zinc sulphide by the use of an alkaline sulphide, with subsequent flotation from the sulphidized pulp—at least his patent claims as much. There are few places, however, where sulphuric acid and sodium or calcium sulphides could be obtained cheaply enough to allow of the application of this process.

We have recently been informed by Frank A. Bird, of Salt Lake City, that he has obtained some success in the flotation of a zinc-carbonate ore, by using the idea seemingly underlying Thornberry's work. After many of the ordinary flotation-oils had failed to do anything with sulphidized or non-sulphidized ore, oleic acid was added to an ore-sample while being sulphidized with sodium sulphide. The result was a fair grade of concentrate and about 50% recovery. Whether the sulphur in the sodium sulphide had anything to do with it or whether alkalinity was all that was necessary, was not determined.

OTHER MINERALS. Flotation on a commercial scale seems to be possible only after sulphidizing. We are not certain but that cuprite and similar minerals of highly developed cleavage or crystalline character can be floated direct without sulphidizing. From private parties we hear of laboratory successes in the flotation of scheelite, fluorite, and similar minerals. The flotation of magnetite seems well established. J. T. Terry, in a paper re-printed in this book, also reports the successful sulphidizing of cassiterite, followed by flotation.

THE FLOTATION OF GOLD AND SILVER MINERAL

By T. A. Rickard

(From the *Mining and Scientific Press* of August 25, 1917)

In the title to this article I have avoided the use of the word 'ore,' because the object of flotation is to float not the 'ore' but the valuable mineral in the ore, leaving the gangue to sink. It is a selective process, based upon the idea that the ore consists of valuable and of valueless components, which must be separated so that the valuable component may be concentrated as cleanly as possible previously to a final treatment in which the metal or metals are extracted and prepared for the market.

Some of the earliest work in flotation, such as that at the Glasdir mine, in 1896-1899, was done on an ore containing gold and silver, but the recovery of the precious metals was incidental to the concentration of the chalcopyrite with which they were intimately associated. Likewise the saving of the silver in the Broken Hill ore was incidental to the recovery of the sulphides of lead and zinc. In such cases—and they are typical—the floatability of gold and silver in the native state, or of their mineral compounds, does not present any special problem because the recovery of the gold and silver follows the concentration of the base-metal sulphides by which they are usually so closely accompanied in ore deposits. However, the floatability of native gold, as of native silver, hardly needs special demonstration here. 'Float gold' has been a bugbear of processes in which water is used, whether in the sluice-box of the gulch or in the stamp-mill on the hillside. Small particles of gold, particularly when flaky, are easily transported on water, as every miner has learned to his sorrow. The platy form of gold, so common in veins, lends itself readily to flotation, if the particles are small, by offering a large surface to the play of surface-tension and to the adhesion of air. The high metallic lustre of gold is a characteristic that experience in flotation would lead us to associate with easy buoyancy in the presence of air and of oil. If the gold is 'rusty,' that is, coated with iron oxide or with manganese di-oxide, or, as more rarely happens, with a film of silica, we should not expect it to float, as we should not expect it to amalgamate or to cyanide freely, until it had undergone such abrasion as would expose a fresh clean surface. Similarly gold in a clayey ore may make trouble for any process in which water is used, but this, like the 'rustiness,' is nothing new and is not peculiar to flotation.

As regards silver, the same general ideas apply. Silver in flaky form is elusive when running water is used, because it is readily floated; likewise when it presents a clean surface it is easily amenable to the guidance of the ascending bubbles. One would expect native silver and those of its compounds that are either highly lustrous, or have a marked cleavage, to float easily. This is a fact. Experiments made at Cobalt* showed a recovery of 92 to 97% for metallic silver, 77 to 89% for argentite, 85 to 87% for pyrargyrite, 78 to 80% for proustite, and 69% for frieslebenite. These experimental results have been confirmed in practice, a recovery of 96% having been made by using oil-flotation to supplement gravity-concentration.† Of manganiferous silver ores, a type familiar to the Mexican miner, it can be stated that when they cannot be cyanided they also cannot be floated. The obstacle probably is the double oxide of silver and manganese. Even preliminary sulphidization appears ineffective because the sodium sulphide will not attack the manganese-silver compound.

As regards the economic gold minerals, namely, the tellurides, they are so lustrous that one would expect them to be eminently floatable. That would apply to the silver tellurides also. Such has been the experience at Cripple Creek, provided, of course, that oxidized ore is carefully excluded from the mill-feed. At the Vindicator mine the practice is to wash the oxidized material out of the ore before it goes to the flotation plant. At the mines on the Mother Lode, in California, where the carbonaceous slate causes trouble by re-precipitation of gold in the cyanide solution, it has been found advantageous to apply flotation after amalgamation.

However, even if sundry gold and silver minerals will float, that does not mean that they can be recovered successfully as a concentrate by the frothing process. Direct floatability would refer to the surface-tension methods, such as those of Wood and Macquisten.

For the success of the older methods, such as that introduced by the Minerals Separation company, employing mechanical agitation, it is necessary that the pulp should contain finely divided mineral able to pass into the oil-water interface and in quantity sufficient to stabilize the air-bubbles by armoring them. Thus, a clean gold-bearing quartz is unsuitable to a machine working on the principle of violent agitation unless, of course, it contain enough gold, so sub-divided by

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*Canadian Mining Institute. Bull. No. 62. J. M. Callow and E. B. Thornhill.

†At Cobalt the flotation-cell has replaced the slime-table in the McKinley-Darragh mill, while in the Nipissing, Buffalo Mines, and Dominion Reduction mills the cyanidation of tailing has given way to re-grinding and flotation.

the time it reaches the flotation-cell as to suffice for froth-making. The tailing from a vanner is not as suitable for the agitation-froth process as the pulp before it has undergone concentration on the vanner. Similarly, a gold-quartz ore containing 5% gold-bearing pyrite or other sulphides is better adapted to agitation-frothing than one containing 1% only. This applies to the mechanical stirrer; it does not apply to the pneumatic machine, in which air-bubbles, supplied lavishly, rise quietly through the pulp. In such a machine it is not necessary to have a large proportion of mineral for stabilizing the froth because the plentiful supply of bubbles obviates that requirement. As one bubble breaks, another is ready to take its place, so that the float, or concentrate, does not fall, but is lifted successively until it passes over the lip of the cell.

Another important phase of the subject is the recovery of the base metals associated with the precious metals. In mills using amalgamation and cyanidation, the presence of base-metal sulphides may be so detrimental that an ore containing any considerable percentage of them is likely to be left in the mine. In some cases the presence of base-metal sulphides, insufficient to be a source of revenue, but sufficient to interfere with the milling, has rendered it unprofitable to treat an ore. For such mines the use of flotation comes as a real boon. In the San Juan region of Colorado at this time there is a pronounced growth of productive activity because flotation has facilitated the recovery of the base metals associated with the precious, and so long as the metal markets remain propitious, we may expect a further expansion in this direction. Flotation is superior to any of the older wet processes—amalgamation, chlorination, and cyanidation—in that it will enable the miner to recover not gold and silver only, but copper, lead, and zinc as well.

These general remarks will serve to introduce some analyses of specific conditions—a more satisfactory method of discussing a problem that is economic as well as scientific.

North Star. Early in 1916 the management of the North Star Mines, at Grass Valley, undertook a critical analysis* of the milling methods then in use, with a view to consolidating the existing plants and obtaining greater economy of treatment. The ore was being reduced in two 40-stamp mills, each with a cyanide annex, situated at the two main openings of the mine. The combined capacity of the two plants was 110,000 tons per annum, development work during 1915 had

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*For this information I am indebted to William Hague, managing director of the North Star Mines.

been highly successful, and it was anticipated that by centralizing the entire plant at one shaft a considerable saving in operating expense might be made.

The ore was being crushed by 1050-lb. stamps to pass 20-mesh screens, the treatment involving amalgamation in the mortars and on plates, then table concentration, followed by classification into sand and slime for separate cyanidation. The concentrate was re-ground in tube-mills to pass 200-mesh and treated in the slime-plant. The total extraction averaged $10 in gold per ton of ore; of this, $5 was obtained in the stamp-mortars, $3 on the amalgamating plates, and $2 from the concentrate, sand, and slime. The tailing averaged 25 to 35 cents per ton, so that the extraction averaged 97%. To treat 108,000 tons in 1915 the cost of milling was $51,000, for cyanidation $42,000, a total of $93,000, besides the tailing-loss of $30,000—a total deduction of $123,000.

Whatever process might be adopted, it was deemed advisable to retain amalgamation, since fully 50% of the gold extracted was caught in the mortars and 30% on the plates. It seemed wise to use amalgamation to catch as much of the free gold as possible early in the operations, as a sportsman tries to shoot his bird with the first barrel rather than the second.

The necessary experiments in flotation were made by the firm of Hamilton, Beauchamp & Woodworth, of San Francisco. Samples of plate-tailing were sent to them. The assay-value of these samples ranged from $2.50 to $2.90 in gold per ton. The first tests indicated that the material required re-grinding, to pass 80-mesh, in order to obtain a good recovery in the flotation-cell. When the heading assayed $2.50 the residue from these tests ranged between 10 cents per ton on pulp ground to 200-mesh, and 40 cents on pulp reduced to pass 65-mesh. When the plate-tailing was ground to pass 80-mesh the flotation residue averaged 25 to 30 cents per ton, like the residue after cyanidation.

The treatment of the flotation concentrate was the next step in the investigation. To ship the concentrate to a smelter—the Selby smelter, near San Francisco—would cost $17 per ton, for sacking, haulage, freight, treatment, and losses. This cost, on an ore containing 3⅓% sulphides, would mean 50 cents per ton of ore. Smelting therefore was not to be recommended. There remained the possibility of cyaniding the concentrate. The ratio of concentration being 30 to 1, the flotation product was worth from $70 to $90 per ton. The residue from the working-tests, when cyaniding the flotation concentrate, averaged $6 per ton. The average consumption of cyanide was 6 lb. per ton. Experiments were made also to learn what effect the flotation-oil had on the precipitation of the gold or on the fouling of the cyanide solution. The results indicated that no difficulty was to be anticipated from the presence of small quantities of oil in the concentrate.

Given the results of these flotation experiments and comparing them with the results obtained in cyanide practice, it appeared that three methods were available for use in the consolidated plant which was to treat 110,000 tons per annum:

No. 1. To use 60 stamps of 1500 lb. each and crush to 0.04 inch diameter, employing amalgamation, classification, concentration of the sand, the classifier overflow and the concentrator tailing each going by separate conduits to the cyanide plant; the concentrate to be re-ground to 200-mesh and to undergo separate treatment in the cyanide annex, in order to ensure sufficient contact with the solution before being delivered to the slime-plant.

No. 2. To use 40 stamps of 1500 lb. each, crushing to 8-mesh, followed by amalgamation, classification, and re-grinding; to re-grind 70% of the stamp-product in tube or ball-mills to pass 80-mesh, this product to be treated by flotation, re-grinding the flotation concentrate to 200-mesh before cyaniding it.

No. 3. The same as No. 1 except that, instead of cyaniding the slime, to treat everything finer than 150-mesh by flotation and to leach the coarser material with cyanide solution; the flotation concentrate to be cyanided with the re-ground product of the water-concentrators.

Tests made in the mill showed that the 1500-lb. stamp falling 6 inches 105 times per minute would crush a little more than 5 tons per day to 0.04 inch, the screen having an open area of 36%; and also that this weight of stamp, crushing to 8-mesh, would have a duty of 7½ tons, yielding a product 70% of which would be coarser than 80-mesh.

The question of using ball-mills, both as primary and secondary crushers, had to be considered. The fact that 50% of the gold could be saved in the mortars was favorable to the retention of the stamps. Furthermore, in referring to descriptions of South African practice, it was noted that from 5 to 10% less gold was recovered by amalgamation after coarse crushing followed by tube-milling was introduced. If 5% more of the gold in the North Star ore, formerly saved by amalgamation, were thrown into the cyanide annex, the extra loss in cyanidation would off-set the saving of power and supplies to be anticipated from the substitution of ball-mills.

In estimating the operating cost of the 60-stamp mill and cyanide annex, the management was able to supplement its own experience with that of a neighboring plant having a capacity equal to that of the one being planned. In estimating the cost of flotation treatment, the North Star management was less confident, having to depend largely upon the advice of others; but by giving due weight to the evidence available it was possible to come to a fairly trustworthy conclusion, namely:

No. 1 method, applied to 110,000 tons in one year, involved a working cost of $75,000, plus a tailing-loss of $33,000, making a total deduction of $108,000.

No. 2 would require a working cost of $69,000 on the same tonnage and in the same time, plus a tailing-loss of $27,000, plus a loss of $20,000 more (3300 tons of flotation concentrate per annum in which $6 per ton would be left after cyanidation) in the residue of flotation concentrate after cyanidation. The total deduction would be $116,000.

No. 3 required an operating cost of $75,000, plus a total tailing and residue loss of $39,000, making $114,000. In this estimate, as in No. 2, royalty has not been included in the operating cost.

The capital cost to be incurred was estimated at $52,000 for No. 1, $42,000 for No. 2, and $50,000 for No. 3 method.

It was decided that the saving of $15,000 per annum to be made by consolidating the plant, under No. 1 method, was justified, this decision being strengthened by the disadvantage, occurring under No. 2 and 3 methods, of having "to choose between paying a royalty or fighting a patent suit."

A Mexican Mill. Next I shall quote figures relating to a silver mine in Mexico. The question had arisen of substituting flotation for cyanidation. Experiments, made by the same firm as had tested the North Star ore, indicated that this Mexican ore was amenable to flotation. The silver sulphides floated readily; the recovery ranged from 70 to 83% of the combined silver and gold, varying according to the proportion of oxidized minerals in the ore—oxidation being a deterrent to flotation, of course. This compares with an extraction of 91% by the existing method, which gives 77% of the metallic content as bullion and 14% as concentrate. But a closer analysis of more detailed data is required to make a trustworthy comparison. The present method of treatment includes crushing in cyanide solution followed by concentration of the sand on Wilfley tables and of the slime on Deister tables, re-grinding the sand and cyaniding an all-slime product. The capacity of the plant is 150,000 tons per annum and the ore assays $10.50 per ton when silver is worth 65 cents per ounce. The ratio of gold to silver in the ore is 10 oz. silver to 0.07 oz. gold. The tailing is worth $1 per ton. The total cost of milling is $1.55 per ton, to which must be added 10 cents per ounce of fine metal for marketing the bullion, this charge including export-tax, expressage, and refining, and 15 cents per ounce of metal for marketing the concentrate, this expense including taxes, freight, smelting, and sacking. The present output yields a bullion 700 fine and approximately 50 tons of $350 concentrate per month.

On the other hand, the flotation plant would cost $50,000 and would produce 100 to 150 tons of $500 to $800 concentrate, to be marketed at a cost of 15c. per fine ounce and leaving a tailing assaying $2.10 per ton. The Mexican export-tax on concentrate is 2% (of gross value) more than on bullion, thus:

	Bullion, %	Ore,%
Federal	5	7
State	2¼	2¼
Total	7¼	9¼

The final comparisons are as follows:

1. Between table-concentration followed by cyaniding and straight flotation, the saving in cost of treatment by flotation is about equal to the extra recovery by tabling and cyaniding, but the increased expense for marketing the large tonnage of lower-grade concentrate plus lower smelter-returns on concentrate than on bullion represents a loss of 90 cents per ton of ore by straight flotation.

2. Between table-concentration and cyanidation, as against flotation and cyanidation of flotation tailing, the extra recovery is 33 cents (extraction 94%) and the saving in cost is 57 cents per ton, while the additional expense of marketing the concentrate plus lower smelter-returns on concentrate than on bullion is 90 cents, so that the difference is extinguished.

Cyanide is taken at 30 cents per pound, 1.8 to 2 lb. being consumed per ton of ore. Lately the precarious character of the cyanide supply has furnished an argument in favor of flotation. Packing the concentrate on mule-back or freighting it by train, with the uncertainty of getting cars for shipment to a smelter, possibly outside Mexico, are points requiring careful consideration. The smelter deductions are important; usually payment is made on 95% of the silver and $19 (or 91.92%) is paid per ounce of gold in the form of concentrate against 100% of these metals in the form of bullion. This represents a net loss of 6 to 8% on this class of ore. At present therefore it is inadvisable to spend $50,000 in erecting a flotation plant to obtain a result no better than that given by the existing system of treatment, but it may prove advantageous in the future to adopt flotation followed by cyanidation when the flotation product itself can be treated safely and profitably on the spot, yielding bullion. This example will serve at least to emphasize the fact that such problems cannot be settled in the laboratory, and to show that the object of metallurgy is to give the greatest net returns rather than the highest percentage of extraction.

The Melones Mill. Another interesting comparison between cyanidation and flotation is afforded by an investigation made by the Melones Mining Company, which treats a low-grade gold ore typical of this part of the Mother Lode region. The existing plant consists* of 100 stamps weighing 1000 lb. each, and dropping 6 inches at the rate of 107 drops per minute. The stamp-duty, when discharging through a 20-mesh screen, is 5.3 tons. No plate-amalgamation is attempted inside the mortar, but mercury is fed into the battery, and the pulp when discharged passes over the usual amalgamating tables. The ore, a gold-bearing quartz containing pyrite, averages \$3.65, from which \$1.83, or 50%, is extracted by amalgamation and cyanidation, leaving a 51-cent tailing and 3.4% of concentrate assaying \$36 per ton. The further extraction of the gold in the concentrate may be disregarded for the moment. Of the total extraction 43% is obtained as amalgam, 17% as bullion in the cyanide annex, and 40% in concentrate, which also is treated by cyanidation. The pulp from 60 stamps passes from the amalgamating tables to Wilfley concentrators, while that from the new mill of 40 stamps undergoes classification in spitzkasten before being concentrated. It has been observed in the Mother Lode region that the pulp from the stamp-battery does not concentrate so well after hydraulic classification as without such preliminary treatment. Sizing seems to be preferable. On the Wilfley tables the gold-bearing pyrite is recovered as a concentrate; at the same time, by the addition of extra water in the feed-box of the Wilfleys, the sand and slime are separated without the intervention of the usual de-sliming classifiers. The sand, assaying \$1.15, goes to the leaching-vats of the cyanide annex; the slime, assaying \$1, passes through cone-classifiers, the underflow from which joins the sand in the leaching-vats, while the overflow runs to the slime-plant. This includes Dorr dewaterers and Devereux agitators,† followed by Dorr thickeners and an Oliver filter. A middling, assaying \$8 per ton, is made on the Wilfleys; this, after

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*For most of the information in these paragraphs I am indebted to W. G. Devereux, manager for the Melones Mining Company.

†For a description of these machines see M. & S. P., March 3, 1917.

classification, goes to six 'finishing' Wilfley tables, the tailing from which is passed to the sand-plant.

The following facts are pertinent to our enquiry. The Wilfley tables recover 95% of the gold that is so intimately associated with the pyrite as to have escaped amalgamation; such gold-bearing pyrite as escapes into the cyanide annex is either in the form of slime or it is material that has been insufficiently pulverized. The pulp after concentration on the Wilfleys assays $1.12, whereas the mill-tailing, discharged from the cyanide annex, assays 51c. per ton. That represents the residual loss, to which must be added the loss in the treatment of the concentrate. The 'sand' and 'slime' are nearly equal in weight. The extraction of gold from the 'sand' and 'slime' together is about 55%, that is, 55% of the 31% of gold remaining after amalgamation and concentration. A solution containing ½ lb. KCN per ton of ore is used in cyaniding the slime, and a 4-lb. solution on the sand. The total cost of milling (excluding concentration) is 50 cents per ton of ore.

What can flotation do on this ore? Samples were sent to the Minerals Separation people in San Francisco and they reported thus:

	Weight %	Gold oz.	Recovery %
Heading	100.0	0.06	100.0
Concentrate	1.4	1.83	42.7
Middling	6.2	0.20	20.7
Tailing	92.4	0.02	30.8

This showed a recovery of 63.4%, including the middling, which, in mill-practice, would be re-treated continuously. However, account is rendered for only 94.2% of the total gold in the heading. The material tested was slime from the Wilfley tables, the screen-analysis showing 98% through 200-mesh. In a later test, made at the same laboratory, a sample of the pulp as it came from the amalgamating tables was subjected to flotation, the result being a failure owing to the coarseness of a large part of the product. After the sample had been re-ground, until only 4% remained on a 200-mesh screen, the flotation machine did as follows:

	Weight %	Gold oz.	Recovery %
Heading	100.0	0.085	100.0
Concentrate	1.7	4.400	88.4
Tailing	98.3	0.010	11.6

The chief engineer (E. H. Nutter) for Minerals Separation reported that this test "indicates very definitely that the ore as submitted can be given flotation treatment usefully," but it must be noted that the sample "as submitted" was much too coarse to undergo successful flotation. The extra cost of re-grinding to 200-mesh is a vital factor in the problem. What would be the cost of re-grinding? At a neighboring mine, producing a similar ore, the cost of re-grinding is 25c. per ton. But all the pulp would not have to be re-ground; only the sand, say, 275 tons in all, out of the daily output of 530 tons. At 25c. per ton on 275 tons, the cost per original mill-feed would be 12c. per ton for re-grinding.

A flotation plant to treat 530 tons of such ore would cost $6000 f.o.b. San Francisco, or $10,000 erected; but the necessary re-grinding plant would cost $20,000 more. The items of operating cost are estimated, by Mr. Nutter, as follows, per ton of dry ore:

	Cents
Reagents	6
Labor	5
Power (35 hp. per 200-ton unit)	2
Royalty at 25c. per oz. gold	2
	15

To this must be added the present cost of crushing and amalgamation, which is 20c.; so that the total cost of combined treatment, to the point of making a concentrate, would be

	Cents
Crushing	20
Re-grinding	12
Flotation	15
	47

This compares with the present cost of 50c. Allowing a 90% recovery by flotation, as against the present 86%, on a $3.65 ore, the additional winning would be 14.6c. per ton.

The Melones concentrate, representing 3.4% of the weight of ore, is re-ground, at a cost of 50c. per ton, to pass 200-mesh and is then cyanided, without roasting. The cost of treatment is $5.50 and the extraction is 92%. The cost is 19c. per ton of crude ore and the tailing retains 9½c. in gold.

In making this comparison the treatment of the concentrate is assumed to be the same, whether it be the product from the Wilfley tables or from the flotation-cells. No doubt exists as to the successful treatment of the flotation concentrate, which would not require re-grinding, so that the present cost of re-grinding the concentrate, which is 50c. per ton of concentrate, or 1.5c. per ton of mill-feed, would be saved. Moreover, the concentration would be higher, if one may judge from the results of the test made on the re-ground pulp. In that experiment the concentrate was only 1.7%, but it assayed $88, that is, it was half in quantity and double in richness as compared with the Wilfley product. Apparently the re-grinding had liberated some gold, which had become included in the concentrate; on the other hand, some of the quartz attached to pyrite had been loosened so as to join the rest of the gangue in the tailing. The reduction in the weight of concentrate would decrease the cost of treating concentrate from 19c. per ton to, say, 15c. The higher-grade concentrate would require more careful handling, and the extraction, at the same ratio of 92%, would leave a higher residue, namely 8% of $88, or $7.04, as compared with 8% of $36, or $2.88, making a difference, however, of only 2c. per ton of original ore, owing to the higher rate of concentration by flotation. In the event of adapting flotation to a stamp-mill, such as that of the Melones, it would be advisable to take the pulp from the amalgamating tables to the re-grinding machinery, in preparation for flotation, and not to attempt any table-concentration, because flotation would be better when leaving the pyrite in the pulp than when treating pulp after concentration. It only remains to remark that the Melones treatment might be changed to all-sliming and cyanidation, discarding concentration and separate treatment of the concentrate.†

The cost might be reduced 3c. per ton, but it must be remembered that the flotation figure is only an estimate as against the actual cost by the existing method. The increased extraction might be 15c. per ton. The total gain, of 18c. per ton, would be attractive if confirmed by further experiment, and if the use of flotation did not involve inquisition by, and subservience to, a patent-exploiting company. That undoubtedly, in my opinion, is a deterrent now. If it were a question of erecting a mill on a mine that had no reduction plant, and that produced ore of the kind we have been discussing, it would be rational to adopt flotation, not only for the sake of the small extra extraction but on account of the first cost of plant. The Melones cyanide plant cost $50,000.

THE DUTCH-APP MILL. At the Dutch and App, a neighboring group of mines, in Tuolumne county, a conventional Californian mill of 40 stamps of 1050 lb. each, followed by amalgamation and concentration, has been changed from concentration by Wilfley tables and Frue vanners to flotation, so that a closer comparison is possible. I am informed‡ that the cost in the old mill was 74 cents, of which 38c. was for stamping, amalgamation, and concentration, and 36c. was for the transport and treatment of the concentrate. The Californian custom

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†Compare this with the Nickel Plate experience. 'The Nickel Plate Mine and Mill.' By T. A. Rickard. M. & S. P., January 20, 1917.

‡By W. J. Loring, who, I hope, at a later date, will contribute his own testimony on the subject.

of reporting the cost of milling without including the expense of realizing upon the concentrate is misleading; so also is the practice of ignoring the loss or smelter-deduction from the assay-value of the concentrate. This item should be added to the assay of the mill-tailing in order to ascertain the total loss, and therefrom the total extraction of valuable metal. Thus the total cost in the old mill was 74c.; in the modified mill it was found to range between 88c. and $1 per ton. The modified plant, however, is at best a mill patched-up for the purpose of testing the ore by flotation; therefore, the cost should be much reduced. The tonnage treated was at the rate of 200 tons daily, whereas the proposed new mill will treat 600 tons daily.

The tailing in the old mill, treating daily 200 tons of $3.75 ore, assayed 90 cents (excluding the loss in concentrate-treatment), but when flotation replaced concentration by Wilfley tables and Frue vanners on the same grade of ore, the tailing was reduced to 35c. during the first month of operation, showing a saving of 55c. per ton. The comparative cost of a plant to treat daily 200 tons of ore carrying 5% of concentratable pyrite is estimated under normal conditions as follows:

(1) Twenty stamps of 1250 lb. each, with two re-grinding tube-mills, plates, and vanners—including rock-breaker, $48,000.

(2) Same mill, using flotation in place of vanners, $55,000.

(3) Same mill, concentrating on tables, the sand and slime treated by cyanide, $65,000.

No. 3 does not include the treatment of concentrate, because it is the usual custom to send it to the smelter at Selby. It will be noted that, for a comparison of plant-cost, No. 3 must be compared with No. 2. Flotation has given a slightly higher concentration of the gold-bearing pyrite in the Dutch-App ore; thus:

Old mill, 4½% of $35 to $40 concentrate.

Flotation, 5% of $50 to $65 concentrate.

The cost of transport and treatment is 38c. per ton of ore. The cost of haulage, freight, and smelter deductions is $9.50 per ton of concentrate. The cost of stamp-crushing and ball-mill re-grinding together is 35c. per ton. The cost of flotation by itself is 15c., making 88c. per ton in all for the extraction of the gold.

When the new mill is treating 500 to 600 tons daily, it is expected to reduce the cost to 68c. and the tailing-loss to 20c. per ton.

By way of further comparison I may quote the cost of milling at an up-to-date plant, using stamps, amalgamation, and table-concentration, namely, at the Plymouth Consolidated in Amador county, also on the Mother Lode. There the cost of milling is 36c. and the concentrate realization 24c. more, making 60c. per ton. The treatment is most satisfactory because, among other reasons, the yield of concentrate is only 1½%. On such an ore flotation would not be as beneficial as on the Dutch-App ore, which contains 5% concentratable gold-bearing pyrite.

THE ARGO MILL. A tribute to the elasticity of the flotation process is furnished by the use of it in a plant treating custom ores. In the Argo mill, at Idaho Springs, Colorado, it has been found highly advantageous to substitute flotation for cyanidation, after stamp-milling and classification, as shown on the accompanying flow-sheet.* Most of the ore comes through the Argo (formerly Newhouse) adit, which taps the veins of Clear Creek and Gilpin counties. These contain gold and silver associated with pyrite, chalcopyrite, and tetrahedrite, so that it is a question of concentrating the sulphides encasing the precious metals. Much of the ore is of the so-called 'free-milling' kind, that is, it is amenable to stamp-mill amalgamation. The coarse gold is caught on the tables before flotation; the fine gold is caught in the flotation concentrate. Good results are obtained by classifying before flotation, particularly on oxidized ore. A trial on an oxidized gold ore from the Paris mine yielded 86% by flotation and 98% by cyanidation. The mill levies the same charges for treatment as the smelter at Denver and has helped, by its competition, to lower the smelter-rates. Its own concentrate is sold to the smelter. Rens E. Schirmer, the manager, and Jackson Pearce, the metallurgist, informed me that they are able to treat ore assaying $40 to $80 per ton. They quote $10.50 for treatment on a $50, and over, ore, but the bulk of the custom ores that come to this mill range between $9 and $20, gross value, and on such material the milling-charge ranges from $4.75 to $5.50 per ton.

For zinc there is no pay and also no penalty.

For lead they pay the regular smelter rate, namely: "Deduct 1.5% from wet assay. The prices paid per unit for lead ore are based upon a quotation of $4 per hundred pounds, 1c. up or down for each change of 5c. in this quotation, which shall be 90% of the sales prices in New York of the A. S. & R. Co. for common desilverized lead, provided said price does not exceed $4 per hundred pounds. When price does exceed $4 per hundred pounds, the quotation used as a basis of settlement shall be $3.60 per hundred pounds, plus three-

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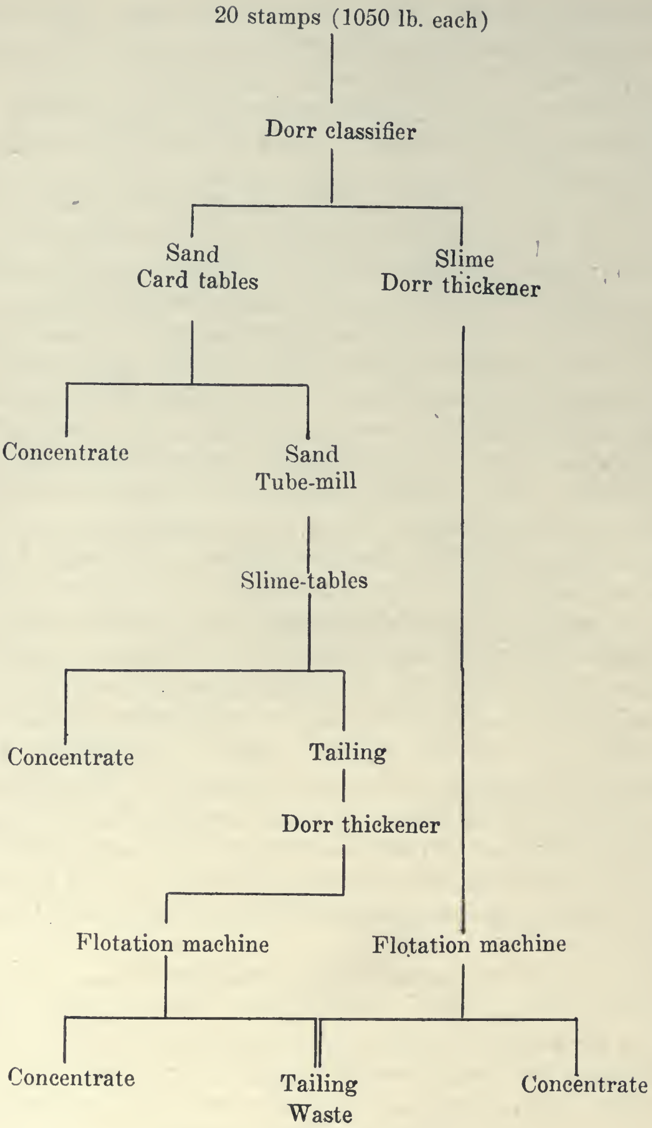
*See also an excellent article by Jackson A. Pearce. 'Flotation Tribulations. M. & S. P., Sept. 16, 1916. Re-printed in this volume.



FLOW-SHEET OF ARGO MILL

fourths the excess of said sales price above $4 per hundred pounds."*

For copper they pay on the dry assay, that is, 1% deduction

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*I quote the exact words in order that the reader may appreciate the hocus-pocus of this smelter method of fixing the price of lead. It is to laugh!

from the wet assay, and the Western Union quotation for casting copper, less 6c. per pound.

For silver, they deduct ½ oz. from assays up to 10 oz. per ton, and pay for the remainder at 95% of New York quotation on date of assay. For ore over 10 oz. per ton, they pay 95% of the quotation, without further deduction.

For gold they pay $19 per oz. between 0.05 and 1.5 oz. per ton; on richer ore they pay $19.50 per ounce.

The Argo mill, with its flotation annex, has treated 4 oz. gold ore, 100 oz. silver ore, 40% lead ore, and 5% copper ore at different times. Such high-grade ore is mixed with the lower-grade before being milled. Money has been made even on a $1.25 ore.

It was found that the recovery by flotation was slightly better than by cyanidation; moreover, the cost was lower, owing to the less expense in chemicals. A much simpler flow-sheet became practicable; there is less pumping, less power, and less labor. Hence the adoption of flotation. A further and decisive advantage is the ability to beneficiate the base metals, notably copper, which was a cyanicide. Since flotation was introduced the mill finds a wider scope and is able to command a larger custom. The flotation machine in use is one devised and patented by Mr. Pearce. It is of the mechanical-agitation type, but it consumes less than one-third of the power required by the Minerals Separation machine previously used in this mill. A 6-cell Pearce machine requires only 5.3 horse-power. Two such 6-cell machines are employed, one to treat sand (80% + 200-mesh) and the other to treat slime. The former gives the higher recovery. I watched them at work and can testify that they produced a uniformly good froth and appeared to be operating admirably. Two pounds of an oil-mixture, consisting of two parts of gas-oil to one part of pine-oil (Pensacola Tar & Turp. Co.'s No. 400), is used per ton of ore. The gas-oil comes from Wyoming; it is one from which the lighter gasoline has been removed. The more sulphidic an ore the larger the proportion of oil required. As soon as sulphide particles appear in the tailing, more oil is added. Gas-oil costs 6c. per gal. and pine-oil 32c. laid down. The water is neither acid nor alkaline. Neither acid nor alkali is added. Fresh water is used, there being no return of water from the tailing. By using fresh water the millman avoids fouling of the liquid by an accumulation of colloids. Formerly the overflow from the concentrate-thickener was run back to the flotation-cell but it was found that this closed circuit tended to collect colloids detrimental to a high recovery by flotation.

Experiments have been made with as much as 40 lb. oil per ton of ore; the recovery was slightly higher than when using 2 lb. per ton. What a commentary on the 'critical' point! When using 40 lb. of oil the bubbles are smaller owing to the larger proportion of gas-oil, which was increased to 85% of the oil-mixture. When using 5 to 6 lb. oil and storing the concentrate in a wooden bin, Mr. Pearce noticed that the oil seeped visibly.

Ordinary variations of temperature appear to have no effect. In winter the froth freezes occasionally, so that it sinks, but so long as the temperature is just short of freezing the operation is not affected. In summer the recovery is no higher than in winter. The mill recovers 92% of the gross market-value of the various ores and treats 100 tons daily.

THE PORTLAND MILL. As yet scarcely anybody that has tried flotation has discarded it after trial. One example of such a reversal is furnished by the Portland Gold Mining Co. of Cripple Creek, and the reasons for it are interesting.

The ore was dump material assaying $2.25 per ton, carrying half an ounce of silver for every ounce of gold, both minerals being present as tellurides, chiefly calaverite. After treating over 100,000 tons the management decided that flotation was not superior to their older method of treatment by table-concentration and cyanidation, for the following reasons:

(1) Good extractions are obtained by cyanidation when grinding to 20-mesh, whereas flotation calls for grinding to 48-mesh. This extra work costs 10c. per ton, which is a serious item on $2.25 ore.

(2) Cyanide bullion is sold to the Mint, and the small amount of concentrate that is made is so low in silica and so high in iron that it can be marketed at the smelter on easy terms, whereas flotation yields a large amount of silicious concentrate on which the cost of freight and treatment is three times that of marketing the by-product of a cyanidation mill. On this ore the recovery by flotation was found to be inversely proportional to the grade of the concentrate; a high recovery made a large amount of low-grade concentrate; a small amount of high-grade concentrate entailed a poor recovery.

(3) Only $20 per ounce was paid for gold in the flotation concentrate, and nothing for the silver. Cyanide bullion is sold to the Mint at $20.67 per ounce for gold and 95% of New York quotation for silver. Thus 4% more is received for the product from the table-concentrate than for the flotation product. On account of the highly silicious character of the latter it was found that the cost of marketing at the smelter was out of all reason, whereupon it was sent to the

custom roasting-cyanide mills at Colorado Springs. This flotation concentrate proved ideal stuff to treat after roasting, but as the silver is not recoverable after the ore has been roasted, the mill could not pay for it.

(4) The royalty payable to the Minerals Separation company.

The principal difficulty was to make a high-grade concentrate and a low-tailing concurrently. Amorphous slime rises with the froth, and any effort to prevent it involves a loss of the sulpho-telluride mineral; in short, it is difficult to separate the gangue-slime from the mineral in this particular ore. Any free gold in the ore floats with the telluride and sulphide minerals. Incidentally, it is worthy of note that flotation in cyanide solution was accomplished successfully at the Portland by J. M. Tippett. He had to use caustic soda, in preference to lime, in order to ensure sufficient alkalinity. The ore was ground in the presence of caustic soda and cyanide. Mr. Tippett avoided dewatering, and the consequent loss of cyanide, by establishing a closed circuit. The pulp flowed from the flotation-cells to thickeners and pachucas, and thence to filters. By this method of treatment he was able to obtain a 40c. tailing on a $20 ore. From $17 to $18 was taken off in the form of a 12-ounce flotation concentrate, the tailing from which assayed $2 or $3 per ton and was reduced to 40c. by treatment in a pachuca.

SUMMARY. In most cases the substitution of flotation means the making of a concentrate instead of bullion. The latter is ready for the market and easily handled or transported. The concentrate is bulky and if it has to be shipped elsewhere for treatment the handling of it entails loss, to which must be added freight and smelter deductions. However, these are troubles that can be obviated if the concentrate is treated at the mine. Some difficulty is said to have been caused by the oil retained by the concentrate; it may interfere with cyanidation, as Paul W. Avery testifies,* but we have the statement of E. M. Hamilton† that he has treated several samples of flotation concentrate with complete success. The experience at the Melones mine is to the point. Speaking generally, I infer that if an ore can be cyanided, then its concentrate, obtained by flotation, can also be cyanided successfully. In short, any gold and silver ore that can be amalgamated or cyanided is amenable to flotation, and the resulting concentrate is equally amenable to treatment by cyanidation. In some cases, as with Cripple Creek tellurides and the Cobalt silver minerals,

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*'Cyanidation of Flotation Concentrate.' M. & S. P., May 16, 1916.

†M. & S. P., March 11, 1916.

it may be necessary to roast first, but the use of flotation on precious-metal ores need not involve dependence upon a smelter. That is important. On the concentrate made at Cobalt, for example, the total cost of marketing is $38 per ton. A chloridizing roast followed by leaching appears to be the only escape from this exaction. In California, the marketing of concentrate from a Mother Lode mine involves a cost, in freight, treatment, and other deductions at the smelter, of $9 to $15 per ton. This can be avoided, at many mines, by cyanidation on the spot without roasting, at a cost of about $5 per ton.

Thus we see that the substitution of flotation for the older processes of amalgamation and cyanidation is an economic rather than a metallurgic problem. In most of the specific cases discussed in detail it is safe to assume that if the manager were starting today to equip his mine with a mill, he would select the flotation process rather than the older methods, or make flotation a part of his flow-sheet. The scrapping of an existing, and expensive, plant is quite another matter. Usually the simple flotation plant would cost half that of the more complicated cyanide annex. Yet, in conversation with various managers, I have ascertained that the control or assumed control of the basic flotation patents by the Minerals Separation people is a strong deterrent. Most of us do not like to be inquisitioned by the agents of a patent-exploiting company, nor do technical men care to be placed under pledges of professional secrecy to anybody. The royalty on gold is only 25 cents per ounce and on silver 2½%, so that the tax is not onerous, but a tax of any kind is an irritation to most men, particularly when the right of the tax-gatherer is still undecided by the courts of law. If and when this question of Minerals Separation's right to collect a royalty is decided satisfactorily we may expect a wide extension in the application of flotation to ores chiefly valuable for gold and silver.

FLOTATION LITIGATION

By T. A. Rickard

(From the *Mining and Scientific Press* of April 14, 1917)

The story of American litigation over the flotation patents is interesting and perplexing. The first contest over the validity of the Minerals Separation company's principal patent was caused by James M. Hyde, who, in August 1911, introduced the use of froth-flotation at the mill of the Butte & Superior Copper Company,[1] applying the process successfully to a zinc ore carrying a small amount of lead. On October 3, 1911, suit for infringement of patent 835,120 was brought by Minerals Separation against Mr. Hyde. The trial took place before the U. S. District Court at Butte and there, on July 28, 1913, Judge Bourquin decided that the patent was valid ''in respect to all claims in issue.''

It will be well to outline the nature of the patent in suit. The first claim says: ''The herein-described process of concentrating ores which consists in mixing the powdered ore with water, adding a small proportion of any oily liquid having a preferential affinity for metalliferous matter (amounting to a fraction of one per cent on the ore), agitating the mixture until the oil-coated mineral matter forms into a froth, and separating the froth from the remainder by flotation.''

Claim No. 12 states: ''The process of concentrating powdered ore which consists in separating the minerals from gangue by coating the minerals with oil in water containing a fraction of one per cent of oil on the ore, agitating the mixture to cause the oil-coated mineral to form a froth, and separating the froth from the remainder of the mixture.''

The patentees—H. L. Sulman, H. F. K. Picard, and John Ballot—refer in their specification to the Cattermole patent, No. 777,273, in which mention is made of using ''an amount of oil varying from four per cent to six per cent of the weight of metalliferous matter present,'' and they then proceed to explain:

''We have found that if the proportion of oily substance be considerably reduced—say, to a fraction of one per cent on the ore—granulation ceases to take place, and after vigorous agitation there is a tend-

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[1] This company did not produce copper, but zinc, lead, and silver. In 1916 the name was changed to Butte & Superior Mining Company.

ency for a part of the oil-coated metalliferous matter to rise to the surface of the pulp in the form of a froth or scum. This tendency is dependent on a number of factors. Thus the water in which the oiling is effected is preferably slightly acidified by adding, say, a fraction of one per cent up to one per cent of sulphuric acid or other mineral acid or acid salt; the effect of this acidity being to prevent gangue from being coated with oily substance, or, in other words, to render the selective action of the oil more marked; but it is to be understood that the object of using acid in the pulp according to this invention is not to bring about the generation of gas for the purpose of flotation thereby, and the proportion of acid is insufficient to cause chemical action on the metalliferous minerals present. Again, we have discovered that the tendency for the oily substance to disseminate through the pulp and the rapidity with which the metalliferous matter becomes coated is increased if the pulp is warmed. The formation of froth is assisted by the fine pulverization of the ore, and we find that slime mineral most readily generates scum and rises to the surface, while larger particles have less tendency to be included in the froth."

Application for this patent was filed on May 29, 1905, and the rights accruing under the patent start from this date. The patent was granted on November 6, 1906, and the life of the patent, 17 years, is measured from this later date.

Judge Bourquin's decision was sweeping.[2] It rested largely on a reply to the question whether Froment's British patent No. 12,778, of June 4, 1902, anticipated the patent in suit. On this point the Court expressed itself as follows:

"Froment's [patent] requires several times the quantity of oil that does this in suit, both by examination of the patents and working description and by tests in evidence. Froment crushes the ore in two operations, and de-slimes it before treatment, because the slime is too fine to be treated by his process, while the process in suit needs but one crushing operation, and finds slime advantageous and most easily recovered. Froment employs carbonate of lime; the process in suit does not. Froment requires acid, and in greater quantity and for a different function than does the process in suit, which latter may or may not use acid. Both may use heat, and both require agitation—Froment's agitation only to disseminate the oil, the process in suit for that purpose and also to aerate. Froment's result is by flotation by gas generated *in situ*; this in suit is by flotation by air introduced by vigorous agitation. Froment's product is like unto a magma, a spongy, pasty

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[2] For full text of this decision see M. & S. P., August 16, 1913.

mass of oil and metallic particles, and more or less gas bubbles, while this in suit is a froth of oil and metallic particles and air-bubbles. Froment's requires oil in such quantity that he deems it worthy of recovery from the concentrate, so far as it can be; this in suit so little oil it disappears, is not sensible to sight or touch upon the concentrate but only to analysis. In Froment's it would seem that the metallic particles are floated like the basket of a balloon, while in this like the very envelope of a balloon. Froment's is costly, while this is cheap. And from the evidence it would seem that Froment's process would fail in practical operation, while this in suit has succeeded. In Froment's he oils the metallic particles by agitation; then, when the mixture is quiescent, generates gas therein by quick reaction, followed by immediate and direct rising of the gas bubbles to the surface in which they may come into contact with but few metallic particles. In this in suit vigorous agitation of the mixture beats great and excess volumes of air therein, likely bringing the ultimate air bubbles into repeated contact with many metallic particles. The action of the gas in Froment's is almost explosive in nature. He speaks of the proportion of carbonate of lime to be sought as, in his test-tube example, the reaction may be so sudden and violent as to project the metallic particles out of the tube. Froment's gas bubbles, quick formed and quick rising it may be, arrive at the surface with expansion still in progress. These or analogous reasons may account for Froment's magma breaking gas bubbles and fragile evanescent froth in so far as his result is like unto froth, and also may account for the process in suit's strong and lasting froth.''

On appeal to the Ninth Circuit in San Francisco the decision of the lower court was reversed, on May 4, 1914. The opinion of the Court of Appeals, pronounced by Judge Gilbert, stated that ''the fact that the appellees use a smaller quantity of oil than was used in the prior art is not of itself, and is not claimed by them to be, sufficient to distinguish their process so as to render it patentable.'' This Court held that ''the agitating of the mixture to cause the oily-coated mineral to form a froth'' was ''clearly anticipated by the prior art.'' It is noteworthy that the Examiner of Patents rejected claim No. 12 ''in view of 763,260, Cattermole, June 21, 1904; or 793,808, Sulman et al, July 4, 1905, . . . as expressing merely a difference of degree thereover as to the proportion of oily matter employed.'' Thus the Examiner refused to allow patentability on the mere use of a small percentage of oil. The claim thus cancelled, not the No. 12 of the final patent, quoted above, was the only one that was based exclusively on the use of a fraction of 1% of oil, without reference to a particular kind of agitation or a particular kind of froth. The Appellate Court took cognizance of this interesting disclosure, for Judge Gilbert said.[3]

"We hold that to sustain the appellees' patent would be to give to the owners thereof a monopoly of that which others had discovered. What they claim to be the new and useful feature of their invention, as stated by their counsel, is 'agitating the mixture to cause the oily-coated mineral to form a froth.' As we have seen, that feature was clearly anticipated by the prior art, and when the elements of the appellees' claims are read one by one it will be found that each step in their process is fully described in more than one of the patents of the prior art, with the single exception of the reduced quantity of oil which they use. The patentees of the appellees' patent made a valuable contribution to the art in discovering the smallest quantity of oil which would produce the desired result. In doing so they pursued the course which all skilful metallurgists would be expected to pursue. They made a series of experiments to determine how small a quantity of oil could be used successfully. They found, as all must find who apply the oil flotation process, that certain oils are adapted to use with certain ores, and that a larger quantity of oil is necessary for one kind of ore than for another. The appellees admit that for some ores they use four times as much oil as for others. Their discovery that a small fraction of one per cent of oil is sufficient to produce flotation of the metalliferous matter cannot, as we have seen, be made by itself or in a combination the subject of a patent. The appellees cannot take from others the right to use oil economically. This was evidently the ruling of the Patent Office on their application for a patent. One of their claims in the original application was 'the process of concentrating powdered ore, which consists in separating minerals from gangue by coating the minerals with oil in water containing a fraction of one per cent of oil on the ore, and recovering the oil-coated minerals.' This was rejected in view of the Cattermole patent 'as expressing merely a difference of degree thereover as to the proportion of oily matter employed.' Counsel for appellees admit that the claim was properly rejected for the reason that it leaves out the agitation and froth, and say 'our invention is something else than the mere reduction of oil.'"

Thereupon Minerals Separation obtained a hearing before the Supreme Court of the United States on a writ of certiorari. The case was argued in October 1916. The court expressed its opinion through Mr. Justice Clark on December 11, 1916. It was laid down that the patent was valid on three counts, (1) the use of a 'critical' and minute

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[3] For the full text of this decision see M. & S. P., May 9, 1914.

proportion of oil, (2) the use of a particular kind of agitation, namely "by beating air into the mass," and (3) the production of a "peculiarly coherent and persistent" kind of froth. The most important parts of the opinion are to be found in three paragraphs.[4] The first defines the patent:

"The process of the patent in suit, as described and practised, consists in the use of an amount of oil which is 'critical,' and minute as compared with the amount used in prior processes 'amounting to a fraction of one per cent on the ore,' and in so impregnating with air the mass of ore and water used, by agitation—'by beating air into the mass'—as to cause to rise to the surface of the mass, or pulp, a froth, peculiarly coherent and persistent in character, which is composed of air bubbles with only a trace of oil in them, which carry in mechanical suspension a very high percentage of the metal and metalliferous particles of ore which were contained in the mass of crushed ore subjected to treatment. This froth can be removed and the metal recovered by processes with which the patent is not concerned."

"It is obvious that the process of the patent in suit, as we have described it, is not of the Metal Sinking class, and while it may, in terms, be described as a Surface Flotation process, yet it differs so essentially from all prior processes in its character, in its simplicity of operation, and in the resulting concentration, that we are persuaded that it constitutes a new and patentable discovery."

The third declares the validity of the patent, but restricts its application.

"While we thus find in favor of the validity of the patent, we cannot agree with the District Court in regarding it valid as to all of the claims in suit. As we have pointed out in this opinion there were many investigators at work in this field to which the process in suit relates when the patentees came into it, and it was while engaged in study of prior kindred processes that their discovery was made. While the evidence in the case makes it clear that they discovered the final step which converted experiment into solution, 'turned failure into success' (*The Barbed Wire Patent,* 143 U. S. 275,) yet the investigations preceding were so informing that this final step was not a long one and the patent must be confined to the results obtained by the use of oil within the proportions often described in the testimony and in the claims of the patents as 'critical proportions' 'amounting to a fraction of one per cent on the ore,' and therefore the decree of this court will be that the

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[4] For full text see M. & S. P., December 30, 1916.

patent is valid as to claims No. 1, 2, 3, 5, 6, 7, and 12, and that the defendant infringed these claims, but that it is invalid as to claims 9, 10, and 11. Claims No. 4, 8, and 13 were not considered in the decree of the two lower courts and are not in issue in this proceeding.''

Meanwhile a number of Western mining companies had begun to use flotation. One of them was the Miami Copper Company, in Arizona. On October 10, 1914, suit was brought by Minerals Separation for infringement of patent No. 835,120 and also of No. 962,678 and 1,099,699. The first trial took place in the District Court at Wilmington, Delaware, and the decision, by Judge Bradford, was pronounced on September 30, 1916.[5]

In this case the issue differed from that involved in the previous litigation. Hyde had denied, not infringement, but the validity of patent 835,120. The Miami company denied infringement, claiming that it was using a method similar to that described in a patent of earlier date, namely No. 793,808. Judge Bradford accepted this contention. He said:

''The evidence shows that the defendant in its concentration of ore in its pneumatic flotation plant employs the process of patent No. 793,808, of July 4, 1905, to Sulman & Picard, hereinbefore discussed, as modified by the use of certain apparatus, substantially the same as a portion of the apparatus, the operation of which is described in the above-mentioned Callow patent,'' namely, No. 1,104,755 of July 21, 1914, to John M. Callow.

He decided that the Froment patent was not an anticipation because ''it does not appear that there was present in the Froment process the very minute quantity of oil of the first patent in suit.''

The essential part of the Wilmington decision is that the diminution of oil to less than 1% of the weight of the ore is patentable. Judge Bradford said:

''On the whole I am satisfied that the first patent in suit must be sustained as to claims 1 and 12, but not as to claim 9. The two former are definite, specifiying and limiting the amount of oil to be used; claim 1 mentioning 'a small proportion * * * amounting to a fraction of one per cent on the ore,' and claim 12 'a fraction of one per cent of oil on the ore.' Claim 9 mentions 'a small quantity of oil.' This is so indefinite as to render the claim void, unless on consideration of the patent as a whole the claim can by construction be limited to the use of oil amounting to only a fraction of one per cent. The patentability of the process of the first patent in suit resides in the use of oil in the ex-

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[5] For full text of this decision see M. & S. P., October 14 and 21, 1916.

tremely minute proportion disclosed in the descriptive portion of the patent to effect separation of froth with its metallic particles from the remainder of the mixture by flotation. The amount there disclosed is not in excess of 'a fraction of one per cent on the ore' and may be only one-tenth of one per cent on the ore, or even less. If, then, by construction claim 9 should be so limited as to be restricted to the use of oil amounting to only a fraction of one per cent on the ore, that claim is in substance, though not in exact phraseology, the same as claim 1 for the reason that in any event from the nature of the invention it would be necessary to read 'by flotation' into claim 9, if in other respects valid. But a limitation by construction producing such a result is inadmissible. It is suggested by one of the plaintiff's counsel in his consideration of claim 9, that one for the purpose of securing immunity from the consequences of infringement might use an oil useful in the process, and add to it an oil not useful as applied to his particular ore, and, on being sued for infringement contend, 'I am using 1.1% of oil. I do not infringe. I am using more than a fraction of 1% of oil.' But the existence of this possibility does not, I think, warrant such a construction of claim 9 as is urged; for the disclosure of the patent does not extend to the use of 1.1% of oil, but is limited to a fraction of 1%."

In regard to the second patent in suit, No. 962,678, of June 28, 1910, to Sulman, Greenway, and Higgins, the Court quotes part of the description in the patent:

"According to this invention the crushed ore is mixed with water containing in solution a small percentage of a mineral-frothing agent (that is of one or more organic substances which enable metallic sulphides to float under conditions hereinafter specified) and containing also a small percentage of a suitable acid such as sulphuric acid, and the mixture is thoroughly agitated; a gas is liberated in, generated in, or effectively introduced into the mixture and the ore particles come in contact with the gas and the result is that metallic sulphide particles float to the surface in the form of a froth or scum, and can thereafter be separated by any well-known means. Among the organic substances which in solution we have found suitable for use as mineral-frothing agents with certain ores are amyl acetate and other esters; phenol and its homologues; benzoic, valerianic, and lactic acids; acetones and other ketones such as camphor. In some cases a mixture of two such mineral-frothing agents gives a better result than a single agent. * * * The present process differs from the two before mentioned types and from other known concentration processes by the introduction into the acidified ore pulp of a small quantity of a mineral-frothing agent, that is, an organic compound in solution of the kind above referred to and by the fact that the metalliferous particles are brought to the surface in the form of a froth or scum not by mechanical means but by the attachment of air or other gas bubbles thereto. In the frothing process hitherto known the substance used to secure the formation of a mineral-bearing froth has been oil or an oily liquid immiscible with water. According to this invention the mineral-frothing agent consists of an organic compound contained in solution in the acidified water.''

The Court then proceeds to say:

''It will be observed that no one of the claims of the second patent in suit requires as an element an oily substance or liquid as is essential in the process of the first patent in suit, and all of the claims relied on require the introduction into the mixture of a 'small quantity' of a 'mineral frothing agent' or an 'organic mineral frothing agent.' The amount of the mineral frothing agent employed in the process is not confined to a fraction of one per cent on the ore, but must be a small quantity evidently to be determined by the metallurgical engineer conducting or superintending the operation according to the requirements of the different ores. The novelty of this invention is to be found, not in any restriction of the amount of the mineral frothing agent to any stated proportion, for there is none, but in the fact that a mineral frothing agent as the means of separating the metallic particles from the gangue is substituted for the oil, fatty acid, or other oily substance essential to the process of the first patent in suit. Such substitution has produced sucessful results, and, I think, involved invention. Frothing agents had theretofore been used in ore concentration, but not in the absence of an oily ingredient. Even were the grounds on which the validity of the patent can be sustained less clear, it should have the benefit of the presumption of validity arising from the grant of letters. That the defendant has infringed the claims in suit of the second patent is established by the evidence.''

The third patent, No. 1,099,699, was not sustained and need not be discussed.

The most remarkable feature of Judge Bradford's opinion is that he states flatly that the Miami is using the process of patent 793,808 yet he holds that the company has infringed patent 835,120, the numbers of these patents indicating their relative age.

An analysis of the decisions up to date shows that three courts out of four have sustained the validity of patent 835,120 but the reasons have been dissimilar and even contradictory. For the sake of brevity, I shall refer to the courts by the cities in which the issue was tried.

Butte said that Froment did not anticipate Sulman et al.

San Francisco said that he, and others, did do so. This court refused to consider the mere diminution in the proportion of oil as a subject for patent.

The Examiner of Patents had decided likewise.

Washington granted validity on account of limitation of oil, peculiar agitation, and peculiar froth. This court decided that Froment's process "was little more than a laboratory experiment" and did not anticipate the workable process described in 835,120.

Wilmington granted validity on account of the specification of critical proportion of oil, and adversed the one claim that did not specify that limitation.

Moreover, the Supreme Court differs with everyone that has passed on patent 835,120. It holds the Patent Office wrong for having granted indefinite claims, it holds the Butte court wrong in deciding that such indefinite claims were valid, it holds the San Francisco court wrong for invalidating the whole patent, by inference it holds the Wilmington court wrong for basing patentability on a small proportion of oil alone.

It is a curious fact that the practicability of producing an effective froth by means of more than 1% of oil was not tried on a working scale before these suits were started. Such experimental demonstrations as were made, out of court or before the judges, were apparently unconvincing, for the sufficient reason, I believe, that the minimum proportion was considered best even by the defendants, but as soon as the Supreme Court had given its opinion and placed so much emphasis on the 'critical' proportion, the use of more than 1% of oil was applied successfully on a scale of over 1000 tons per day in the mills of the Utah Copper and Butte & Superior companies, in Utah and Montana, respectively. The 'critical' point was proved fallacious early in 1917.

An appeal from the Wilmington decision was taken promptly by the Miami company to the Court of Appeals for the Third Circuit, at Philadelphia, where the case was heard in February 1917. As was to have been anticipated, the appellees made the most of the Supreme Court's decision in the Hyde case, in so far as it defined and limited the scope of patent 835,120. Counsel argued that the Miami company had not infringed because its operations differed radically from those described in the Supreme Court's decision, both in the kind of aeration employed and in the character of the froth produced. Whereas Hyde, and Minerals Separation also, used mechanical means for causing violent agitation and for producing the 'cauliflower' froth, as described by Mr. Ballot, the Miami company used a Callow cell, an inclined trough having a porous bottom through which compressed air at a low pressure was admitted, producing a froth without the aid of mechanical agitation, and the froth thus formed was described as thin, tender, and evanescent. This froth broke and disappeared as soon as the supply of air was withdrawn, while the froth produced by beating air into the pulp would last for days. While the Miami used less than 1% of oil, it did not employ the two other elements essential to patent 835,120, namely the violent mechanical agitation and the formation of a peculiarly coherent and persistent froth. It was argued that a patent claim for a combination of any three elements, such as those specified by the Supreme Court in patent 835,120, created a monopoly only in the use of a process in which all three of the stated elements were used. No monopoly was secured of any one of the elements used singly and apart from the others. Therefore, there was nothing in the Supreme Court's decision giving Minerals Separation a monopoly of the use of a fraction of oil *per se;* on the contrary, the Supreme Court stated that the patent derived its validity from the three factors taken together. So the Miami company contended that it had a perfect right to use any quantity of oil however minute, provided it used the oil in a process that did not include the violent agitation and the persistent froth characteristic of the Minerals Separation process. Whereupon the patentees had to repudiate the limitations specified by the Supreme Court and depart from the contention that they had made in the Hyde case concerning the special and remarkable character of the froth produced by their process. In the District Court the great difference between the two kinds of froth, one due to beating air into the pulp during violent mixing and the other to the simple introduction of compressed air through a porous bottom, had been emphasized heavily and the statement had been repeated that a shovel had been seen to rest on the froth of patent 835,120, whereas even a match would sink through the kind of froth made at Miami. In the appeal at Philadelphia another tack had to be taken, so counsel for Minerals Separation, in their reply brief, stated:

"With respect to the character of the froth, there can be no serious contention. Before the discovery of these patentees nothing in the nature of froth (a collection of bubbles on the surface) remained long enough to permit recovery of the metal. By reason of the discovery of these patentees a froth was produced, composed of 'modified' air bubbles, coherent and persistent enough to permit of recovery of the metal. That was the unique thing—the peculiarity adverted to by the

Supreme Court. In defendant's practice the froth produced by it is similarly composed of 'modified' air bubbles, and so is coherent and persistent enough to permit of recovery of the metal. There is no point and nothing of importance in the degree of coherency or persistency beyond and in excess of that required for the recovery of the valuable metal.''

The decision of the Court of Appeals at Philadelphia is expected at any moment. Meanwhile it is to be noted that after Minerals Separation won the preliminary decision in the Hyde case at Butte they brought suit against the Butte & Superior company and moved for a preliminary injunction. This was in the autumn of 1913. The Butte & Superior case was brought before the same court as that in which the Hyde case was first tried, and this court, at Butte, ruled that no injunction would be issued if the Butte & Superior company would file a bond and also file monthly reports of its flotation operations with the Clerk of the Court. This condition was fulfilled. No injunction was issued and the case has rested in *statu quo* up to the present. The trial began on April 16, 1917. It proved most interesting because a number of new scientific witnesses were placed on the stand and in the course of their evidence they gave the results of recent research into the principles of flotation. In my article on this phase of the subject I have quoted from the testimony given by some of these gentlemen at Butte. As regards the legal argument, it is noteworthy that the 'critical point' was demolished by the evidence of large-scale mill-operations in Arizona, Utah, and Montana, showing that the use of 20 to 22 pounds of oil, or over 1%, per ton of ore had given even a higher recovery than the 2 to 5 pounds heretofore customary in these mills.* The question was also raised, and answered, whether the excess of oil was inert. Minerals Separation shifted its ground so as to broaden its claims to cover all processes in which an air-froth is a factor, regardless of the amount of oil used. They repudiated the peculiar agitation, the extraordinary froth, and the critical proportion of oil on which they had obtained a favorable decision from the Supreme Court.

[Since the above was written the Court at Philadelphia has recorded its decision in the case of Minerals Separation *v.* Miami Copper Co. This decision, made known on May 24, 1917, was not unanimous, one judge (out of three) dissenting. The majority opinion upheld the validity of patent 835,120, but interpreted the Supreme Court's decision in the Hyde case as meaning that ''invention resides

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*'Flotation—the Butte & Superior Case.' M. & S. P., July 28, 1917.

not alone in the critical proportion of oil, but also in air and agitation.'' The Miami company was held to have infringed because it used agitation similar in ''degree of intensity and time of duration'' to that defined by the Supreme Court as characteristic of the patented process. Such infringement was due to the use of a centrifugal pump and a Pachuca tank before aerating the pulp in a Callow cell. Inferentially the opinion suggests that infringement would not have been found if the Callow cell had been used without the pump and the Pachuca, both of which were discarded by the Miami company before the trial began, but evidence to that effect was not in the record. Apparently the use of the pneumatic machine in flotation is validated. The Court says, concerning the Callow cell, ''Aeration is direct and is not the result of or caused by agitation. On the contrary, agitation results from aeration, and such agitation, though present in some measure, is not even approximately of the violence and duration of the agitation of the patent.'' As it stands, the Philadelphia decision clears the ground in that it leaves free the use of the Callow cell, and other pneumatic machines of the same type, in conjunction with such agitation as was used in the prior art solely for the purpose of bringing the oil in contact with the mineral in the pulp; in other words, unless the use of flotation involves an agitation characterized by great intensity and long persistence it will not infringe patent 835,120. The minority opinion confirms this view, stating that ''steps of the process 'agitating the mixture until the oil-coated mineral matter forms into a froth' meant the novel *air-entraining* agitation which the patentees disclosed, and did not cover the novel *air-releasing* agitation which the defendants disclosed.'' The majority opinion sustained the validity of patent 962,678 for a ''soluble frothing agent,'' but tied it to a violent and persistent type of agitation. On the other hand, the exception made in favor of the Callow cell as not infringing 835,120, under given conditions, was not, apparently, made to apply to metallurgical operations under 962,678; so that the definition of what is a 'soluble frothing agent' becomes crucial.]

Some reference to the previous litigation in England and Australia may be made, although it is now only of secondary importance. It is vital to the proper understanding of the patent litigation as a whole to recognize the fact that the decisions in the British and Australian cases did not establish the validity of the British equivalent of U. S. patent 835,120. That issue was not before those courts; indeed, the prior art, except as it had a bearing on the validity of the Elmore bulk-oil patents, was not under consideration. Moreover it was the Elmore bulk-oil patent of 1898 and not the vacuum-air patent of 1904 that was at stake. The question before the British and Australian courts was the validity of Frank Elmore's British patent No. 21,948 of 1898 and Stanley Elmore's British patent No. 6519 of 1901, the first the principal bulk-oil patent and the second a modification specifying the use of acid. No account was taken of the patents issued between the dates of these Elmore patents and the date of the Minerals Separation patent of 1905, nor was the question of how such intervening patents would affect the validity of 835,120 considered. To establish the fact that Elmore's bulk-oil patent is not valid or that the M. S. process is not the Elmore process does not prove anything with regard to the validity of the M. S. patent. That question was not before the British courts and it is remarkable therefore that these cases should have been cited at all in the American courts. The effect of the citation has been only confusing.

Most of the English suits were between Minerals Separation and the Elmores, or the company with which they were identified. Personal quarrels and charges of bad faith were made in Sulman & Picard *v.* Wolf, in 1905, and in Ore Concentration Company [Elmores] *v.* Webster and others [the Minerals Separation group] in 1908, but the two cases involving basic patent-rights were both brought by the Elmores against Minerals Separation.

In the first case, ended in 1909, British Ore Concentration Syndicate, Ltd., and Alexander Stanley Elmore *v.* Minerals Separation, Ltd., the principal issue was the validity of the Elmore bulk-oil patents of 1898 and 1901 against the Minerals Separation process as described in British patent No. 7803, the equivalent of U. S. 835,120. The Court (Mr. Justice Neville) gave judgment against the Elmores and decided that:

(1) The selective action of oil for sulphides was known before Elmore obtained his patents, and was disclosed in prior expired patents.

(2) Elmore's patent was for a process wherein a large quantity of oil was used, sufficient to carry all the sulphides to the surface by the buoyancy of the oil.

(3) The Minerals Separation process used only an infinitesimal amount of oil for the purpose of attaching air-bubbles to the sulphides, causing them to float by the buoyancy of the air-bubbles, and did not infringe F. E. Elmore's patent.

(4) The use of acid in oil processes was known before A. S. Elmore

obtained his patents and was disclosed in prior expired patents, therefore, Elmore's patent was not infringed by Minerals Separation.

The plaintiff appealed and the decision of the court was reversed, it being held that Minerals Separation was infringing the 1901 patent, involving the use of acid with oil. The Court of Appeals found that

(1) The first Elmore patent was not anticipated by previous expired patents [such as those of Robson and Everson].

(2) If Minerals Separation used a thin oil they would not infringe Elmore [who used a thick oil; so also Minerals Separation used a thicker oil (oleic acid) than is now customary in the United States].

(3) The second Elmore patent [that of A. S. Elmore of 1901] was not anticipated by previous expired patents [such as Everson's, in which acidulation is mentioned].

(4) Minerals Separation infringed the second patent by using acid.

An appeal was then taken to the House of Lords and on November 16, 1909, the judgment of the Court of Appeals was reversed, that of the trial court being upheld.

The Lord Chancellor (the Earl of Loreburn) said that the Frank Elmore patent of 1898 need not be discussed, because it had no place in the controversy, ''into which it has nevertheless been introduced with no other result than to confuse the issue.'' He held that the Stanley Elmore patent of 1901 was ''framed with great subtlety, being partly narrative, partly claim'' and ''designed in order that the claim might be expanded or contracted as occasion might require in the interest of the patentee;'' that the only definite claim was for acidulation, and that this claim was anticipated by Everson; therefore the patent could not be sustained.

The Earl of Halsbury was of the opinion that the inventions of Elmore and Minerals Separation were ''essentially different,'' the one being dependent on ''the selective action of oil, the other upon surface tension''; that acidulation had been ''invented and patented'' before the date of Stanley Elmore's patent, and that this patent was so ambiguously stated that it should be held bad.

Lord Atkinson likewise described the specification of the patent as ''framed, somewhat craftily, in terms of studied vagueness and ambiguity''; he held that it could not claim ''the mere addition of acid in small quantities to a mixture of ore, water, and a relatively infinitesimal quantity of oil reduced to a 'freely flowing pulp'.'' If the patent was for the addition of a small quantity of acid and a relatively large quantity of oil to a mixture of ore and water, where the oil, in accordance with some obscure law of affinity, seized upon the minute particles of ore in preference to the earthy particles, and, by the buoyancy of oil, floated them to the surface, then the Minerals Separation did not infringe this process, because their process was one where they made use of the known selective action of oil, yet the oil was used in relatively small quantities, and the metallic particles were only coated with a thin film of it, and the lifting force was found, not in the buoyancy of the oil, but in the natural buoyancy of the air-bubbles, which, introduced into the mass by violent agitation, envelop or become attached to the oiled mineral particles and raise them to the surface.

Lord Shaw of Dunfermline said: "It has already been determined that the use of thin oil instead of thick imports no infringement of the 1898 patent, nor do I see my way to hold that there has been any contravention of the 1901 patent by the application of the acid to a mixture in which the oil has been reduced from bulk to the merest fraction, and especially when froth instead of oil has been secured, along with the law of capillarity or surface-tension, as the main floating and separating agent." He held that the processes were essentially different and that there was no infringement.

Lord Ashbourne concurred with the decision of their lordships, thus making the judgment of the Court unanimous.

Meanwhile, in 1910, the Elmores had brought suit against the Sulphide Corporation, a licensee of Minerals Separation, operating at Broken Hill. The issue was tried in Australia with a result adverse to the Elmores, who then appealed to the Judicial Committee of the Privy Council, which heard the case in November 1913 and gave a decision on March 6, 1914. This decision confirmed the lower court and was in accord with that of the House of Lords; the Judicial Committee found that the Everson patent did not anticipate the Elmore acid-oil patent, but, on the other hand, that the Minerals Separation process was not an infringement of the Elmore patent, because it relied on surface-tension, and not oil, for the flotation effect.

I quote one of the decisive paragraphs in this decision of the Privy Council:

"The Appellants place considerable importance on the second form of apparatus described in the patent. In this apparatus a thin stream of oil is thoroughly mixed with the pulp, and the oil 'by its selective action coats or absorbs the metallic particles, sulphides, tellurides, and the like.' The whole mixture then flows over a weir and down an incline over a number of wave-like steps or baffles by which the stream of pulp and oil globules is thrown against an oiled apron continuously moving in the opposite direction. Separation is effected by the oiled surface of the apron taking up most of the oil globules and by also picking up from the pulp such particles of metallic substances as have escaped oil selection in the mixer. The patentee distinctly draws attention to the fact that separation in this apparatus does not depend upon the buoyancy of the oil, and that consequently tar, heavy residuum oils, and other like substances of a greater gravity than water may be employed as the selective agent. The question arises whether the selective action of the oil or tar when the separation is effected by the second apparatus differs from the selective action of oil when the separation is effected in the first apparatus. The answer is in the negative. The 'coating or absorbing' described in connection with the second apparatus is not different in character from the entrapping described in the first apparatus. The 'oil globules' hold and carry the metallic particles and are taken up by the oiled surface of the apron, which also picks up from the pulp such particles of metallic substances as have escaped selection by the oil in the mixer, that is to say, such particles as have not been coated and carried in the 'oil globules'.''

Throughout these British and Australian litigations the validity of the bulk-oil patents, of 1898 and 1901, and not of the vacuum patent, of 1904, was at stake. It is a curious fact that whereas the Elmore vacuum method depends upon surface-tension and the use of air quite as much as the Minerals Separation method, it was not cited in the litigation and it was ignored by the courts. It is also curious that during the six years of litigation in the United States the Elmore vacuum patent was not used to attack the validity of 835,120, although this patent of Minerals Separation was taken out in England on April 12, 1905, as compared with Elmore's vacuum patent of August 16, 1904. It may be asked, why did not the Miami company fall back on this defence and use Elmore to fight the Minerals Separation? The answer is the fear to establish another patent monopoly, possibly no more pleasant than the one already on the ground. However, in May 1915, after the Miami suit had been heard at Wilmington, the Elmore vacuum patents were purchased for $50,000 by a syndicate headed by Messrs. D. C. Jackling and J. Parke Channing, representing the Utah, Miami, and other important copper-mining companies in the United States. It is possible that the possession of these Elmore patents may prove an interesting factor in later litigation, but it is even more likely that the use of oil will be discarded before this litigation is ended.

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