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AMERICAN
SULPHURIC ACID PRACTICE

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Lunge

AMERICAN
SULPHURIC ACID
PRACTICE

BY
PHILIP DeWOLF
AND
E. L. LARISON
Anaconda Copper Mining Company

WITH A SPECIAL CHAPTER
BY
W. M. LeCLEAR

First Edition

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PREFACE

During a period of several years in close contact with the manufacture of Sulphuric Acid the writers have a great many times been asked to recommend some published work upon the subject from which a knowledge of the practical essentials of modern American acid making could be obtained. This inquiry has come from men working in association with, and under the supervision of, the writers, and also from men in allied lines who wished to acquaint themselves quickly with this information.

So far as the writers know, such a work in English does not exist. Lunge's "Sulphuric Acid and Alkali" is admirable in many ways, and certainly every one permanently connected with the manufacture of acid should have it for reference: it does not, however, cover modern American practice, nor is it suitable to present to a new chamber operator as a source of information. Besides Lunge, there are several books which include a few chapters on sulphuric acid, but none is satisfying.

The writers' purpose in preparing this volume has been to provide some fundamental information for the man with little preliminary knowledge of the subject. It does not in any way pretend to cover acid manufacture with the thoroughness of Lunge. History, chemical and physical theory, and many other things are treated from the *technical,* not the *scientific,* view-point, in an effort to avoid the error, so common in "Handbooks," of not devoting much time to **Why,** while very thoroughly covering **How.**

NOTE.—"Sullivan's Handbook" so thoroughly covers the laboratory end that we have not included laboratory practice, and recommend his methods.

The writers are much indebted to several manufacturers of acid plant equipment for photographs and drawings of machinery and apparatus.

PHILIP DEWOLF.
E. L. LARISON.

ANACONDA, MONTANA,
April, 1921.

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AMERICAN SULPHURIC ACID PRACTICE

CHAPTER I

ALCHEMY, HISTORY, DEVELOPMENT, STATUS

When the old and bewhiskered alchemist mentally planned his transmutations from lead to gold, he no doubt considered his reagent "spiritus vitroli" second only to his trusty Philosopher's Stone in power and usefulness; for we read of sulphuric acid back through Alchemical times, but the name of the true discoverer will probably always remain unknown.

The Arabian, Geber (A.D. 960), was formerly thought to have been the first to describe thc "spirit of alum" and its solvent powers, in the mythical literature of the time, but there is a question now whether this did not creep in during the Latin "translations" of the same. The Persian Alchemist, Abn-Bekr-Alrhases (A.D. 930), and also DeBeauvais (A.D. 1240) are conceeded probable discovers, but direct evidence is woefully lacking.

Basil Valentine (A.D. 1425), in that landmark of Alchemical lore, "The Triumphal Car of Antimony," is the first to refer to any method of manufacture, and therein describes the burning of sulphur with saltpeter in glass vessels. This method was adopted by the apothecaries of the time, for the manufacture of sulphuric acid on a small scale for pharmaceutical use. From the apothecaries' laboratory to an industrial installation was the logical sequence, and about 1746, at Richmond, near London, we find what was then considered a large plant, operated by a quack doctor named Ward.

From this point the manufacture branches off from alchemy and quackery, and its development is along scientific and mechanical lines. The development and introduction of lead chambers instead of glass, took place about 1746, when Dr. Roebuck, and later a Mr. Garbet, erected plants with lead chambers six feet square. Later factories were built at Worcestershire, London, and Glasgow.

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FIRST AMERICAN ACID PLANT

The house now known as Harrison Bros. & Co., Inc. was founded in 1793 by Mr. John Harrison of Philadelphia. Mr. Harrison received his early education in Philadelphia, and then spent two years in Europe investigating the arts and processes of the manufacture of chemicals and in studying under the celebrated chemist, Dr. Joseph Priestley. Mr. Harrison became deeply impressed with the belief that many staples were imported which could be produced to advantage in the United States, thereby rendering the citizens independent of foreign producers and aiding the industrial development of the youthful Republic. Following this thought, in 1793 he began in Philadelphia the manufacture of chemicals, notably Sulphuric Acid, of which he was the first maker in the United States.

In that year, he had a lead chamber capable of producing 300 carboys per annum. The competition of foreign makers was so overwhelming at first, that his enterprise was confined to manufacturing for his own use and filling orders on a small but very remunerative scale for a few of his patrons, his investment at the start not exceeding $5,000. In 1807 he built what was for that time quite a large lead chamber; it was 50 ft. long, 18 ft. wide and 18 ft. high and capable of making nearly half a million pounds of Sulphuric Acid annually, the price of the staple being then as high as 15c. per pound. According to a letter addressed by Mr. Harrison to President Jefferson, dated November 1, 1808, and now in the archives of the State Department at Washington, it is learned that he had then developed his Sulphuric Acid Plant to such an extent as to have a possible annual output of 3,500 carboys and he had also extended the line of products in his laboratory by adding the various preparations of mercury, antimony, copper, etc., used in the arts and medicines at an investment of some $40,000. This was at his establishment on Green Street, west of Third.

As is well known, acid produced in lead chambers is not the Oil of Vitriol of commerce and the only method known at that time to concentrate it to the required strength was by boiling it in glass retorts—a very precarious and dangerous process. The constant breakage of the glass largely increased the cost of the concentrated acid and the dangers of the work. To obviate this great trouble Mr. Harrison, in 1814, introduced the use of Plati-

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num for the manufacture of Sulphuric Acid, for the first time, at least in this country. In the previous year, 1813, Dr. Eric Bollman, a Dane, had come to Philadelphia. Dr. Bollman was familiar with the metallurgy of platinum and a highly scientific man. He brought with him from France Dr. Wollaston's method for converting the crude grains of platinum into bars and sheets. About the first use that Dr. Bollman made of these platinum sheets was the construction, early in 1814, of a still for the concentration of Sulphuric Acid for the Harrison Works. It weighed 700 oz., had a capacity of 25 gal., and was in continuous use for 15 years. This early application of platinum for such purposes was highly characteristic of the sagacity and ingenuity of the American manufacturer. At the time the use of this rare metal was a novelty in Europe and known only to a few persons and certainly entirely unknown in this country. It follows, therefore, that Mr. John Harrison was not only the earliest successful manufacturer of Sulphuric Acid in America, but the first in this country to concentrate it in platinum. Too great praise cannot be given him for, as Liebig has said, "The quantity of Sulphuric Acid made in a country is a sure index to its wealth and prosperity."

In 1806, Mr. Harrison began the manufacture of white lead and he and his successors have continuously marketed their product since that date. In fact, with one exception, the "Harrison" lead is the oldest established brand of white lead in the United States. In later years, he introduced into his works apparatus for making pyroligneous and acetic acids and their dependent products, white and brown sugar of lead, also oxides of lead, colors, alum, coppers, iron liquors, etc. Mr. Harrison may be credited with doing more to influence the establishment and development of the chemical industries than almost any man of his time.

The Green Street Works soon grew too small for such large operations as Mr. Harrison had undertaken and an eligible location was secured in Kensington, now the Eighteenth Ward of this city, where extensive buildings were erected and large manufacturing facilities provided. In 1831 he admitted his sons to partnership, under the title of John Harrison & Sons. He died in 1833 and in that year the firm name was changed to Harrison Brothers. In 1859, by the admission of the founder's grandsons, John Harrison, George L. Harrison and Thomas S. Harrison, the

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firm name became Harrison Bros. & Company and in 1898 was incorporated. In 1917 the Greys Ferry plant was taken over by the Du Pont Company and is now known as the Harrison Works.

Holker, in 1766, introduced the first lead chambers into France, and at his Rouen plant the two important ideas of introducing steam into the chambers during combustion, and continuous air feed, were mechanically developed. In Germany the first lead chambers were probably those at Ringkuhl, near Cassel. Dr. Richard's plant near Dresden (1820) was one of the oldest, and although it was erected some time after the idea of continuous air feed had been perfected, it represented the old intermittent type.

The last 150 years has seen little or no change in the fundamental idea of the English, or chamber process. True, the chambers have been increased tremendously in size, the generation of SO_2 has undergone marvelous mechanical development, and the utilization of valuable waste products has become of great importance; methods of handling the product have been rendered many times more efficient: but for the original idea we are indebted to the pseudo-scientists of the Alchemical period.

One of the promoters of the Contact Process once said, "The alchemists and the early English chemists could hardly have helped stumbling onto the discovery and manufacture of oil of vitriol by the Chamber Process, but it remained for a nation of real scientists to discover and develop the Contact Process." For nowhere in the field of industrial chemistry can the chemical engineer see so clearly the result of systematic, painstaking research, experiment, and accurate interpretation of observation.

Up to the close of the eighteenth century the little fuming acid demanded by the arts had been produced almost exclusively by the firm of Joseph Starck, in Bohemia, by the distillation of dry ferrous sulphate and the absorption of the evolved SO_3 in a high strength pan concentrated acid. From the place where it was stored it was called Nordhausen acid.

About 1875, Cl. Winkler, and later Squire and Wessel, showed that SO_3 is easily formed by the interaction of SO_2 and O_2, in the presence of a number of substances in a finely divided state, with certain other requirements as to temperature, humidity, and pressure. Although the oxides of iron and cobalt, and metallic gold, iridium, and silicon produce this result, none of them

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approach the efficiency of conversion obtained with small percentages of metallic platinum. The platinum itself is unacted upon and termed a catalyzer, after the suggestion of Berzilius, in 1835.

The commercialization of Winkler's idea has been rapid during the last forty years, owing to the increased demands of the dye makers and oil refiners, so that today the old distillation process is obsolete.

About 1875, the promoters of the process that later became known as the Hanish and Schroder, using Winkler's ideas, secretly tried out the catalysis of SO_3, using first pure SO_2 and oxygen, and later dilute SO_2 from pyrites, with platinized asbestos as the catalytic agent, and a heated entrance gas, under a pressure of three atmospheres.

But the great obstacles in the way of the development of the process were the failure to get a dry and arsenic free entrance gas, the false idea that SO_2 and oxygen must be present in stoichiometrical proportions, and that nitrogen was detrimental. These three difficulties alone must be considered the causes of the failures of the pioneers, and the financial losses through semi-commercial experiments were startling.

Through the disloyalty of a workman at the Badische works (Ludwigshaven) the important secrets of their process were obtained by their competitors, and simultaneously, 1898, patents were issued to three different companies: THE BADISCHE ANILIN UND SODAFABRIK OF LUDWIGSHAVEN; THE FARBEWERKE VORM MEISTER, LUCIUS & BRUNING, OF HOCHST; AND THE VEREIN CHEMISCHER FABRIKEN OF MANHEIM.

These three companies at once set about the commercial perfection of the process, as secretely as possible, the only important variation being in the catalytic agent. To trace the foreign development would indeed be interesting, but we are limited by title to American practice.

American manufacturers, due to their lack of appreciation of the results of organized research and experiment, refused to finance any work along these lines, and followed the usual course of importing the developed process and trained men for installations in this country. The Schroder process, employing platinized magnesium sulphate, and the Badische, with platinized asbestos, have been the most favored in America.

An eminent chemical engineer has called sulphuric acid the

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back bone of the chemical industry, for like soda, its uses are so diversified and its production so great, that in any country it is a true barometer of chemical and industrial progress. It finds its greatest use in fertilizer manufacture (80 per cent), and is indispensable in the manufacture of coal tar dye stuffs, petroleum products, paper, stearine, oleine, sodium sulphate, soda; hydrochloric, nitric, citric, and tartaric acids; sulphates of iron and copper; alums, shoe blackings, coke plant by-products, electrolytic refining of metals, mostly copper; it enters, directly or indirectly, into almost every chemical process. In some of the more important branches of the chemical industry it is a raw material costing millions. The amounts used in the manufacture of explosives, during the late War, were enormous. This huge war increase was of course only temporary, and there are many plants, paid for by the War, that should make very cheap acid.

While the Contact process has many advantages over the Chamber process, such as no bulky chambers of concentration pans, it is very doubtful if it will ever completely replace the chambers. It cannot make 50° and 60° Bé. acids to compete, and requires some method of producing weak acid to keep it going. But on the production of higher strength acids it is supreme, and statistics show that it is gaining in the United States today. The cost of platinum for concentrating pans is excessive and increasing, and that required for contact mass is negligible in comparison. Both processes are being improved steadily, and the patent rights are costing less each year, and in a few years will become public property. Supervision, regulation and yield are all better on the contact process, while depreciation and maintainance are less.

In April, 1920, the Department of Commerce had no figures for production since 1915. They show a 25 per cent increase in production during 1915 over the previous year, and one war time plant alone, completed in 1916, produced a quarter of a million tons of fuming acid a year, against 49,000 tons for the whole country in 1914.

A few figures on the world's production will give an idea of the rate of development:

1880	1,850,000 tons
1892	2,818,000 tons
1902	4,450,000 tons
1909	8,000,000 tons

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CHAPTER II

ELEMENTARY CHEMISTRY OF SULPHURIC ACID

When sulphur, either brimstone or a metallic sulphide, is burned in air, sulphur dioxide, SO_2, is produced. This is the starting point of the sulphuric acid industry.

SO_2 is a colorless gas of a suffocating odor, and will not burn nor support combustion directly, under ordinary conditions. It is very injurious to plants. It contains 50.05 per cent sulphur, and 49.95 per cent oxygen. Molecular weight, 64.04 per cent. Specific gravity, 2.2136. A liter of SO_2 at 0°C. and 760 mm. pressure weighs 2.8608 g. Its heat of formation is given (Richards) as 69,260 as a gas, or 77,600 in dilute solution.

Anhydrous sulphur dioxide will not act upon iron, up to 100°C., but the commercial product, containing up to the 1 per cent H_2O that it carries at saturation, does act slightly.

Owing to the catalytic action of the hot iron of the burners, some SO_3 is formed when brimstone is burned but not enough to influence the process. With pyrites, however, the SO_3 formed is considerable, as the catalytic action of the red hot iron oxides is very marked; in fact the oxides of iron, copper and chromium are the only catalytic (?) agents that have been seriously experimented with, outside of platinum. The generally accepted theory for the action of the metallic oxides is that they are more oxygen carriers than actual catalyzers: doing their work more as the nitrogen oxides do theirs, than as platinum does its work.

The yields, when ferric oxide is used, are not high enough to permit it to seriously compete with platinum as the catalytic agent used in this industry, in the present state of our knowledge.

The reactions are probably two, both taking place at very nearly the same temperature, viz.:

$$2Fe_2O_3 + 3O_2 + 6SO_2 = 2Fe_2(SO_4)_3$$

which splits up into

$$Fe_2O_3 + 3SO_3$$

the Fe_2O_3 being ready to repeat the cycle

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and

$$3Fe_2O_3 + SO_2 = 2Fe_3O_4 + SO_3$$

and

$$4Fe_3O_4 + O_2 = 6Fe_2O_3$$

when the Fe_2O_3 is again ready to repeat.

SO_2 is pretty soluble in water, one volume of water, at atmospheric pressure, and 32°F., dissolving about 80 volumes SO_2. However, this does not appear to be a chemical compound, H_2SO_3, sulphurous acid, because SO_2 evaporates from it even at ordinary temperatures.

Bunsen and Schonfeld published the following table, in 1905, of the solubility of SO_2 in water, at 760 mm. pressure:

TABLE 1

TEMPERATURE, °C	1 LITER H_2O DISSOLVES LITERS SO_2
0	79.8
5	57.5
10	56.6
15	47.3
20	39.4

Solutions of SO_2 slowly oxidize in the presence of air.

Sulphuric acid is a compound, in varying proportions, of sulphur trioxide and water. Several different compounds exist, showing all the properties of definite chemical compounds. The mono- and the duo-hydrates have been the most frequently studied. Acid of a concentration of 98.3 per cent or better seems to hold the 1.7 per cent or less of water present chemically, and this is the absolute limit to which a concentration by distillation can go. In practice, 98 per cent is rarely reached, however.

Sulphuric acid has a tremendous affinity for water, combining with it violently, with evolution of great heat. Of the entire molecular heat of formation, 192,200 calories, 100,300 calories, or 53.5 per cent, results from the combination of the anhydrous SO_3 with the water. A very common manifestation of this affinity is the charring of carbo-hydrates by sulphuric acid, the water in the combination being removed, leaving the carbon behind.

Another familiar result of this affinity is the dense white cloud that forms when SO_3 escapes into the air. Air at all times contains moisture-humidity and the SO_3 combining with this moisture forms H_2SO_4 in minute particles. These particles are

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small enough to remain suspended in the air for a long time, forming a white cloud, or "fume" not properly a fume at all, because it is not a gas, but a mass of small liquid particles.

As there is always some moisture in the air we always have an indicator as to whether SO_3 is going through our system and being lost out our stacks. While "fumes" come from other causes, if there is no "fume" there is no SO_3 escaping.

The moisture in the air has a very direct effect upon the contact process in keeping down the strength of the acid that can be made. The air introduced into the system carries with it its own share of humidity, which must be absorbed, and thus dilute the acid made. In the Middle Atlantic States this will average 60 lb. of water per ton of 100 per cent acid made, or 3 per cent: less in winter, and more in summer, for the saturation point of air increases rapidly with the temperature. Consequently, if it is desired to make very high concentration fuming the location must be in the driest climate possible.

There are three distinct steps in the evolution of sulphur into sulphuric acid, either naturally, or directed by man. They are the burning of the sulphur to SO_2, the oxidation of the dioxide to the trioxide, and the hydrating of this trioxide.

In the chamber process the last two steps proceed simultaneously, the water acting both as an assistant to the catalyser, various oxides of nitrogen, and as the hydrator. The oxidation will not proceed at a commercially practicable rate unless water is present in excess, consequently the acid produced is dilute, and to make strong acid must be concentrated.

We know what results may be attained by different methods of handling the process, but the intermediate changes that occur are the subjects of very heated controversy. There is no doubt that nitrososulphuric acid, $SO_2(OH)(ONO)$ is formed, which breaks up into H_2SO_4 and NO. The NO becomes oxidized to NO_2, N_2O_3, and N_2O_4, probably a mixture of all three, and HNO_3, deriving the oxygen from the excess of air present, and the H_2SO_4 immediately takes up an excess of water and condenses.

In a work of this character, written as an operating handbook, not as a treatise, it would not serve any useful purpose to go into the theories of Weber, Winkler, Raschig, and Lunge, regarding changes within the chambers.

The saving of the nitrogen oxides is of the uttermost importance, as without this saving the process would not be com-

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mercially practicable. The Gay-Lussac tower was the first nitrate saver, and now, in conjunction with the Glover tower, reduces the nitrate from 11 per cent to 4 per cent.

Strong sulphuric acid absorbs nitrous acid, forming nitrososulphuric acid as follows:

$$2H_2SO_4 + N_2O_3 = 2SO_2(OH)(ONO) + H_2O$$

it absorbs nitric peroxide, forming nitrososulphuric acid and nitric acid:

$$H_2SO_4 + N_2O_4 = SO_2(OH)(ONO) + HNO_3$$

Nitrososulphuric acid is decomposed by water alone, (1) or by water and SO_2, (2):

(1) $2SO_2(OH)(ONO) + H_2O = 2H_2SO_4 + N_2O_3$
(2) $2SO_2(OH)(ONO) + SO_2 + 2H_2O = 3H_2SO_4 + 2NO$

and the nitric oxides are ready to repeat.

The recovery of the nitrogen gases is accomplished by taking advantage of two of the reactions that proceed within the chamber—the absorbtion of N_2O_3 and N_2O_4, in the Gay-Lussac tower, by strong sulphuric acid, and the decomposition of the product, at a point where it is available, by burner gas, (SO_2), to H_2SO_4 and NO.

N_2O_3 and N_2O_4 are absorbed by strong sulphuric acid, forming nitrososulphuric acid, as shown in the reactions of the chamber. This prevents the escape of the nitrogen gases into the atmosphere, with the attendant loss of nitre and the damage done, but the nitrososulphuric acid is of little value, and must be made into a useful product.

The Glover tower accomplishes this. As shown in the chamber reactions, water and SO_2 decompose $SO_2(OH)(ONO)$—nitrososulphuric acid—to H_2SO_4 and NO, so by bringing the hot burner gases, rich in SO_2, in contact with the nitrososulphuric acid that reaction is brought about, and in addition the heat present effects a considerable concentration, the water from the concentrated acid going on with the burner gas and the NO back to the chambers, thus being used over and over again.

CONTACT PROCESS

In the contact process SO_2 is produced by the same means that are employed to make it for chambers. The last two steps are separate and distinct, however, and instead of an excess of water,

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giving a dilute acid, there is an excess of SO_3, producing fuming acid.

Burner gases must be cleaned of certain impurities, before touching the catalytic agent, which in this country is always finely divided platinum, on either asbestos or roasted magnesium sulphate.

The following is from a paper by Dr. Charles L. Reese, *Journal* of the Society of Chemical Industry, March 31, 1906:

"Water—it was thought at one time to be essential that the gases be dried by sulphuric acid not weaker than 60°Bé., but this was found to be an error, in that the gases could be saturated with moisture, by passing them through water before introduction into the contact mass, without affecting the conversion in any way. Fuming sulphuric acid was produced, but, of course, such a procedure could not be carried out on a manufacturing scale, where it is necessary to use iron pipes.

"Carbon dioxide had no effect whatever, whenever introduced into the gas, as was to be expected, but I was surprised to find that carbonic oxide had no deleterious effect, in spite of its reducing qualities. On one occasion the conversion in a certain plant ceased altogether, and we were at a loss to know the cause. We, however, soon found that some coal had got mixed with the pyrites in the burners. In this case there was carbon dioxide, and possibly carbonic oxide, present, but there was also evidently a lack of oxygen, and when the coal was consumed, conversion began again.

"Sulphur will at times find its way through two or three scrubbing towers, and, before the filtering system was adopted, it became necessary to determine whether the presence of sulphur in the gas would affect the catalytic action of the contact material. Experiments were carried out to determine this point. It was desirable to introduce sulphur into the gas in as finely divided condition as possible. This was accomplished by introducing hydrogen sulphide into the gas. When hydrogen sulphide is mixed with sulphur dioxide the reaction between these two gases takes place, producing sulphur and water, and thus sulphur was introduced into the mass. It was found, on discontinuing the introduction of hydrogen sulphide, the conversion continued to be normal, and the sulphur was simply carried through the tube. This experiment was repeated a number of times with the same result, showing that the presence of sulphur does not affect the reaction. Of course, hydrogen sulphide would affect it, in that it would reduce the sulphur dioxide.

"The above substances do not affect the reaction of the contact mass, but hydrochloric acid, chlorine, silicon tetra-fluoride, arsenic, and lead do seem to affect it in two distinct ways: first, by their presence in

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the gas, and only when present in the gas; and second, affecting the catalytic property of the contact material. In the first case we have hydrochloric acid, chlorine, and silicon tetra-fluoride. In the second we have arsenic and lead.

"When **Hydrochloric Acid** gas is introduced, the effect is instantaneous, reducing the conversion from 98.5 per cent to 42 per cent, but when the hydrochloric acid gas is discontinued and air passed through for a while to displace it, the conversion becomes normal in a short time.

"The presence of **Chlorine** in the gas seems to have an effect similar to that of hydrochloric acid, although not so intense. In both cases the dry chlorine or the hydrochloric acid was introduced, until a minimum yield was obtained, which in the case of HCl was about 42 per cent, and that of the Cl was 57 per cent. After discontinuing the HCl and the Cl, air was passed through and the operation was continued at the same temperature. As will be seen by the curve the percentage conversion gradually arose again to the normal. Although at one point the gas showed a trace of HCl, the conversion amounted to 94 per cent.

"The introduction of a small quantity of silicon tetra-fluoride caused the conversion to drop immediately, but on discontinuing, the conversion rose in a few minutes to normal. In each case some silica was undoubtedly deposited upon the contact mass, but most of it passed through the tube, as was made evident by the fact that the silica separated out when the gas came in contact with the water solution used in testing the exit gas. Of course a minute quantity of silicon tetrafluoride in the gas would gradually deposit silica on the contact mass, and would eventually cover the contact agent, so as to render it inactive; but when contact mass is so affected it can be easily rendered active by simply removing it from the converter and putting it back again. The handling will be sufficient to expose surfaces.

"The injurious effect of arsenic upon the contact mass is extremely marked. Arsenious acid was placed in the front end of the tube, heated, and carried into the contact tube by the flow of gas. The effect of the arsenic was to reduce the conversion absolutely to zero, owing to the large amount introduced, but after 40 min. it rose again to 40 per cent. At this time HCl was introduced for 50 min. to remove the arsenic, and then air drawn through for 15 min. more. The process was then continued, and the conversion then rose to 96.5 per cent. Several attempts were made to find a simple means of removing As from the contact mass, and at first Cl was used for this purpose. The mass was placed in a tube, heated, and Cl passed through. This did remove some of the As, but did not regenerate the mass sufficiently. A very interesting observation was made, however, during this experiment. It was found the Cl carried over platinum to the exit end of the tube, and deposited it in the form of a chloride. This was done at a temperature of 400°–450°C.

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"It was found in attempting to regenerate or remove arsenic, that HCl mixed with the reduced sulphurous gas was much more effective, as is shown by the curve referred to, *all* arsenic having been removed.

"It is well known that when platinum is heated in the presence of lead or lead salts, lead combines with the platinum either to form an alloy or a compound, and this combination of lead with platinum undoubtedly destroys the catalytic property of the platinum. The effect of lead, however, was not determined in the regular way, but can be shown very readily by one or two experiments.

"It is well known that when a platinum spiral is heated in a gas flame, the gas turned off for a few minutes, and on again, the spiral will reignite the gas. A small piece of contact mass will do the same, but if either is moistened with a small quantity of lead acetate and then ignited, it will lose this property of reigniting gas, unless it is heated sufficiently long to volatilize the lead. A similar experiment will show in a rough way the effect of arsenic on contact mass or a platinum spiral."

The above quotation shows very clearly the necessity for very careful scrubbing. The loss of sulphur, and consequently of acid, from unconverted SO_2 that passes on out the stacks is anywhere from 60 per cent to 80 per cent of the entire loss, and anything that throws the mass off at all will enormously increase that loss. The operation costs the same, with the exception of the small item of handling the finished acid, with a low as with a high conversion and the yield, and consequently the income, is cut down in the proportion that the conversion falls off.

Arsenic is by all odds the worst of the contact "poisons" with which we have to deal.

Opl's theory is that the destruction of the activity of the contact mass is caused by the deposition of a glass-like coating over the platinum, thus mechanically preventing its contact with the gas. This coating is, he says, a deposition product of As_2O_3 and SO_3, with a formula $3As_2O_3, 2SO_3$. Lunge says this product has actually been found in dust chambers.

Dr. Krauss holds that the arsenic is oxidized to a non-volatile oxide, which combines with platinum.

In a plant on the Pacific coast, operating on the Schroeder-Grillo process, using pyrites, it is necessary to regenerate the mass about every four weeks, and an astonishing fact has been noted—that while the platinum recovers its activity, the arsenic remains in the mass. It appears to exist after the regeneration in the form of Realgar, arsenic disulphide, As_2S_2, and in that

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form is apparently not a contact poison. I have been informed that after 3 years the quantity of arsenic in the mass is actually greater than the amount of platinum, but the old arsenic seems to be perfectly inert, having no effect, good or bad, and it is not until fresh arsenic compounds are introduced that the mass again loses its activity.

Of course there is a loss of the efficiency of the mass in regenerating, because the platinum becomes distributed through the grains of magnesium sulphate, instead of all being on the outside, thus reducing the area that can come in contact with the gas.

The absorbtion system requires conditions proper for the combination of SO_3 and H_2O. The principal interferences with these conditions are vapor pressures, as follows:

(*a*) Vapor pressure due to H_2O,
(*b*) Vapor pressure due to SO_3, and
(*c*) Vapor pressure due to foreign acids, as HNO_3 or HCl.

Heat increases vapor pressures, so temperature control is necessary.

The vapor pressure due to H_2O exists when the strength of the absorbing acid drops below 98.3 per cent H_2SO_4. Above that figure the H_2O seems to be chemically combined with the H_2SO_4 and no water vapor exists. SO_3 coming in contact with water vapor forms very small drops of sulphuric acid, almost impossible to condense, and any SO_3 used in this way may be considered as lost beyond any reasonable hope of recovery, as even a very long condensation and absorbtion apparatus will catch very little of it.

The second vapor, that of SO_3, is only met with in making fuming acid. A glance at the absorbtion curve will show how rapidly the absorbtion drops, as the strength of the absorbing acid increases. But SO_3 passing through fuming acid unabsorbed is in no way changed, and is caught perfectly by the close to 100 per cent acid in the back of the system.

The vapor pressure of foreign acids comes of course from impure materials. Sometimes it is necessary to clean out the system after foreign acids have gotten in; but frequently any trouble of this character can be cured by letting the system get as hot as possible and simply "boiling out" the foreign substance. It is necessary to watch weak acid from chamber plants closely, to prevent nitric acid getting in.

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As fuming acid has high melting points, the exact varying with the strength, the temperature must be kept up sufficiently high to prevent freezing. In shipping fuming acid it is general practice to add a little nitric, if the intended use will not be interfered with by nitric acid. Five per cent of nitric acid will drop the freezing point of fuming acid to −10.5°F.

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CHAPTER III

CHARACTERISTICS AND USES

Sulphuric acid is a viscous, colorless (when pure) liquid, composed, by weight, of 2.04 per cent hydrogen, 32.64 per cent sulphur, and 65.28 per cent oxygen. It is very strongly acid.

Its most outstanding characteristic is its affinity for water, either free or combined, and violent combination, with evolution of much heat, with it.

The sulphuric acid industry is a business barometer, as the acid enters into most other industries, and general trade conditions are very soon reflected in both sales and prices.

Sulphuric acid forms sulphates with all the metals, replacing any other acid radical, and freeing the other acid. Its affinity for water makes it the most important desiccating agent known. It readily forms bisulphates (acid sulphates) and double sulphates. Most of its combinations are characterized by extreme stability. Below 65 per cent H_2SO_4 it attacks iron vigorously; above that, very little. Below 92 per cent H_2SO_4 its action upon lead is slight—it increases fast with strength. Hot acid acts more vigorously than cold. The water in sulphuric acid of 98.3 per cent concentration seems to be, not a diluent, but an actual part of the acid, exerting none of the characteristics of water in the less high concentrations.

Upon these main characteristics depends the important place of sulphuric acid in modern life. A list of the industries using it would be a catalogue of the industry of the world.

The LeBlanc process for soda ash, dating from the end of the eighteenth century, took the manufacture of sulphuric acid out of the drug business, and made it a major industry.

Common salt, treated with sulphuric acid, gives off hydrochloric acid, with the formation of sodium sulphate, after the formula

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$$

The sodium sulphate, roasted with coal and slaked lime, gives soda ash (sodium carbonate), oxide and sulphide of calcium, and carbon dioxide.

There are other methods of making sodium carbonate from the sulphate, with by-products of sulphur and hyposulphites, but the LeBlanc process is still a tremendous producer.

Nitric acid is made from its natural sodium salt, Chile saltpeter,

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by treatment with sulphuric acid, the result being nitric acid and sodium sulphate, or salt cake. By the use of twice the theoretical amount of sulphuric acid a bisulphite is formed, which is fusible, and easily removed from the stills. This bi-, or acid, sulphate, has many of the characteristics of the acid itself, and is frequently used for pickling iron castings, its 31 per cent of free H_2SO_4 being sufficient to accomplish this purpose.

Petroleum refining consumes large quantities of sulphuric acid.

Without sulphuric acid and its product, nitric acid, the coal tar dye industry could not exist.

The fertilizer industry depends upon sulphuric acid for its sulphate of lime, or land plaster; and even more, as a means of converting cheap phosphate rock into a soluble form, from which phosphoric acid is made.

The medical profession uses it in many ways. The quinine we are brought up on is the sulphate of that alkaloid. The manufacture of "sulphuric" ether from ethel alcohol uses sulphuric acid as a catalytic agent.

In all nitrating processes, whether for celluloid, nitro-cellulose, either for ammunition or some form of soluble cotton, the action of sulphuric is a desiccating one, removing, and holding fast to the OH radical released, preventing its doing any harm.

Fuming Sulphuric Acid is a solution of SO_3 in H_2SO_4—it is largely used in the manufacture of coal tar dye stuffs. Its most important use is the "butting up" the 96 per cent to 97.5 per cent acid of the best concentrators to the 100 per cent that is needed in many industries.

The popularity of the sulphate method of pulping wood is growing, and with it the use of H_2SO_4. It is not necessary to pick the wood so carefully, as in the sulphite or caustic methods, as resinous parts, such as knots or sappy wood, are pulped by it to an extent impossible by any other method.

An extensive use for sulphuric acid is (**was**) in the preparation of the mash for distilling.

The large number of alums, used especially in the textile industry, are double sulphates. Originally sulphate of alumina was invariably one of the sulphates, chromium, iron, sodium, potassium and ammonium being the usual others, and from the aluminum it took its name—but today other pairs of sulphates go under the name of alum. Sulphate of alumina, free from iron, is used as a mordant and dyeing agent, to escape the injurious iron that alum frequently carries.

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Both alum and sulphate of alumina have wide application for clarifying drinking water, and in coagulating and settling sewage.

Sulphate of zinc is used as a drier for paints, a disinfectant, and a mordant in dyeing.

Much of the electroplating industry, including the electrolytic refining of copper and other metals, uses the suphate of the metal as the electrolyte.

Copper sulphate, or blue vitriol, and iron sulphate, or green vitriol, have large application in the dyeing industry, also in recovering silver by the amalgamation process. Green vitriol, perhaps better known as copperas, is very largely used in ink manufacturing.

The leaching of low grade copper ores with weak solutions of sulphuric acid has become a great industry within the last few years.

"Shoddy" wool is freed from cotton by "carbonizing" the goods with sulphuric acid, which consists in letting a solution of acid dry on, when the cotton or other vegetable fibre gives up its OH radical, only the carbon remaining, and that in the form of a powder, which is easily shaken off.

The foregoing is only a brief list of some of the most important uses to which sulphuric acid may be put, and is not intended to do more than show how dependent modern civilization is upon this industry.

The Bureau of Mines *Bulletin* No. 184 reports for the period June to August, 1918, the following distribution of sulphuric acid among the industries:

TABLE 2

Industry	Tons acid used per month. On basis of 100 per cent H_2SO_4	Tons per year. 50°Bé. basis	Per cent of total acid used
1. Explosives (military and domestic)	140,000	2,700,000	36.0
2. Fertilizers	111,000	2,130,000	28.0
3. Oil refineries	35,000	671,000	8.8
4. Chemicals, drugs, and ammonium sulphate	38,500	740,000	9.9
5. Steel pickling and galvanizing	36,500	700,000	9.3
6. Fabrics, textiles, etc	5,200	100,000	1.3
7. Paints, lithophone, glue, etc	5,300	104,000	1.4
8. Metallurgical, including storage batteries	15,200	292,000	3.9
9. Miscellaneous	3,800	73,000	1.0
Total	390,500	7,510,000	100.0

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TABLE 2.—SULPHURIC ACID MAKERS IN THE UNITED STATES

List of plants

Name	Address	Shipping facilities	Plant	Raw material used	Source of raw material	Acid made	By-products (if any)
Naugatuck Chemical Co., (U. S. Rubber Co. System).	Naugatuck, Conn.	N. Y., N. H., & H. R. R.	Chamber	Brimstone	Purchased	50°, 60°, & 66° high grade	Nitre cake
Franklin Kalbfleisch Corp.	Waterbury, Conn.	Rail	Chamber	Brimstone	Purchased	50°–66° Bé.	None
Lowell Fertilizer Co.	Boston, Mass.		Chamber				
Merrimack Chemical Co.	148 State St., Boston, Mass.	Rail & water	Chamber & contact	Brimstone & pyrites	Purchased	All	Pyrites cinder
Buttorworth Judson Corp.	Newark Transfer, N. J.	Rail & water	Chamber & contact	Sulphur & pyrites	Purchased	60° & 66°Bé., 98% & 20% oleum	Dyes & intermediate
American Agricultural Chemical Co.	No. Weymouth, Mass.	Rail	Chamber	Brimstone & pyrites	Purchased	50°B.é	None
Avery Chemical Co.	88 Broad St., Boston, (plant) Lowell, Mass.	All rail	Chamber	Brimstone	Purchased	60° & 66°	None
Merrimack Chemical Co.	Woburn, Mass.	Rail	Chamber & contact	Brimstone & pyrites	Purchased	All	Pyrites cinder
General Chemical Co.	Claymont, Del.		Contact				
American Agricultural Chemical Co.	Baltimore, Md.	Rail	Chamber	Brimstone & pyrites	Purchased	50°Bé.	None
Baugh Chemical Co.	25 S. Calvert St., Baltimore, Md.	Rail & water	Chamber	Brimstone & pyrites	Purchased	56°Bé.	None
Standard Acid Works	Baltimore, Md.		Chamber				
F. S. Royster Guano Co.	Baltimore, Md.		Chamber				
Virginia-Carolina Chemical Co.	Baltimore, Md.		Chamber				
Griffith & Boyd Co.	Baltimore, Md.	Rail & water	Chamber	Brimstone	Purchased	52°Bé.	None
Davison Chemical Co.	Curtis Bay, Baltimore, Md.	Rail & water	Chamber	Pyrites & Brimstone	Own mines & Purchased	52°Bé to 66°.	Pyrites cinder Magnesium fluor-silicate.
Naval Proving Grounds	Indianhead, Md.		Contact				
Lancaster Chemical Co.	Perryville, Md.		Chamber.				
General Chemical Co.	Bayonne, N. J.		Contact				
Standard Oil Co*	Bayonne, N. J.		Chamber	Brimstone	Purchased	50°, 60°, & 66°Bé.	None

* All acid used at the plant—none sold.

TABLE 2 (*continued*).—SULPHURIC ACID MAKERS IN THE UNITED STATES

List of acid makers

Name	Address	Shipping facilities	Plant	Raw material used	Source of raw material	Acid made	By-products (if any)
Calco Chemical Co.	Boundbrook, N. J.		Contact				
King Chemical Co.	Boundbrook, N. J.	Rail	Chamber	Brimstone	Purchased	60°Bé.	None
General Chemical Co.	Camden, N. J.		Contact				
American Agricultural Chemical Co.	Carteret, N. J.	Rail	Chamber	Brimstone & pyrites	Purchased	50°Bé.	None
American Agricultural Chemical Co.	Chrome, N. J.	Rail	Chamber	Brimstone & pyrites	Purchased	50°Bé.	None
Armour Fertiliser Works	Chrome, N. J.		Chamber				
Franklin Kalbfleisch Corp.	Elisabeth, N. J.		Chamber	Brimstone	Purchased	50°–66°Bé.	None
American Agricultural Chemical Co.	Elisabethport, N. J.	Rail	Chamber	Brimstone & pyrites	Purchased	50°Bé.	None
General Chemical Co.	Edgewater, N. J.		Chamber				
E. I. duPont deNemours & Co.	Deepwater Point, N. J.		Chamber & contact	Brimstone	Purchased	Fuming	None
E. I. duPont deNemours & Co.	Gibbstown, N. J.		Chamber & contact	Brimstone	Purchased	Fuming	None
Grasselli Chemical Co.	Grasselli, N. J.	Rail & water	Chamber & contact		Both purchased & owned		All strengths
Mutual Chemical Co. (Plant, Jersey City, N. J.).	110 William St., N. Y.	Rail	Chamber	Brimstone	Purchased	60°Bé.	None
Hercules Powder Co.	Kenville, N. J.		Contact				
American Smelting & Refining Co.	Maurer, N. J.		Chamber				
Butterworth-Judson, Corp.	Medford, Mass.	Rail	Chamber		Purchased	60°–66°Bé.	Dyes
Harrison Bros. (Inc.)	Newark, N. J.		Contact				
Harrison Bros. (Inc.)	Paulsboro, N. J.		Contact				
E. I. duPont de Nemours & Co.	Pennsgrove, N. J.	Rail	Contact		Purchased	Fuming	None
American Cyrnamid Co. (Plant, Warners, N. J.).	511 Fifth Ave., New York	Rail & water	Chamber	Brimstone	Purchased	50° & 60°Bé.	None
Atlas Powder Co.	Hopatcong, N. J.		Contact				
Franklin Kalbfleisch Corp.	Brooklyn, N. Y.	Rail	Chamber	Brimstone	Purchased	50°–66°Bé.	None
Robinson Bros.	Montrose & Seneca Ave., Brooklyn, N.Y.	Trucking	Chamber	Brimstone	Purchased	All	None
General Chemical Co.	Laurel Hill, Long Island, N. Y.		Contact				
American Agricultural Chemical Co.	Buffalo, N.Y.	Railroad	Chamber	Brimstone & pyrites	Purchased	50°Bé.	None

Contact Process Co.	Buffalo, N. Y	Railroad	Chamber & contact	Pyrites	Purchased	50°, 60°, 66°, & 20% oleum	None
General Chemical Co.	Buffalo, N. Y.		Contact				
Titanium Alloy Manufacturing Co.	Niagara Falls, N. Y.		Contact	No acid for sale. Use entire output			
Eastman Kodak Co.	Rochester, N. Y.		Contact	No acid for sale. Use entire output.			
Pennsylvania Trojan Powder Co.,	Allentown, Penna.	Rail from Seiple, Pennsylvania.	Chamber	Brimstone	Purchased	All	None
Chas. Lennig & Co.	Bridesburg, Pa.		Chamber				
Harrison Bros. Part of E. I. du-Pont deNemours & Co.	Philadelphia, Pa.		Chamber & contact				
I. P. Thomas & Sons	Philadelphia, Pa.		Chamber				
Pennsylvania Salt Manufacturing Co.	Philadelphia, Pa.		Chamber				
Powers-Weighton-Rosengarten Co.	Philadelphia, Pa.	Rail	Chamber	Brimstone	Purchased	52°, 60°, & 66°Bé.	None
United Gas Improvement Co.	Broad & Arch Sts. Philadelphia, Pa.	Rail & water	Chamber	Brimstone	Purchased	60° & 66°	Usual
(Plant, Delaware River)		Own cars					
New Jersey Zinc Co.	(office) 160 Front St., New York City, N.Y.	Tank cars Own cars	Contact	Zinc ores	Owned & Purchased	From 60°Bé. to 20% oleum	
(Plant, Palmerton, Pa.)							
Atlas Powder Co.	Tamaqua, Pa.		Contact				
York Chemical Works	York, Pa.	Rail	Chamber	Brimstone	Purchased	50°–60°	None
American Agricultural Chemical Co.	Alexandria, Va.	Rail	Chamber	Brimstone & pyrites	Purchased	50°Bé.	None
E. I. duPont deNemours & Co.	Hopewell, Va.	Rail	Contact	Brimstone	Purchased	Oleum	None
Virginia-Carolina Chem. Co.	Lynchburg, Va.		Chamber				
Robertson Fertilizer Co., Inc.	124 Atlantic St., Norfolk, Va.	Rail	Chamber	Brimstone	Purchased	60°Bé.	None
F. S. Royster Guano Co.	Norfolk, Va.		Chamber				
General Chemical Co.	Pulaski, Va.		Contact				
Virginia-Carolina Chemical Co.	Pinners Point, Va.		Chamber				
Virginia-Carolina Chemical Co.	Richmond, Va.		Chamber				
Richmond Guano Co.	1106 E. Main St., Richmond, Va.	Rail & water	Chamber	Brimstone & pyrites	Purchased	50°–60°	
Grasselli Chemical Co.	Canton, Ohio	Rail & truck	Chamber		Purchased & owned		
Grasselli Chemical Co.	Cleveland, Ohio		Chamber				
General Chemical Co.	Cleveland, Ohio		Contact				
American Agricultural Chemical Co.	Cleveland, Ohio	Rail	Chamber	Brimstone & pyrites	Purchased	50°Bé.	None
American Agricultural Chemical Co.	Cincinnati, Ohio	Rail	Chamber	Brimstone & pyrites	Purchased	50°Bé.	None

TABLE 2 (*continued*).—SULPHURIC ACID MAKERS IN THE UNITED STATES

List of acid makers

Name	Address	Shipping facilities	Plant	Raw material used	Source of raw material	Acid made	By-products (if any)
Jarecki Chemical Co.	Cincinnati, Ohio		Chamber				
Virginia-Carolina Chemical Co.	Cincinnati, Ohio		Chamber				
Farmers' Fertilizer Co.	Columbus, Ohio		Chamber				
Smith Agricultural Chem. Co.	Leynord & Hayes Aves., Columbus, Ohio.	Rail	Chamber	Brimstone	Purchased	Up to 60°Bé.	Nitre-cake
Grasselli Chemical Co.	Lockland, Ohio	Rail & truck	Chamber		Purchased & owned		
Grasselli Chemical Co.	Niles, Ohio	Rail & truck	Chamber				
New Jersey Zinc Co.	Tiltonville, Ohio, (office, 160 Front St., New York)	Rail Own cars	Contact	Zinc bearing ores	Owned & purchased	From 60°Bé. to 20% free SO_3.	
St. Bernard Acid Works	St. Bernard, Ohio	Out of business					
Virginia-Carolina Chemical Co.	Sandusky, Ohio		Chamber				
American Alkali & Acid Co.	Bradford, Pa.		Chamber				
Grasselli Chemical Co.	Beaver Falls, Pa.	Rail	Chamber		Owned & purchased		
American Steel & Wire Co.		Rail	Chamber	Zinc ores	Purchased	60° & 66°Bé.	Nitre-cake
Donora Zinc Works	Donora, Pa.			Brimstone			
F. H. Kalbfkeisch Corp.	Erie, Pa.	Rail	Chamber	Brimstone	Purchased	50°–66°	None
American Zinc & Chemical Co.	Langeloth, Pa.	Rail	Chamber	Zinc ores Brimstone	Owned & purchased	66°Bé	None
Pennsylvania Salt Manufacturing Co.	Natrona, Pa.		Chamber & contact				
Grasselli Chemical Co.	Newcastle, Pa.	Rail & truck	Chamber		Owned & purchased	52°–66°Bé.	
General Chemical Co.	Newell, Pa.		Contact				
American Sheet Tin & Plate Co.	Vandergrift, Pa.		Chamber				
Riverside Acid Works	Warren, Pa.	Rail	Chamber	Brimstone & pyrites	Purchased	60° & 66°Bé.	None
Fairmount Chemical Co.	Fairmount, W. V.	Rail	Chamber Multiple tangent system	Brimstone	Purchased	60°Bé, 25 tons per day	None
United Zinc Smelting Corp.	Moundsville, W. Va.	Rail	Chamber	Brimstone & zinc ores	Purchased	60°Bé. 100 tons per day	None

International Aluminum Co......	Nitro, W. Va.	Rail	Contact	Brimstone	Purchased	104% oleum, 400 tons per day, 55°, 60°, 60° & 98%	
Nitro Products Co..............	Nitro, W. Va.	Rail	Contact	Brimstone	Purchased	104% oleum, 160 tons a day, 55°, 60°, 66° & 98%	
Hegeler Zinc Co.................	Danville, Ill.	Rail	Chamber	Zinc ores		60°Bé.	None
Mineral Point Zinc Co..........	Depue, Ill.	Rail	Contact	Zinc ores	Purchased	60° to 20% free SO_3	None
Victor Chemical Works	Chicago Heights (Office, Fisher Bldg., Chicago, Ill.	Rail	Chamber	Brimstone	Purchased	60°Bé.	Nitre-cake
Monsanto Chemical Co..........	East St. Louis, Ill.	Rail	Chamber & contact	Brimstone	Purchased	60°–66° & 98%	Nitre & salt cake
American Zinc, Lead & Smelting Co.	East St. Louis, Ill. (Office, 1009 Pierce Bldg., St. Louis, Mo.)	Rail	Chamber	Brimstone & zinc ores	Purchased	60°Bé.	None
American Zinc, Lead & Smelting Co.	Hillsboro, Ill. (Office, 1009 Pierce Bldg., St. Louis, Mo.)	Rail	Chamber	Brimstone & zinc ores	Purchased	60°Bé.	None
Eagle Picher Lead Co...........	Hillsboro, Ill.	Rail	Chamber	Brimstone & zinc ores	Owned & purchased	60°Bé.	Nitre-cake
Matthiessen & Hegeler Zinc Co...	LaSalle, Ill.	Rail	Chamber	Zinc ores		60°Bé.	None
Illinois Zinc Co................	Peru, Ill.		Chamber				
General Chemical Co............	South Chicago, Ill.		Contact				
Central Chemical Co...........	West Hammond, Ill.		Chamber				
Grasselli Chemical Co..........	Grasselli, Indiana	Rail & truck	Chamber & contact		Owned & purchased	52°Bé. to 20% oleum	
Smith Agricultural Chemical Co..	Indianapolis. Ind.	Rail	Chamber	Brimstone	Purchased	Up to 60°Bé.	Nitre-cake
E. Rauth & Sons, Fertilizer Co....	Indianapolis, Ind.		Chamber				
Detroit Chemical Co	Detroit, Mich.		Chamber				
Cleveland Cliffs Iron Co	Marquette, Mich.		Chamber				
Atlas Powder Co................	Atlas, Mo.		Contact				
Mineral Point Zinc Co..........	Mineral Point, Wis.	Rail own cars	Contact	Zinc ores	Owned & purchased	From 60°Bé. to 20% free SO_3	None
E. I. duPont deNemours & Co....	Barksdale, Wis.		Contact				
Vinegar Hill Mining Co., (National Zinc Separat. Co)........	Platteville, Wis.	Rail from Cuba City, Wis.	Contact	Zinc-iron sulphide ores	Purchased	52° Bé. to 104½% oleum	
Wisconsin Zinc Co..............	New Diggings, Wis.		Contact				
Jefferson Fertilizer Co...........	Bessemer, Ala.		Chamber				
Grasselli Chemical Co...........	Birmingham, Ala.	Rail & truck	Chamber		Owned & purchased	52°–66°Bé.	
Virginia-Carolina Chemical Co...	Birmingham, Ala.		Chamber				

TABLE 2 (*continued*).—SULPHURIC ACID MAKERS IN THE UNITED STATES

List of acid makers

Name	Address	Shipping facilities	Plant	Raw material used	Source of raw material	Acid made	By-products (if any)
Virginia-Carolina Chemical Co.	Dothan, Ala.		Chamber				
Home Guano Co.	Dothan, Ala.	Rail	Chamber	Pyrites	Purchased	50° & 60°Bé.	Cind. Metallic Iron
Virginia-Carolina Chemical Co.	Mobile, Ala.		Chamber				
Alabama Chemical Co.	Montgomery, Ala.		Chamber				
American Agricultural Chemical Co.	Montgomery, Ala.	Rail	Chamber	Brimstone & pyrites	Purchased	50°Bé.	None
Virginia-Carolina Chemical Co.	Opelika, Ala.		Chamber				
Roanoke Guano Co.	Roanoke, Ala.	Rail	Chamber	Pyrites	Purchased	52°–60°Bé.	None
Virginia-Carolina Chemical Co.	Selma, Ala.		Chamber				
Planters Chemical & Oil Co.	Talladega, Ala.		Chamber				
Standard Chemical & Oil Co.	Troy, Ala.		Chamber	Brimstone capacity, 75 tons per day	Purchased	50°Bé.	None
Southern Sulphur Oil Co.	Albany, Ga.		Chamber				
Empire State Chemical Co.	Athens, Ga.	Rail	Chamber	Brimstone	Purchased	52°Bé.	None
Armour Fertilizer Co.	Atlanta, Ga.		Chamber				
Morris Fertilizer Co.	801 Citizens and Southern Bank Bldg., Atlanta, Ga.	Rail, own cars	Chamber	Pyrites	Purchased	50°, 60°, & 66°Bé., 50 tons of 50° per day	None
Swift Fertilizer Co.	Atlanta, Ga.		Chamber	Brimstone	Purchased	52°Bé.	None
Virginia-Carolina Chemical Co.	Atlanta, Ga.		Chamber				
Virginia-Carolina Chemical Co.	Augusta, Ga.		Chamber				
Southern States Phosphate & Fertilizer Co.	Augusta, Ga.		Chamber				
Blackshear Manufacturing Co.	Blackshear, Ga.		Chamber				
Mandeville Mills	Carrolton, Ga.		Chamber	Pyrites (Acid is	Purchased used in making	50°–60°Bé. acid phosphate)	None
Home Mixture Guano Co.	Columbus, Ga.		Chamber				
Southern Sulphur Ore Co.	Columbus, Ga.		Chamber				
Virginia-Carolina Chemical Co.	Columbus, Ga.		Chamber				
Furman Farm Improvement Co.	East Point, Ga.		Chamber	Plant being	dismantled		
Troup Co.	Lagrange, Ga.		Chamber				
Cotton States Feed & Fertilizer Co.	Macon, Ga.	Rail, 270 tons per week	Chamber	Brimstone & pyrites	Purchased	60°Bé.	None
F. S. Royster Guano Co.	Macon, Ga.		Chamber				
McCabe Chemical Co.	Macon, Ga.		Chamber				
Virginia-Carolina Chemical Co.	Macon, Ga.		Chamber				
Virginia-Carolina Chemical Co.	Rome, Ga.		Chamber				

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Pelham Phosphate Co.	Pelham, Ga.	Rail	Chamber	Brimstone & pyrites	Purchased	50°–60°Bé.	None
American Agricultural Chemical Co.	Savannah, Ga.	Rail	Chamber	Brimstone & pyrites	Purchased	50°Bé.	None
Mutual Fertilizer Co.	Savannah, Ga.	Rail	Chamber	Brimstone & pyrites	Purchased	52°Bé.	Nitre cake & cinder
The Phosphate Mining Co.	124 Bay St., East, Savannah, Ga.	Rail	Chamber	Brimstone & pyrites	Purchased	50° & 60°Bé.	None
The Reliance Fertilizer Co.	Savannah, Ga.	Rail	Chamber	Pyrites	Spain	60°Bé.	None
Savannah Guano Co.	Savannah, Ga.		Chamber				
Southern Fertilizer & Chemical Co.	Savannah, Ga.		Chambers				
Virginia-Carolina Chemical Co.	Savannah, Ga.		Chambers				
Georgia Fertilizer & Oil Co.	Valdosta, Ga.		Chambers				
Barker Chemical Co.	Office, Savannah, Ga.	Rail	Chambers	Brimstone	Purchased		None
Plant	Ingles, Florida						
Armour Fertilizer Works	Jacksonville, Fla.		Chambers				
Wilson & Toomer Fertilizer Co.	Jacksonville, Fla.		Chambers				
American Agricultural Chemical Co.	Pensecola, Fla.	Rail	Chambers	Brimstone & pyrites	Purchased	50°Bé.	None
E. O. Painter Fertilizer Co.	Jacksonville, Fla.	Rail & water	Chambers	Brimstone	Purchased	50°Bé.	None
American Cotton Oil Co.	P. O. Box 900, New Orleans, La.	Rail & water	Chambers	Brimstone	Purchased	50°–60°Bé.	None
Planters' Fertilizer & Chemical Co.	508 Hibernia Bank Bldg., New Orleans, La.	Rail	Chambers	Brimstone (Known in the	Purchased trade as "the	50°–60°Bé. Armour Fert.	None Works)
Swift & Co.	Harvey, La.		Chambers	Brimstone	Purchased	52°Bé.	None
Virginia-Carolina Chemical Co.	Shreveport, La.		Chambers				
Gulfport Fertilizer Co.	Gulfport, Miss.	Rail	Chambers	Brimstone	Purchased	60°Bé.	None
Meridan Fertilizer Factory	Meridan, Miss.		Chambers	Brimstone	Purchased	50°–60°Bé. 300 tons per month	None
Meridan Fertilizer Factory	Hattiesburg, Miss		Chambers	Brimstone	Purchased	50°–60°Bé. 300 tons per month	None
Jackson Fertilizer Co.	Jackson, Miss.		Chambers				
Tupelo Fertilizer Factory	Tupelo, Miss.	Rail	Chambers	Brimstone	Purchased	52°–60°Bé.	None
Acme Manufacturing Co.	Acme, N. C.		Chambers	Brimstone	Purchased	52°–60°Bé.	None
McCabe Chemical Co.	Charlotte, N. C.		Chambers				
Virginia-Carolina Chemical Co.	Charlotte, N. C.		Chambers				
Virginia-Carolina Chemical Co.	Durham, N. C.		Chambers				
Virginia-Carolina Chemical Co.	Selam, N. C.		Chambers				
Virginia-Carolina Chemical Co.	Wadesboro, N. C.		Chambers				
Virginia-Carolina Chemical Co.	(Almont Works), Wilmington, N. C.		Chambers				
Virginia-Carolina Chemical Co.	(Navassa Works), Wilmington, N. C.		Chambers				
Virginia-Carolina Chemical Co.	Winston-Salem, N. C.		Chamber				
Caraleigh Phosphate & Fertilizer Works.	Raleigh, N. C.	Rail	Chamber	Brimstone	Purchased	60°Bé.	None

TABLE 2 (*continued*).—SULPHURIC ACID MAKERS IN THE UNITED STATES
List of acid makers

Name	Address	Shipping facilities	Plant	Raw material used	Source of raw material	Acid made	By-products (if any)
American Agricultural Chemical Co.	Wilmington, N. C.	Rail	Chamber	Brimstone & pyrites	Purchased	50°Bé.	None
Swift & Co., Fertilizer Dept.	Wilmingron, N. C.	Rail	Chamber	Brimstone	Purchased	52°Bé.	None
Morris Fertilizer Co.	Wilmington, N. C.	Rail, own cars	Chamber	Brimstone	Purchased	50° & 60°Bé.	None
Anderson Phosphate and Oil Co.	Anderson, S. C.	Rail	Chamber	Brimstone	Purchased	52°Bé.	None
					All acid used in fertiliser manufacture		
Virginia-Carolina Chemical Co., (3 plants in this town).	Blacksburg, S. C.		Chamber				
Virginia-Carolina Chemical Co., (3 plants in this town).	Charleston, S. C.		Chamber				
Etiwan Fertilizer Co.	Charleston, S. C.	None Shipped-all used in fertilizer manufacture	Chamber	Brimstone	Purchased	52°Bé	None
Maybank Fertilizer Co.	Charleston, S. C.		Chamber				
McCabe Chemical Co.	Charleston, S. C.		Chamber				
Planters' Fertilizer & Phosphate Co.,	Charleston, S. C.	Rail & Water	Chamber	Pyrites	Purchased	50°Bé.,	None
Read Phosphate Co.	Charleston, S. C.		Chamber				
Royster Guano Co	Columbia, S. C.		Chamber				
Tennessee Copper Co.	Copperhill, Tenn.	Rail	Chamber	Pyrrhotite ore, from own mines.		60°Bé. 20–40 cars daily	Nitre-cake
Ducktown Sulphur, Copper, and Iron Co.,	Isabella, Tenn.	Rail	Chamber	Blast furnace gases from semi-pyritic smelting of chalcopyrite ores.		60°Bé,	None
Virginia-Carolina Chemical Co.	Memphis, Tenn.		Chamber				
Armour Fertilizer Works	Nashville, Tenn.		Chamber				
Federal Chemical Co.	Nashville, Tenn.		Chamber				
Read Phosphate Co.	Nashville, Tenn		Chamber				
U. S. Smokeless Powder Plant	Nashville, Tenn.		Contact				
Victor Chemical Works	Nashville, Tenn.		Chamber	Brimstone	Purchased Use practically all acid made	60°Bé.	Nitre-cake
Commercial Acid Co.	Augusta, Ark.		Chamber				
Arkansas Fertilizer Co.	Little Rock, Ark.		Chamber				
Everly M. Davis Chemical Corp.	Little Rock, Ark., and 480 Lexington Ave., New York City, N. Y.	Rail	Chamber & concentrators	Brimstone	Purchased	60° & 66°	Nitre-cake

Calumet & Arizona Mining Co.,	Douglas, Arizon	Tank cars	Chamber	Cuprous Pyrites	Own mines	60°Bé. extra clear	None
Western Chemical Manufacturing Co.,	Denver, Col.		Chamber & contact				
E. I. duPont deNemours & Co.	Louviers, Col.	Rail	Contact		Purchased		None
National Zinc Co.	Kansas City, Kan.	Private tank cars	Chamber	Brimstone & blande	Purchased	60° & 66° battery electrolite	Glauber's salt, salt cake
Anaconda Copper Mining Co.	Anaconda, Mont.	21 private tank cars	Chamber & Larison packed (cell)	Copper concentrates	Own mines	60°Bé.	Mineral acid acid phosphate
E. I. duPont deNemours & Co.	Ramsay, Mont.		Contact		Purchased		None
Mid-Continental Chemical Co.	Sand Springs, Okla.		Chamber				
Armour Fertilizer Works	Houston, Tex.		Chamber				
Gulf Refining Co.	Port Arthur, Tex.	Rail & water	Contact	Brimstone	Purchased;	98%	
Commercial Acid Co.	Port Arthur, Tex.		Contact				
Sugarland Manufacturing Co.	Sugar Land, Tex.	Rail	Chamber & contact	Brimstone	Purchased	All strengths	Nitric, usual
Hercules Powder Co.	Bacchus, Utah		Contact				
Garfield Chemical & Mfg. Co.	Garfield, Utah	Rail	Chamber	Copper concentrates	Purchased	60°Bé.	(50 tons nitre cake per month
Office	McCormick Block, Salt Lake City		Acid all sold	to Utah Coppe	r Co.		
General Chemical Co., of Cal.	Bay Point, Cal.		Contact				
American Agricultural Chemical Co.,	Los Angelos Cal.	Rail	Contact		Purchased	50°Bé.	None
Mountain Copper Co.	Martinez, Cal.	Rail	Meyer Tangential Chamber	Pyrites	Own mines	60°Bé.	None
Metals & Chemicals Extraction Corp.	Oakland, Cal.	Rail	Chamber	Pyrites and calcopyrite	Purchased	66°Bé. & 93.5%	Copperas
Hercules Powder Co.	Pinole, Cal.		Contact				
Stauffer Chemical Co.	San Francisco, Cal		Chamber				
Pacific Guano & Fertilizer Co.	Stege, Cal.		Chamber				
E. I. duPont deNemours & Co.	duPont, Wash.	Rail	Contact	Brimstone	Purchased	Fuming	None

This list of the 238 plants now operating in this country shows how widely the industry is scattered, Sulphuric acid is expensive to ship, but from this list it will be possible to find a manufacturer not far from your place of business, no matter where that may be.

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This table shows, eliminating the acid used for munitions and explosives, and allowing about 10,000 tons per month for domestic explosives, an indicated requirement for normal peace purposes of possibly 260,000 tons per month (basis, 100 per cent H_2SO_4), or about 5,000,000 tons per year (basis, 50°Bé.).

There is no question that the use of phosphate fertilizer will increase all over the country for many years. And as acid is expensive to transport, it will have to be made near the place it is used.

Sulphur, the primary raw material, either as pyrites or brimstone has recently been described by Drs. Raymond F. Bacon and Harold S. Davis before the American Institute of Chemical Engineers. The following extracts have been taken from their paper.[1]

America now dominates the sulphur industry and virtually all the American sulphur is produced by three companies—viz., the Union Sulphur Co., the Freeport Sulphur Co. and the Texas Gulf Sulphur Co. These three companies produce not only virtually all the sulphur used in the United States but also a considerable surplus which is exported. The only other sulphur which normally enters the American market in quantity comes from Japan and its percentage calculated on the consumption of the United States is small and is not likely to increase. Rising costs of living have meant much higher wages in Japan, as well as in other parts of the world; in fact, the percentage increase has probably been greatest in Japan, due not only to world conditions affecting all countries but to the rising standards of living of the Japanese. These facts, together with present higher transportation costs, will make it increasingly difficult for Japanese sulphur to compete on our Pacific coast with the American product.

Expansion of Industry During War

During the World War, and especially after America's entry into it, the demand for sulphur grew enormously. Some time previous to our declaration of war consideration had been given by a certain group of New York capitalists to the opening up of the sulphur deposit (known as the "Big Dome") located near Matagorda, Tex. These plans were hastened to realization by our Government's need and demand during the war for the maximum production from every possible source of sulphur. The plans eventuated in the formation of the Texas Gulf Sulphur Co., which, however, did not get its plants into operation until after the armistice. Production has been practically continuous since

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[1] *Chem. & Met. Eng.*, January 12, 1921.

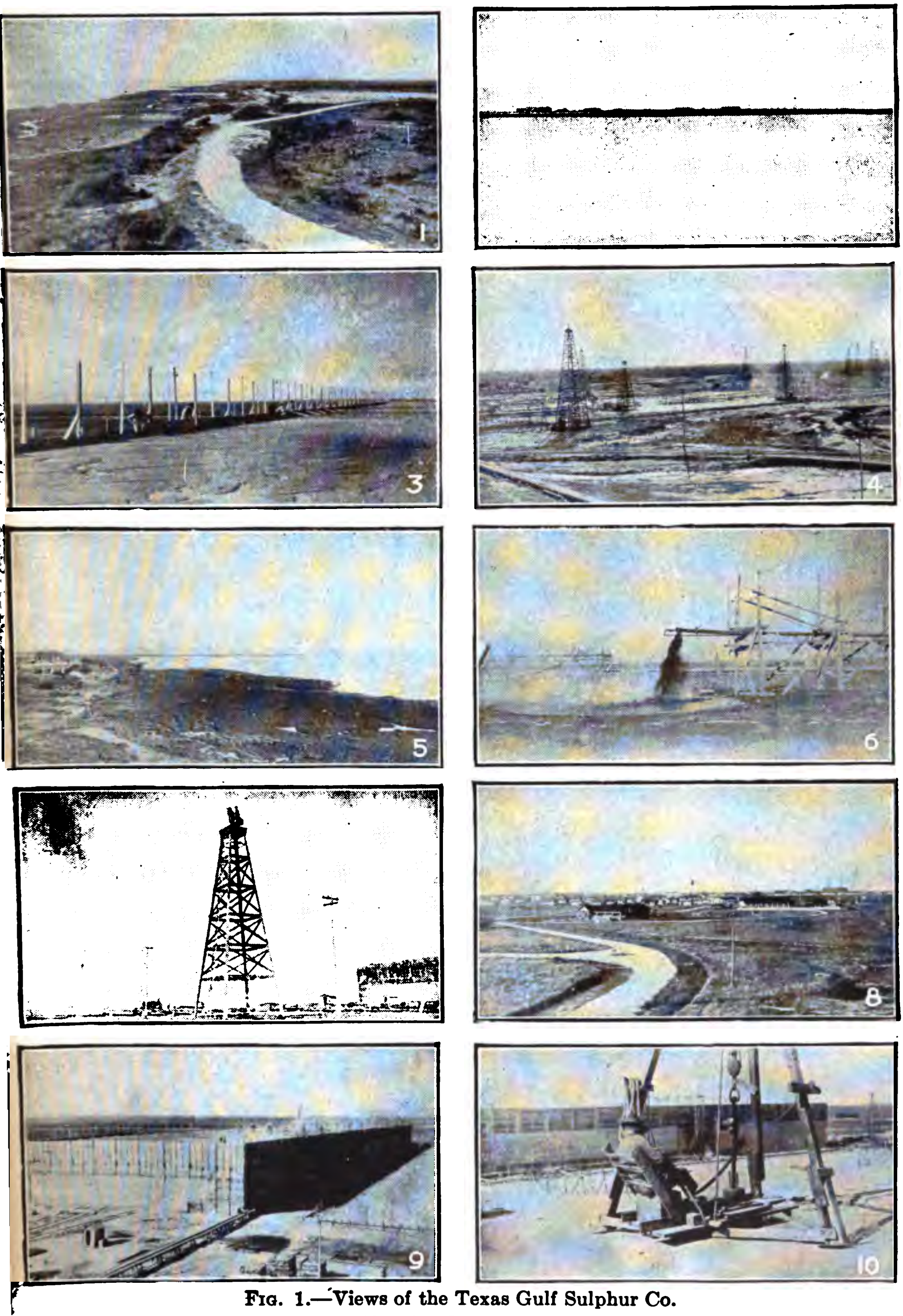

Fig. 1.—Views of the Texas Gulf Sulphur Co.
General Views Showing Topography, Figs. 1, 2, 5, 8.
Sulphur Tank Storage System, Figs. 3, 6, 9.
Well Driving Equipment, Figs. 4, 7, 10.

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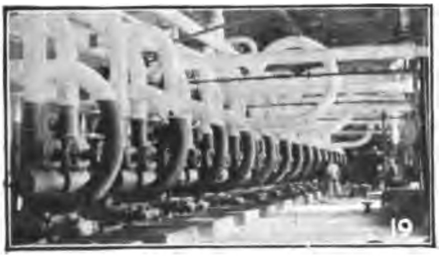

Fig. 2.—Views of the Texas Gulf Sulphur Co.
Houses, Pavilion and Hospital, Figs. 11, 14, 17, 20.
Method of Loading for Shipment, Figs. 12, 15, 18.
Exterior and Interior Views of Power House, Figs. 13, 16, 19.

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the company first mined sulphur on March 19, 1919. The plant of this company, which has been described elsewhere,[1] was designed to have a capacity of 1,000 tons of sulphur per day, but for months at a time during the past year it has produced on an average 2,000 tons per day. The total production for the year 1920 exceeds 800,000 long tons, while in all probability the production for 1921 will be the largest of any sulphur company in the world. The possible daily production with the present plant, under favorable conditions, could be forced to 3,000 or 4,000 tons per day. The deposit contains upward of ten million tons of sulphur; and a brief description of its character is as follows:

DESCRIPTION OF BIG DOME AT MATAGORDA

The main deposit has a diameter of about 4,000 ft. and is situated 800 to 1,000 ft. below the surface of the ground. The sulphur occurs in an almost flat stratum, whose general shape is like that of a flat-topped umbrella. Above the sulphur stratum is an unconsolidated sediment consisting of bands of shale, gumbo and boulders. Below is a layer of salt and gypsum, and then a layer of salt of undetermined but very considerable thickness. The sulphur content of the deposit runs quite uniform with a slightly higher percentage of sulphur on one side of the dome. The mining operations are carefully checked, and a large-sized model of the deposit enables the engineers constantly to visualize what is taking place underground.

PRODUCTION AND STOCKS EXCEED POST-WAR NORMAL DEMAND

At the time the Texas Gulf Sulphur Co. entered the market the situation was about as follows: The Union Sulphur Co. had on top of the ground, in unsold stock of sulphur, upward of one million tons and the Freeport Sulphur Co. had several hundred thousand tons. The normal consumption of sulphur in the United States had been between four and five hundred thousand tons per annum, which quantity could be readily supplied by the two older companies.[2] A new sulphur company entering the market with a large production of sulphur was therefore compelled to pursue one of two policies—either to attempt to obtain a share

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Read before the American Institute of Chemical Engineers, New Orleans, December 6, 1920. By RAYMOND F. BACON and HAROLD S. DAVIS.

[1] *Chem. & Met. Eng.*, vol. 20, No. 4, pp. 186–188. *Eng. Min. J.*, vol. 107 (1919), pp. 555–557.

[2] It may be stated, in passing, that any economic data given regarding either the Union Sulphur Co. or the Freeport Sulphur Co. are subject to the usual statement on advertisements of bond sales; that is, "they are gathered from sources we believe to be reliable, but are not guaranteed by us."

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of the business by cutting prices or to place the sulphur in markets which had not hitherto used sulphur; in other words, to increase the sulphur consumption of the country.

With reference to the first possibility, competition based on cutthroat slashing of prices always has proved disastrous to the whole industry. Moreover, the mining of sulphur by the Frasch process, to be carried out economically, must be conducted on a very large scale, so that even if a company under the conditions outlined above had obtained a third of a possible 500,000-ton consumption, this would not have insured profitable operation. The company has chosen what is surely the wiser course, in attempting to place its sulphur by increasing the total consumption in the industries.

It was possible to do this owing to the prevailing economic conditions. The United States had in recent years consumed annually, for the manufacture of sulphuric acid, upward of 500,000 tons of sulphur in the form of pyrites, most of which came from Spain. The older sulphur companies, either because of some agreement with the pyrites importers or because of a desire to hold the price of sulphur at a certain level, had not attempted seriously in past years to substitute sulphur for pyrites as the raw material of sulphuric acid manufacture. Importation of Spanish pyrites, due to war transportation conditions, fell off very seriously during the war years. This caused many producers of sulphuric acid to discard the pyrites roasters and to install sulphur-burning equipment, while new producers in this field erected plants which were almost entirely so equipped. The new company was able to obtain its fair proportion of the new business and the net result has been that the total consumption of sulphur of the United States during the past year has been upward of 1,000,000 tons, as compared with a normal consumption in recent years of about half that figure.

PYRITES VERSUS SULPHUR AS A SOURCE OF SO_2

It is interesting, in this connection, to give just a little history, for if the subject is examined it is found that in the early days of sulphuric acid manufacture all the sulphuric acid of Europe, excepting Nordhausen acid, was made from brimstone. This includes the period from about 1750 to 1839, when pyrites first was used commercially for the manufacture of sulphuric acid in England. This use of pyrites was due to the fact that the Neapolitan Government in 1838 granted a monopoly for the exportation of sulphur to Taix & Co., of Marseilles, which firm immediately raised the price of sulphur from $25 to $70 per ton. By so doing, it killed the goose that laid the golden egg, for pyrites was substituted immediately for sulphur in most European countries and the era of high-priced sulphur was but short lived. The loss of this market was a permanent setback to Sicilian sulphur.

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The subsequent history of the sulphur industry is one of violent ups and downs. If one considers this history up until some time after Frasch made America a factor in the business, it will be noted that it has been characterized at all times by short periods of prosperity, followed by a short-sighted, selfish, destructive competition on the part of certain interests. Following this would come a period of such marked depression as to threaten the life of the entire industry, and it would be necessary for some governmental or other outside agency to exercise pressure to get the producers together on a common-sense basis and thus gradually put the industry again on its feet.[1] Since the time when Frasch made possible America's sulphur industry the stability of the whole industry has been much greater. While at the present time there is an extremely lively competition among the companies for business, there is every reason to believe that American common sense, spirit of fair play, and co-operation will prevent this competition going to the extent of threatening the industry itself, as has happened many times in the past. Present indications are that all the sulphur companies are pursuing an enlightened policy, in that all are doing more or less research and development work having as its ultimate object the opening up of broader markets for sulphur, of which sulphuric acid manufacture affords but one.

ADVANTAGES OF SULPHUR OVER PYRITES

For sulphuric acid manufacture sulphur has many very marked advantages over pyrites. Using pyrites means handling into the works a comparatively large quantity of material, its slow combustion in expensive roasters, a certain inevitable dust nuisance and the disposal of a large tonnage of cinder. As against this, sulphur of less than one-half the weight of pyrites for a given tonnage of acid produced is handled into the works, is burned cleanly in inexpensive equipment and leaves no residues to be taken care of. Sulphur is constant in composition, and its freedom from arsenic and other impurities allows the production of a purer acid. It is also claimed that, in practice, the burning of sulphur means a higher rate of production for a given size of lead chamber space.

These acknowledged advantages of the use of sulphur over pyrites for sulphuric-acid manufacture have been demonstrated by the willingness of acid producers to pay a higher price per unit for elementary sulphur than for combined sulphur in the form of pyrites. An example of this is the fact that one of our largest and best organized chemical companies, in making a large contract, chose sulphur over pyrites for sulphuric acid manufacture, where the differential in offered prices was 8c. per unit of sulphur.

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[1] In this connection, see FRASCH, Perkin Medal Address, *Met. & Chem. Eng.*, vol. 10, No. 2, pp. 73–82, and *J. Ind. Eng. Chem.*, vol. 4 (1912), p. 139.

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When one considers the present high prices of labor, the uncertainty of the copper market and the fact that sulphur may be purchased in a competing market, from concerns which have large stocks on hand, so that delivery is certain, it would seem to be a wise business policy to use sulphur rather than pyrites for sulphuric acid manufacture even with a very large differential in price. This is especially true when one considers the other side of the situation—namely, that in buying imported pyrites the consumer is putting himself at the mercy of one large set of interests which, while it may at the present time offer pyrites at low prices and even below actual cost, will almost certainly at some time in the future reap its profit by much higher prices. It is said that imported pyrites has been offered for large contracts in this country at about 10c. per unit of sulphur, ex-vessel, Atlantic seaboard, while at the same time pyrites was selling in England, much nearer the base of supplies, at 20c. to 22c. per unit of sulphur. It reminds one somewhat of the tactics of Standard Oil in the old days before "trust-busting" became fashionable with politicians; and everyone knows that those who bought cheaply when the company was extinguishing a competitor never reaped any permanent advantage, but later more than paid for temporary reductions in price.

Sulphur is today one of the few substances which have not risen in price since pre-war days. In fact, sulphur is cheaper today than at any other time in the history of the industry. The price for large contracts is about $20 per ton, Atlantic seaboard. This makes sulphur one of the cheapest raw materials available and should, it would seem, greatly extend its usefulness. Sulphur as mined and sold by all three companies is of remarkably high grade. In fact, many so-called C.P. chemicals do not possess the purity of crude sulphur, as sold by these companies. The sulphur is free from arsenic, selenium and tellurium, and often for days at a time wells will yield a product running higher than 99.9 per cent sulphur, as calculated on a moisture-free basis; in fact, sulphur companies selling the crude sulphur on contracts guarantee the purity to be over 99 or 99½ per cent.

Effect of Traces of Petroleum on Combustion

One impurity occurring in traces in the sulphur of all three companies is oil. There is a dearth of information in the technical literature respecting the subject of oil in sulphur. Since the effect of this impurity is very interesting, it is appropriate to discuss it here. The peculiar effect of oil is its influence on the burning qualities and also on the color and odor of sulphur. *A priori*, one would not assume that mere traces of a combustible substance like petroleum oil could affect adversely the combustion of another combustible substance like sulphur, but such is indeed the case.

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If one will make a simple experiment by attempting to burn two small lots of sulphur, one being chemically pure and the other containing 0.2 per cent of petroleum oil, he will note the following phenomena: The pure sulphur will burn quietly until it is totally consumed; the sulphur containing the oil will burn for a very short time, when it will be observed that a thin, elastic film is being formed over its surface. Very soon combustion is taking place only in spots, and within an exceedingly short time the flame goes out, although only a small percentage of the sulphur has been consumed. The explanation is quite simple. Sulphur and oil at a moderate temperature react together to form asphalt, and if the reaction is carried to completion the final result is carbon.

In the burning of sulphur containing oil the oil reacts with the sulphur to form an asphaltic material, which quickly spreads as a film over the surface. The result, as combustion proceeds, is a film of carbon over the surface of the sulphur. The ignition temperature of carbon, or of the intermediate asphaltic material, is so much higher than that of sulphur itself or than the temperature developed during the burning of the sulphur that this film is not ignited and consequently the whole flame is extinguished.

The remedy for burning such sulphur is also quite obvious. If the devices for sulphur combustion are such as to agitate the surface of the burning sulphur or in any other way break this film of asphaltic material, no difficulty will be experienced. Acid manufacturers who use mostly modern types of sulphur burners, such as the rotary or cascade type, which allow the sulphur to drop from one level to another, have absolutely no difficulty in burning sulphur containing 0.2 per cent of oil, which figure represents more oil than any of the commercial sulphurs contain at the present time. On the other hand, many of the small paper-pulp manufacturers still adhere to types of burners in which the burning sulphur is more or less quiescent. With such a type there is no agitation of the burning liquid surface, so that some of these paper-pulp manufacturers have had difficulty in burning sulphur when they happened to obtain a shipment comparatively high in oil.

The sulphur deposits of all three operating companies are located in close proximity to oil fields. When a sulphur deposit is first opened some of the product may be high in oil, running as much as 0.2 per cent, but as production proceeds the oil becomes progressively lower until finally, for days at a time, it may amount to only 0.04 per cent, which is totally negligible, even for burners which provide no agitation of the surface. We have assumed that hot water carried this small quantity of oil from small crevices in the oil-sand formation to the sulphur below when the well was first opened. After a region has become heated up by the hot water, these traces of oil are pretty well washed out; consequently, sulphur mined later in the same area is virtually free from it. Examination of drill cores of native sulphur showed such *in situ* sul-

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phur to be oil-free. We are informed by ex-employees of the Union Sulphur Co. that this corresponds with the experiences of that organization in heating up any new area of sulphur ground. The examination of a very large number of samples of sulphur, representing the production of all three companies, has shown quite positively that none of their sulphur contains enough oil to cause any difficulty in its combustion with rotary burners or other burners which agitate the surface of the burning sulphur during combustion. It is only very exceptionally that one will find a car of sulphur whose oil content is high enough to make difficulties in its combustion in a stationary type of burner.

PROPERTIES AND USES OF SULPHUR

Sulphur is now and is likely to be for some time one of our cheapest raw materials, and accordingly should and undoubtedly will find a much wider range of usefulness. It is by studying the physical and chemical properties of a substance that one first obtains ideas as to possible new uses therefor. The chief physical properties of sulphur are tabulated in Table 4. The present tonnage uses of sulphur are presented in the chart. Those properties which suggest certain possible tonnage uses for sulphur are its very poor conductivity of heat and electricity, its resistance to being wetted by water and its inertness toward most acids, all of this combined with a fair degree of physical strength. These properties suggest heat-insulating materials, electrical insulators of various types, water- and acid-proof cements, and acid-proof construction materials.

As against the properties of sulphur which might make it very desirable for certain construction purposes are certain objectionable ones, such as its brittleness and its flammability. The brittleness can be overcome sufficiently for many purposes by making mixtures of sulphur with other materials, such as sand, asbestos, or paper pulp, or by reinforcing with wire screen. In many cases the flammability is not a serious objection.

A survey of the literature, especially the patents, on the subject of sulphur mixtures reveals that almost every conceivable thing has been suggested as a perfective admixture for sulphur to obtain a material which has all the air- and acid-resistant properties one could desire or to get a completely resistant kind of concrete useful in building. We have tested out most of the recipes which appeared to be promising and find as usual that the claims have been much overstated. However, the ordinary mixture of sand and sulphur which has been repeatedly mentioned in the literature has merits which should make it better known. The mixture which has seemed to us the best for most uses is that of 40 of sulphur and 60 of sand (parts by weight). The tensile strengths of sulphur-sand mixtures as measured in the usual manner for testing cement were as follows:

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TABLE 3.—TENSILE STRENGTHS OF SULPHUR-SAND MIXTURES

PERCENTAGE OF SULPHUR BY WEIGHT	TENSILE STRENGTH, LB. PER SQ. IN.
25	90
35	310
40	400
45	310
50	110
100	250

We have also used other fillers which have given tensile strengths of 800 and even 1,100 lb. measured in the same manner and have to a large extent overcome the brittleness of the sulphur in some of these mixtures. Sulphur-sand briquets kept on hand for one year show no deterioration in strength. It is evident that the 40:60 sulphur-sand mixture can be used as an acid-resistant concrete, for making acid-resisting pipe, tanks, gutters, launders, etc. The manipulation of such a mixture is much like that of pouring concrete and is as follows:

Practical Manipulation.—It is evident that the sand should contain no constituent which will be attacked by any material which is to come in contact with the finished product; for instance, in the case of acid tanks it should be free from limestone or other acid-soluble constituents. If necessary, it should be washed and dried. The sulphur may be melted in a kettle with constant stirring, and the sand, which has been heated separately, poured into it while the stirring is continued. Unless the sand is heated, it will lump when poured into the sulphur. When the material is thick enough (40 per cent sulphur and 60 per cent sand) it is ladled into the molds.

Considerable flexibility is possible in handling this material. For instance, a small tank was made which was 2 ft. square, 18 in. deep, and 2 in. thick. The mixture was poured into a wooden mold in twelve different lots. Although several of these lots had solidified before the next was poured upon them, nevertheless the resulting joints were strong. Apparently the hot mixture melts sufficient of the solidified part to form a solid joint. There was no contraction of the tank as a whole and no tendency to split in the mold. This mixture can be worked with a trowel, like mortar. It can also be reinforced by wire netting placed in the mold before it is poured. The specific gravity of a sulphur-sand mixture (40 : 60) was found to be 2.46.

Weight of 1 cu. ft..............................	154 lb.
Weight of sulphur required per cubic feet.....	62 lb.
Weight of sulphur required per cubic yard....	1,670 lb.

Taking the value of sand as $1 per cu. yd. and of sulphur as $20 per ton, the price of the materials per cubic yard will be about $18. It may be possible to decrease appreciably the amount of sulphur necessary and

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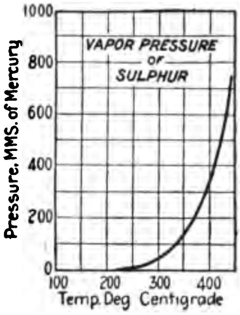
hence the cost by imbedding larger pieces of crushed rock or some such substance in the mass. Tests of the material in sea water are being made, but it is too early to give results. It is apparently standing up well to date.

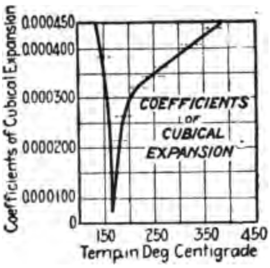
Pipes cast of this sulphur-sand mixture show no deterioration after one year in 5 per cent hydrochloric or 5 per cent sulphuric acid. The ordinary organic acids have no effect on such a mixture.

TABLE 4.—THE PHYSICOCHEMICAL PROPERTIES OF SULPHUR



VAPOR PRESSURE CURVE[1]

Forms of sulphur:	
Crystalline	Sp. gr.
(*a*) ***Rhombic.*** Ordinary form stable below 96°C. (205°F.)..	2.07[1]
(*b*) ***Monoclinic*** Stable above 96°C. (205°F.)............	1.96[1]
(*c*) ***Milk of Sulphur.*** Formed, *e.g.*, by action of diluted acids on polysulphides. Generally called amorphous, but shown by Smith and Brownlee to be crystalline.[2] There are several other modifications of crystalline sulphur of scientific interest but not of general importance.	
Liquid. At 113°C. (235°F.)............................	1.81[1]
Contains:	
Sulphur (liquid, soluble), Sλ.	
Sulphur (liquid, insoluble or amorphous), Sμ.	
The proportion of Sμ to Sλ increases with the temperature.	
Amorphous. Sμ (solid)................................	1.89[3]
Plastic Sulphur. Formed by heating sulphur above viscous stage, 162°C. or 324°F., and cooling quickly........	1.88[3]
Elastic Sulphur. Formed by heating sulphur above 400°C. or 752°F. and pouring in a thin stream into liquid air. Its elastic properties are soon lost.	
Black Sulphur. "When sulphur mixed with very little oil is thrown into a hot platinum dish, a black substance is obtained which has been looked on as a modification of sulphur. The product contains 55 per cent of sulphur and 33 per cent carbonaceous material."—Watts, *Dictionary of Chemistry.*	



The coefficients of cubical expansion over various ranges of temperatures are shown at horizontal broken lines.

ELECTRICAL CONDUCTIVITY[1]

Measured as reciprocal value of resistivity in ohms of 1 cm. cube.

TEMP.		CONDUCTIVITY
C.	F.	
22	72	1×10^{-17}
69	156	0.254×10^{-15}
115	239	0.105×10^{-11}
130	266	0.5×10^{-10}
430	806	0.1×10^{-7}

Compare:

Porcelain	1×10^{-14}
Mica	1×10^{-12}
Ebonite	1.5×10^{-11}

FRICTIONAL ELECTRICITY

When rubbed with practically any other substance, *e.g.*, glass, fur, silk, wool or hard rubber—sulphur becomes charged with negative electricity.

COEFFICIENT OF LINEAR EXPANSION[1]

Temp.		Ex. coeff.
C.	F.	
0–13	32–56	0.000046
13–50	56–122	0.00007
50–78	122–173	0.00009
78–97	173–207	0.0002
97–110	207–230	0.001

SURFACE TENSION[4]

Temp.		Surface tension, mg./mm.
C.	F.	
120	248.0	5.71
131	267.8	6.12
146	294.8	6.05
195	383.0	6.62

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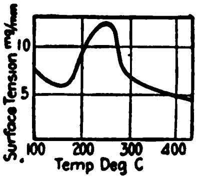

APPROXIMATE CURVE OF SURFACE TENSION

COMPRESSIBILITY[5]

Average fractional change of volume caused by 1 megabar change in pressure between 100–500 megabars 0.0000125.

1 megabar = 0.987 atmosphere

CONDUCTIVITY OF HEAT[1]

Measured as the number of gram-calories transmitted in 1 sec. through a plate 1 cm. thick and having surfaces 1 sq. cm. in area when opposite faces differ in temperature by 1°C.

20°–100°C. (68°–212°F.)	0.0006
Compare:	
Ice	0.002
Copper	1.00

International Atomic Weight, 1920 = 32.06

Vapor Density:

At boiling point corresponds approximately to formula S_8[13].

At 1,000°C. (1,832°F.) corresponds approximately to formula S_2.

ECONOMICS OF NATURAL SULPHUR

Until 1900, 95 per cent of world's supply from Sicily
In 1912, 50 per cent of world's supply from Sicily
In 1917, 14 per cent of world's supply from Sicily
In 1917, 80 per cent of world's supply from U. S. A.

United States Exports and Imports

1909 exports	37,142 long tons
1909 imports	30,589 long tons
1918 exports	131,092 long tons
1918 imports	82 long tons

United States Production

1894	494 long tons	1909	303,000 long tons
1899	1,590 long tons	1914	347,491 long tons
1904	196,888 long tons		

1919 Texas Gulf Sulphur Co.

Only 9 months production after start, 348,380 long tons.

PROPERTIES OF COMMERCIAL SULPHUR

Insoluble in Water

Insoluble in Most Acids

Tensile strength, 200 lb. per square inch (approx.).

Heat conductivity, low: ½ that of cork, ¼ that of ice.

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Electrical conductivity lower than that of practically any other solid substance.

Melting point, depending on conditions, 110.2°–119.25°C. (230.4°–246.7°F.).

Ignition temperature, 248°C. (478°F.).[7]

Boiling point, 444.6°C. (832.3°F.).[6]

Melting Point[1]

Type of sulphur	Temp. C.	Temp. F.
Rhombic	112.8	235
Monoclinic	109.25	246.7

Natural freezing point $S\lambda$ and $S\mu$ in equilibrium (96.3 per cent $S\lambda$, 3.7 per cent $S\mu$), 110.2°C. (230.4°F.).

Specific Heat[1]

Type of sulphur	Temp. C.	Temp. F.	Sp. ht.
Rhombic	0–95°	32–203°	0.1751
Liquid	160–201	320–393	0.279
	201–233	393–451	0.331

Heat of Combustion[1]

	G. cal. per g. S	B.t.u. per lb.
$S + O_2 \rightarrow SO_2$	2,200	3,960
$S \rightarrow H_2SO_3$ (dilute)	2,450	4,410
$S \rightarrow H_2SO_4$ (dilute)	4,450	8,010

Heat of Vaporization[1]

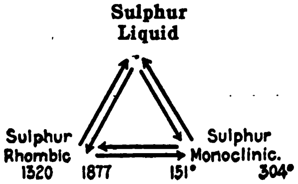
Temp. C.	Temp. F.	G. Cal. per g.	B.t.u. per lb.
444.6°	832.3°	70	126
			(Approx.)

Transition Temperature[1]

S Monoclinic ⇆ S Rhombic

Pressure, kg./sq. cm.	Lb./in.	Temp. C.	Temp. F.
10.6	15	96°	204.8°
123	175	100	212.2
638	907	120	248
1,350	1,920	150	302

TRIPLE POINT



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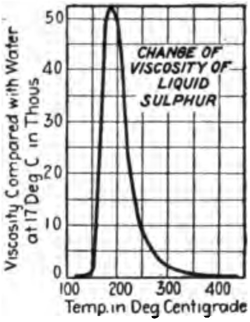
Heats of Solution in CS_2[9]

	G. cal. per g.	B.t.u. per lb.
Dilute solution	−11.89	−21.4
Saturated solution	−11.55	−20.9

Heats of Fusion[10]

	G. cal. per g.	B.t.u. per lb.
Rhombic at 100°C. (212°F.)	14.9	26.8
Monoclinic at 100°C. (212°F.)	11.5	20.7
To form pure liquid sulphur (Sλ):		
From rhombic	14.5	26.1
From monoclinic	11.1	20.0

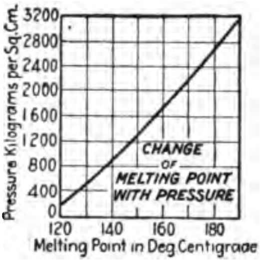


CHANGE IN VISCOSITY WITH TEMPERATURE[1]

Solubilities in Various Solvents[11]

	Temp.		Solubility, G. in 100-g. solution
	C.	F.	
Amyl alcohol	95	203	1.5
	110	230	2.1
Aniline	89.5	193.1	8.3
	130	266	46.2
Benzene	25	77	2.1
	70	158	8.0
Carbon disulphide	−20	−4	10.5
	−10	14	13.5
	0	32	18
	20	68	29.5
	50	122	59
	100	212	92
Carbon tetrachloride	25	77	0.86
Chloroform	22	71.6	1.2
Coal-tar oil, sp. gr. 0.87	15	59	2
	100	212	13
Sp. gr. 1.02	15	59	6.5
	110	230	53.5

Ethyl ether	23.5	74.3	0.97
Linseed oil	15	59	0.4
	160	320	9.0
Olive oil (sp. gr. 0.885)	15	59	2.2
	130	266	30
Sulphur chloride	0	32	11
	55.2	131.4	43
	86	186.8	89
Phenol	175	346	26.7
Toluene	23	73.4	1.48
Turpentine (oil of)	16	60.8	1.33



CHANGE OF MELTING POINT WITH PRESSURE[1]

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CHAPTER IV

RAW MATERIALS

The raw materials for Sulphuric Acid are sulphur, oxygen (supplied from the air), and water. The oxides of nitrogen, either as Chile saltpeter or nitric acid, might be called indirect raw materials.

Water and air need no introduction nor description, so this chapter will be devoted to the description of the sources of sulphur and the nitric oxides. The amount of acid produced by distillation from natural sulphates is practically nothing, leaving brimstone and the metallic sulphides as our commercial sources.

Sulphur occurs native, as brimstone, in all parts of the world, particularly rich deposits existing in Iceland and Sicily; but the enormous deposits of Calcasiou Parish, south-western Louisiana, furnish the United States. A small amount is mined in Utah and Wyoming for local use, and the Pacific Coast is supplied from Japan.

The Louisiana beds, worked by the Frasch process, were discovered in boring for oil, and a most interesting and ingenious method of recovering the sulphur was devised by Herman Frasch, for which he was awarded the Perkin medal.

The sulphur ore, containing up to 90 per cent sulphur, occurs 450 ft. down, under quicksands that make usual mining methods impossible. The limits of the bed have never been determined, although 40,000,000 tons have been locked out.

The Frasch process, described in United States patents, No. 799,642 and No. 800,127, is as follows: A 13-in. hole is drilled to a depth of 800 ft., cased, and inside, concentrically, a 10-in., a 3-in., and a 1-in. pipe is placed. Between the 3-in. and the 10-in., and the 10-in. and the 13-in. pipes superheated water, heated by superheated steam to a temperature where sulphur begins to darken, is forced by its own expansive force, and by steam pressure, into the deposit. The hot water, after melting the sulphur, passes into the crevices of the rock, the molten sulphur separating from the water by gravity, and being forced up the inner pipe by steam pressure. The steam pressure is kept less than the head of a column of molten sulphur reaching

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to the ground, and the sulphur is lifted the last part of the way by compressed air.

The molten sulphur is run into huge spaces fenced in with boards, where it solidifies and is then blasted down for shipment. It will run over 99.6 per cent S, and practically no As.

Louisiana sulphur is shipped from Sabine Pass, Texas, to supply all the eastern United States. It was quoted (1916) at $22 a ton, and was reported to cost, f.o.b. mines, under $3.

The Japanese sulphur, greyish in color, comes in large blocks, about 3 by 2 by 1 ft., wrapped in matting. It supplies the Pacific coast demand.

PYRITES

Iron pyrites, FeS_2, bisulphide of iron, is one of the most widely distributed of ores, and has been, since about 1840, a material of prime importance in the manufacture of sulphuric acid.

Pyrites crystallizes in the regular system, as a cube, octohedron, and pyrihedron, and often as twin crystals. The crystals are frequently well developed, and become very large. It is greenish yellow in color, its popular name, "Fool's Gold," describing it well. Small crystals show darker colors, and the powder is greenish black. Fracture is conchoidal or irregular. Hardness 6 to 6.55; sp. gr., 4.83 to 5.2; it contains 46.58 per cent of iron, and 53.42 per cent of sulphur.

Volcanic pyrites contains no water, while sedimentary deposits do. Some of the pyrites containing water bursts upon roasting.

The principal North American deposits of pyrites are at Tilt's Cove; New Foundland; Capleton, Quebec; Ely, Vermont; and Pulaski, Virginia. Cuba is becoming a large producer.

Pyrrhotite, magnetic iron sulphide, Fe_7S_8, is not a practicable source of sulphur: first, because of its low sulphur content (39.5 per cent sulphur, 60.5 per cent iron), but even more important, the sulphur that it does contain is not readily given up, the lumps crusting with oxide of iron, and extinguishing whatever flame is started. It has been successfuly roasted in powdered form in a Herreshoff roaster. E. D. Peters speaks, in "Principles of Copper Smelting" (p. 169), of $200,000 thrown away on an acid from pyrrhotite proposition.

Copper-bearing pyrites, of the general form of chalcoperite, Cu_2S, Fe_2S_3, is a valuable source of sulphur, either when the ore is roasted and the SO_2 given off used for acid making, and the

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cinder for copper; or as at the Tennessee Copper Co., the gases from semi-pyritic smelting are used direct to the chambers.

Zinc blende, ZnS, the principal ore of zinc, is an important raw material, the SO_2 derived from its being roasted to ZnO being used. Blende contains 32.9 per cent sulphur when pure—ores usually contain some PbS and other impurities, so that the sulphur content may drop as low as 20 per cent. Very little arsenic occurs with blende, and the acid produced from it is in demand for that reason.

The SO_2 produced by the roasting of zinc blende would probably never be used to make sulphuric acid if the gases were not injurious to vegetation, for the gas from a material so low in sulphur is very dilute. And in addition, sufficient air must be introduced, not only to burn the sulphur, but to oxidize the zinc as well:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2.$$

As is shown, 50 per cent more oxygen than is required to burn the sulphur is required, and the nitrogen from that air serves to dilute the gas formed. So sulphuric acid from blende is less a by-product than a means of taking care of the harmful gases, that otherwise, if let free, destroy all vegetation near the plant. Consequently, while an important source of acid in this country, the burning of blende is properly a part of zinc metallurgy, and for thorough treatment the reader is referred to works on that subject.

Zinc ores must be well roasted, so the cinder should contain under 0.75 per cent sulphur, either as ZnS or as $ZnSO_4$. If the furnace temperature is too low the sulphate will form, and that must be specially treated to get it into the form of ZnO, for distillation.

The muffle type of furnace, with a mechanical stirrer, is in use in all modern works.

Lead ores are too low in sulphur to be used for a raw material for sulphuric acid, pure galena only containing 13.4 per cent sulphur.

I cannot find that spent oxide of iron is used in this country as a raw material, although it is used abroad. Gas works remove the H_2S from gas by a mixture of hydrated iron oxide and sawdust, according to the formula:

$$Fe_2(OH)_6 + 3H_2S = 2FeS + 6H_2O + S,$$

and upon exposure to the air precipitates more sulphur, as follows:

$$4FeS + 3O_2 + 6H_2O = 2Fe_2(OH)_6 + 2S_2$$

This regeneration is repeated perhaps thirty times, before the quantity of sulphur is sufficient to interfere with the use of the oxide as a purifier. It contains as high as 60 per cent sulphur then, and is used as acid material.

NITRATE OF SODA

Nitrate of Soda, usually called Nitre, or Chile saltpeter, has been the source of practically all our nitric acid, and still accounts for the largest part of it, although the various fixation processes are making the nitrogen of the air available in ever increasing quantities.

Formula—$NaNO_3$; hardness, 1½ to 2; sp. gr., 2.09 to 2.39; the large crystals are colorless, transparent, and brilliant; small crystals white and opaque; crystallizes in rhombohedra; has a bitter, cooling taste; upon heating it first melts and then decomposes, at a red heat, into sodium nitrite and oxygen; fuses at 316°C.; and it dissolves very readily in water, with absorption of heat.

There are many known deposits of nitre, but the world's supply comes from northern Chile. There it is found under a cap, up to 7 ft. thick, of "costra," a hard conglomerate. The actual nitrate bearing ore, called "caliche," occurs in horizontal beds, up to 5 ft. thick, containing 45 per cent to 85 per cent of sodium nitrate, 20 per cent to 40 per cent sodium chloride, and sodium, potassium, and magnesium nitrates, sulphates, iodates, and chlorates, and guano. It is an old ocean bed.

The caliche is crushed and the soluble salts leached out; then the sodium nitrate crystallized out in a very pure form, carrying the chlorates and iodates, which are recovered during the nitric acid manufacture. The mother liquor retains most of the sodium chloride.

An average analysis of commercial Chile saltpeter is:

96.00 per cent $NaNO_3$ (including nitrate, iodate, etc.),
0.05 per cent NaCl,
0.75 per cent sulphates (calculated as Na_2SO_4),
2.75 per cent moisture.

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The imports of this material into the United States have grown steadily, from 125,000 tons in 1898, to 519,000 tons in 1910. About 80 per cent of this goes into commercial fertilizers, the remaining 20 per cent into our chemical industry.

Being deliquescent, the salt becomes damp and adheres to the bags it is shipped in, not only causing loss of nitre, but danger of fire, as the bags will ignite spontaneously. The bags are therefore usually washed out with hot water, and dried, the saltpeter being crystallized out of the water. The mother liquors from this crystallization contain $NaNO_3$, KNO_3, I, NaI, KI, $KClO_3$, 20 per cent to 30 per cent insoluble, water, and small quantities of borates and chromates.

The mother liquor is run into a wooden vat, equipped with a mechanical stirrer, and is slightly acidulated with sulphuric acid; the result is $NaHSO_4$ and I, from the iodates—now $NaNO_2$ is added, reacting as follows:

(1) $$NaNO_2 + H_2SO_4 = HNO_2 + NaHSO_4,$$

(2) $$2HNO_2 + 2HI = 2I + 2NO + 2H_2O,$$

Bubbling air through gives

(3) $$2NO + O_2 = N_2O_4,$$

which reacts with HI as

(4) $$N_2O_4 + 4HI = 4I + 2NO + 2H_2O,$$

and the reaction repeats.

Agitation is then stopped, and the liquor is allowed to settle over night, decanted, filtered, and washed with soda-ash. The product is a paste, running 75 per cent iodine and 25 per cent water.

The decanted liquor contains 0.02 per cent I, which is treated with sodium sulphite, to fix the iodine, so it will not pass off as a fume, and goes back to the bag house to be reconcentrated. The proper amount of sulphite is known to have been added when the color of the liquor changes from black to dark brown.

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CHAPTER V

PRODUCTION OF SO_2

By far the largest part of the sulphuric made is from SO_2 produced especially for that purpose. A very considerable tonnage, however, is made from gases which are by-products of certain metallurgical operations.

High grade brimstone is the ideal material for making SO_2 for acid manufacture. The equipment for burning it is comparatively small and inexpensive, and as it all burns, there is no expense for handling cinder. Moreover, a very rich and uniform gas can be obtained. Several very satisfactory brimstone burners are made and regularly marketed in the United States. The two most used and perhaps best suited for burning large quantities of sulphur, are the rotary type and the shelf type.

The rotary type is shown in Fig. 3. This burner is similar in appearance to the Bruckner or White-Howell roasters, except that no fire box is required.

Brimstone melts at a temperature below its combustion point, so whether it is in lumps or in powder or is run into the burner molten, is not important to the actual burning, although the condition in which it is to be fed will determine the nature of the feeding apparatus if it be a mechanical one.

If a pile is made of lump sulphur and a fire started at the bottom of the pile, the sulphur melting and running down will smother the flame; so a small depression is made in the top of the pile, a piece of oily waste lighted and thrown in, the sulphur begins to melt and run down to the bottom of the cavity and to take fire. The pool enlarges itself rapidly by melting down new sulphur, and soon the entire mass is burning but all on the top.

The molten sulphur is sticky, and this property is taken advantage of in rotary burners, of which the Glenn Falls Machine Co. makes the best known. This burner is a plate iron cylinder with cast iron truncated cone-shaped ends, mounted upon trunnions, horizontally, the sulphur and air going in at one end, the SO_2 and partly comsumed air, with a little vaporized sulphur, passing out at the other into a large fire-brick lined vertical cylindrical

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combustion chamber. In the combustion chamber entrance further air is admitted and the vapor of sulphur is completely burned. (See Fig. 3.)

The advantage of the rotating burner is that the molten sulphur sticks to the inside of the cylinder as it revolves and burns all the way around, which, with the dripping sulphur adds in small compass very largely to the combustion area and so increases the capacity. The burner revolves slowly, being adjusted to have the sticky film almost burned up when that portion of the side of the cylinder dips into the molten sulphur again.

FIG. 3.

The labor of attending these furnaces is very light. One man can easily feed two of them with a shovel in addition to looking after oiling, adjusting dampers, and all other operation. If the sulphur is supplied to the burners by mechanical means they require very little attention. The sulphur may be fed, in either the solid or molten state. If solid, the material is carried into the burner from a small hopper by a short screw. If molten, an iron tank containing a steam coil is placed somewhat above the burner, the molten sulphur is carried to the burner through a steam-heated pipe, and the flow controlled by a steam-jacketed valve. Either method works well if properly handled.

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Control of the quality of gas and its volume lies in the handling of dampers at the feed end and the entrance to the combustion chamber, and in the quantity of sulphur fed. The production of gas of the grade most desirable for making sulphuric acid, *i.e.*, not over 10 per cent SO_2 is not at all difficult. The chief trouble which occurs in the operation of sulphur burners, especially in producing high strength gas, is that if dampers are not properly adjusted some sulphur vapor may go through the combustion chamber without being burned. This sulphur on being cooled in the flues or in the towers becomes solid and chokes the passages.

Rotary burners are regularly made in sizes with capacities ranging from 200 to 300 lb., to 15 tons per 24 hours. Floor space 12 ft. by 40 ft. will accommodate even the largest size mentioned. The power consumed in driving them is very small.

Rotary type burners have been likened to Bruckner roasters, and the shelf type may properly be said to resemble the McDougall roaster. It employs the superimposed tray or hearth construction. Of course a stirring mechanism is unnecessary because the sulphur is molten and simply overflows one tray and drops to the next and so on. A burner of this type is shown in Fig. 4. It consists essentially of a cylindrical cast-iron or steel, brick-lined chamber containing several cast-iron hearths or trays. At the top is a chamber or reservoir into which the sulphur is charged and in which it melts. A valve in the bottom of this chamber controls the flow of molten sulphur into the burner proper.

In operation a charge of sulphur is put into the top reservoir, a fire is started in the tray immediately below and allowed to burn until the sulphur starts to melt. The valve is then opened and the molten sulphur trickles in and ignites. Any part not burned on the first tray overflows to the second, and so on. Most of the ash and dirt is carried by the flow to the bottom pan. Doors are provided however to give access to any hearth.

In capacity range these burners are regularly made to burn up to 10 or 12 tons of sulphur per 24 hours. The manufacturers point out the following advantages for this type of burner:

1. No moving parts or power required.
2. Small floor space. A 9-ft. diameter cylinder burns 10 to 12 tons per 24 hours.
3. Better heat conservation than any other type.

As mentioned before, brimstone burning allows the production

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of very rich and uniform gas. The percentage of SO_2 is limited by the fact that for either chamber or contact work a certain minimum oxygen percentage must be maintained. This oxygen percentage should be at least per cent $\frac{SO_2}{2} + 4$, since one volume of SO_2 requires ½ of one volume of oxygen to form SO_3, and about 4 per cent excess is desirable. Since air contains about 20.8 per cent oxygen, the sum of SO_2 and oxygen in the gas from the burner will be 20.8 per cent. The maximum SO_2 then should

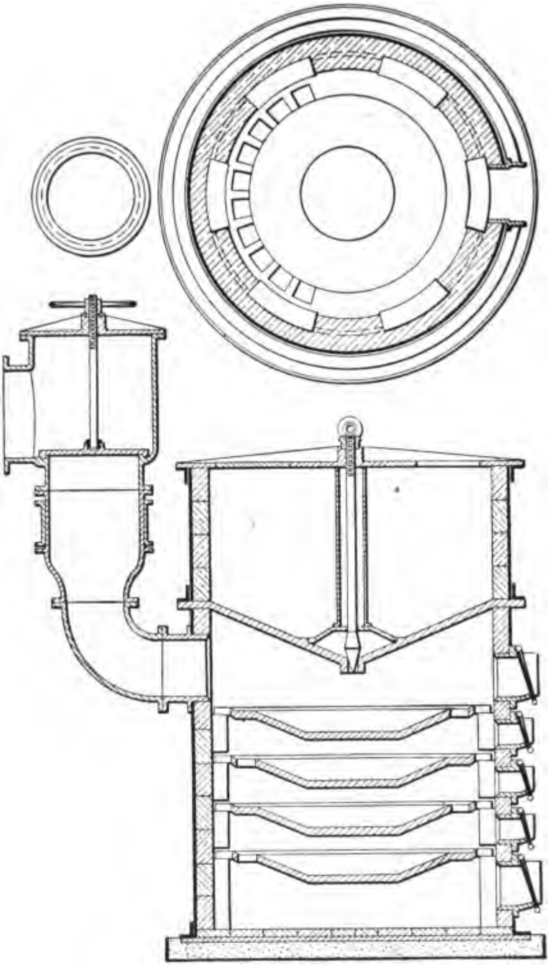

FIG. 4.

be, in accordance with the above proportion, 11.2 per cent and oxygen 9.6 per cent.

BURNING PYRITES

Iron pyrites, when pure, has the formula FeS_2, and contains 46.7 per cent iron and 53.3 per cent sulphur. It is never obtained entirely pure, although material containing over 50 per cent sulphur is sometimes found. The general range is from 40 per cent to 50 per cent sulphur.

Sulphides of the metals burn in air, with the production of the metallic oxides and SO_2; and if the operation, called roasting, is not complete, intermediate sulphates and bisulphates.

Iron pyrites when roasted gives off of its FeS_2 nearly one atom of sulphur very easily. At comparatively low temperatures the sulphur burns at once to SO_2 leaving behind Fe_7S_8. At higher temperatures it is at first volatilized as a dense cloud of yellow smoke, and then burns to SO_2. At the second stage of the process begins the oxidation of the iron in the ore along with that of the remaining sulphur. This is much slower and less vigorous than the burning of the primary atom of sulphur, and as the various iron oxides formed are fairly active catalytic agents or "contact substances," a considerable quantity of SO_3 is formed at this stage. For purposes of calculation the net result of these reactions may be written:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

Pyrites is obtained and burned in two different forms, viz., as lump pyrites and as fines. The former is material in pieces from the size of the fist down to about ¼ in. Fines is material under ¼ in. These two classes are burned in distinctly different forms of burners.

The lump burners used in this country are quite simple. The general scheme is similar to the burning of lump coal on grates except that the bed of fire is carried much deeper, *i.e.*, around 2 ft. Fines in any appreciable amount are not permissible as they prevent free draught. In brief, a single burner consists of a brick box up to 6 ft. long from front to back, and 4 or 5 ft. wide. It is divided by a grate into an upper or burner compartment, and a lower or ash pit compartment. A charging door is placed at such a level above the grate as to allow a bed of ore about 2 ft. deep. A small door at the grate level allows the grates to be

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shaken. A door in the ash pit provides for removal of cinder. Grate bars made of cast iron, of square section about 2 in. on a side are used. They are supported by cast-iron bearers at two or three points. The bars are made with circular section at the points of support in order that they may be turned. When their diagonals are set vertical and horizontal a considerably smaller space exists between them than when they are turned with their diagonals 45° from horizontal. By turning the bars from one position to the other with a wrench the lumps are crushed and the shaking out of the spent cinder is accomplished. Figure 5 shows the general features of a lump burner and grates.

Most of the modern plants using the lump burner have improved its details making it tighter and more convenient to operate. Burners are now made practically encased in steel or cast-iron plates. Door frames and doors are planed to give tight joints without using putty. In some cases the ash pits discharge into cars in a tunnel below the burner set. These improvements have made labor less and gas more uniform, but the nature of this form of burner demands a considerable amount of hand labor which cannot well be eliminated.

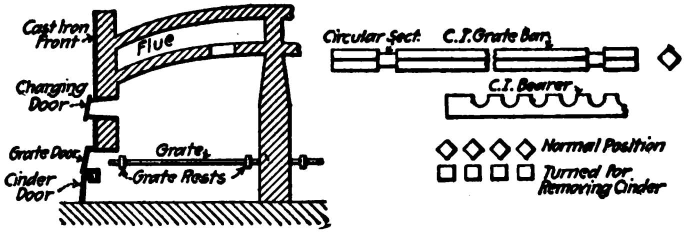

FIG. 5.

The capacity of a burner depends somewhat upon the sulphur tenor of the ore and its melting point. High grade pyrites containing little copper can be burned to give much more SO_2 per unit of grate area than low grade ore high in copper or which contains pyrrhotite; in other words ore of low fusing point. We cannot in any event expect to get much more than one ton of 60° acid from one good sized burner. Driving a burner too fast causes fusing and sticking and much hot laborious effort to clean.

It will be seen that to provide gas for a large set of chambers the ground area and buildings required for lump burners is very great. Lump burners are built in blocks back to back and consisting of almost any number desired. Sets of 24 to 30 are

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common, and some up to 40 are to be seen. To decrease ground area the obvious thing to do would be to carry greater depth of ore on the grates. This presents several difficulties however. Heat would get too high if rate of burning per square foot were increased. Shaking out cinder uniformly would be uncertain. If fusing occurred, cleaning would be difficult. Burning of lump pyrites is practiced almost entirely on acid units of not over 50 tons 60°Bé. acid daily capacity.

INSTRUCTIONS FOR STARTING LUMP BURNERS

Be sure the brickwork is not too green upon starting. The moisture should be dried out of the bricks by means of a very light fire in the bottom before starting up.

Uniformity of size of charge is important and money spent on this will pay well.

First clean out the furnaces thoroughly; see that the top flues are clean; put in the grate bars. See that all doors are in place. Manhole doors should have a thin joint of tar and fireclay.

The top buckstay rods should not be too tight, which is readily seen by striking them with a hammer, so as to allow for expansion as the furnace heats up. This must be watched carefully.

Before putting a fire in the furnace provision should be made for taking off the smoke, which is best done by means of a temporary stack on the uptake to the Glover tower, over the opening in one of the top plates. This stack should have a tight damper in it so it will not be necessary to remove it when its use is discontinued.

The damper in the Glover flue must be closed to prevent smoke from getting into the system. It is necessary to cover the grate bars with something like pyrites cinder to protect them from warping. If cinder is not to be had, broken stone or brick will do. Spread out this protector a foot thick except in the corners, where it should be 15 in. A wood fire is then started in each furnace on top of the cinder. The fire is kept burning until the whole interior is well warmed up and there is a bed of red ashes over the entire area of the furnaces. The fire is then increased until the interior of the furnaces is red hot, including the top of the bed of cinders.

The best material for firing is oak or hickory as these make little smoke. Broken coke and coal are used but as these make a very

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hot fire, care must be taken that no clinkers are formed with the cinder. If any are formed they must be removed before changing ore.

As the mass of brickwork and iron is bound to expand as it heats up, the buckstay rods must be loosened from time to time. A tap with a hammer shows if they are too tight, a hard metallic ring indicating that they should be slacked off. Do not loosen them too much as it is hard to tighten them again owing to the great pressure of the arches, which may crack in consequence. Care must be taken that a furnace does not get hot too quickly. Firing should take 30 to 36 hours for a new furnace, less time being required for an old one being restarted.

After the final heating the wood should be burned off about the same time in each furnace, leaving a bed of hot embers. Before ore is charged withdraw any unburned fuel, at the time making sure there is no matte where the main fire was. Distribute the hot embers evenly then charge sufficient pyrites to cover the whole grate. The pyrites should be placed in front of the furnaces beforehand so that no time is lost in charging, for it is very important that they go in quickly before the furnaces lose heat. This is best done by having several men charging at the same time. When the charges are in, the gas can be turned into the system. When the first charge is burning well, the furnaces should receive a second charge so as to insure a sufficient quantity of ore in the furnace to prevent any possibility of running low and losing its heat.

The gases leaving the furnace contain for a time some carbon dioxide in addition to SO_2, due to the residual fuel. It is highly important to charge the furnaces with clock-like regularity. For example, if there are 24 furnaces one will be charged every hour or every half hour as desired. A regular schedule is followed in any event. The charging time of each furnace should be marked upon it.

FINES BURNERS

Fines burners are by far the most used and most important of the apparatus for producing SO_2 for making sulphuric acid. The main reasons for this are:

1. Large capacity with small ground area.
2. Charging ore and discharging cinder are continuous and are accomplished without opening the furnace, and the gas is in consequence uniform.

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3. Handling of ore and cinder are done by machinery, practically eliminating hand labor.
4. Several well-designed and satisfactory furnaces are on the market and can be bought practically from stock.

In the early days of acid making pyrites fines were burned in the crudest way. The favorite method was on a brick hearth, the pyrites being fed by hand with shovels, and rabbled by hand. This method produced cinder high in sulphur and most ununiform, besides being very costly in labor.

The first improvements over the hand method in rabbling were along the line of mechanical rabbles in the form of plows which were dragged through the furnace on a chain, pulling the ore along with it and turning it over, giving a much better roast with lower labor costs. But to get a complete roast the temperature had to be high and maintenance costs were heavy. Also the plows were heavy and the wear on the hearths considerable.

The next step was an annular furnace with arms branching out from a revolving central axis, the arms carrying rakes for stirring the ore. The roof of the furnace had to be supported from the outside as the arms entered the furnace through a slot in the inner wall. A great deal of air entered through this slot so it was often covered by an iron apron revolving with the arms.

In 1868, McDougall introduced his circular multiple hearth furnace. The McDougall furnace consists essentially of a cylindrical steel shell lined with about 9 in. of brick and containing several self-supporting arched brick hearths. Through the center of the furnace runs a vertical iron shaft or column. To it are fastened horizontal iron arms, one, two, or even three to each hearth, and these bear iron rabble teeth. This shaft with its arms is supported on a bearing beneath the furnace and in operation is revolved slowly. Alternate hearths have drop-holes near the central column and near the outside wall. The rabble teeth stir the burning ore and move it across the hearths so that it passes uniformly down through the furnace, crossing each hearth and falling to the one below.

The original McDougall furnaces did not include any provision for keeping the shaft and arms and rabbles cool, and this was probably the chief reason that the furnace gave trouble and was not more widely used for many years. Mr. J. B. F. Herreshoff

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of the Nichols Chemical Co. on investigating the problem built a furnace with a hollow iron shaft and hollow arms, and blew cold air through them, in that way keeping the temperature of the metal at such a point that its strength was not impaired. Herreshoff also arranged to admit controlled amounts of the heated air issuing from the shaft and arms, into the hearths at any desirable points. Frasch also applied water cooling to the hollow shaft and arms.

Other improvements and refinements have been made on the McDougall furnace and we find to-day that the name McDougall has largely disappeared, and these furnaces are known by the names of those who have made the modifications.

The chief differences in the furnaces of this type now on the market are in the shafts and arms, and the following classification is made on that basis:

1. Furnaces having water-cooled shafts and arms.
2. Furnaces having air-cooled shafts and arms.
3. Small shaft furnaces, *i.e.*, shafts into which a man cannot enter.
4. Large shaft furnaces, *i.e.*, shafts large enough to allow a man to enter and work.

In roasting any of the pyritic materials suitable for acid making it should be understood that furnace temperatures, *i.e.*, temperatures of gas, ore, and brickwork, are influenced only to a small extent by either the air or water which may be circulated through the shaft and arms. This statement applies in greater degree to large than to small furnaces. The prime function of the air or the water is to regulate the temperature of the iron parts themselves. A rough heat balance sheet of a roaster burning a pyritic ore of moderate sulphur tenor is interesting in showing the disposal of the heat units.

As this balance is intended to show only the relative amounts of heat going to the various products, etc., rather than acutal heat units, only the iron sulphid is considered.

This ore contains 34.7 per cent S as FeS_2.

The calcine contains 7.0 per cent S.

The calcine weight is 80 per cent of that of the ore from which it is made.

For each 100 parts of ore there is burned 34.7–80 per cent of 7 or 29.1 parts of sulphur

Assume that one half this is "volatile atom" and its dissociation heat requirement is negligible. The heat evolvers are then:

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29.1 parts S to SO_2 @ 2,170 calories = 63,200
29.7 × 1.75 parts Fe to Fe_2O_3 @ 1,750 calories = 44,500
Total calories per 100 parts ore = 107,700

Heat is absorbed by dissociation of FeS.

40 FeS @ 273 calories = 10,920
Net calories evolved per 100 parts ore = 96,780

Assume that the furnace roasts 100 lb. ore per minute and that the gas issuing from it contains 9 per cent SO_2, 8 per cent oxygen and 83 per cent nitrogen.

29.1 lb. S make 320.6 cu. ft. SO_2. Total gas per minute then = 3,562 cu. ft. Assume the air enters the furnace at 20°C. and the gas leaves it at 620°C. Then the heat carried away by the gas is:

SO_2....... .09 × 3,562 (.0226 × 600 × .0000187) = 10.80
O........ .08 × 3,562 (.0189 × 600 × .0000017) = 5.65
N........ .83 × 3,562 (.0189 × 600 × .0000017) = 59.80

Calories per degree.............................. 75.35

Calories for 600° = 45,210.
Calcine from 100 lb. ore = 80 lb.

The ore enters the furnace at 20°C. and the calcine is discharged at 420°C. Heat carried away by calcine is 80 (.1456 × 400 × .000188) = 17.664 pound calories per degree. Calories for 400° = 7,066.

This furnace is assumed to be air cooled. There are 1,000 cu. ft. per minure of air at 20°C. blown in through the arms, and this air issued at 220°C. Calories carried away by this air = 3,848.

RECAPITULATION

Total heat envolved =		96,780 calories
Heat to gas	45,210	
Heat to calcine	7,066	
Heat to air	3,848	
Total accounted for		56,124
Balance for radiation		40,650

Radiation surface of the furnace, 2,200 sq. ft.
Loss per square foot per minute = 18.4 lb. calories.

This calculation shows that the two chief ways in which the heat is carried off from a roasting furnace are by the gas and by radiation. The heat units carried away by the cooling medium circulated through the shaft and arms, and by the calcine, are

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insignificant. As the radiating capacity of a furnace once built is not variable at will, it is apparent that control of furnace temperature must lie in feed of ore and volume of air admitted.

When air cooling of the iron parts can properly be used it is to be preferred over water cooling for several reasons. When water is used for cooling, the temperature of the arms is so low that the iron becomes sulphated and the rabbles soon become cemented to the arms and can often be removed only by breaking. With air cooling, the temperature of the metal is usually so high that this sulphating does not occur. Another advantage is that slight leaks at joints or chaplet plugs do no harm if air cooling is employed, while with water even slight leaks cannot be tolerated. Often a water-cooled arm must be removed on account of a persistent small water leak where an air leak of the same size would scarcely be noticed.

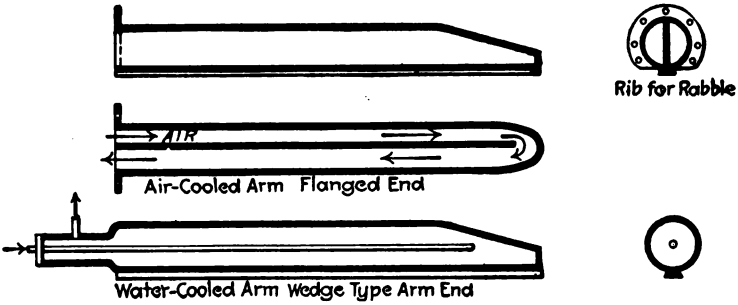

FIG. 6.

Air-cooled arms and shaft must have much larger passages in them than necessary when water is used for cooling. Indeed the success or failure of air cooling depends much upon whether or not the passages are of ample area. The thickness of metal in air-cooled arms is less than in water-cooled arms.

Figure 6 shows the essential features of an air-cooled arm with flanged end for bolting to shaft, and a water-cooled arm with end-detail as used in the Wedge furnace.

The other major difference in the McDougall types is in the large and small central columns. Until the advent of the Wedge furnace all the McDougall furnaces had small central columns, *i.e.*, not above 18 or 20 in. diameter, and hence too small for a man to enter. When anything became wrong with an arm which necessitated replacing it, it was necessary to stop the furnace and allow it to cool down enough to permit men to enter the hearth, unfasten the bad arm from the shaft and fasten on a new one. This always required several days and meant that the furnace had to be restarted with fuel. Such a loss of time is a serious thing to an acid plant, especially if a single furnace is being depended upon.

Many attempts have been made to devise arrangements whereby arms could be replaced without cooling and entering the hearths. It is not difficult to do this if air cooling or no cooling is sufficient. If water cooling is necessary and water-tight connections have to be made it seems impossible unless one can get at the inner end of the arm, which with the small column furnace means getting into the hearth. While this feature of the small shaft furnaces is disagreeable, it should not be overestimated. Well made arms properly taken care of last for long periods, and there are other things beside failure of arms which demand cooling down a furnace at times, failure of brickwork for example. It is often possible to get along with a sick arm for a time until a general overhauling is desirable.

Small column furnaces of which the Herreshoff is an example have their columns made up of cast-iron sections flanged together. When water cooling is used a water supply pipe extends down the middle. It is provided with a tee fitting corresponding to each arm, into which is screwed a pipe which extends well out toward the end of the arm. The water enters the arm through this pipe and returns around it into the annular space in the column. Usually the arm itself has a flanged end which is bolted to a corresponding flange on the column casting. There are variations in this method of fastening but the flange is most used.

For air cooling a partitioned arm, as shown in Fig. 6, is used and an interior column construction as shown in Fig. 5.

The Wedge furnace, shown in Fig. 6*B*, is the only furnace made with the large column. This column is 4 or 5 ft. in internal diameter, built of steel plates riveted together, and covered on the fire side with fire brick and insulating material. The arms project through the wall of this column and are fastened inside. The air or water connections are likewise inside the column. It is a simple matter in case of the failure of an arm for a man to enter the column immediately, disconnect the pipes, and loosen the latch. The arm can then be pulled out and a new one in-

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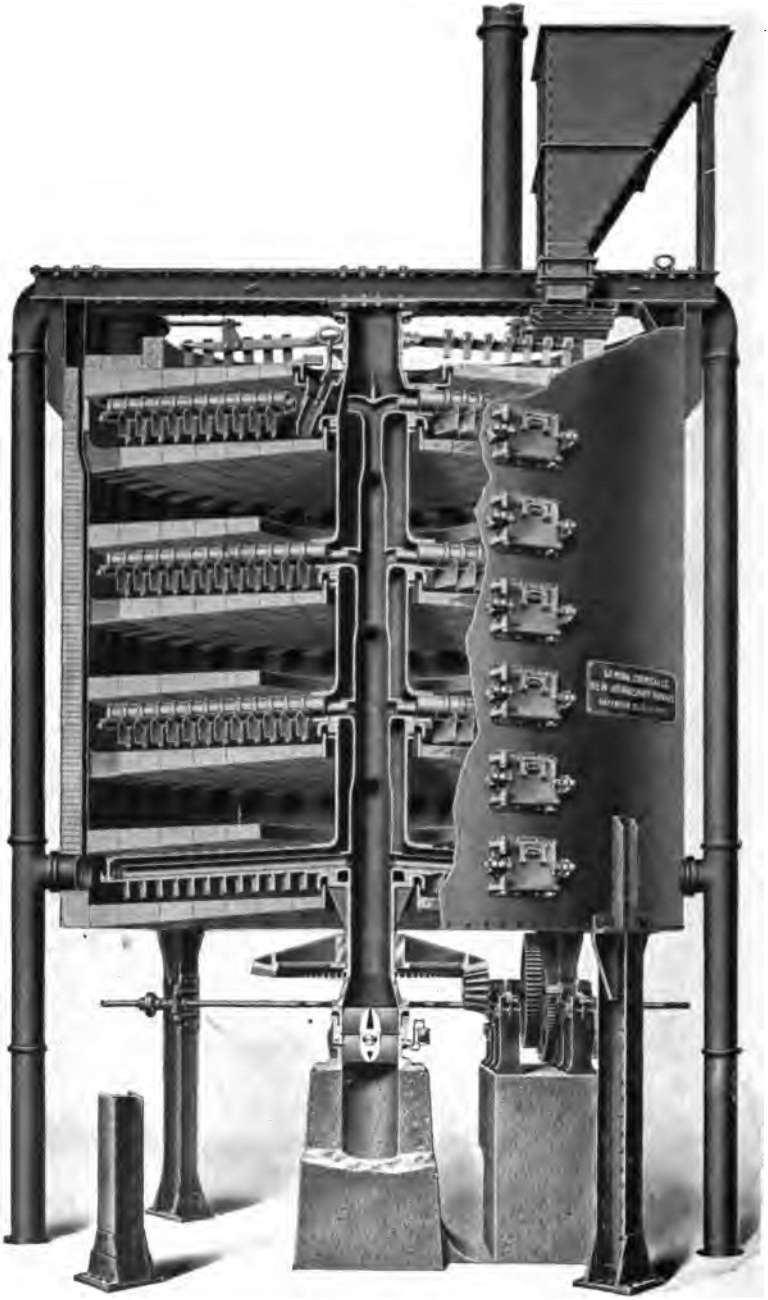

FIG. 6*A*.—Herreshoff furnaces.

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serted and connected. It is not a pleasant job because the inside of the column is decidedly warm, but it can be readily and safely done by any men who are reasonably accustomed to furnace work. There are certainly many more severe tasks about metallurgical furnaces. If proper arrangements are made an arm may be removed and a new one inserted and connected ready to go in 4 hours.

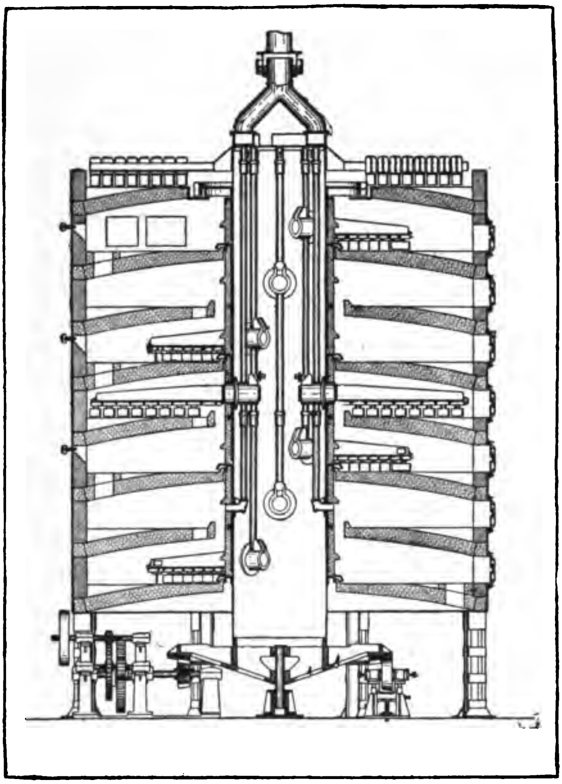

FIG. 6*B*.

One feature of the large column which has given some trouble is the carrying of the great rotating weight in a satisfactory way. The customary design for the larger sizes provides a set of six large beveled rollers upon which the cast spider carrying the column revolves. In the middle is a small guide bearing. The trouble with this arrangement is in maintaining the shaft plumb, and the load equally distributed upon the rollers. The side

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thrust causes some wear of the rollers and their thrust bearings, which is not equal all the way around. As soon as one roller is further away from the center than the others it ceases to carry its proper share of the load, or else the shaft goes out of plumb. This cannot be said to be a very serious fault, but it makes the arrangement less satisfactory than the old step bearing.

In the 25-ft. furnaces of this type erected at Anaconda a few years ago, the columns are supported on 9-in. step bearings of very rugged construction. The column is held plumb by a set of vertical rollers bearing against a ring fastened around the top of the column.

Fines burners are started by bedding the upper floors with ore then heating with wood, coal, oil, gas, or powdered coal, with the mechanism stationery. When sufficiently heated the floors are cleared and the mechanism started with a light feed of ore. It is usually necessary to use a little fuel for a time after starting feed. The variables used in the control of a furnace are amount of ore fed, and volume of air admitted, also sometimes the rate of revolution of the arms. The usual speed of revolution is from 1 to 2 R.P.M. The operation is watched through peep-holes. A 15-ft. (diameter) furnace requires one horse power.

BY-PRODUCT GAS FROM COPPER REDUCTION WORKS

About one-half million tons per year of acid is made from gases evolved from the reduction of copper ore. The only two sources of such gases at present are roasting furnaces and blast furnaces. The roasting furnaces used at copper reduction works in connection with acid making are all of theMcDougall type, and of several different makes, embracing all the types described above. The materials roasted show wide range and are all materially different from the pyrites ores regularly bought for acid making. However as the gas used is really a waste product and no charge for sulphur is made against the acid, these acid plants can well afford to work with less favorable ores.

The chief difference between the materials available at copper reduction works and the ordinary ores is that the former are lower in sulphur and higher in copper, are of irregular analysis, and are often exceedingly fine. While pyrites ores range from 40 per cent to 50 per cent sulphur and contain little copper, the ores and concentrates used at copper works range from 25 per

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cent to 40 per cent sulphur, and contain up to 12 per cent or 15 per cent copper. Moreover at some plants the sulphur content of the material varies 5 to10 per cent from day to day.

The copper-iron sulfide, and the copper sulfide minerals fuse at a considerably lower temperature than does straight pyrites, so in roasting copper ores and concentrates accretions are found to form on the brickwork and on the shaft of the furnace much more than they do when roasting pyrites. This fact makes it necessary to watch the furnace temperatures carefully or serious formations of matte may occur. A good deal of barring and plowing of the hearths is necessary even with the most careful attention.

As the cinder from the roasted copper ore is usually treated in a reverberatory furnace to make a copper matte, some sulphur should be left in the cinder. For example at Anaconda where the copper content of the cinder is about 10 per cent, it is desirable to leave about 7 per cent sulphur in the cinder to make matte.

THE BLAST FURNACE

The blast furnace is a very unusual source of SO_2 for acid making. The only place in this country where it has been used is at the reduction works of the Tennessee Copper Co. and the Ducktown Sulphur, Copper, and Iron Co., in the Ducktown district in southeastern Tennessee. There exists a peculiar set of conditions there which will rarely be duplicated, but the tonnage of acid produced is so large, and the plants themselves present so much of interest in their construction and operation, that some description of the operations is in order.

The ore treated at these works is a heavy sulfide carrying substantially:

	PER CENT
Copper	2.5
Iron	30.0
Sulphur	20.0
Insoluble	30.0
CaO, MgO	10.0
Zinc	3.0
Al_2O_3	3.0

This ore is treated directly in blast furnaces with no preliminary dressing or concentration whatever. It is very near self-fluxing when making a 15 per cent copper matte, and it can be smelted with about 5 per cent coke. This permits the production

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of a gas containing 7 per cent to 8 per cent SO_2, 5 per cent to 6 per cent CO_2, and about 3 per cent to 4 per cent oxygen.

At the time the first acid plants were built, about 1907, no experience was available to say what could be done with such gas. However it was necessary to undertake the manufacture of acid because the United States Supreme Court had enjoined the smelteries from allowing to escape more SO_2 than the state of Georgia deemed reasonable. The redeeming feature of the situation lay in the fact that Ducktown basin is in the heart of that portion of the country which consumes the greater part of all the acid phosphate fertilizer made in the United States, that is to say there is an excellent market for sulphuric acid.

For some time after the completion of the plants troubles of various kinds were experienced and many curious phenomena arose. The chief differences between this blast furnace gas and the gases usually used for making sulphuric acid are the high CO_2 content and the low oxygen. It was necessary to revise ideas about the oxygen content of exit gases, or else if the customary 6 per cent were maintained there, to take a gas entering at about 2 per cent to 3 per cent SO_2. One solution of this devised at the Ducktown plant, was to adjust the gas entering to contain about 3 per cent oxygen, and to introduce air into each chamber sufficient to maintain 3 to 4 per cent oxygen at all stages of the process. Working without this arrangement the best way seemed to keep the oxygen in the exit gases above 2 per cent and get as good SO_2 entering as that would allow.

It should perhaps be explained that in near-pyritic smelting the gases issuing from the charge contain almost no oxygen and if the furnace top and flues are tight the gas entering the acid plant contains only such oxygen as may be voluntarily admitted.

The high percentage of CO_2 in this gas along with the unusually low oxygen makes the reactions in the chambers very sluggish. In order to get reasonable tonnage from the plant is is necessary to use much more than the normal nitre circulation and this in turn tends to make high nitre loss.

A very serious feature of the blast furnace work is the irregularity of the gas due to the mode of operating the furnace. It is necessary to open the furnace top several times an hour to charge and barring and cleaning are necessary every day. If the flues are dampered so as to cause some pressure at the furnace top, the working conditions on the charge floor are

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almost impossible. If suction is maintained, every time the furnace is opened false air rushes in and dilutes the gas. In spite of these difficult conditions these acid plants must be considered very successful both technically and financially.

COPPER CONVERTERS

It has many times been suggested that the gases from copper converters might be used for making acid, but as yet this has not been attempted.

Taken without modification the gas from a single converter ranges in a period of a few hours from almost no SO_2 to perhaps 20 per cent. As a reasonable approach to uniformity is a necessity in the chamber process, such a gas would not do. It may be possible with a battery of several converters working on a schedule and equipped with tight hoods and dampers to get a workable gas. It must be said that the converter is not an attractive source of gas for acid making, although perhaps a not impossible one.

SO_2 FROM ROASTING ZINC ORES

In the reduction of the sulfide ores of zinc it is necessary to roast off sulphur, and the gas so produced is utilized in making sulphuric acid. The zinc reduction works in this country are usually so located geographically that the sulphuric acid produced is readily marketed.

In roasting zinc sulfide ores preliminary to distillation for metal it is necessary to convert, as nearly as possible, all the zinc to zinc oxide. In order to do this certain temperature and oxygen percentage figures must be observed which make the roasting operation more difficult and the gas less favorable for acid making than in roasting pyrites.

The essentials of this are that in roasting zinc sulfide some sulphates of zinc form; these are not broken up completely at temperatures much below 900°C.; after the sulphur content of the roasting ore is down to about 8 per cent it no longer burns with sufficient vigor to maintain a roasting temperature, much less a temperature sufficient to break up the sulphates. It is therefore necessary at the later stages of the roast to add heat by means of the hot gases from burning carbonaceous fuel. As this fire gas would be a serious diluent of the roaster gases going to the chambers, it is kept separate from the latter.

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The roasting furnace most used in this country for zinc roasting in connection with acid chambers, is the Hegler furnace, first used at the Matthiesson and Hegler works, LaSalle, Ill. The Hegler furnace is a multiple hearth, rectangular furnace, with the lower hearths of muffle construction. The ore is moved longitudinally over each hearth falling to the one below. The rabbles mounted on frames of steel shapes are drawn through the hearths by means of long rods. After each passage through, the rabbles are drawn clear out of the furnace and allowed to cool for a short time. Their temperature therefore never becomes high enough to impair their strength and rigidity. The latest Hegler furnaces have seven hearths, and producer gas is used to heat the muffled hearths in the lower parts of the furnace.

In order to properly roast zinc ores a plentiful supply of air must be allowed to pass over the roasting ore, *i.e.* the oxygen percentage must be kept well up. Observing this requirement then, the gas going to the chambers contains only 4 to 5 per cent SO_2. There is of course some dilution due to rabbles entering and leaving the furnace and to the doors leaking air.

BURNING PYRITE CINDER

Even with the most careful handling some where about 2 to 3 per cent of sulphur will remain in the cinder from roasting pyrites. This causes two losses, that of the sulphur, and that of the market for the cinder as iron blast furnace material, as with so high a sulphur content good iron is an impossibility, and many acid plants have a potential market for their iron "ore." The Dwight & Lloyd sintering machine, as sold by the American Ore Reclamation Co., 71 Broadway, New York City, overcomes the twin difficulties of high sulphur content and fineness, and is best described by the company as follows:

"Sintering is a comparatively recent art in the iron industry. It is the process of agglomerating fine ore material into a mass that is suitable for blast furnace use. Sintering may be illustrated as the making of flour into biscuits. With the use of the fine ores from the Mesaba Range in Minnesota and the resulting making of flue dust at blast furnaces, many attempts were made to recover the valuable iron in the flue dust by briquetting. This means of treatment has not proven very satisfactory, since, to secure a firm bond, the process is expensive, and when the bond is fickle the briquettes quickly return to dust.

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"The briquette is a porous mass and the spaces are filled with air, so that the mass must be heated first to expel the air to allow the reducing mass of the furnace to come in contact with the ore particles, which delays the reduction and the mass is easily disintegrated into dust. Sinter made by the continuous down draft process is cellular in structure, providing an open and large area of contact between ore and reducing gases; and as the cell walls are quickly heated to the temperature required for reduction, an economy in coke consumption results from the use of sinter.

"To quote Shinz's law (in his "Action of the Blast Furnace"): 'A chemical action can only take place between two bodies, however great their affinity, if they are in intimate contact with each other and the rapidity of this action will be much greater the more numerous the points of contact are.' The material which provides the greatest area of contact is more readily and economically reduced in the furnace.

"The iron-bearing materials treated by sintering include blast-furnace flue dust, roll-scale, magnetite concentrates, magnetic sands, high sulphur ore, pyrites cinder, etc. Any finely divided ore or ores, containing high sulphur or high moisture and combined water, can be converted into ideal material for use in the blast furnace. Flue dust sludge from blast-furnace gas washers may be sintered by adding the sludge to a dry sintering mixture instead of moistening the charge with water.

"Sintering was first applied in the iron industry to the reclamation of flue dust, but it has since widened out into other fields and demonstrated its adaptability for treating pyrites cinder, magnetic ore concentrates, and other fine ores or hydrated ores.

"A plant installation is made up of two main parts, the sintering machine proper, and the raw materials plant, both forming a unit, of which the former is more or less standardized, but the latter made to conform to local conditions and materials. The following is a description of a typical plant.

"The materials to be sintered are delivered to a series of bins, the number and size of which depend on the kind and quantity of materials to be treated; or the raw materials may be dumped from the cars into a pit and transferred to the bins by a grab bucket.

"In the case of flue dust the screening of it is necessary, and a considerable quantity of coke is recovered for furnace use.

"The bins are fitted with feeders of a special type which are driven as a group in synchronism with the sintering machine. The required composition of the sintering mixture is made up by adjusting the feeder gates and the total amount of sintering mixture delivered by the feeders is adjusted to suit the needs of the sintering machine at various speeds. The sintering mixture is carried to, and thoroughly mixed and moistened in, a pug mill or other mixing device, and is delivered onto the grates of the sintering machine in a continuous layer of desired thickness and

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uniform permeability. This continuous layer is moved under an ignition burner where the fuel in the upper surface of the layer is ignited and the charge then continues its movement over a wind box connected to a suction fan which draws air down through all parts of the charge and the sintering action is progressive through the whole depth of the layer down to the grates. At the end of the sintering machine the sinter is discharged over a grizzly screem which thorouhly separates all fines from the sintered material and the fine sinter is returned to the sintering machine to increase the permeability and thereby the rate of sintering is increased."

The whole operation of regulating the feeding of material and speed of sintering is controlled by a single lever.

SINTERING MACHINES

Capacities of the three machines made by the Dwight & Lloyd people are as follows, all in tons per 24 hours:

Material	Type A	Type B	Type C (two strand)
Flue dust	125–150	260–310	550–650
Pyrites cinder	150–175	300–375	650–750
Magnetic concts	175–200	350–400	750–900

Pyrites cinder and high sulphur ores are sintered and desulphurized in one operation. The cinder contains from 1.5 per cent to 5 per cent sulphur, and is reduced to 0.10 per cent to 0.15 per cent in the sintered product. About 8 to 10 per cent fuel is required.

Contents	Pyrites cinder, per cent	Sinter, per cent
Iron	56.28	61.00
Sulphur	4.41	0.07

Mixture of Pyrites Cinder and Flue Dust

Contents	Pyrites cinder, per cent	Flue dust, per cent	Average mixture, per cent	Sinter
Iron	56.28	33.00	46.97	57.10
Sulphur	4.41	0.18	2.72	0.12
Carbon	......	24.00	9.60	......

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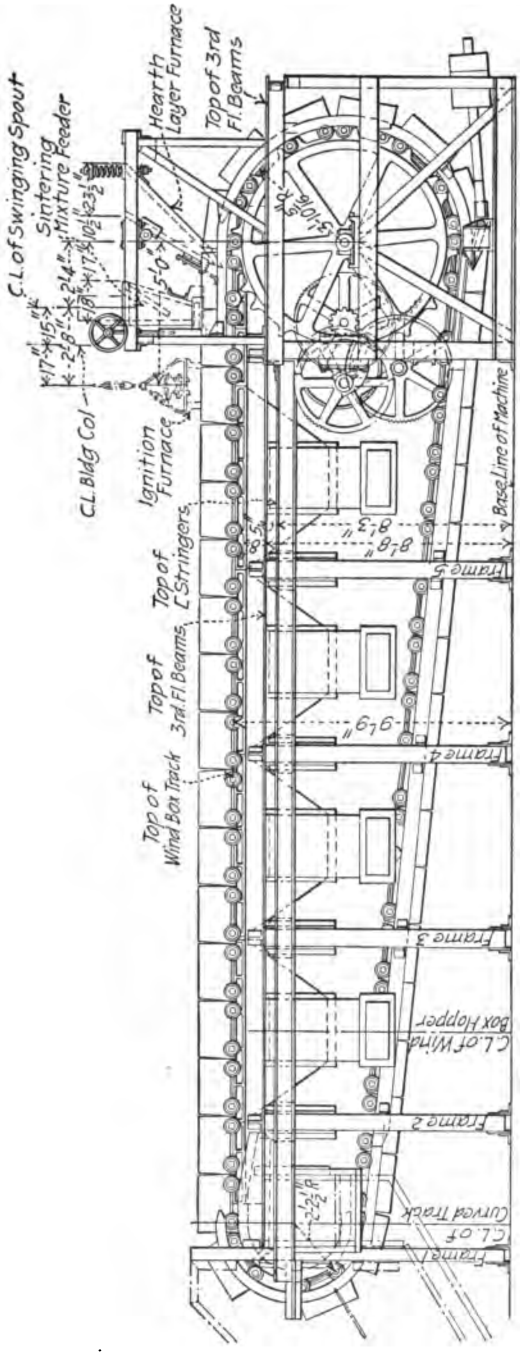
C.L. of Swinging Spout
Sintering Mixture Feeder
Hearth Layer Furnace
Top of 3rd Fl. Beams
C.L. Bldg Col
Ignition Furnace
Top of C Stringers
Top of 3rd Fl. Beams
Top of Wind Box Track
Base Line of Machine
Frame 5
Frame 4
Frame 3
Frame 2
Frame 1
C.L. of Wind Box Hopper
C.L. of Curved Track
17" 15"
2'-8"
24"
17½" 10½" 23½"
5'-0"
3'-10 9/16"
8'-3"
8'-8"
9'-9"
2'-1½" R

Fig. 7.

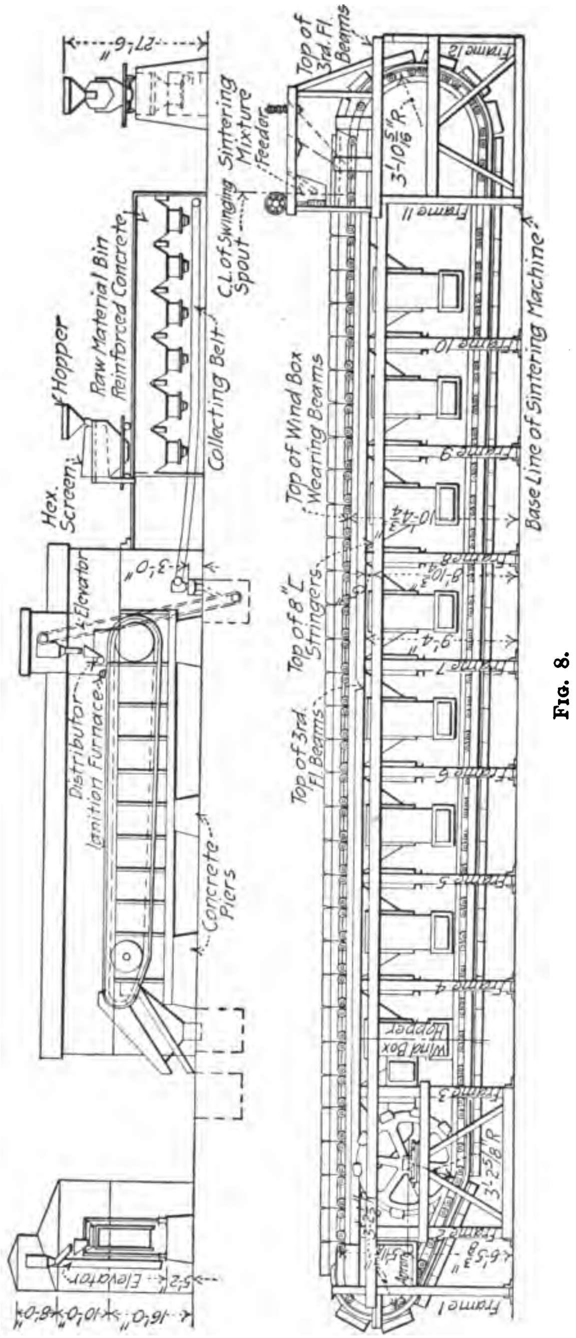
27'-6"
Hopper
Hex. Screen
Raw Material Bin Reinforced Concrete
Collecting Belt
C.L. of Swinging Spout
Sintering Mixture Feeder
Top of 3rd. Fl. Beams
3'-10 5/16" R.
Frame 12
Frame 11
Elevator
3'-0"
Distributor
Ignition Furnace
Concrete Piers
Top of Wind Box Wearing Beams
Top of 8" ⊏ Stringers
Top of 3rd. Fl. Beams
10'-4 1/4"
8'-10 3/4"
9'-4"
Frame 10
Frame 9
Frame 8
Frame 7
Frame 6
Frame 5
Frame 4
Frame 3
Frame 2
Frame 1
Wind Box Hopper
Base Line of Sintering Machine
3'-2 5/8" R
5'-2"
5 1/8"
6'-5 3/8"
Elevator
5'-2"
8'-0"
10'-0"
16'-0"

FIG. 8.

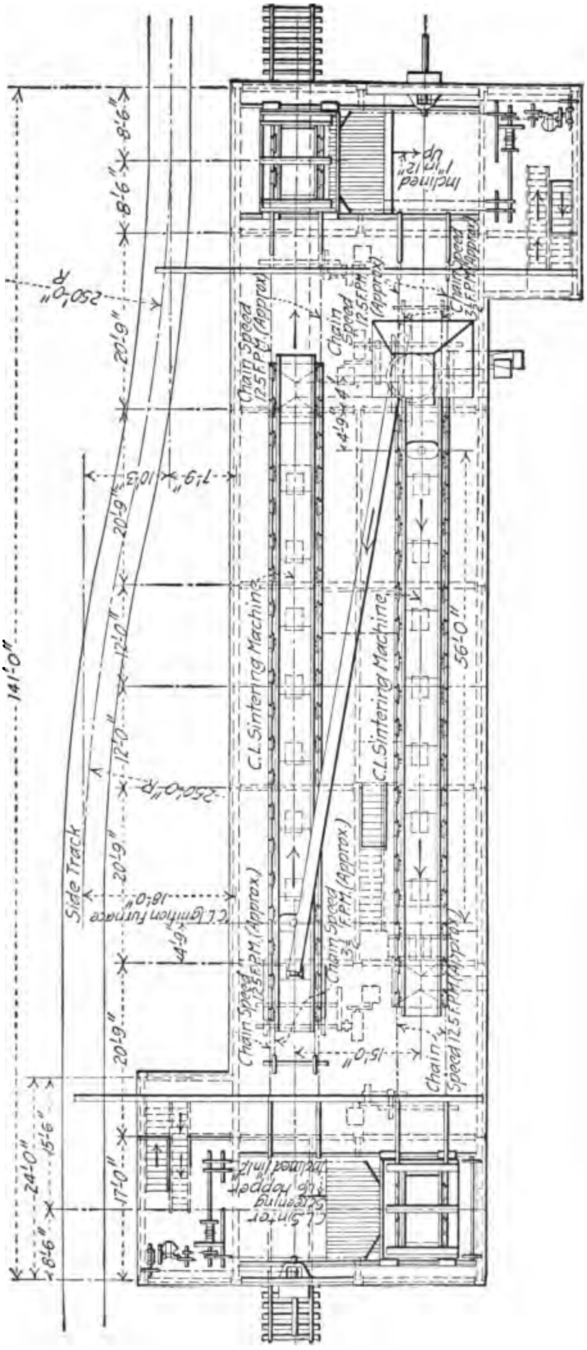
141'-0"
250'-0" R
20'-9"
8'-6"
8'-6"
10'-3"
7'-9"
20'-9"
12'-0"
12'-0"
250'-0" R
20'-9"
Side Track
18'-0"
C.L. Ignition furnace
4'-9"
20'-9"
24'-0"
15'-6"
6'-6"
17'-0"
Inclined 1" in 12" Up
Chain Speed 12.5 F.P.M. (Approx)
C.L. Sintering Machine
Chain Speed 12.5 F.P.M. (Approx)
4'-9"
4'-3"
Chain Speed 3½ F.P.M. (Approx)
C.L. Sintering Machine
56'-0"
Chain Speed 13½ F.P.M. (Approx)
Chain Speed 12.5 F.P.M. (Approx)
15'-0"
Chain Speed 12.5 F.P.M. (Approx)
C.L. Sinter Screening & Hopper Inclined Unit

FIG. 9.

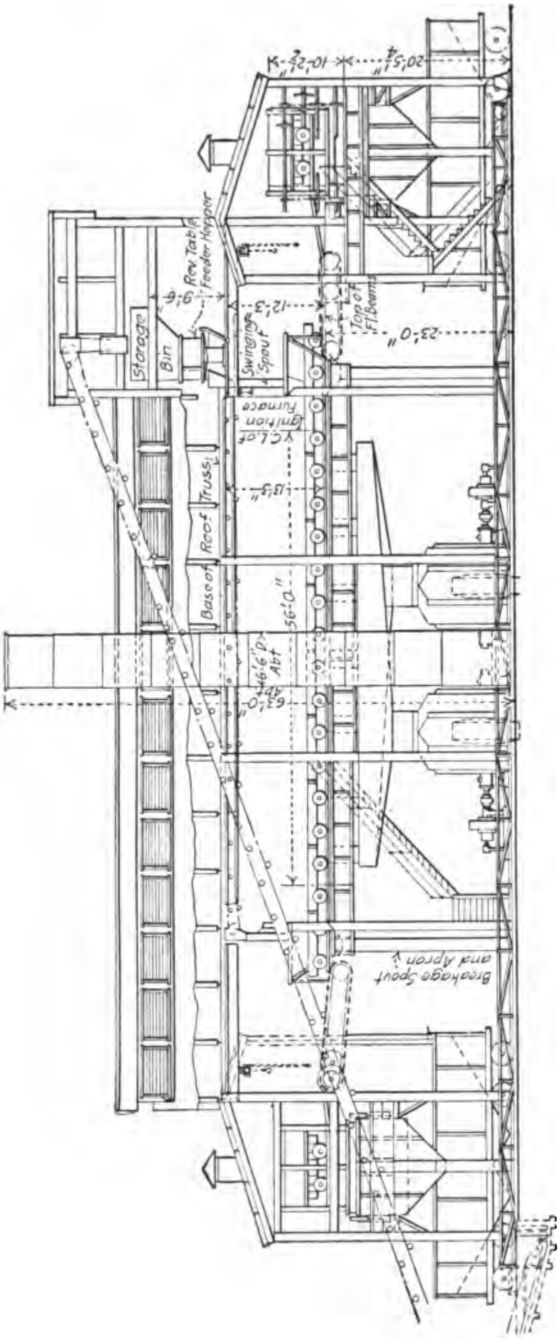
10'-2½"
20'-5¼"
Storage Bin
Rev. Tab. & Feeder Hopper
9'-6"
12'-3"
Swinging Spout
Top of Fl. Beams
23'-0"
C.L. of Ignition Furnace
13'-3"
Base of Roof Truss
56'-0"
6'-6" D. Abt.
63'-0"
Breakage Spout and Apron

FIG. 10.

Sintering machines of this type are also used to treat lead ores as a preparation for blast furnacing.

The gas from a sintering machine is not only low in SO_2, but as it is high in CO_2 and CO, it is not good acid material. SO_2 has been hard to concentrate up to recent years, but a new process is now on the market which makes available very weak gases.

Silica gel is put out by the Davison Chemical Co. at Baltimore. While this material has been known for years, its commercial production was not possible until the researches of Prof. W. A. Patrick of Johns Hopkins, on gas mask absorbers during the war. Apparently any condensible gas is adsorbed by this material, the capacity of which is very great, and a small rise in temperature serves to drive out the adsorbed gas. This is so much the case that the additional gas pressure produced by the slight increase in temperature caused by laying ones hand on the apparatus is easily measured.

The action is unquestionably surface condensation, the small drops of "gel" being full of sub-microscopic cracks, so that Prof. Patrick says, "if you consider the measure of the 'gel' drop in centimeters, you must measure the area of the cracks in acres."

This plant consists of three towers in series, each capable of being cut out. Only one is used at a time, one being discharged and the third in reserve. The temperature is raised or lowered by forcing steam or brine through horizontal pipes laid in the gel mass. Vertical pipes were tried, but the channeling action of the gas was too great. This opens up a new type of contact plant where the concentration of SO_2 in the gas can be very high, thus cutting down plant and particularly mass, very greatly. The advantage of being able to mix air and SO_2 instead of air and sulphur, is at once apparent. When sulphur is burned in air and that mixture taken into the system, the nitrogen that was in the air, the oxygen of which helped form the SO_2 goes along and dilutes the gas, whereas by having the SO_2 ready burned, that dead gas is avoided.

If there is sufficient oxygen present, the contact mass is more efficient as the concentration of the gas increases. By sufficient oxygen is meant the excess that is needed to give good results. So the use of a gas mixture made from SO_2 direct works out as follows: In a gas made by burning sulphur in the air and containing 7 per cent SO_2, 12.3 per cent of the total is the nitrogen that accompanied the 3.5 per cent oxygen necessary to make the

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SO_2. This concentration process reduces the amount of gas to be handled, raises the concentration of the gas, and leaves just as much oxygen to form SO_3 and furnish the excess necessary for this formation.

Silica gel should be tried out along the following lines, as the concentration of platinum in the mass drops the conversion drops, also, but not in the same proportion. Therefore, there is a point, to be determined, to which it will pay to drop the conversion, catching the unconverted SO_2 with silica gel, and returning it to the gas stream.

The saving will be in plant cost of platinum. Suppose that with 10 per cent of the amount of platinum required for a 97 per cent conversion you are able to get a 60 per cent conversion and recover the SO_2 at reasonable expense. At the standard rate of platinum used, for a plant burning one ton of brimstone an hour, 90 pounds avoirdupois, of platinum would be required. At $95 an ounce, troy, that is $1,385 a pound avoirdupois or, $124,650 for platinum. Ten per cent of that would be $12,465, quite a difference.

Without anywhere near sufficient research work done upon this subject, I do not state the above as either an accomplished fact, nor as a certainty—it is simply a possible lead. The Davison Chemical Co., Baltimore, Maryland, hold the basic patents on silica gel, and will furnish the most complete information upon this subject that exists.

Water is an obstacle to the adsorption by silica gel, as it is a great moisture adsorber, and the moisture would be given up, under certain conditions, along with the SO_2, which would have to be dried again before conversion. Of course there would be no moisture in the gas just leaving the strong acid of the absorption towers.

When the contact process first became an accomplished fact many people looked for it to displace chambers entirely, but the cost of the platinum required has prevented the fulfilment of their hopes. Is it too much to hope that silica gel may bring this about?

OTHER USES OF SO_2

Liquid SO_2 was first made commercially from zinc smelter gases in this country by the Davison Chemical Co. in Baltimore around 1870. It is interesting to note that the first sulphite

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paper pulp in this country was made with liquid SO_2 by the Mitcherlich process, then the pulp mills began to burn their own sulphur, and now the pendulum has swung back again.

For liquid SO_2 the normal boiling point is.................... −11°C.

For liquid SO_2 the latent heat of vaporization, at −10°C. (diminishes as the temperature rises)............................ 93.4 cal.

Vapor pressure temp. C....	−10	0	10	20	30	40	50
Pressure (atmospheres).....	1.0	1.53	2.26	3.24	4.51	6.15	8.18

Critical temperature = 155°C. Critical pressure = 78.9 atmospheres.

Specific heat, between − 20° and + 130°C. = $0.31712 + 0.0003507t + 0.00000672t^2$

ACTION OF METALS

The commercial product, containing 0.07 per cent H_2O, attacks iron above 70°C., forming a solid crust of ferrous sulphate and thio-sulphate, but the metal is not further attacked. Anhydrous SO_2 does not attack either iron or steel.

USES

For refrigeration, because of its cheapness, ease of handling, and the fact that it is neither acid nor alkalin in its action.

In the manufacture of sulphite pulp.

For petroleum refining.

As a solvent for organic fats and resins.

As a sewage disposal agent.

So far as I know, there are three plants in this country making liquid SO_2. The Tacoma Smelter, of the American Smelting and Refining Co., Tacoma, Wash., has a plant that has been in operation about 5 years,—operating as follows: The gas from the converters, containing 2.5 per cent to 3 per cent SO_2, and at about 300°C., is lead to a scrubber tower, brick lined and loose brick packed, into the top of which is fed a small amount of water, just enough to prevent it all vaporizing. The run off cleans the gas, but because of its temperature contains practically no SO_2. The gas then goes to another tower, of the same construction, but larger in diameter, to which water is admitted through spray nozzles at the top, the water being in sufficient quantity to cool down and absorb practically all the SO_2, the scrubbed gases going out the stack. See Fig. 11.

The liquor flows by gravity to a heat exchanger, made of lead pipe, outside of which flows the desulphurized liquors,

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hot, from the following process. Then to 12-in. lead pipes, horizontal, into the bottom of which is blown steam, which vaporizes the SO_2, which comes off through a gas outlet on top, and thence to the compressor. The water, after the SO_2 has been blown off, flows down to heat the heat exchanger.

Before the compressor is a scrubber, fed with 66°Bé. acid, to remove moisture from the SO_2. This 66° acid drops to 60° in a week, and has to be renewed.

The compressor is a bronze, single-stage, direct-driven one, compressing to about 60 lb., although under perfect conditions 45 lb. will do it. The liquid SO_2 then goes to lead cooling coils, over which water drops, and thence to a tank car.

An iron cylinder for the compressor only lasts six weeks.

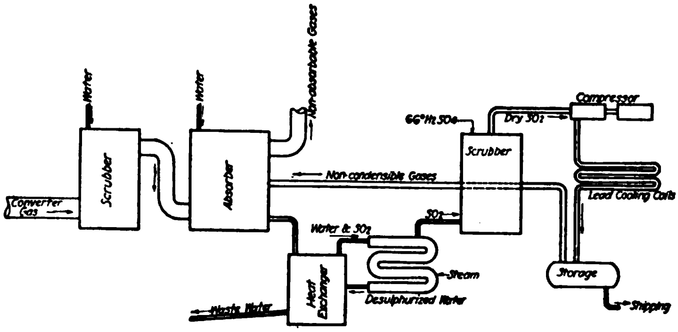

FIG. 11.

The storage tank, built to stand 300 lb., has a safety valve with a pipe running to the absorber tower, where any SO_2 will be caught and the non-condensible gases will escape to the stack.

This plant started to produce in 1917, making 10 tons of liquid SO_2 per day. In 1920 the production was increased to 30 tons per day, and in 1921 it will be 50 tons. The product is shipped partly to Crown Willimette, where it is combined with SO_2 produced on the ground, to make a 25 per cent gas to make a strong cooking liquor for making sulphite pulp. The rest of the production goes to Los Angeles for oil refining.

At Tacoma, with coal at $8, SO_2 from a 3 per cent gas, including overhead, but with no charge for the gas, is (1920) $8 per ton.

The plant of the Virginia Smelting Co., at Norfolk, Va., has

Without steam or power plant, a 10-ton per day plant costs (1920) $30,000.

Without steam or power plant, a 30-ton per day plant costs (1920) $45,000.

been leased to Beer, Sondheimer, & Co., who are recovering the SO_2 in a process very similar to the one at Tacoma, except that it is much smaller, and the liquid SO_2 is shipped in cylinders.

There is a small plant in Wisconsin which produces SO_2 from brimstone directly for the purpose of compressing and selling. I have been unable to get any details.

Dr. Ralph McKee, head of the Department of Chemical Engineering at Columbia, is a world's authority on liquid SO_2. He has furnished some of the information contained in this section, and sees a great future for the industry, some of the reasons for which are given below.

Liquid SO_2 will not burn nor explode, will not attack steel containers, and costs ½¢ a pound, F.O.B. point of manufacture, against 7¢ for gasoline and 15¢ for carbon-tetrachloride (1920).

The U. S. Bureau of Chemistry does not like the use of liquid SO_2 for the extraction of oils to be used for food, if any other solvent can be used.

Mr. James E. Steely, of the West Virginia Pulp and Paper Company, Inc., has furnished some notes on the production and use of SO_2 in the pulp industry.

In the manufacture of bi-sulphate liquor, it is desirable to have SO_2 gas at as high a percentage as possible, as the solubility of the gas in water increases in the per cent of SO_2 in the gas. This solubility also increases with a reduction in temperature; therefore the gas is cooled as low as possible, usually in some form of lead-pipe cooler.

It is also necessary to keep the SO_3 in the gas as low as possible, SO_3 being a very undesirable component of gas for sulphite pulp manufacture.

A 15 per cent to 18 per cent SO_2 gas meets the above requirements. Liquid SO_2 is a most desirable material to work with, and if it could be delivered at the mill at slightly above the cost per pound of sulphur, as compared to elemental sulphur, it would be in very wide demand. However, under present (1920) conditions, the cost of producing liquid SO_2 together with increased cost of freight and containers for handling would make the proposition prohibitive in ordinary times. The efficiency of operation in a sulphite acid plant is very high, and maintainance cost of first-class equipment comparatively low; therefore it would seem that only in special cases would liquid SO_2 be attractive to sulphite pulp manufacturers.

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The chief source of SO_2 for sulphite pulp manufacture is elemental sulphur, burned in the same types of burner that are used in acid manufacture. Very little SO_3 is produced by any of these machines, but to make assurance doubly sure, at some plants a pyrometer is installed in the combustion chamber and the temperature maintained around 1500°F., at which point SO_3 dissociates into SO_2 and O. Other plants depend solely upon gas analyses.

Pyrites, particularly from Spain, used to be the chief source of SO_2 for pulp making, but the Louisiana sulphur discoveries, and the interruption to Spanish deliveries by the War, cut down its use so that today (1920) Mr. Steely does not know a single plant in this country running on pyrites. The market price of Spanish pyrites has not gone low enough to justify plants that used to use it returning, and also most important, the burners, usually of the Herreshoff or Wedge type, must be operated with the greatest care to prevent formation of SO_3, due to the catalytic action of the hot iron oxides in the cinders.

There are two general schemes for making bi-sulphite liquor. In each case the SO_2 is cooled as low as possible. The first scheme is to use a tall tower filled with lumps of lime stone, over which a slow stream of water is passing. The gas is admitted to the bottom of the tower, and is absorbed by the water, forming sulphurous acid, which in turn dissolves the stone to make calcium-bi-sulphate liquor.

The second scheme consists of passing the gas through towers containing a solution of milk of lime. The two are brought together in such a way that they combine and form a clear solution of bi-sulphite.

When rosin is extracted from yellow pine waste, enough SO_2 remains in the wood to cook the pulp. Both United States and Canadian patents on this process are applied for by Ralph McKee and A. A. Holmes.

The city of New Haven has experimented with liquid SO_2 on sewage disposal. The sewage was going into the bay; if an acid was added the colloidal sludge was precipitated. H_2SO_4 was first used, then SO_2. If this sludge is dried and extracted, considerable amounts of fats and oils are recovered, gasoline being used as the solvent. The report says the recovery will pay costs, including bond interest.

Liquid SO_2 is a solvent for di-ethylamine, analine, di-phenyl-

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amine, benzylamine, P-toluidine, A-naphthylamine, B-naphthylamine, phenyl, B-naphthylamine, benzidine, chrysaniline, carbazol, quinolin, pyridine, acetanilide, acetnaphtalid, benzene, toluene, tri-phenyl-methane, di-phenyl-flouren, phenanthren, naphthalene, nitro-benzene, limonen, pinene, anthracene, B-dibromnaphthalene. All fatty alcohols from methyl to capryl, benzyl alcohol, menthol, borneol, O-cresol, B-naphthol, hydroquinone, picric acid, phenol-chloro (and di-chloro) acetic acid, A-brom-butyric acid, benzoic acid, salicylic acid, M-oxybenzoic acid, B-naphthoic acid, acetic-ethyl-ester, succionic-acid-di-ethyl-ester, asopropyl-aceto-acetic-ester, fumaric-acid-di-ethyl-ester, cinnamic-acid-di-ethyl-ester, malic-acid-di-methyl-ester, mandelic-acid-di-ethyl-ester, acetic-acid-bornyl-ester, ricanelic-acid-propyl-ester.

The following are also soluble—KI, NaI, NH_3I, RuI, tri-methyl-sulphoneum-iodide, tri-methyl-ammonium,-iodide, KBr, ammonium-thio-cyanate, methyl-ammonium-chloride, di-, tri, and tetra-methyl-ammonium-bromide, sublimed ferric chloride, cobalt-thio-cyanate. More compounds for which liquid SO_2 is a solvent are continually being discovered.

CANADIAN SITUATION

Dr. McKee shows a picture of the smelter of the International Nickel Co., with clouds of SO_2 coming out of the stack—1,000 tons a day. There are numerous copper, nickel, and zinc smelters in the Dominion, and the large pulp mills near at hand are importing sulphur from Louisiana and Japan, while this SO_2 is worse than thrown away—it is acutally hurting the nearby farms.

The Tennessee Copper Co. showed that the production of acid from smelter fume was not an impracticable dream, and when the acid was produced a market was found for it. The method of producing liquid SO_2 from smelter fumes is already in successful operation, and the market for the product is ready and waiting at the door.

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CHAPTER VI

A BRIEF DESCRIPTION OF THE CHAMBER PROCESS

The Chamber Process for the manufacture of sulphuric acid takes its name from the lead chambers which constitute the chief essential part of the apparatus. It differs from the other important process of making sulphuric acid, the contact process, both in nature of the plant proper and in the chemical reactions involved. The purpose of each is to oxidize SO_2 up to H_2SO_4. The chamber process does this by means of the reactions between SO_2, the higher oxides of nitrogen, oxygen, and water, at low temperatures, while the oxidation in the contact process is accomplished by a catalyzer, usually finely divided platinum, at a comparatively high temperature.

The normal product of chamber plants is sulphuric acid of 50° to 60°Bé. Contact plants normally produce acid of 98 per cent H_2SO_4 or higher strengths. The chamber process makes 50° to 60° acid more cheaply than the contact process can make acid of that grade. The chamber process cannot, however, make high-strength acid. Each process therefore has its distinct field.

The essential parts of a modern chamber plant are:

1. Burners of some kind for the production of SO_2.
2. Dust settling apparatus, except in those cases where brimstone is burned to make SO_2.
3. Glover Tower.
4. Chambers.
5. Gay Lussac Towers.
6. Acid Circulating Apparatus.
7. Fans and flues.
8. Apparatus for introducing the oxides of nitrogen.

The gas produced in the burners is derived from the oxidation of elemental sulphur, iron sulfide, iron-copper sulfides, zinc sulfide or mixed sulfides. It contains from 5 per cent to 10 per cent SO_2, depending on the material burned, 8 per cent to 12 per cent oxygen, and nitrogen, with, in special cases some CO_2 or possibly CO.

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When necessary this gas is drawn through some form of dust-settling apparatus to remove the greater part of the dust which would otherwise contaminate the acid.

If nitre potting is practiced, the gas next passes around the nitre pots. These are cast iron vessels set in the gas flue, into which are introduced nitrate of soda and sulphuric acid. The hot gases cause these compounds to react to form nitric acid vapor, and a mixture of sodium sulphate and sodium bisulphate. The latter is tapped off molten, at intervals. The nitric acid vapor is reduced to NO by the hot SO_2 and is carried along with the gas.

The gas mixture next enters the Glover tower at a temperature of 800°F. to 1,000°F. It is in this tower brought into intimate contact with a mixture of 60°Bé. sulphuric acid carrying in solution N_2O_3, and chamber acid of about 50° Bé. The hot gas with its considerable SO_2 content, reacts with the acid and denitrates it or removes from it its N_2O_3, forming some H_2SO_4 and converting practically all the N_2O_3 into NO, a gas, which goes on with the main gas stream. Steam and some weak sulphuric acid vapor are also formed and go on with the gas. Leaving the Glover tower the gas mixture contains then a somewhat reduced percentage of SO_2, nitric oxide (NO), oxygen, nitrogen and steam or weak acid vapor. Its temperature has been reduced to about 200°F.

If nitre potting is not practiced it is customary to introduce some fresh nitric acid into the Glover tower top.

The acid issuing from the Glover tower at the bottom is maintained at a gravity of about 60° Bé. It has a temperature of 200°F.-300°F. and is passed through a cooling system consisting of a tank containing lead pipe coils through which cold water is circulated. The acid should leave this cooler at as low a temperature as possible, certainly not over 80°F. A part of this acid is elevated and introduced into the Gay Lussac towers, and the remainder is shipped.

The gas mixture from the Glover tower is conducted into the chambers, usually from 3 to 10 in number, in series. From 1 to 2 hrs. is occupied by any given portion of the gas in passing through the set of chambers. Steam or atomized water is introduced at various points. By the reactions between SO_2, oxygen, the oxides of nitrogen and water, sulphuric acid is formed. This collects in the bottoms or pans of the chambers.

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When these reactions have gone on for the proper period of time and the gas finally reaches the end of the last chamber the SO_2 percentage has been reduced to less than $\frac{1}{10}$ of 1 per cent, and the nitrogen oxides are practically all in the form of N_2O_3. It is highly important that the SO_2 percentage be reduced below $\frac{1}{10}$ of 1 per cent or else the recovery of the nitrogen compounds will be incomplete. It is almost as essential that the SO_2 percentage be not less than $\frac{2}{100}$ of 1 per cent for the same reason, and also because of increased corrosion of the lead. These points will be taken up in more detail later on.

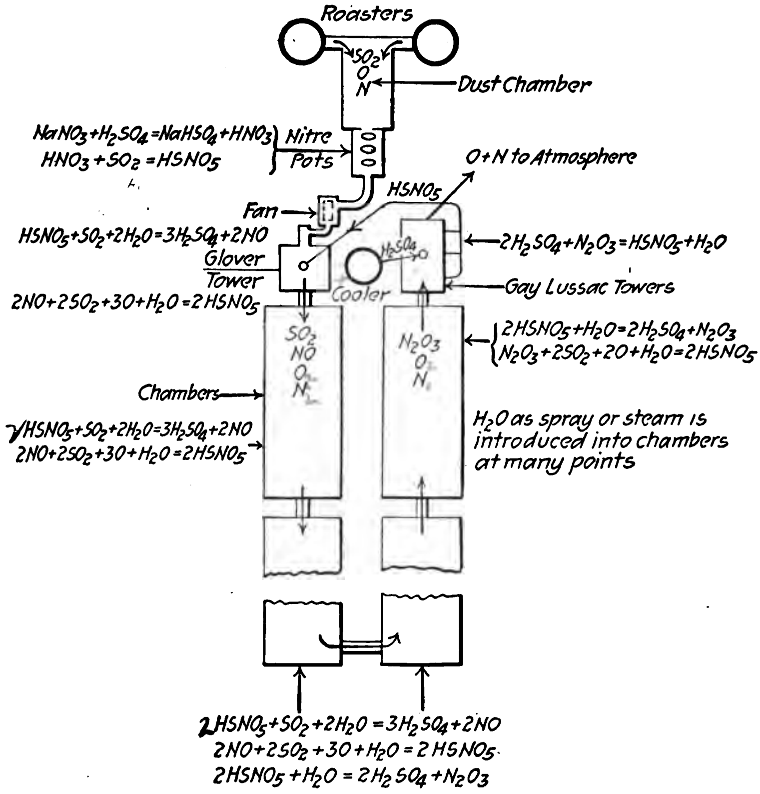

FIG. 12.—Flow Sheet of Chamber Process.

By properly regulating the amount of water or steam introduced the acid made in the chambers is kept at approximately 50°Bé. It is not permissible to allow the continued formation of acid of much greater concentration because of the tendency of

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such acid to take into solution some of the oxides of nitrogen, in which case they are no longer available for reaction with SO_2.

The acid-making reactions generate a large amount of heat which is carried off mostly by radiation from the lead chamber walls. The chambers should therefore be housed in a well-ventilated building.

From the chambers the gases pass into the Gay Lussac towers. Their function is to recover the N_2O_3. This is accomplished by bringing the gas into intimate contact with cold 60° Bé. sulphuric. acid, which takes 85 per cent to 90 per cent of the N_2O_3 into solution, forming what is known as nitrous vitriol. Perfect recovery of the N_2O_3 is never attained because the cost of apparatus to accomplish it is prohibitive.

The gas which leaves the Gay Lussac towers consists of 94 to 96 per cent nitrogen, 4 to 6 per cent oxygen with traces of other things. It is discharged into the atmosphere through a stack.

The acid issuing from the Gay Lussacs, carrying usually from 1 per cent to 2 per cent N_2O_3, is elevated to the top of the Glover tower and the N_2O_3 there reintroduced into the system.

Figure 12 shows a conventional plan of a chamber plant and indicates the reactions which occur in the various parts of the apparatus.

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CHAPTER VII

DUST SETTLING APPARATUS

A chamber acid plant will usually require some provision for removing dust from the burner gases. This varies from almost nothing in the case of brimstone burners, to rather large and elaborate chambers for use when very fine sulphide ore is burned. It is highly important in order to insure uninterrupted operation to provide suitable and adequate means for dust removal. If any considerable amount of dust is carried into the Glover tower by the gas it causes the following disagreeable and serious results: The packing of the Glover tower will become obstructed, interfering with passage of the gas. The acid will be contaminated and rendered impure. Even though this may not be of importance to the consumer of the acid, it will cause gradual fouling and obstruction of pipes, valves, tanks etc., in the acid plant and will make uniform running impossible.

There are two general principles applied in dust removal, which are: decreasing gas velocity, and causing change of direction of the gas stream. It is hardly necessary to consider some of the older proposals for washing the gas by water or acid, as these involve cooling the gas so much that the Glover tower will not function properly. In general, it is necessary to retain the temperature of the gases as high as possible from the furnaces to the Glover tower. Dust chambers for acid plants should therefore be compact and well insulated.

The Cottrell apparatus has been used in a few acid plants with considerable success. It probably has a distinct place in acid plant design when the sulphur bearing material burned produces very fine dust. This form of treater is hardly justified otherwise, as it is expensive to install, and involves some operating expense. The following information is furnished by the Research Corporation, 31 West 43rd St., New York:

COTTRELL PRECIPITATORS FOR CLEANING ROASTER GASES

The problem of satisfactorily cleaning the sulphur dioxide gases prior to their oxidation and conversion into sulphuric acid has long been a

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troublesome one for acid makers to solve. In contact acid plants it is of course essential that the gases be completely freed from suspended particles of dust or fume prior to their passage through the catalyst and it is almost equally desirable in the case of chamber plants that the sulphur dioxide gases be thoroughly cleaned if the plant is to operate at high efficiency and produce a clean acid of good quality. In the latter case, however, the problem is complicated by the fact that the sulphur dioxide gases must be cleaned at a very high temperature whereas in contact plants the gases may be cooled during the cleaning process or may be cooled first and then purified.

FIG. 13.

In both cases the Cottrell Processes of Electrical Precipitation offer a very satisfactory method of cleaning the gases, and several Precipitation Installations are today in use for such purposes.

In designing Cottrell Precipitators for cleaning roaster gases the temperature at which the gases must be cleaned and the character of the suspended matter to be removed from such gases are governing factors. Of course the size of the installation depends directly upon the volume of gas to be cleaned and this in turn is fixed by the quantity of material being roasted per unit of time and by its sulphur content as well as by the percentage of sulphur dioxide in the gases leaving the

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furnaces. These factors must therefore be known or approximated in order that a precipitation plant of suitable capacity may be provided. Two types of precipitators are today being installed for cleaning the hot furnace gases in sulphuric acid plants. These types differ widely from each other and the decision as to which type should be installed is based largely upon the temperature and fume or dust conditions in the particular plant under consideration. In cases where the gases must be cleaned at temperatures of 1,000°F. and over and where the suspended matter to be removed is mostly dust rather than fume, precipitators of the so-called plate type, in which the gases pass horizontally between the collecting and discharge electrodes, have proven highly satisfactory. On the other hand, where the gases can be cooled to a temperature of about 600°F. or under before cleaning and where the suspended matter to be removed is fume rather than dust, precipitators of the pipe type, in which the gases pass upwards between the collecting and discharge electrodes, would in general be the more suitable.

Fig. 14.

Figure 14 is a photograph of a Cottrell Precipitator of the pipe type which was recently installed under the supervision of the Research Corporation at a plant in Wisconsin. Here 17,500 cubic feet of gas

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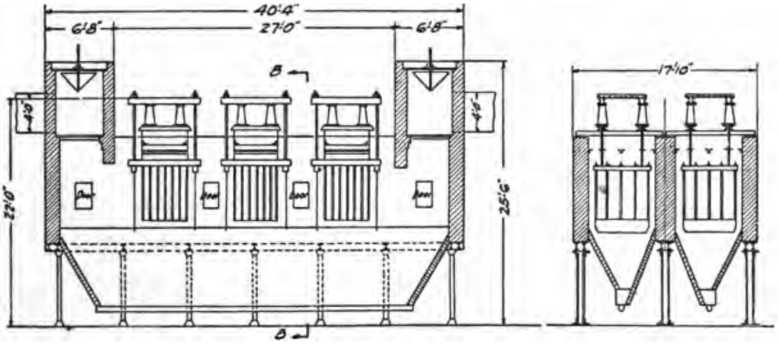
per minute at a temperature of 500°F. are cleaned. These gases come from three Mathey rotary kilns roasting Wisconsin zinc ore concentrates, and after being cleaned are used for the manufacture of sulphuric acid by the contact method. The precipitator as installed consists of two units, each having 36 collecting electrode tubes or pipes. These pipes are of steel, 12 in. in diameter and 15 ft. in height. Means are provided for rapping both the discharge and the collecting electrodes in order to remove from time to time any dust which may have adhered to them. The levers for operating the pipe rappers may be clearly seen in the photograph. The bottom header is a reinforced concrete chamber into which the collecting electrode pipes project and in which the collected material is deposited. This is later removed by hand through doors which are provided for this purpose. Should it be desirable similar installations could be readily provided with hoppers and screw conveyors so that the collected dust could be taken out of the precipitator continuously and automatically. This precipitator occupies a space approximately 17 ft. wide by 28 ft. long and has an overall height of about 35 ft. The amount of power required to operate the installation is about 18 KW.



SECTION A-A SECTION B-B

FIG. 15.

Figure 15 is a drawing giving the general arrangement and overall dimensions of a precipitator of the horizontal flow or plate type, designed and installed by the Research Corporation, and Fig. 13 is a view looking in a lengthwise direction through a precipitator of this kind which was installed in a chamber acid plant near Baltimore, Maryland, and which is particularly designed to withstand the high temperatures at which the gases must be cleaned in such a plant. This installation operates at a gas temperature of 1,100°F., while occasionally temperatures as high as 1,400°F. have been recorded in the precipitator.

A precipitator of the size shown in Fig. 14 will clean the hot gases produced by the roasting of 40 to 45 tons of fines pyrites per twenty-

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four hours. With a sulphur dioxide concentration of 7½ per cent to 8 per cent this means that the volume of gas passing through the installation is about 17,500 cu. ft. per minute at a temperature of 1,100°F.

As will be noted from an inspection of Fig. 15, the precipitator is divided into two sections, each of which is provided with a damper at both inlet and outlet ends. This makes it possible to shut off either section from the system when inspection or repair is required or when it is desired to clean the electrodes. Such cleaning may be necessary every few days if a very dusty ore is being roasted in the furnaces. For the above reason it is desirable to so design the plant that each section will have sufficient capacity to handle all the gas for short periods of time and in this way continuity of operation with clean gas is practically assured.

Among the more important benefits obtained by the use of the Cottrell Processes for cleaning roaster gases in sulphuric acid manufacturing plants the following may be mentioned:

1. The quality of the acid is improved, due to the removal of the dust carried by the furnace gases.
2. More efficient operation of the nitrating pots can be obtained due to the absence of dust in the gas at this point in the system.
3. Plant shutdowns for cleaning the Glover towers, with the attendant loss of acid and limitation of production, are avoided.
4. The life of the lead chambers is increased, due in part to elimination of dust deposition.
5. A material is collected usually having more than sufficient value to carry the operating cost of the installation.

The simplest dust settler is an enlargement of the gas flue to reduce the gas velocity. A considerable amount of valuable data has been gathered on this method of dust settling, and it is possible to design a dust chamber of this kind with assurance as to its performance.

It seems to be well established that reduction of the velocity of the gas stream to not over 5 ft. per second is necessary to allow proper settling within a reasonable distance of travel. Even at this rate of speed a flue of moderate height, say 10 ft., will have to be 50 ft. or more long to allow the dust particles to settle out. It will be readily seen that for a large acid unit a dust chamber of this type requires a great deal of ground space.

Baffle walls to make the gas take a tortuous course are, in this form of dust chamber, of doubtful value. One baffle immediately in front of the inlet opening is good to spread the gas stream, but if a large number of baffles are put in they impede

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the draft, raise the gas velocity, and often give poorer net results than empty chambers.

Wires or chains hung in a dust chamber of this type have a very good effect. Their virtue of course lies in the fact that dust particles impinge on them and lose their velocity and fall or else cling to the wires or chains. They do not interfere with draft to any serious extent. It is well to provide some means of shaking suspended wires or chains as dust clings to them to some extent.

An interesting account of the performance of dust chambers hung with wires at the Copper Queen smeltery is given in an article by Geo. B. Lee in the *Engineering and Mining Journal* of September 10, 1910. Two tests described showed that in a 100 ft. long chamber with gas velocity about 4½ ft. per sec., 62.8 per cent of the total dust was deposited with the chamber empty, and 77 per cent when hung with wires.

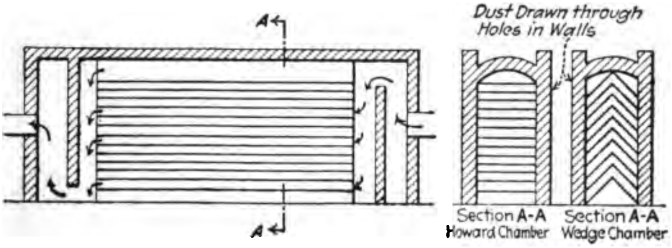

FIG. 16.

Several interesting proposals have been made along the lines of inserting shelves into the chambers, the idea being that by using them the distance which a dust particle must fall before it finds a resting place is greatly reduced. The Howard dust chamber which provides horizontal metal shelves a few inches apart is one example of this. The Wedge dust chamber does the same thing except that the shelves slope sharply toward the outside walls and in that way the dust all slides down against the walls and can be more easily drawn. This principle is a good one so far as settling dust is concerned, but the structural difficulties are considerable for large units or where the gases are very hot.

Figure 16 shows a longitudinal section which applies to either the Howard or the Wedge chambers described, while the transverse sections show the horizontal position of the Howard shelves and the inclined position of the Wedge shelves. The Howard chamber has been installed in several plants with

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satisfactory results. I do not know whether any chambers following the Wedge plan have been built.

Dust chambers employing the centrifugal principle have been used in some places for acid work. They have not been as popular as their merits warrant. A. P. O'Brien many years ago used such a dust chamber at Richmond, Va. This is described in the *Mineral Industry*, Volume 9, as retaining 75 per cent of the dust entering, which is very good. More modern applications of this plan have been made at the American Steel and Wire Company's acid plants at Donora, Pa., in connection with Hegler roasters, and at the Garfield Chemical and Manufacturing Company's plant at Garfield, Utah, where fine copper concentrate is roasted in Herreshoff furnaces.

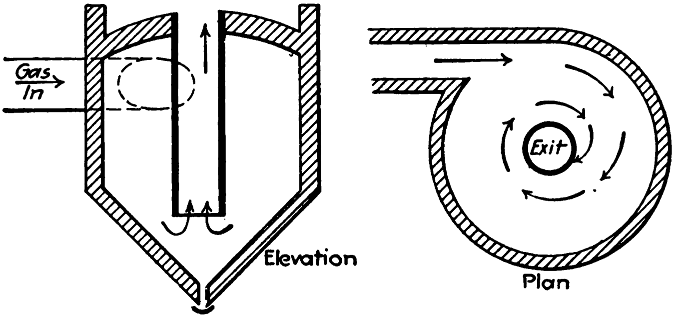

Fig. 17.

Chambers of this type are cylindrical with gas inlet tangential and near the top, and with gas outlet through a central pipe leading from a point near the bottom. Figure 17 shows the essential features. The velocity of the entering gas should be as high as possible without too much impeding the draught. Good clearance requires entering gas velocity not under 25 t. per second.

Centrifugal dust chambers are very small and compact for the work they accomplish and have much to recommend them for acid plants for that reason. In cases where it is desirable to hold up the temperature of the furnace gases so that the Glover tower will concentrate well, the small radiating surface of the centrifugal chamber is an advantage.

The Anaconda Copper Mining Co. has in its acid plants two dust chambers of a unique design which has probably not been used elsewhere. These chambers have given excellent results and are so compact that they deserve description. They

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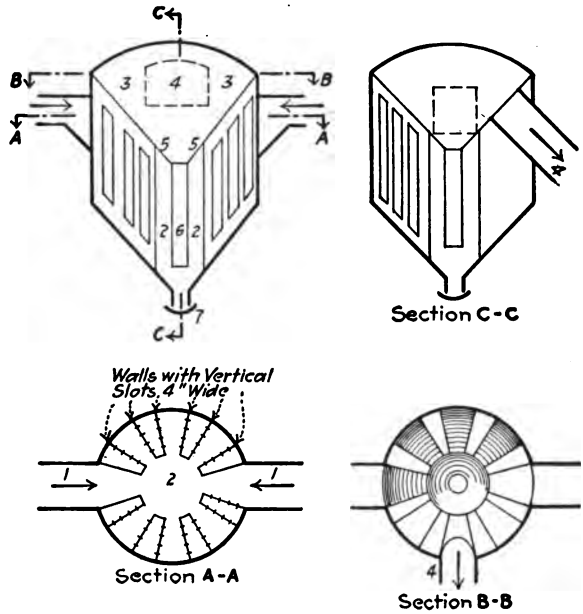
use both the principles of decreased velocity and change of direction to accomplish clearance. The form of this chamber is a cylinder with inverted conical bottom, and in general appearance resembles the centrifugal chambers.

Referring to Fig. 18, the gas enters through flues 1–1 into space 2, distributes radially, passes through the 4-in. vertical slots, and rises into space 3. Space 2 is separated from space 3 by reinforced concrete cone 5–5. From space 3 the gas leaves the chamber through passage 4 which does not communicate with space 2. The dust which drops in space 3 falls through the vertical cast iron pipe 6 and is drawn off with the dust which falls in space 2, at gate 7. This chamber is entirely self cleaning.



Section C-C

Section A-A

Section B-B

FIG. 18.

The original chamber at Anaconda cleans the gases from roasting 150 tons of copper concentrate per 24 hours, all of which passes ¼-in. screens. It is 32 ft. in diameter and 43 ft. high outside. It offers very little resistance to the passage of the gas and in this respect is better than the centrifugal chambers. Its cost of construction is somewhat higher than that of a centrifugal chamber, but it is a very satisfactory apparatus from an operating point of view.

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CHAPTER VIII

THE GLOVER TOWER

The Glover tower is the first division of the acid plant proper. It receives through a flue entering it near its bottom the gas from the burners. This gas contains essentially SO_2, oxygen, nitrogen and—if nitre is potted in the flue—a small amount of NO. Its temperature may be up to 1,000°F. or 1,200°F. Into the top of the Glover tower are fed nitrous vitriol (60° sulphuric containing N_2O_3 in solution), and chamber acid about 50°Bé. The purpose of the tower is to produce an intimate contact between the gas and the acid.

With this statement of the duties of the Glover tower in view, it is clear that the tower must be constructed in such a way as to be acid and gas tight against pressures of a few ounces, and it must be of such materials and built in such a way as to withstand the action of gas at 1,000°F. and sulphuric acid of 60° or 61°Bé. at 300°F.

A modern Glover Tower consists of a lead shell supported by steel or wood framework, a lining of acid- and heat-resisting brick, and a packing of acid- and heat-resisting material placed in such a way that gas may ascend through it freely and acid descend over its surfaces. The structure is built in a lead, brick-lined pan which may be integral with the tower or fairly distinct from it. A brick-lined flue enters near the bottom to deliver the hot furnace gases into the tower, and another flue of bare lead leaves the top of the tower and carries the gases to the chambers.

As it is desirable that the acid which issues from the Glover tower shall flow by gravity to coolers and tanks, the tower proper is built on a suitable foundation from 10 to 20 ft. high.

The weight of the tower is very great and the stability of the foundation must be beyond question. In modern plants reinforced concrete, or structural steel on a heavy concrete base or piers, are the forms of construction used. A smooth level floor at the desired height is obtained by one of these methods, and on it is laid down a sheet of light lead—6 or 8 lb. per square foot

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—as a protection against leakage or overflow of acid. This lead extends out beyond the edge of the foundation a few inches, or is turned up to form a shallow pan which is drained by pipes.

The pan of the Glover tower is frequently made of lead weighing 60 lb. per square foot *i.e.*, about 1 in. thick. It may be made somewhat lighter with safety if the masonry lining is well done.

The sides and top of the Glover tower are of lead not less than 10 lb. per square foot and better 15 or 20 lb.

A sturdy framework of wood or steel or a combination of the two, supports the lead, and, above the top of the tower, a platform carrying acid tanks. This frame consists usually of 4 posts or columns with horizontal members between them which support the lead, or which carry small vertical pieces which support the lead. Horizontal or vertical straps are burned to the lead sheets and nailed or bolted to the supporting members of the framework. As the lead sheets are supported inside by close contact with the lining wall, the outside straps on the side sheets need not be very close together.

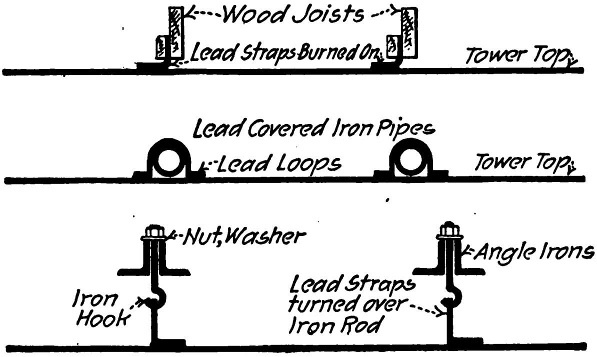

Fig. 19.

The top lead is supported by straps nailed to wooden joists or by loops of lead passing over iron pipes, or by small iron hooks supporting rods burned to the lead. Several of these schemes are shown in Fig. 19.

As mentioned earlier the pan of the Glover tower is often quite distinct from the tower proper which sits in it, though sometimes the upper edge of the pan and the lower edge of the side sheets are burned together, in which case the pan is not very

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clearly defined. It cannot be said that either plan is very distinctly better than the other though it is easy to get into trouble with the latter method if the details are not carefully designed.

The pan and the sides of the Glover tower are lined with brick, usually in recent years laid up in acid proof mortar, though formerly and sometimes now, laid dry. So much stress has been put upon the quality of the brick used for this purpose that it seems to be a rather common idea that very exceptional clays, and methods of manufacture are necessary. It is difficult to lay down any analysis figures which show the fitness of brick for this purpose. Of course the higher the sum of silica and alumina the better. The sum of CaO and MgO should not be over 3 or 4 per cent. Very satisfactory acid resisting brick may contain up to 6 or 7 per cent FeO. As a matter of fact in almost any part of the United States one can find within two or three hundred miles entirely satisfactory brick for making tower linings. As a test if the brick is mechanically sound and strong, it should be soaked for a week or more in sulphuric acid and then allowed to stand in the weather for several weeks or as long as one can wait. If no spalling or cracking or swelling occurs after a long period of weathering, the brick will stand up well in the tower.

The mortar used in laying the brick consists of silicate of soda and finely ground silica with a small percentage of barium sulphate if desired. This mortar sets up very slowly as the set is due to evaporation of water only. After this initial set has taken place, sulphuric acid is run over the brickwork. This reacts with the silicate of soda and gives the mortar a permanent set. The bottom of the pan is lined with 4 or 6 in. of brick. If the pan is open, the sides are lined with 4 in. of brick. The lining wall of the tower proper is 18 to 24 in. thick in the lower part where the heat is high. A few feet above the top of the gas inlet flue the thickness can be decreased and after the middle of the tower is reached 9 to 12 in. thickness is correct.

Figure 20 shows the lining and packing of a Glover tower. The packing of Glover towers is essentially acid-resisting solid material which shall present a large amount of surface to the gas and acid passing through it, thereby causing intimate and thorough contact between them. Many materials have been used for packing. Coke was formerly well thought of because it offered much surface and was light. It is rarely used now because it is not so permanent or satisfactory as other things. In

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the course of months or a few years coke breaks up and impedes the passage of the gas and has to be renewed—an expensive and dangerous job. Like any other non-symmetrical packing, coke exerts some lateral pressure on the walls of the tower, which is undesirable.

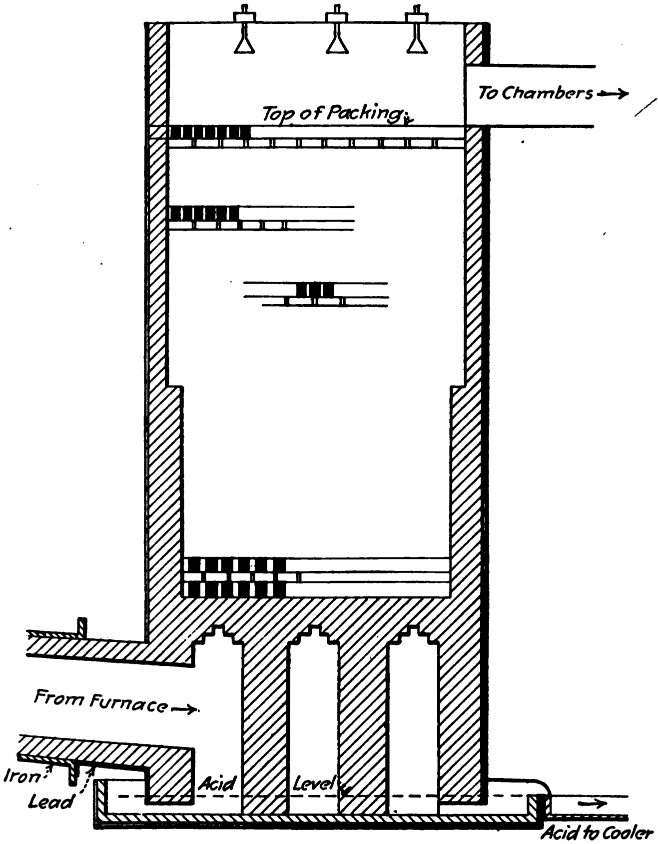

Fig. 20.

Another class of material used formerly but not much now, is rough fragments of quartz or other natural or artificial silicious material. This is better than coke in that it does not break down readily, but it is open to the objection of creating lateral thrust. In using these rough unsymmetrical packings one cannot foretell very accurately what resistance to gas passage will be encountered, and sometimes very unexpected things in this way are encountered.

Much the most satisfactory kind of packing is acid-resisting brick or shaped pieces of symmetrical form, laid up so that all the thrust is downward and none on the walls. With such packing one can accurately determine how much area for gas passage exists and how much wetted surface for gas acid contact. In using unsymmetrical packing these things are very indefinite. With symmetrical packings also there is no thrust on the walls of the tower.

There are many kinds of symmetrical packings, some patented and some for which very exclusively superior virtues are claimed. In deciding between the various kinds available one should consider that the most elaborately designed shapes do not as a matter of hard practical fact give much better results than plain rectangular brick of standard dimensions. If packing is to be used at a point near to the factories which make the special shapes it is well enough to take advantage of the fact and use them. It does not pay however to ship fancy packings many hundreds of miles if good standard brick can be obtained locally.

Above the top of the Glover tower are located two tanks, one to receive nitrous vitriol and the other chamber acid. These acids are fed into the tower through suitable distributors which should uniformly spread the acids over the entire top surface of the packing. The nitrous vitriol and chamber acid are best kept separate until they are inside the tower, because on mixing them some fuming off of the nitrogen oxids occurs.

The chief function of the Glover tower is to denitrate the nitrous vitriol, the solution of N_2O_3 in sulphuric acid, which comes from the Gay Lussac towers. This nitrous vitriol is broken up by the hot SO_2, the acid is freed from its nitrogen compounds, which are mostly reduced to the form NO, a gas, which proceeds with the gas stream into the chambers.

In order that this action may be complete and the acid issuing from the Glover tower be entirely free from nitrogen-oxides it is necessary that the nitrous vitriol be diluted with water or weak acid at the top of the tower. It is necessary however that the acid issuing from the tower be not less than 59°Bé. as that is what the Gay Lussacs require. This requirement limits the amount of weak acid which may be introduced. Fortunately the usual roaster or burner gas has a sufficiently high temperature to allow the introduction of much more weak acid that the amount necessary to accomplish complete denitration, and the

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Glover tower becomes a means of concentrating almost all of the chamber acid to 59° or 60° acid. This is its second function.

A third function though an incidental one is that the roaster gas is cooled to a temperature at which it will not harm bare lead.

Of course the concentrating capacity of a Glover tower depends largely upon the temperature of the roaster gases. If they enter the tower at 1,000°F. all the chamber acid can be concentrated to 60° or even 61°. If their temperature be two or three hundred degrees lower not all the chamber acid can be concentrated.

In the matter of dimensions and of cubic contents there seems to be a surprising difference of opinion, shown by modern designers. Varying SO_2 percentages and temperatures account for some of the difference but by no means all.

Lunge states that the net packed volume of a Glover tower should be in the neighborhood of 320 cu. ft. per ton of sulphur or about 80 cu. ft. per ton of 60° acid made. This refers to European practice and small units.

A large American plant recently erected has a Glover tower whose net packed volume amounts to 33 cu. ft. per ton of 60° acid.

Many American plants erected within the last few years have around 50 cu. ft. per ton of 60° acid produced, and that figure probably approaches modern opinion of this point.

The vertical dimension of the packing is usually from 20 to 30 ft. There is some possibility of making this dimension too great to be good for the concentrating capacity of a tower in that the gas temperature may fall so low that condensation will take place. If gases entering the tower are hot, say over 1,000°F., a 30 ft. dimension is quite proper, but if the gas temperature is below 800° it is well to hold the vertical dimension of the packing lower.

The horizontal area of the packing will of course be fixed by the cubic contents and the height, and will, from the above, vary between 1.66 and 2.5 sq. ft. per ton 60° acid produced. The overall height of the Glover tower is usually from 10 to 15 ft. more than the height of the packing proper to allow for the gas distribution chamber below and the acid distribution space above the packing.

The outside horizontal dimensions are greater than the horizontal dimensions of the packing by 3 or 4 ft. to allow for the lining walls.

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As an example of the above observations a Glover tower for a unit to produce 100 tons of 60° acid per day would assume dimensions as follows:

Cubic contents of packing @ 50 cu. ft. per ton 60° acid 5,000 cu. ft.
Vertical dimension of packing 25 ft.
Area of packing 5,000 ÷ 25 = 200 sq. ft.

Assume that the tower has square section, than the horizontal dimensions of the paking will be 14 ft. 2 in.

The overall height of the tower will be 25 + 15 = 40 ft.
The outside horizontal dimensions will be about 17 ft. × 17 ft.

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CHAPTER IX

THE CHAMBERS

The gas mixture coming from the Glover tower consists of SO_2, NO, O, N, and water and weak acid vapor. A period of from 1 to 2 hours is required for reaction between them sufficient to convert substantially all of the SO_2 into sulphuric acid.

A place in which the gases may react, a chamber or series of chambers then, will be required of such volume that each portion of gas mixture will occupy from 1 to 2 hours in its passage from entrance to exit of the series. Liquid sulphuric acid forms and condenses within the chambers, which must therefore be constructed of such material and in such fashion as to retain liquid sulphuric acid.

The acid-forming reactions are, taken collectively, exothermic. It is essential for the proper progress of the reactions that the temperature of the gas mixture shall not rise much above the boiling point of water. It is therefore necessary that the chambers be constructed of such material and in such fashion that the heat of reaction can be readily carried away by radiation.

These considerations together with the experience of many years dictate the volume, the materials, and the method of construction of the chambers.

Sheet lead possesses a desirable combination of the essential characteristics so predominantly that it is universally used as the basic material for chamber construction. It is cheap, it resists acid well, it can be readily shaped, and its pieces can be burned together to make gas- and acid-tight joints. Furthermore it conducts heat well. Other materials have been tried from time to time but none so well meets the requirements.

It has been found best to provide instead of one single large chamber several smaller ones, usually three or more. Several good reasons for this exist. Mixing and stirring up the gas mixture accomplished by passing through flues from one chamber to another has been found to accelerate the reactions. By dividing the space into several small chambers more radiating surface is

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provided than if a single chamber were used. It is more convenient structurally to build several small chambers than one large one. A modern chamber set therefore consists of from three to ten chambers in series.

The individual chamber consists of three parts, pan, side or "curtain" walls, and top, all of sheet lead. The pan is ordinarily of lead weighing 8 or 10 lb. per square foot—*i.e.* 1/8 to 3/16 in. thick—with the bottom horizontal and the sides from 18 to 30 in. high. The pan is designed to be a reservoir for the acid made in the chamber and is supported strongly so that it will safely carry acid to within an inch or two of its top edge.

The side or curtain walls extend from the upper edge of the pan to the top of the chamber. They are of sheet lead of 6 to 10 lbs. per sq. ft. in weight. They are supported by lead straps burned to the sheets and fastened to a wood or steel framework surrounding the chamber. It was formerly common to allow the bottoms of the curtain sheets to extend down into the pan to within about 2 in. of the bottom. The acid in the pan then, so long as it was maintained more than 2 in. in depth, made a seal which retained the gas. This plan though followed for years and still used sometimes is not a sensible one. It wastes lead on original construction and after about two years that part of the lead which is immersed in the acid becomes so corroded that holes appear and much repair work or even reskirting becomes necessary. The usual plan of recent years is to burn together the top edge of the pan and the bottom edge of the curtain walls. Figure 21 shows the two methods.

The top of the chamber is usually of lead of the same weight as the curtain walls. It is ordinarily horizontal and the sheets are supported by frequent straps fastened to rafters of wood or steel. The sheets of the top and the curtain walls are burned together when they meet.

The bottoms of the chambers should always be far enough above ground to allow convenient inspection for leakage, say 6 or 7 ft. minimum, so that a man may walk about. This is important because leaks invariably develop and if the chamber pans were laid on the ground much loss of acid and damage to foundations and pans would result before the trouble was detected.

Concrete piers properly placed in the ground to carry the weight of the chamber structure and the pan full of acid are first set. On these are fixed wood or steel posts surmounted by wood

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or steel sills. On the sills is laid down a wood floor to carry the chamber pans. Between and around the pans the floor is of wood slats well apart, or perforated steel, a construction in any event which will allow free circulation of air up the sides of the chambers. It is well to build the floor on which the pans are to rest of plain boards, not matched—tongue and grooved—in order that leaks may be readily located. If the floor is too tight it may be difficult to decide just where the hole in the lead is, as the acid may travel some distance before it finds a crack or crevice through which it can issue.

The lead walls and tops of the chambers are supported by wood or steel framework or a combination of the two. For very large chambers steel is necessary because of the long spans and great height of columns. For small chambers wood is more economical and perhaps better adapts itself to fastening to the lead. Certainly it is not so fireproof though there is not any unusual fire hazard about chambers inherent in the process itself.

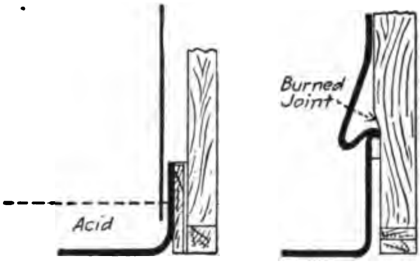

FIG. 21.

Two somewhat different general plans of wood framing for supporting the curtain walls have been used. The first, which is probably most used, provides posts of rather large section spaced perhaps 6 or 8 ft. apart. Secured to these are lighter horizontal rails 3 or 4 ft. apart vertically. Horizontal lead straps to correspond to these rails are burned to the lead curtain walls and nailed or cleated to the rails. On the top of the posts rests a heavy cap or crown timber. The curtain sheets are turned back over the top of this crown piece and part way down its outside and there nailed. The theory of this method of support is that almost all of the weight of the curtain sheets is carried by the crown piece, and the straps on the sides simply prevent lateral movement.

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There are of course many variations of detail in this scheme. Figure 22 shows the essential features.

The other system, shown in Fig. 23 provides vertical posts or studs of comparatively small cross section, much closer together, say 20 to 30 in. No horizontal rails are used. The straps are burned to the curtain walls vertically, a row to correspond to each vertical stud, and cleated to the studs. A light cap at the top of the studs serves merely to hold them in position. The curtain sheets are not turned over it but are curved in toward the center line of the chamber. The studs are appropriately braced and held in position by horizontal and diagonal members spiked to their outside faces. When the sides of the chamber pan

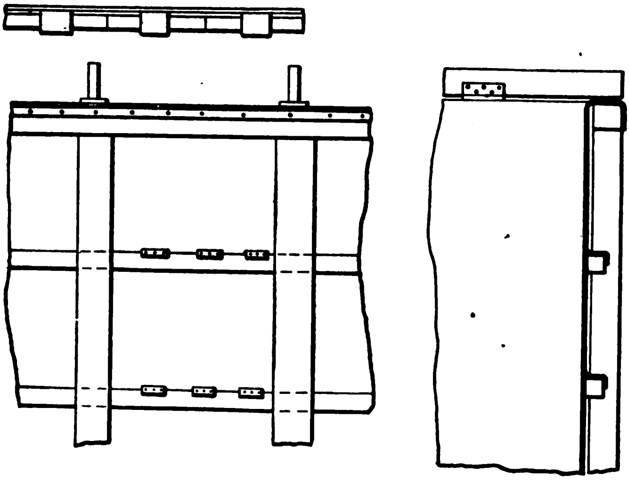
FIG. 22.

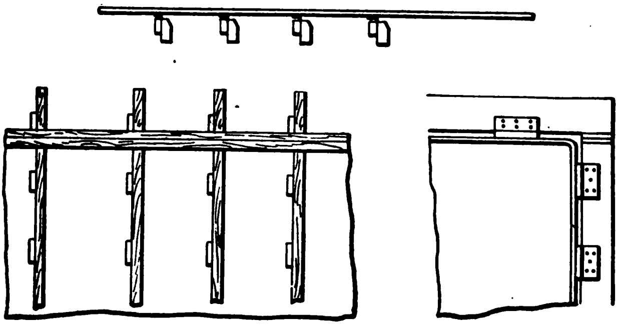
FIG. 23.

are of 10 lb. lead and the studs are not more than 24 in. apart it is not necessary to support the pan sides with planks. The theory of support by this method is that each vertical strap supports its particular small section—perhaps four square feet—of the curtain sheet, and the whole load is uniformly distributed.

There is some difference of opinion as to which is the better of these two general systems of support. The first described plan has been more generally used, but the second plan has some very important advantages in practice as well as in theory. Lead is a metal which has practically no elasticity. Under stress, particularly when warm, it flows. When a sheet 20 or 30 ft. long is suspended from a crown piece as described, with light horizontal straps at rather large intervals to prevent sway, it unfortunately does not all remain just where it was placed. When the chamber is heated up to 200°F. a considerable expansion occurs. When a stop and cooling takes place, it does not go back up again. On again heating, downward expansion again takes place. Furthermore there is some creep caused by stretching or flow. The net result of these influences in the course of a year or two, is that much of the load is transferred to the straps where it does not belong, and distortion of the curtain sheets results, or straps are pulled off, usually both. Another weak feature of this support plan is in the fact that behind the crown piece just where the strain is greatest on the lead, and where radiation is most obstructed, the lead is inaccessible for repair.

In the vertical-stud system each small rectangle of the lead is supported by its strap and the expansion of the lead with heating shows itself in very slight curves between straps. No large unsightly and damaging distortions occur. At the line where the side turns to the top, the lead is entirely accessible. From an erection point of view this framing plan is excellent also.

Steel framing for supporting chamber lead has been increasingly used of late years. Its use has been necessary in some of the large units in which individual chamber dimensions are so great as to make timber construction out of the question, or at least very awkward. In some modern plants of small dimensions the desire for permanency and fireproof construction has dictated the use of steel.

The construction is simple and usually follows the idea described first above under wood framing, *i.e.*, vertical posts or

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columns 8 to 12 ft. apart are used with horizontal members 3 or 4 ft. apart to which the lead is attached with straps. Angles are probably most used for both vertical and horizontal members though sometimes I beams for columns and channels for horizontal pieces are seen. The chamber top is supported by I beams or pairs of channels across the short dimension of the chamber, with pairs of small angles between them running longitudinally of the chamber to which the lead straps are fastened.

Chambers should always be protected by a building. The chief reason for this is to prevent wind pressure from reaching the lead Less important considerations are protection from sun, rain and snow, and facility of proper control of the process in bad weather. The chamber framing should be in no way connected with the framing or walls of the building as it is essential that movement of the building due to wind be not transmitted to the chambers. Ample openings in the walls below the chamber floor, and roomy ventilators in the roof are necessary to assure free circulation of cool air along the side walls of the chambers. Modern chamber plants are housed in steel or brick buildings.

It has been mentioned that one prime object of dividing the chamber space into several small chambers instead of using a single large one is to cause mixing and invigorating reaction by passing through connecting flues. Much thought and experimentation has been spent upon this subject of connections between chambers.

The most simple plan is to run a flue from the centre of the end of one chamber to the centre of the end of the following one. Another similar method is to use two or four direct horizontal flues between the ends of the adjoining chamber. Sometimes the gas is taken from near the bottom of one chamber and led to a point in or near the top of the following one. Or a flue will leave the lower left hand corner of the end of a chamber and enter the upper right hand corner of the next or vice versa, the object being apparently to have entrance to and exit from a given chamber at points most extremely distant from each other. The purpose of all these latter designs is to avoid having dead corners or wedges in the chambers in which the gas moves sluggishly or not at all, or in a word to avoid short circuiting. An arrangement sometimes used which is intended to introduce the gas into a chamber in such a way that it will conform to the natural

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movement of the reacting gases in the chamber is shown in Fig. 24.

This is based on the idea that any given portion of gas mixture will proceed through the chamber in a spiral course. Radiation at the walls causes the gas nearby to cool and descend. On reaching the bottom it is forced in toward the centre and reaction heat there causes it to rise again toward the top where it is drawn toward the side again by the descending stream. There is meanwhile a forward movement. This movement of course takes place on each side of the central vertical plane. The flue connections shown inject the gas on each side near the bottom and direct it toward the centre where it rises and immediately and naturally begins its double spiral progress.

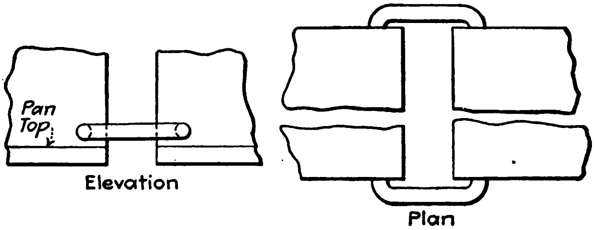

Fig. 24.

Many designers have used special structures between the chambers to insure thorough mixing of the gases and often cooling as well. These often accomplish the work for which they are designed. Sometimes they cost more money than an additional plain chamber which would give the same net result in tons of acid made and the intricacy of their lead work sometimes makes for heavy repair costs after they are a few years old.

In the 1918 "*Transactions of the American Institute of Chemical Engineers*," Dr. L. A. Thiele describes his Multiple Tangent System of introducing gases to the chambers.

His idea is to avoid the large amount of waste space, particularly in the corners, where the circulation in the chambers is sluggish. An additional advantage is a very considerable saving in area.

Gas is introduced from the top of the Glover tower, through flues, which vary in area and length, the largest in area being the shortest; this makes for varying rates of cooling, thus varying pressures and rates of flow-all of which results in more rapid circu-

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lation and better mixing. The flues are arranged as shown in the accompanying sketch, around the circumference of the top, Fig. 25.

If the outlet should be in the centre of the bottom, the gas would be a spiral cone, the outside parts of the bottom being dead space. Thus the outlets are arranged on a circle in the bottom, concentric with the reaction chamber, and with a diameter half that of the reaction chamber.

This arrangement is reported to save floor space and lead, and start remarkably easily.

Such an arrangement is in service at the plant of the Fairmount Chemical Co., Fairmount, W. V. It is running on coal brasses, which of course produce a large amount of CO_2, so the figures are not of the value that they would be if the conditions were more nearly standard, but Dr. Thiele expresses himself as well pleased with results.

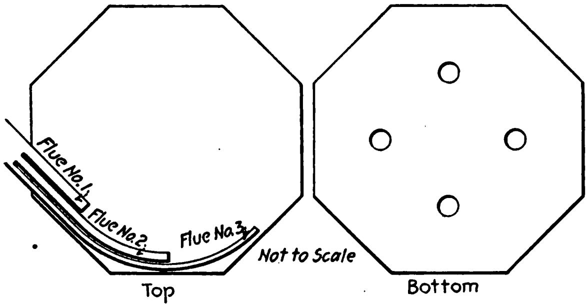

Fig. 25.

To briefly cover a few of the best known arrangements of this kind, the Lunge Plate Column is one of the early proposals. This is essentially a comparatively small lead tower packed with stoneware plates spaced a few inches apart. These plates have numerous small holes in them so arranged that holes in one do not occur directly below those in the next above. The plates have slightly raised circumferences and the rims of the holes are also raised so that some acid always lies on each plate and drips down through the holes and splashes about as fresh acid forms or is fed in. This apparatus is not for big plants for size of plates is necessarily limited.

The Gilchrist Pipe Column is a lead tower with many horizontal lead pipes extending through from side to side, both ends

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being open to the air. Circulation of air through the pipes gives some cooling effect and the mixing is attained by the gas forcing through between them.

Lead towers packed with brick or coke, or quartz, similar in construction to Gay Lussac towers are sometimes used between chambers. These may be used dry or may have cool acid circulated over the packing.

A series of two or three open towers with neither packing nor circulation of acid has been used.

Chambers are fitted with steam or water connections or both, for introducing the necessary water to make acid of proper strength. Steam is usually put into each chamber at two or three places only, as it spreads well. These are usually in the top, sometimes in the front end wall. Water must be introduced at several points and in a very finely divided condition for otherwise drops would go quickly down to the bottom without entering into the reaction. Special atomizing nozzles of glass or stoneware or platinum are made for the purpose. The water for this purpose must be filtered and delivered to the nozzles at uniform pressure usually about 60 lb.

Steam distributes through the reacting gases better than water spray unless the apparatus for introducing the latter is carefully taken care of. Water of course is much cheaper to use if live steam has to be used. If a uniform supply of waste steam is available it is quite acceptable. Water has the advantage over steam in that it exerts a considerable cooling action on the gas mixture which in summer particularly is valuable.

In order that the operator may know the gravity of the acid being made in any given chamber at any time, small gutters are burned to the inside of the chamber walls at one or two convenient points. A portion of the acid running down the walls is diverted by them to an opening in the curtain through which it flows over a sealing lip into a small jar in which is kept a hydrometer. By observing and recording the hydrometer readings from time to time the operator is enabled to control properly the admission of steam or water to the individual chamber.

One or two thermometers are inserted into each chamber. If one only is used it is placed in a side wall at the centre and about 5 ft. above the working floor. If two are used one is placed near each end. These thermometers are made with a

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long stem, usually about 12 in., below the graduated portion. This stem is turned 45° or 90° from the graduated part and is inserted through a rubber stopper inside the chamber wall, the graduated part being vertical and conveniently read. Such thermometers are stock articles with the large supply houses.

The last one or two chambers of a set are frequently equipped with bell jars or sight glasses in order that the color of the gas may be observed.

For drawing off the acid from the chamber pans and for communication between them, pipes are led from the bottom of the pan to a boot near the end or between the chambers, or small alcoves are made on the pan ends which are joined beneath the floor by pipes. In any case at least one end of each such pipe should be accessible for blowing out accumulations of mud. Figure 26 shows details.

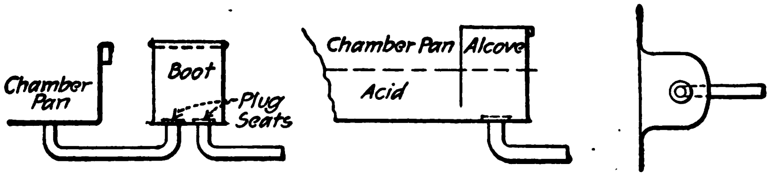

Fig. 26.

CHAMBER VOLUME

The number of cu. ft. of chamber volume which must be provided for making a given tonnage of acid depends upon several factors. It may first be well to note that it is customary to speak of the performance of chambers as using a certain number of cu. ft. per pound of sulphur per 24 hours. This expression of rating was brought into use to do away with the uncertainty that existed when one spoke of volume per unit of acid. It was found that the manufacturer whose product was 50° acid often spoke of his production in terms of 50° acid while he whose product was 60° used that as a basis, and yet others had in mind 66° or even 100% H_2SO_4.

In order to make common ground of comparison the idea of using sulphur itself as a basis has come into general use. Even this is not always common ground as one man will reckon on sulphur contained in the ore burned, another on sulphur burned

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out of the ore, and a third on sulphur in the acid made. Of course only the last is correct.

There is a divergence in claims of performance and a divergence in performance of modern acid plants, in respect of cu. ft. of chamber space per pound of sulphur in acid made per 24 hours, of from about 8 to 20. An average of these two extremes, say 14, is probably not far from the volume actually used in most plants. The plants which run on 8 or 10 cu. ft. per pound of sulphur have special arrangements such as towers fans, etc., in connection with their chambers. Some plants having small plain chambers in which the ratio of radiation surface to volume is comparatively high run on 10 to 12 cu. ft. Some few plants have been constructed in recent years in which large units—100 to 300 tons 60° acid—contained only 4 or 6 enormous chambers. The ratio of surface to volume is very low—mixing, cooling, and impingment are largely sacrificed, but construction cost per cu. ft. of chamber space is very low. In these plants around 20 cu. ft. per pound of sulphur was provided and is used.

These observations bring out the fact that merely to say that a plant is working on so many cu. ft. of chamber space does not determine whether its performance is all that should be expected or not. If two plants of different design are built and each costs $500,000, each produces 100 tons of acid a day with the same operating costs, and one operates on 8 cu. ft. and the other on 20 cu. ft. the performance of the latter is just as creditable as that of the former.

It is the opinion of many designers that plain chambers of moderate size and simple design give the most satisfactory results all things being considered.

LEAD SPECIFICATIONS

One of the largest Chamber Acid plants in the country answers our inquiry as follows:

"It has not been our practice to make any other specification except that lead shall be what is known to the trade as 'chemical lead.'

"We have always purchased this from the same company and the quality has been uniform. It must be free from other metals, and sufficiently ductile to permit of rolling out into thin sheets. The addition of small percentages of copper has been advocated by some engineers, but we have had no experience with this alloy. For the construction of acid valves, fans and other apparatus that require

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structural strength, we use a mixture of chemical lead with 7 per cent to 10 per cent antimony.

LIFE OF LEAD

"The exact life of lead in chamber plants cannot be accurately stated, as it depends too much on local conditions. I would say that the life is influenced chiefly by the temperature and whether or not scouring action obtains. We have had chambers to run without interruption for nearly 10 years, but repairs were made to various parts during the interval."

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CHAPTER X

GAY LUSSAC TOWERS

The Gay Lussac towers follow the chambers in the course of the gas. They receive from the chambers normally a gas mixture consisting essentially of nitrogen about 92 to 96 parts by volume, oxygen about 4 to 8 parts by volume and the oxids of nitrogen NO and NO_2 from $\frac{5}{10}$ to 1 per cent by volume. Of course small amounts of CO_2 and other gases are present but ordinarily have no bearing on the subject. There are a few special cases where carbonaceous fuel is used in the furnaces from which the SO_2 is derived, in which CO_2 must be reckoned with. These are unusual and need not be considered in a general discussion. The temperature of this gas entering the Gay Lussacs is only slightly above that of the atmosphere. The result desired from the Gay Lussacs is the recovery of the oxides of nitrogen by absorption in 60° sulphuric acid which is fed into them.

The Gay Lussac towers then should be built of such material as to resist the action of comparatively cool 60° acid and gas. They should be designed in such a way as to bring the gas and acid into as intimate contact as possible and yet allow reasonably free passage for the gas. They must be of such height as to allow a sufficient degree of contact between gas and acid to accomplish substantially a 90 per cent recovery of the nitrogen oxides.

These requirements differ from those of the Glover tower in the matter of temperature of gas and volume. In the Glover tower the gases enter at temperatures so high as to be injurious to bare lead and it is therefore necessary in constructing a Glover tower to provide a heavy masonry lining wall to protect the lead shell. No such protection is required in the Gay Lussac towers wherein the gas temperature rarely reaches 120°F. The Gay Lussac tower therefore need be simply a well supported lead shell completely filled with packing, excepting of course the gas chambers above and below. This statement does not apply in those cases where non-symmetrical packing such as coke or quartz is used because such material, in a column 20 to 40 ft.

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high, exerts so much lateral thrust as to bulge and cut the lead, and masonry supporting walls are necessary. It is unusual to use such packings now. With the symmetrical packings, bricks, rings or other shapes, the weight is all carried on the bottom.

Some designers still build Gay Lussac towers with lining walls even though symmetrical packing is used, but it is a waste of material and a waste of good absorption space. Also it is actually bad for the lead shell to have an interior wall, in that gas gets in between the masonry and the lead, circulates sluggishly, and the nitrogen compounds oxidize up to nitric acid which often corrodes the lead badly.

With this exception the general construction of the Gay Lussac towers is much like that of the Glover. A massive foundation is put down of sufficient height that the acid issuing from the tower pans may run by gravity to circulation tanks. This usually means on a level site that the top of the foundation will be about 10 ft. above the ground. The top surface of this foundation is carefully levelled and made smooth by trowelling. A sheet of light lead 4 to 6 lb. per square foot is next laid. The edges of this sheet may be turned up a few inches to make a shallow pan and a drain pipe put in, or else the edges are projected a few inches beyond the concrete and turned down slightly to throw any acid leakage away from the foundation. This lead is also turned up around the footings of the columns of the framework.

The tower pans are made of 15 or 20 lb. lead and are usually 24 in. high. False bottoms of 10 lb. lead are placed inside over those portions of the bottom on which the brickwork is to rest. The side sheets of the tower are hung, fastened to the frame and burned together. They may be burned to the pan or extend down inside it. The latter method is not so bad here as in the chambers as the acid is cold. However it wastes lead and has no particular advantages. The side walls are usually of 10-lb. lead.

Ordinarily the top is not put on the tower till the brickwork is in. Through the open top the brick and packing material is introduced. It is perhaps easier and safer to open three or four holes in one side and put in the packing through them. When the packing is finished these holes are closed by the lead-burners. All danger of bricks falling and injuring the workmen is done away with if this plan is followed. The top lead is of the

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same weight as the side sheets. A chamber 4 or 5 ft. high is left without packing at the top to provide for the proper acid distribution and leave the exit flue free.

The base structure for supporting the packing and the packing proper are substantially as described under the Glover Tower.

There should be on each Gay Lussac tower a carefully designed acid distribution system with suitable tanks for feeding it. This apparatus is described under Acid Circulation.

As to volume, dimensions and number of Gay Lussac towers suitable for a unit of given size a considerable difference of opinion seems to exist if one may judge by an examination of different plants. Reverting first to the classic Lunge we find Gay Lussac towers compared in volume to the total chamber space which they serve. Lunge states that the packed volume of the Gay Lussacs should be not less than 1 per cent of the chamber space and better between 2 per cent and 3 per cent. This method of proportioning would be satisfactory if all chamber space did the same work but such is not the case. As mentioned before some chamber sets use 20 cu. ft. of space per pound of sulphur and others less than 10 cu. ft. Lunge of course refers to continental practice of several years ago in which the larger amounts of chamber space were used. It is more pithy in this day to proportion and speak of Gay Lussac volumes in terms of sulphur made into acid of 60°Bé. On this basis Lunge advocates not less than 100 cu. ft. of packed volume per ton 60° acid produced and for really good nitre recovery up to 200 cu. ft.

This range from 100 to 200 cu. ft. of packed volume per ton 60° acid is about what is found in modern American plants. Certainly the upper figure should be approached but this is not always done. With Gay Lussacs well proportioned and skillfully operated whose packed volume amounts to 200 cu. ft. per ton of 60° acid made in the plant, a recovery of about 90 per cent of the nitre can be made. The total nitre introduced into the modern plant amounts to 25 to 30 per cent of the sulphur. The loss of nitre then on the above basis amounts to 2.5 to 3 per cent of the sulphur.

The absorption of nitre in the Gay Lussac towers is of course much more rapid in the earlier part than the late parts. Without attempting to formulate or to give exact figures it may be said that in a case where the Gay Lussac space was divided into three towers in series it was found that the first tower retained about

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65 per cent of the nitre in the gas entering it, the second tower about 60 per cent of the remainder and the third tower about 60 per cent of that yet remaining. It must be considered that probably about 5 per cent of the nitre is not recoverable by solution in Sulphuric acid. The above will then work out as follows:

95 per cent total recoverable.
1st Tower 65 per cent of 95 per cent = 61.75
2d Tower 60 per cent of (95 − 61.75) = 19.95
3d Tower 60 per cent of (95 − 81.70) = 7.98
Total........................89.68

As explained these figures are intended simply to give a rough idea of the relative recovery accomplished by the different zones of Gay Lussac space.

Having decided upon the volume of Gay Lussac towers the number of towers and their dimensions are next calculated. In order to secure uniform distribution of gas and acid throughout the packing, it is well to make the horizontal section not too large and consequently the vertical dimension long. A high tower with small horizontal section makes a much better nitre recovery than a low tower with large horizontal section, the packed volume in both cases being identical. This is to some extent due to more uniform distribution of gas and acid through the packing, but in larger measure to higher gas velocity and consequently more thorough breaking up and mixing of the gas with the acid. The minimum amount of horizontal section will be dictated by the pressure necessary to force the gas through the packing. It is not desirable to use high pressures because the leadwork of the flues, fans and towers will not stand them. Certainly the pressure at the entrance of the first Gay Lussac should be not over $\frac{5}{10}$ or $\frac{6}{10}$ of an inch of water or say 12 to 15 mm. For ordinary packing a gross horizontal sectional area of 2 sq. ft. per ton of 60° acid made should be provided to accomplish the above result. The total vertical dimension of the tower packing should then be 100 ft. if we wish to provide 200 cu. ft. packed volume per ton of 60° acid made. It is not practical to use a single tower 100 feet high because of the difficulty of pumping acid of 1.7 sp. g. to such an elevation, and so it is customary to use two or three towers in series. If two towers be used the height of each will be 50 to 60 ft. allowing 10 ft. in each for the spaces above and below the packing. Likewise if three be used

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the height of each will be 43 ft. As the tower bases will be at the least 10 ft. above the ground and the feed tanks about 12 ft. above the top of the tower it is seen that to the above figures some 22 ft. must be added to get the vertical distance of the acid lift.

It should be remarked that many plants will be found in which the Gay Lussac tower scheme does not check up at all closely with the line of reasoning presented above. Unquestionably somewhat wide variations can be made from it without sacrificing good work. The figures presented are however quite certain to yield excellent nitre recoveries.

To give a concrete example of Gay Lussac towers for a plant to produce 100 tons of 60° acid:

Total packed volume @ 200 cu. ft. per ton........	20,000 cu. ft.
Sectional area @ 2.25..........................	225 sq. ft.
Vertical dimension $\frac{20,000}{2.25}$ =	89 ft.

Using 3 towers packed height each say 30 ft. Total height each allowing 10 ft, for spaces above and below packing 40 ft.

If the section be made square the horizontal dimensions will be 15 × 15. In the writer's opinion it would be better to make the section rectangular say 9 ft. ×25 ft. and to admit the gas at three points on the long side. Such a plan probably more fully utilizes the packing than the square section.

The course of the gas should be upward in all the towers as it has been demonstrated that a given tower performs better absorption with the gas going upward, than downward. The flues between the towers then will leave the top of the first, descend and enter the bottom of the next.

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CHAPTER XI

ACID CIRCULATION

The acid circulating system will be in this discussion taken to include tanks, coolers, pumps, pipe lines and distribution apparatus.

Tanks are almost always provided at the top and bottom of each tower. They are certainly indispensable when intermittent pumping is used, *i.e.*, by acid eggs or montejus. The flow of acid into and out of each tower must of course, be uniform and continuous and during the periods when the eggs are filling there must be a stock of acid at the top to feed the towers and there must be a place at the bottom to accommodate the acid issuing. Even when continuous pumping apparatus such as centrifugal pumps or air lifts is used, it is advisable to have tanks both above and below, although in this case they need not be so large.

Three kinds of tanks are used for this service, viz., lead-lined wood tanks, lead tanks supported by skeleton iron framework, and iron tanks. The lead-lined wood tanks are most used and the iron tanks least.

Wood tanks are always of rectangular section for convenience of framing. Usually they consist of rather heavy sills and caps with upright posts, strongly put together with bolts and dowels. Inside this frame, 2 or 3 in. planks are spiked, making a smooth and solid wall all round. Lead usually 10 lb. per square foot is then put in and turned over the top caps and an inch or two down outside. The burned seams should be some little distance from the corners as they are the places most likely to break open.

A neat way of making a wood tank frame, particularly for small tanks is to build up a crib of 2 × 4 or 2 × 6 material as shown in Fig. 27. This of course, leaves 2-in. strips of the lead open for the air, but no bulging of any moment occurs.

Lead tanks with iron frames are always made circular. The iron frames consist of four or more upright angle iron pieces with flat circular bands or hoops riveted inside. The number of hoops for a tank 4 ft. 6 in. or 5 ft. high is usually four, one at the top,

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one near the middle and two below the middle where the pressure is greatest. The dimensions of the iron parts vary with the size of the tank. For a 10 ft. diameter × 5 ft. deep tank, the angles would be about 4 × 4 × ½ and the bands 4 × ½. Ten- or 12-lb. lead is used in tanks of this type. They are very satisfactory if the details of design are correct, and very neat in appearance.

Iron tanks have come into use to some extent in the last few years for 60° acid. There is no particular reason why they should not be as satisfactory as are iron tank cars or storage tanks. They cannot be so readily repaired in case of leakage as can lead tanks but on the other hand, for several years at least they are not so likely to leak They should not of course, he used for acids much under 60°Bé.

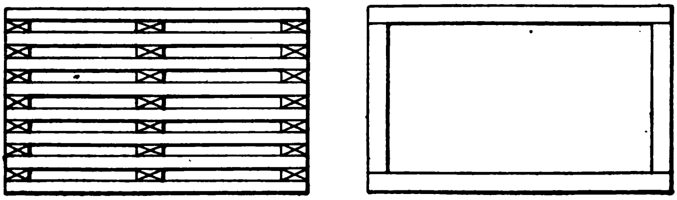

Fig. 27.

Circulation tanks of any construction are usually made from 4 ft. 6 in. to 5 ft. high. This makes them easy to look into and allows light construction as no great pressures are produced.

The capacities of circulation tanks vary widely for plants of a given size. It is not desirable to tie up too great a tonnage of acid in circulation and yet reasonable capacities should be provided to carry over periods in which minor repairs to lines, valves, etc., may be necessary. It would seem that tanks large enough to contain at least two hours' normal flow should be provided at the top and bottom of each tower. At the bottom of the Gay Lussac tower which produces finished nitrous vitriol, somewhat more space is desirable, up to six or eight hours' flow, say. This allows a stock of nitrous vitriol to be held which is highly desirable in restarting the acid process in case of a shut down.

It is a very good plan to have two small tanks at each point instead of one large one. If this is done one tank may be cut out to clean or repair without disturbing operations. The pipe lines leaving a circulation tank should have machined seats of hard lead (or iron, if iron tanks are used) at their points of exit

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from the tanks, and plugs or stems to correspond. In case valves in any line have to be changed or the line opened for any reason, the plugs can be set and the flow of acid stopped. It is convenient to have a washout pipe of generous size in the bottom of each tank as well as the service line. This washout is ordinarily closed with a blind flange.

Storage tanks for sulphuric acid are made of mild steel plate with riveted joints. They are of circular section, have flat bottoms and dome or conical tops. They are similar in general features to large tanks used for storage of oil, except that as the liquid they contain has a high specific gravity they are heavier metal. It is highly important that all seams shall be perfectly tight because any leakage, however slight, causes serious outside corrosion in a short time. The bottom of the tank should be supported on masonry walls or piers a short distance above the ground in order that the bottom seams can be inspected. The pipe for drawing off the acid is equipped with a seat and plug or a long stem or with an inside swing pipe so that the flow of acid from the tank may be stopped in case of a failure of a valve or pipe. Every storage tank should have one or two manhole castings with blind flanges bolted on in its side near the bottom in order that the mud may be cleaned out of it from time to time. If such cleaning is necessary only at long intervals, say over one or two years, the mud may be flushed out with a strong stream of water. There will be produced during the time of such washing acid solutions of a strength which attacks iron, but the injury done the tank during the few hours required for washing out is negligible. Removal of mud from a storage tank by hand is a serious and dangerous task.

The acid issuing from the Glover tower is so hot as to be injurious to pipes etc., and far too hot to absorb nitre when it is put over the Gay Lussacs, hence coolers are necessary at the base of the Glover tower. These are open-top tanks containing lead-pipe coils through which cold water is circulated.

This is sometimes augmented by spraying water on the outside of the tank or by making it with double walls and circulating cold water between them. The hot acid is discharged into the top of the tank and leaves it at the bottom through a pipe which rises up almost to the top again. In this way the cooler is always kept full and the acid takes its natural course, *i.e.*, as it is cooled it sinks to the bottom and runs off.

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The tanks are made with wood boxes lined with lead or with iron framework, as described above. Some times a brick lining is put inside the lead. If the tank is jacketed it is made with the shells heavy enough to be self sustaining. The coils are made of $1\frac{1}{4}$-in. or $1\frac{1}{2}$-in. lead pipe. They may be made flat spirals or upright spirals. If flat, several are placed superimposed. If vertical, they may be of different diameters and set concentrically or may be of the same size and set side by side. The cold water enters at the bottom and circulates upward and leaves the top, in this way the cold water is brought into contact with the cooler acid, and the warmed water with the hot acid. Superimposed flat coils are not to be recommended on account of the inconvenience of repairing or replacing them. Uniform upright coils are best in this respect and give fully as good results as regards cooling. A sketch of a cooler with this type of coils is shown in Fig. 28.

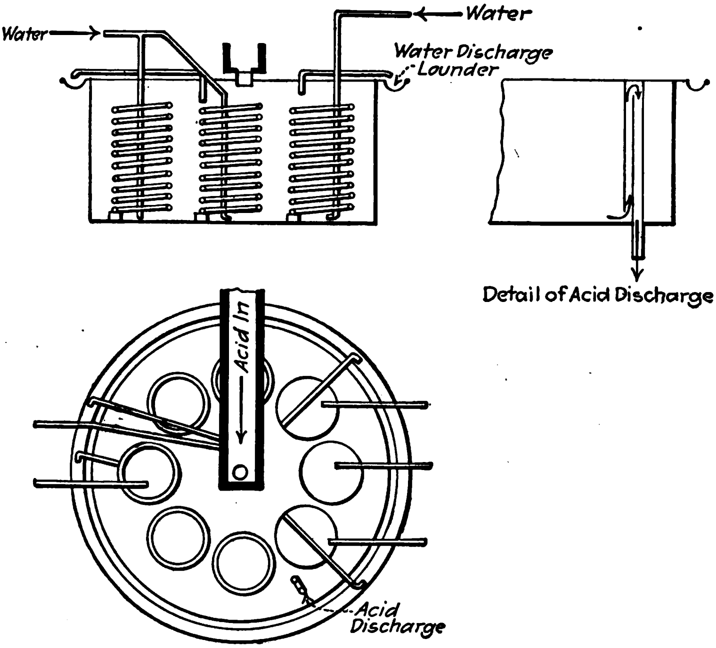

Fig. 28.

Between 1 and 2 sq. ft. of coil surface should be provided per ton of acid per 24 hours going through a cooler tank. The

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cooler tanks should have an acid capacity such that the acid will be in contact with the coils from 1 hour to 1½ hours. For example, if the tower is discharging 300 tons of 60° acid per 24 hours, the total surface of the pipe coils should be perhaps 450 sq. ft. and the acid capacity of the coolers should total around 15 tons or 285 cu. ft. These proportions may be varied properly with the temperature of the acid issuing from the Glover and the temperature of the cooling water. They work well if the former is 275°F. and the water 60°F., *i.e.* the acid will issue from the cooler at a temperature around 70°.

There should always be at least two coolers with the inlet launders and discharge pipes so arranged and of such size that any one cooler may be cut out, emptied and washed while the entire acid stream goes temporarily through the others. A generous washout pipe leading to the sewer should be provided on each cooler tank.

Pumping sulphuric acid presents difficulties which are not encountered in pumping water, oil and other familiar liquids. It is corrosive to many metals and it quickly destroys any packing material. Hence, any pump which depends upon a flexible packing for tightness is out of the question. Reciprocating, or plunger pumps cannot be used at all and even centrifugal pumps which involve glands packed with flexible material are troublesome. These facts have led to the almost universal use of an apparatus known variously as the acid egg or blow case, or montejus. The air lift or pulsometer is also widely used and to an increasing extent, the vertical submerged centifugal pump.

The acid egg is a cast- or wrought-iron vessel provided with three openings for pipe connections. One of them which just enters the egg is connected to the supply tank and through it the acid enters the egg by gravity flow. The second which also just enters the egg, serves alternately for the admission of compressed air and the blow-off. The third pipe extends almost to the bottom of the egg and through it the acid is forced out of the egg and up through the discharge line to a tank on top of the towers. To operate this device, the blow-off valve is opened to atmospheric pressure and the compressed-air valve is closed. The valve in the feed line is opened and the egg allowed to fill with acid. Next the valve in the feed line is closed, the blow-off valve is closed and the compressed-air valve is opened. The compressed air flows into the egg and forces out the acid through

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the discharge line. When the egg is empty or nearly so, the compressed air is shut off and the blow-off valve is opened. When the pressure is relieved, the feed line is once more opened and the cycle begins again. Figure 29 shows a typical layout. It is important that the blow-off pipe be carried up above the level of the top of the feed tank in order that acid may not run out through the blow-off line when the egg is filled. The blow-off valve is of acid proof construction. The arrangement shown is operated by hand. A convenient modification is to have a check valve in the feed line instead of a hand-operated valve. There have been many clever automatic devices developed for operating the compressed air blow-off valves. Almost all of them depend upon the action of a float within the egg to open and close the valves or ports. The Kestner Automatic Egg was an early and much used apparatus of this type but is probably not being installed in this country now. Descriptions of it can be found in Lunge and other publications of several years ago. Simpler and more satisfactory automatic valves are now being made by the Schulte and Koerting Co. and the Monarch Manufacturing Works, both of Philadelphia. Both of these consist essentially of a small lead casing in which a float works. When the egg is empty the lower part of this float, which is conical, seats in a depression whose sides are pierced by ports connected with high-pressure air, and closes them. When the acid rises up about the float it rises off these ports and its upper surface seats against the orifice of the blow-off pipe, thus admitting air to the egg and closing the blow off. The acid is blown out through the usual discharge pipe and when all out the air also escapes and the

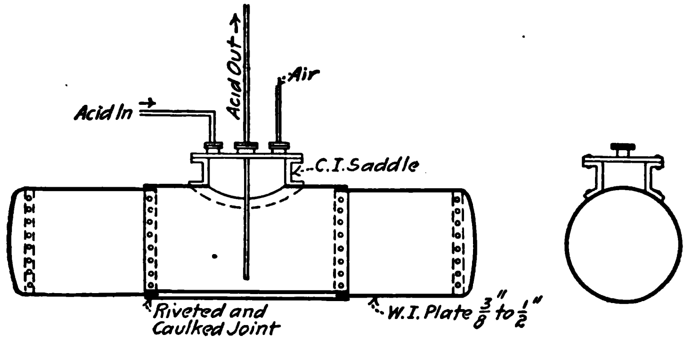

FIG. 29.

pressure within the egg decreases to such an extent that the float drops and closes the air inlet and opens the blow off.

It is to be considered that any automatic apparatus requires a certain amount of attention to keep it in order. Also that the flows of acid into and out of tanks must be kept under observation. One man can easily operate a large battery of hand-operated eggs and the latter are almost trouble proof. It is a question therefore, whether or not, everything considered, automatic apparatus is more satisfactory than hand-operated. As regards economy of air and power, the matter is largely one of the care with which the apparatus is operated and maintained. To be sure, a careless pumpman can waste a great deal of air. On the other hand an automatic valve which is not working properly can do the same. Air pumping at best, is a very inefficient method of using power.

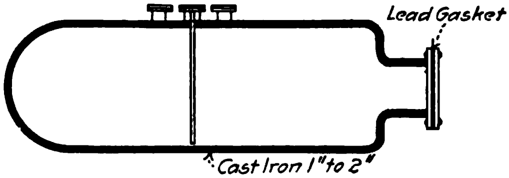

FIG. 30.

Eggs for pumping sulphuric acid were formerly almost always made of cast iron, but as the size of chamber units increased and the volumes of acid to be raised correspondingly increased, it became desirable to make very large eggs. In cast-iron, these would be enormously heavy and expensive and so the egg made of wrought-iron plates, riveted together was evolved. Such eggs are now in use of a capacity up to 250 cu. ft.

Cast-iron eggs are made in several different shapes, one of which is shown in Fig. 30. Usually only two pieces are necessary to make up the complete egg, *i.e.*, there is just one flanged joint to be made. This joint is made tight with a gasket of 10- or 12-lb. sheet lead. Three flanged nipples are cast integral with the egg body. In some cases a depression, or well, is made below the nipple designed for the discharge pipe and the latter dips into it, the idea being to get all the acid out of the egg at each pumping. This is a rather unnecessary refinement as in a short time the bottom of the egg accumulates some sediment and the end of the discharge pipe is in a "well" in this sediment anyway.

It is unwise to line iron eggs with lead as some minute opening in the latter is sure to develop. When this occurs the lead is very soon blown away from the iron by the action of the air and soon the iron is exposed to the action of the acid anyway. Cast iron eggs of ample thickness, up to 2 in. last for many years if only acids near 60°Bé. are handled in them.

Wrought-iron eggs should be made of as high grade wrought-iron plate as can reasonably be obtained. The usual design is shown in Fig. 29. A cast-iron saddle is riveted on one side and this covered with a plate on which are cast the usual nipples. This plate is bolted to the saddle which also serves as a manhole. As mentioned, eggs of this type are especially suitable in the large sizes.

For elevating acid of 50° or less, iron eggs are not suitable as too much corrosion results. For this service the air lift is much used. It is a satisfactory device but it uses a very large amount of power and has some other disadvantages which make it less suitable than eggs for pumping 60° acid.

In its simplest form, the air lift is a U-shaped pipe with one limb longer than the other and with a pipe for carrying compressed air entering the long limb just above the turn at the bottom. The acid to be elevated is fed into the short limb and the long limb discharges into an elevated tank. To operate, acid is allowed to flow into the pipe until the acid is level in both limbs, then the compressed air line is opened somewhat. The air produces an emulsion or mixture of acid and air bubbles. When sufficient air has become mixed with the acid that the column of mixture filling the long limb is lighter than the column of solid acid in the short limb, a flow is established. To get good results with an air lift the long limb should be not more than two times the length of the short limb and it is preferable to make the ratio 1½ to 1 when elevations permit.

Ordinarily, as in elevating acid from the chambers to the top of the Glover tower, the elevations are such that a single air lift cannot be arranged above ground, *i.e.*, the height of the chambers above the ground is very much less than one half the height of the Glover tower top above ground. In order to get a sufficient length of the short limb of the lift a pit or well is sunk into the ground and the pipe extended down into it. While this is a very common procedure, it sometimes leads to considerable trouble and serious loss of acid in case of leakage. In a well particularly,

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inspection is impossible and a leak may exist for some time before it is suspected. To repair, it is necessary to draw the pipes out.

In order to do away with the well, or pit, the multi-stage lift was developed. This simply amounts to putting together several simple lifts of increasing height until the final elevation is reached. It has the advantage of being all above ground and in sight. It is necessary of course, to so adjust the admission of air to each lift that it will take away all the acid which the preceding lift delivers to it. Once properly set, an air lift goes on elevating acid without supervision. It would seem from the theory of this method of lifting acid that the air should be forced in through many small orifices rather than a single larger one. We find in practice both arrangements and from the author's experience, it must be said that there does not appear

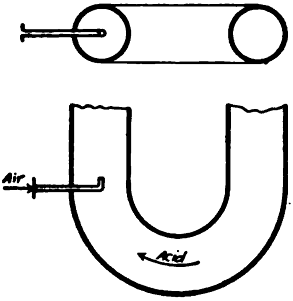

FIG. 31.

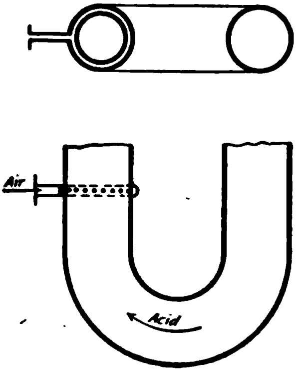

FIG. 32

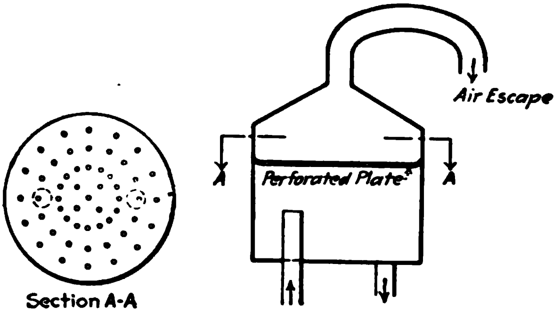

FIG. 33.

to be any great difference in general results. Details of two common schemes are shown in Figs. 31 and 32. At the top of the long limb it is necessary to provide a box, or pot, to receive the mixture of acid and air, in which the two can separate and from which the acid can run into a tank or another lift and the air escape. A baffle of some kind prevents acid from splashing out of the air exit. Figure 33 shows such an arrangement.

From the standpoint of economy of power and supervision, the centrifugal pump would appear to be the best way of elevating acid. Concerning power, there has never been any question as to the economy over air pumping. Maintenance of centrifugal pumps has for years been the thing that has prevented their general use and the stuffing box where the shaft enters the case the particular point of trouble. Sixty degree acid rapidly destroys rubber, or flax, or any of the ordinary flexible materials used for packing. Many metallic packings and combinations of metals with the flexible materials have been tried with indifferent success. Special, and often highly ingenious glands have been devised but so far as the author knows, all of these leave much to be desired.


FIG. 34.

A centrifugal pump which approaches the problem from a different angle has been put into use during the past three or four years and appears to be very satisfactory. This is a pump with a vertical shaft. The whole pump is placed in the tank from which the acid is to be pumped or in a boot connected with it. The shaft extends a short distance up above the top of the tank or boot and is driven by a belt or direct connected motor. The stuffing box trouble is entirely sidestepped. This pump is shown in Fig. 34. One of these pumps working in 60° acid has been under the author's personal observation for more than

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a year, during which time not a cent has been expended for repairs. To give an idea of power consumption, it may be said that one of these pumps equipped with a 5 H.P. motor elevates about 250 tons 60° acid per 24 hours to a height of about 90 ft. The vertical pump has no particular advantage of course, over the horizontal pumps in the matter of power.

The pipes used for conveying acid from one part of the apparatus to another are mostly of lead. They are joined together and to lead tanks by burning. When lead pipes are joined to iron apparatus or when the joints are not permanent as in case of valves, iron flanges are used. The method of making a flanged joint is shown in Fig. 35. Oval flanges with two bolts are suitable for small pipe, but for larger sizes, 2-, 3-, 4-in. or larger, the 4- and 6-hole circular flanges are better.

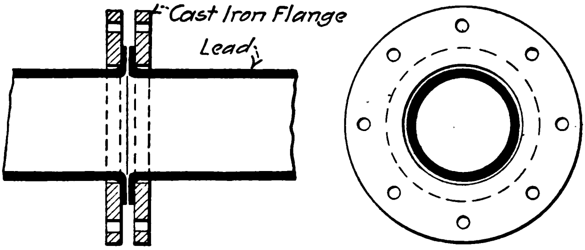

FIG. 35.

Iron pipe is very successfully used in certain places in an acid plant. For example, the lines carrying 60°Bé. acid from the eggs or centrifugal pumps to the tanks at the tower tops can much better be of iron than of lead. These lines often have to sustain pressures of 75 to 90 lb. per sq. in. If they are of lead, they gradually swell and grow thin and sometimes suddenly split open and deluge a large area with acid. Iron pipes, particularly extra heavy iron pipes, last for years in this service and when they do fail they give ample warning by first showing minor leaks. They are best made up with flanged joints using lead gaskets, so that any piece may be replaced without taking down a long run of pipe. Turns should be made by bending the pipe in fairly long radius arcs instead of using fittings. Another advantage which iron pipe possesses is its superior rigidity. Lead pipe is likely to be badly shaken and eventually cracked by the blow off of eggs, while iron pipe can be very securely bolted to framework to prevent such shaking.

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As the discharge lines from eggs or centrifugal pumps deliver acid at rather high velocity, provision must be made at the points of delivery to prevent splashing. This is done by running the pipes into splash eggs or covered boots as shown in Fig. 36. If the form shown in sketch A is used, it can well be made of cast iron.

It is necessary to have some method of knowing how much acid each top tank has in it, in order that the pumping may be done at proper times and the flows maintained. Three schemes of merit are in use, viz., floats, pneumatic indicators and electrical indicators.

In the float system a hollow lead float rests on the acid in the tank and has fastened to it a chain or cable or wire which runs over pulleys to a convenient point near the pumps where it is fastened to a weight running on a graduated board. As the acid rises and falls the float moves the weight up and down and indicates the level. This works well enough but it is rather cumbersome.

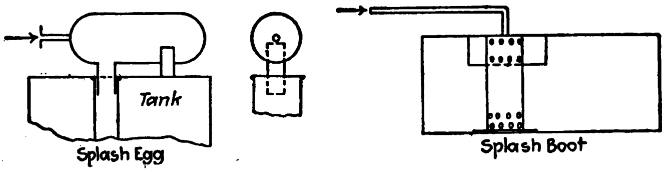

FIG. 36.

In the pneumatic scheme a bell or pot is set on the bottom of the tank. A small bore metal tube is connected to it and runs to a mercury gauge at the desired point. A compressed air line or a small air pump communicates with this tube. Air is admitted to the tube until all the acid is blown out of the latter and out of the bell in the tank and then shut off. The head of acid in the tank then compresses the air in the bell and the tube and the pressure exerted is indicated in the mercury gauge which is graduated to show the stage of acid in the tank. Absolute tightness of this apparatus is imperative as the most minute leak renders it unreliable.

Electrical indicators are simplest and best. An ordinary direct or alternating light circuit is employed. Lead rods of varying lengths are hung in the tank to be indicated. An incandescent lamp on a board is provided at the desired point of observation

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to correspond to each. One side of the light circuit is connected to one socket terminal and the other side to the lead rod. The metal of the tank is connected with the other socket terminal. When the acid in the tank is in contact with the lead rod the current flows through the acid and lights the lamp. When the acid falls below the rod, the circuit is opened and the light goes out. It is customary to use at least two rods and lights to each tank or as many levels as desired can be shown by using more. It is a good plan to provide a bell or horn connected to all the tanks to call attention to any tank which is in danger of overflowing. Figure 37.

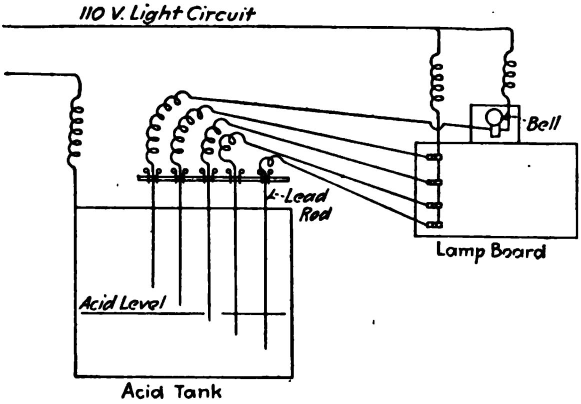

FIG. 37.

DISTRIBUTION

The fundamental purpose of the towers, both Glover and Gay Lussac, is to bring acid and gas into as intimate contact as possible. This makes it necessary to distribute or sprinkle the acid over the entire area of the tower packing as uniformly as possible so that in flowing down through the tower the surfaces of the packing material may be covered with a constantly changing film of the acid. There are two general methods of doing this. One of these divides the total acid stream into many small streams before entering the tower tops and introduces each stream through a small pipe, or opening. The other plan is to divide the total acid stream into a few comparatively large portions which are further broken up and distributed inside the tower by spray nozzles or splash plates. The former method

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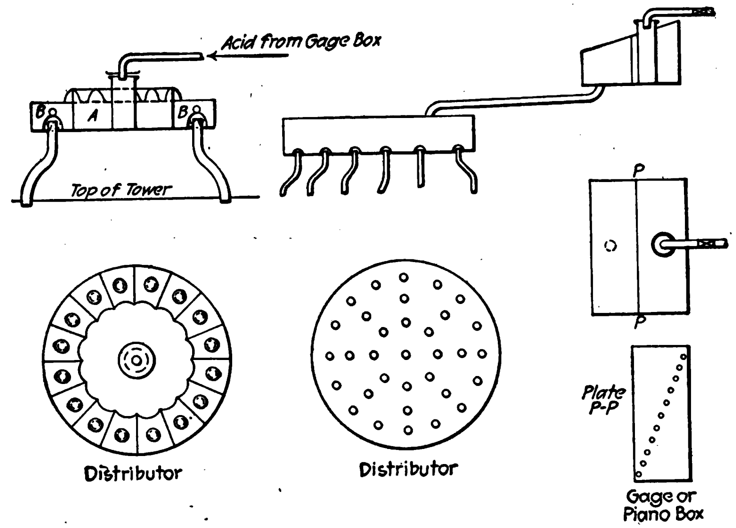
is older and probably more used than the latter. It works very well if the acid is clean and the tower small. In some of the large units built in this country in recent years, the towers have such great areas that the first described plan involves a tremendous number of feed pipes and the second method is more suitable.

There are many ways in which the division of the acid and introduction into the tower can be accomplished. Two of these are shown in Figs. 38 and 39. In Fig. 38 the acid is delivered into a central compartment A. Around A are small compartments B, from each of which a luted pipe runs to some point in the tower top. Acid overflows from A into B over lips on the partition. These lips are all dressed to the same level so that equal volumes of acid flow over all. This apparatus is made of lead and may of course, be square or rectangular or any desired shape.



FIGS. 38 and 39.

In Fig. 39 the internal compartment is omitted, the acid being delivered into the shallow pan from which the small pipes run directly to the top of the tower. These pipes project up into the pan an inch or two and are covered by cups whose lower edges are notched. The equal distribution of the acid depends upon having each of these upstands precisely level and exactly

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the same height. This is a difficult thing to determine and maintain and this apparatus is consequently not to be recommended. In any form of distributor box the individual streams should be in sight at all times and any inequalities easily corrected.

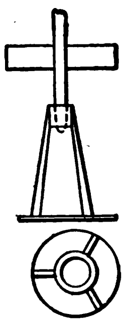

FIG. 40.

With either of these arrangements or any similar ones, the small streams of acid simply trickle down into the tower and on to the packing. Some designers consider it essential to provide one of these small streams for each square foot of packing area, *i.e.*, for a tower 10 ft. × 10 ft. there would be 100 small streams. Other designers consider one stream sufficient for 6 or 7 sq. ft. It can be appreciated that if one pursues a middle course in the matter, the number of individual pipes required for a large tower of say 250 or 300 sq. ft. area, is very great, costly to install, and rather troublesome to keep in order, especially if the acid carries some sediment.

The second described general method of distribution, *i.e.*, by introducing a few comparatively large streams which are sprayed out inside the tower, has much to recommend it. The original division of the main stream of acid can be carried out in much the same way as shown in Fig. 38. The secondary compartments are much fewer in number. Each pipe enters the tower top through a luted opening and has burned to its end a

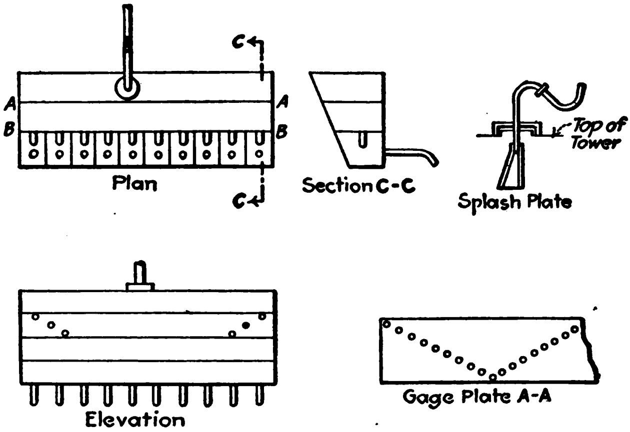

FIG. 41.

spraying device. The simplest of these devices is the splash plate as shown in Fig. 40. This is a casting of hard lead. Other more elaborate spray nozzles of acid resisting material are also suitable. Such sprayers can be depended upon to quite uniformly distribute acid over a 4- or 5-ft. circle, at a distance of 4 ft. below the nozzle. At 6 ft. below the nozzle they will spray a 6- ft. circle. It is important that each pipe should originate in an individual compartment so that if an obstruction occurs in any sprayer it will be immediately known by the corresponding compartment filling up. The nozzle can than be withdrawn through the luted hole and cleaned. The distribution afforded by such an arrangement is even better than that given by the multiple pipe scheme, and it is obviously much simpler, and cheaper to build and less trouble to keep in order. Figure 41 shows a convenient layout embracing the described features and including a gauging compartment.

INTRODUCTION OF WATER INTO THE CHAMBERS

While this subject does not properly come under acid circulation, it may well be discussed at this point.

Water is put into the chambers as steam or as finely divided liquid. If there is available to the plant an unused supply of exhaust or by-product steam, or if there is no fairly pure water available, it is proper to use steam in the chambers. Otherwise atomized water should be used because it is better for the acid-making process and it involves no fuel expense. The only cost is for driving a very small pressure pump.

When steam is used it is ordinarily introduced at two or three points in the top of each chamber, more rarely at a point in the front end wall. A convenient arrangement is to run the steam main under the floor of the working aisles and to carry up one or two risers alongside each chamber to the top where they run in to the points of introduction. A cock or throttle valve is placed in each riser 4 ft. above the working floor. A pointer mounted on the wrench or handle swings in front of a graduated arc and enables the operator to judge how much of a change he is making when it is necessary to change the flow. Iron pipe is used to carry the steam to within 2 or 3 ft. of the point of admission to the chamber then a lead pipe is flanged to it, bent to form a trap and its end burned into the chamber. Low pressure steam even

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so low as 2 or 3 lb. can be used, but the pressure should be uniform at all times.

In using liquid water, the introduction is done through many small nozzles rather than through two or three large ones. There are two reasons for this. One is that control of the amount of water admitted into a chamber is accomplished by completely opening, or completely closing a number of the supply pipes. The other that even well atomized water does not spread out into a very large volume of the reacting gas and so the sprays must be numerous to assure each portion of the chamber of its proper amount of water.

The spray nozzles used in this country are made of hard lead with platinum liners, or of stoneware or glass. The former are much more expensive than the latter though they usually last much longer. With platinum prices where they now are, one can buy eight or ten stoneware or glass nozzles for the price of one platinum nozzle. The principle used in all nozzles is to produce a swirl in the water stream just before it leaves the orifice. This is done in several ways, two of which are illustrated. When working properly the water issues in a cone shaped sheet which breaks into innumerable small drops. Figure 42.

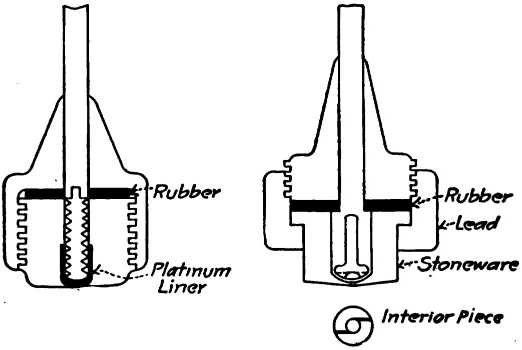

Fig. 42.

As all the passages in these nozzles are small, the areas ranging up to 1 sq. m.m., it is essential that the water entering the nozzles be very free from solid impurities or they soon become plugged up. The water should not carry more than small quantities of salts in solution because when a nozzle is not used for some hours the water remaining in it evaporates and salts deposit and choke it.

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Pressures used on this equipment are usually around 60 lb. per sq. in. at the nozzle. It is important that the pressure what-ever it may be shall be kept uniform within a few pounds.

There are two or three manufacturers in this country who have made up excellent combinations of apparatus for filtering and pumping water for chamber sprays. Figure 43 shows the arrangement of an individual spray nozzle with cock and strainer, lute, etc. The water is filtered through sponges and uniform pressure maintained in the lines by an electric plunger pump with relief valve. In addition to this it is advisable to use a strainer as shown just preceeding each individual nozzle to catch any pipe scale or anything that escapes the main filter. In cold weather when there is danger of the small spray lines freezing, a steam pipe leading into the supply tank warms the water.

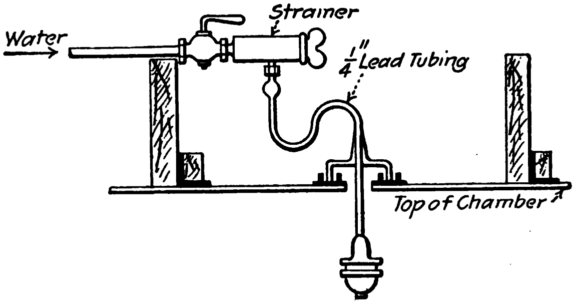

Fig. 43.

CHAPTER XII

INTRODUCTION OF NITRE

The recovery of the nitre in the chamber process is never complete. The average loss is probably from 3 per cent to 4 per cent (96 per cent $NaNO_3$) of the sulphur in the acid actually produced. It is necessary then to introduce into the plant per 24 hours from 15 to 20 lb. of new nitre for each ton of 60° acid produced.

While it is the custom to speak of introducing "nitre," the thing actually wanted and done is to introduce into the gas mixture the gaseous oxides of nitrogen. This is done in two ways. The first and probably most frequent is to decompose sodium nitrate by sulphuric acid and heat in cast iron pots placed in a flue between the furnaces and the Glover Tower. The heat of the furnace gases is depended on to produce the reaction. Sometimes the nitre pots are placed in brick settings alongside the gas flue and heat is supplied by means of coal fires beneath them. The nitric acid vapor is led immediately into the gas flue however.

The other plan is to make liquid nitric acid in a separate plant and introduce it into the top of the Glover tower.

In either case the chemical reactions and the end results are the same. The reactions which take place in the nitre pot whether it is in the gas flue, in a separate setting or in the nitric acid plant are these:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$
$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$$

The nitric acid comes off as a vapor. The acid sodium sulphate and normal sodium sulphate remain in the pot as a liquid mass and are tapped off from time to time. If the pot is in or near the gas flue the nitric acid vapor mingles with the hot burner gas and reacts with it substantially as follows:

$$2HNO_3 + 3SO_2 + 2H_2O = 3H_2SO_4 + 2NO$$

In the nitric acid plant the nitric acid vapor is cooled sufficiently to condense it to liquid HNO_3. This when introduced

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into the Glover tower is reacted upon in the same way, *i.e.*, H_2SO_4 and NO are formed.

Nitre pots are used in the gas flue and are of very simple design. They are generally of rectangular shape, open at the top and have a spout at one end for tapping off the nitre cake. Figure 44 shows a conventional design. These pots have capacities ranging from about 3 to 4 cu. ft. up to 20 cu. ft. Larger sizes become difficult to handle when they break and have to be replaced. The small sizes accommodate 25 to 50 lb. charges and the larger up to 200 lb. The thickness of metal is from 2 to 4 in. The matter of material is somewhat puzzling. Some foundries claim great superiority for their special cast iron formulas. I have seen pots of these special irons, which also cost a special price, give very poor service, and some have very long lives. The same can be said of pots made of good ordinary cast iron by local foundries. Probably design and care in pouring have as much to do with the life of a pot as special metals. Pots usually fail by cracking or going through flaws rather than by actual corrosion.

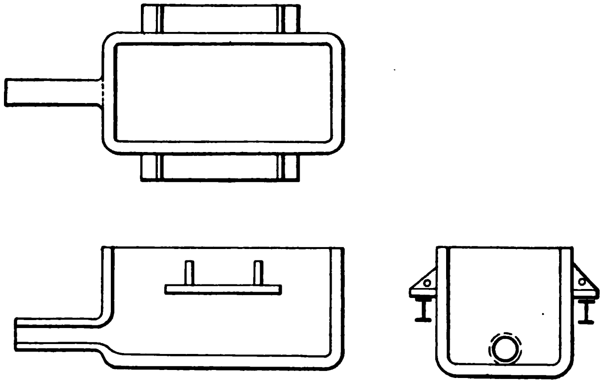

FIG. 44.

The number of pots which should be provided varies with the size of the unit somewhat, but should be never less than two and preferably more.

This on account of the desirability of having as nearly uniform evolution of nitric acid vapor as possible, and to carry over the periods of changing a broken pot for a new one. If the unit is of 50 tons 60° capacity, the normal amount of nitre introduced per

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24 hours will be from 750 to 1,000 lb. There will be times when more than that will have to be potted for a few hours so it will be well to have pot capacity to introduce at the rate of 2,000 lb. per 24 hours. Two hours per charge is the minimum time which should be allowed for the decomposition of the size charges ordinarily used. If therefore two pots are provided each should be able to handle 1,000 lb. per 24 hours in 12 charges or 83⅓ lb. per charge and should have a volume of about 10 cu. ft. If three pots are provided they should be of 7 cu. ft. volume or if four pots of 5 cu. ft. volume.

The pots are supported well above the bottom of the flue on beams, in order that the hot gas may play freely around them. The spout extends out through the wall a short distance. If the pots are small and the span for the beams is not long ordinary I beams are used for support and last very well. In case large pots are used and the flue is 10 or 15 ft. wide, deep cast channels filled with reinforced concrete stand up splendidly.

Charging of the pots with nitre and acid can be done from top of the flue or from the side. In many respects charging from the top is more satisfactory. It does away with the rather laborious handling of a heavy loaded charging ladle and it puts charging and tapping at different levels which is desirable. If both operations are done on the same floor the cake pans or launders are most inconvenient to work over. The nitre is put into the pot through a cast iron pipe with bell top if the charging is done from the top. If the charge opening is in the side of the flue a large scoop or ladle with a sufficiently long handle is used. The acid is fed in from a measuring pot or box through a heavy cast iron pipe. The special high silicon irons and also fused silica are being used for these pipes of late as even a heavy cast pipe does not last long. Figure 45 shows an arrangement of nitre pots in a flue.

The nitre cake is usually tapped off into shallow pans, allowed to cool and harden, then broken up and removed. When conditions permit and there is no use for the nitre cake, a simple means of disposal is to tap into a launder in which a stream of water runs, when the molten cake dissolves and is flushed away. Several ways have been devised for closing the spout after the charge has been tapped. A plate and screw clamp is sometimes used. Or the end of the spout is machined out to take an iron plug. Sometimes wooden plugs are used. If the spout is long outside

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the flue a ball of mud will be sufficient. It is well to use a scheme which does not depend too much on machined surfaces for tightness.

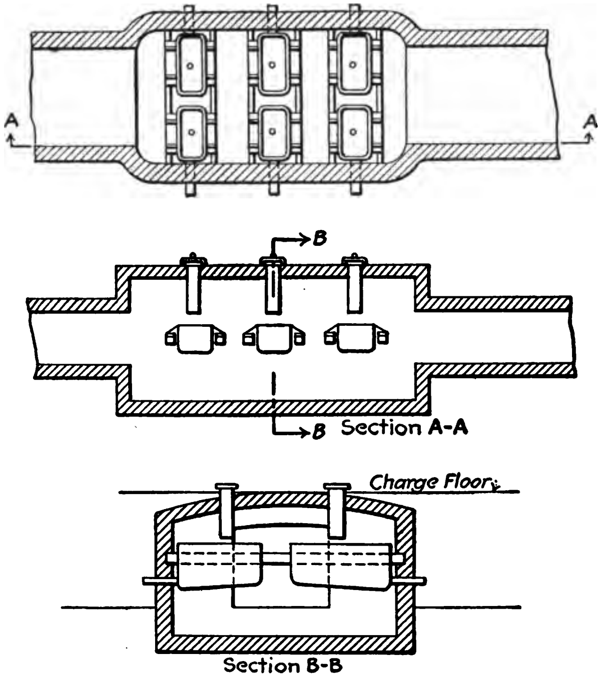

FIG. 45.

POTTING WITH FUEL

While the general features of the method just described, *i.e.*, in placing nitric pots in the flue and utilizing the heat of the SO_2 gas to effect the decomposition of the nitre, would seem the best and most economical possible arrangement, it has some drawbacks which are so annoying that many acid plants are now equipped with nitre pots in independent settings and fired with fuel. When this plan is used the operator can have at all times just the degree of heat he wishes to decompose his nitre. If the process has become badly disturbed by some breakdown or stop he can decompose the extra nitre the emergency demands and get into normal condition quickly. The weakness of the flue potting lies in the fact that just at those times when an unusually large amount of nitre should be potted the flue is cold, *e.g.*, when starting up the plant after a shutdown or when any unusual occurrence disturbs the flow of hot furnace gas about the nitre pots. In choosing between flue pot and independent pots the source of the SO_2 must be regarded. If the sulphur supply is in the form of a uniform high-grade pyrites which will make a hot gas and allow long campaigns with the roasting furnaces, flue potting is quite proper. If the gas is cold or if it is an unreliable metallurgical by-product gas, independent fuel fired pots probably are most economical. Fuel cost is not a very important consideration as with well designed settings a ton of ordinary soft coal will decompose 3,000 to 4,000 lb. of nitre.

The best form of pot for fuel fired settings is shown in Fig. 46. This is a modern retort such as is used in nitric acid work. It is simple and strong and is a design which has been very generally adopted of late years.

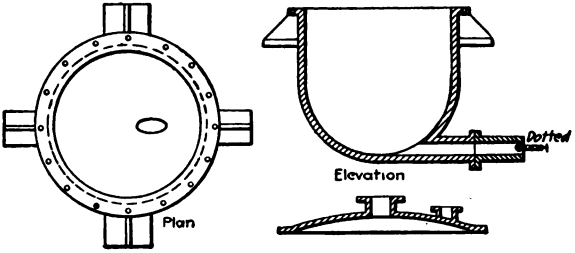

FIG. 46.

An ingenious plan used in connection with fuel-fired pots is used at the works of the Tennessee Copper Co. The retorts are substantially standard nitric acid casting as shown in Fig. 46. The nitre is fed in continuously by means of a conveyor and at the same time the proper amount of sulphuric acid for decomposing it is run in. Both nitre and acid may be varied as desired to meet the demands of the acid process. When a retort is filled up to a certain point with fused nitre cake it is tapped. There are several retorts in the battery and the introduction of nitric acid vapor into the flue is continuous. This arrangement is described in an article by A. M. Fairlie in *Chemical and Metallurgical Engineering* of September 25, 1918.

At some sulphuric acid works liquid nitric acid is made in a separate plant and the nitric acid is introduced as needed into the Glover tower. A comparatively recent modification of this

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scheme is to make instead of straight nitric acid, mixed acid, *i.e.*, a mixture of nitric and sulphuric acids.

In either case the nitre retorts are the same and are about as shown in Fig. 46. Other forms of retort and setting are to be found in some of the older plants, but the larger and more enlightened manufacturers of nitric acid seem to have come to the conclusion that the form shown is most satisfactory.

In making straight nitric acid the condensation of the vapor to liquid is effected in what is known as the Hart condenser. It consists essentially of a pair of upright manifolds of stoneware or high silicon iron with glass tubes between them. The glass tubes are cooled by trickling cold water over them. The final condensation of nitric vapor and recovery of the most of the lower oxides of nitrogen is done by passing the gases through several stoneware towers in series. A counter current stream of water, then weak nitric acid is advanced over the towers. The liquid nitric acid made is received and stored in glass or stoneware vessels. It is possible to use with fair success iron or lead tanks if only strong nitric acid be put into them and if they are kept tight from air leakage. The high silicon irons can be used with success for containing nitric acid of any strength.

The nitric acid made in this way is conveyed to the top of the Glover tower sometimes by elevating the glass carboys containing it, sometimes by pumping it up through stone or special iron pipe lines. More rarely it is mixed with sulphuric acid and the mixed acid then handled in any apparatus suitable for sulphuric acid. This mixing of nitric and sulphuric acid must be done in a closed vessel provided with cooling coils as it fumes badly otherwise.

The handling of straight nitric acid especially in large quantities is rather troublesome and this fact led to the development of the plan of making mixed acid directly, which will now be described. Mixed acid as mentioned can be handled in lead or iron apparatus with very little more wear and tear than straight sulphuric acid causes.

The plant for making mixed acid directly consists of retorts similar to those used when making straight nitric acid. The nitric acid vapor issuing from them is conducted through pipes of silicon iron into a small tower of acid-proof masonry construction packed with acid-proof bricks or shapes, over which cold sulphuric acid of 60°Bé. or higher strength is circulated. The

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nitric acid vapor is condensed and a warm mixture of nitric and sulphuric acids issues into a cooler whence it is pumped up and again introduced into the tower. The operation is exceedingly simple and gives a high recovery. The product containing up to 20 per cent HNO_3 is contained and pumped in lead apparatus. Its volume is such that it is very nicely controlled in introducing it into the Glover tower. The Fig. 47 shows an installation in which 4,000 lb. of nitrate of soda is comfortably handled in an eight hour shift. The fuel used amounts to about 900 lb. ordinary bituminous coal per ton of nitre. The recovery is 96 per cent or better. Some of these plants have been operating at least 3 years. Except for charging the retorts the operation is conducted by one man.

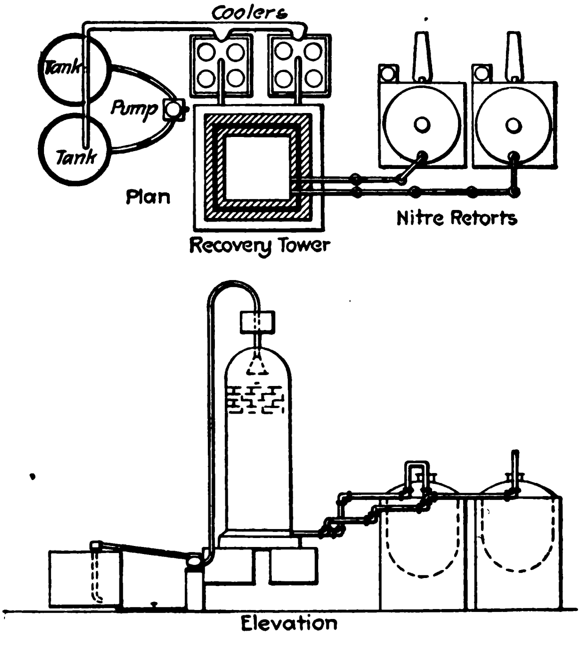

FIG. 47.

In the writer's opinion this last described method is the most satisfactory and economical way of handling the matter of getting the nitre into the chamber process.

It should be mentioned that a water solution of nitrate of soda is used to a limited extent in the Glover tower and in the chambers as a means of nitre introduction. It is a plan which has the serious disadvantage of fouling the acid with sodium sulphate: if the acid is to be used for the manufacture of fertilizer this is no particular drawback. If more than a small proportion of the total necessary nitre is put into the Glover tower as a regular procedure in this way it very soon makes trouble in that pipe lines and valves become obstructed and the tanks and coolers fill up with it. As an emergency measure to tide over a few days when for some reason the regular source of nitrogen oxides is out of commission a solution of this kind can be used in the Glover without serious results. Certainly though a few days is the limit. If the solution be introduced into the chambers and the chamber acid is drawn off for use in making acid phosphate or some other use in which sodium sulphate is not objectionable, very little trouble results. In any event it is unusual to use a nitrate solution as anything more than as in an auxiliary, or a temporary way of putting nitrogen oxides into a chamber system.

NO FROM AMMONIA OXIDATION

About 30 per cent of the European acid plants are supplying the oxides of nitrogen to their chambers by oxidizing ammonia and introducing the gas. So far but one plant in this country, that of the American Cyanimid Co., at Warners, New Jersey, has used this process, which gave them splendid results. It is not in operation at the present time, as nitrogen from Chile saltpeter costs less than from ammonia now.

In January, 1919, the British Ministry of Munitions issued a booklet on "*The Oxidation of Ammonia Applied to Vitriol Chamber Plants.*" This is the most complete publication on the subject, and I will quote from it very freely.

Mr. W. S. Landis, of the American Cyanimid Co., has furnished the following information regarding their New Jersey installation.

In their process of oxidation the platinum gauze is heated by a current of electricity, instead of depending upon the heat of the reaction entirely. Of course the current costs money, but the operation is so free from trouble of any kind, the labor required practically negligible, and the product so uniform, that opinion differs as to the best practice. (Though it will be noted in all (so far as I know) reports on this subject that when results have

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been wanted electrical heating of the catalyzer was practiced.) At Warners an oxidation unit was set up under each chamber, and the operator looked in as he went by. The gas was controlled by a 2-in. valve, and the plant ran steadily, with no adjustment beyond change of quantity of NO made, as the condition of the chambers demanded it, which adjustment simply meant open or close the 2-in. valve.

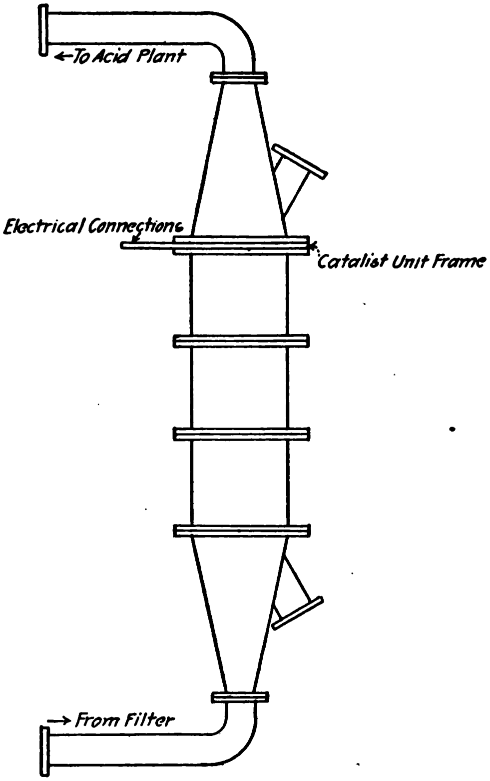

FIG. 48.

Outside of the ease of operation, stronger acid may be made. Both denitration and nitre potting absorb heat, which, if not required for other purposes, may be utilized in the Glover to concentrate. At Warners this was done. The nitric oxides from the converters were fed to the Glovers, all the heat that was saved from the potting went to concentrating, and the result was a constant return of 61°Bé. acid, which often, for long periods, stayed up to 62°, and occasionally reached 62.5°—with complete denitration—which is pretty fair chamber acid.

A patent on this subject, U. S. Patent #1,173,524, was issued on Feb. 29, 1916.

It is necessary to introduce the nitric acid through the roof of the Glover or chamber, as otherwise the acid, running down the side walls will quickly destroy the lead.

The British Ministry of Munitions standard converter consists of an upper and a lower cone, of aluminum, the small ends of the cones being flanged to the inlet and outlet pipes, the large ends also being flanged, but to the catalyzer frame. The internal section of the catalyzer frame, was about 4-in. × 6-in. (that at Warners was larger), and was simply a pair of aluminum flanges between which the platinum wire, gauze-wire being 0.065 (.003″) in. mm., square mesh, 80 mesh per inch—was held in place and insulated by mica and asbestos. The English used two gauzes in each frame, held apart by silica rods, the lower gauze alone having silver terminals. When electric current is *not* used to heat the gauze, three or four gauzes are necessary.

Ninety per cent to 95 per cent efficiency of oxidation will be attained without electric heating of the gauze, and 98 per cent with the current.

The capacity is 1.5 tons of HNO_3 per square foot of converter cross section per 24 hours.

The aluminum used in this construction must be very pure; and either mica or clear silica must be used for the peep holes.

The catalyst container must fit tight. Any air leaks may be luted with a mixture of asbestos powder and thick water glass. Allow this paste to set before heating the catalyzer.

The following precautions are essential in handling the catalyst:

1. Great care should be taken that the platinum gauzes are absolutely clean. They are boiled in pure concentrated hydrochloric acid and rinsed in distilled water before fitting, and should on no account be touched with the fingers afterwards or otherwise soiled.

2. The box containing the catalyst as sent from the makers should not be opened except immediately before fitting.

3. Fitting should be done in a clean room free from dust, not on any account in a workshop, and the fitter should have clean hands and clothes.

4. It is essential that the greatest possible care be taken to

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keep the gauzes clean while the catalyst unit is being fitted to the converter. If the completed converter is not at once connected to the inlet and outlet pipes, the apertures of the lower cone and bend pipes at the top should be closed with corks to keep out dust until this is done.

As the electrical resistance of the gauze is low, the current must be low voltage, but high in amperage. The maximum, or starting, current for a 4-in. × 6-in. gauze is 12 volts, 300 amperes.

The mixture of air and ammonia may be supplied to the converters in either of two ways:

1. By producing air and ammonia gas separately, and mixing them in the proper proportions—1 vol. NH_3 to 7.5 vols. air—in an aluminum mixing chamber, with tangential inlets and baffle-plates.

2. By passing a stream of air through aqueous ammonia in a suitable apparatus.

The second method is by far the better, and will alone be described.

Purified ammonia liquor, 20 to 25 per cent. NH_3, "free from sulphur," is the source of the ammonia. It is fed at the proper rate to an ammonia still, and there met by low pressure steam blown in at the bottom, either directly or through coils, and a current of air. Ammonia gas is liberated, mixed with the right proportion of gas for oxidation, and if the top of the column is kept cool, the gas is fairly dry. Moisture has no influence upon the oxidation, but is liable to condense in the filters and impair their efficiency. Iron pipe, fitted with red lead and oil, may be used up to the filters.

This still should work uniformly and with little attention, and not be liable to breakdowns. It should have a low steam consumption, which depends upon its being kept hot below and cool above. It should deliver ammonia, or air and ammonia, at a definite rate.

The kind of ammonia available and the amount required will of course influence the design.

Where the amount required is small the ammonia may be generated by boiling ammonium sulphate or ammonium chloride with milk of lime in an iron boiler with a reflux cooler, with a small balancing gas holder between the boiler and the converter. This method would be useful at coke ovens or gas works, where such salts are by-products. It has the additional advantage

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that the ammonia is pure, as there is no sulphur. On a large scale ammoniacal liquor is more economical. Gas liquor should not be used directly, because of the impurities.

An ammonia still of Brunner, Mond & Co. is shown (Fig. 49). Purified ammonia liquor of 25 per cent is run in at such a speed

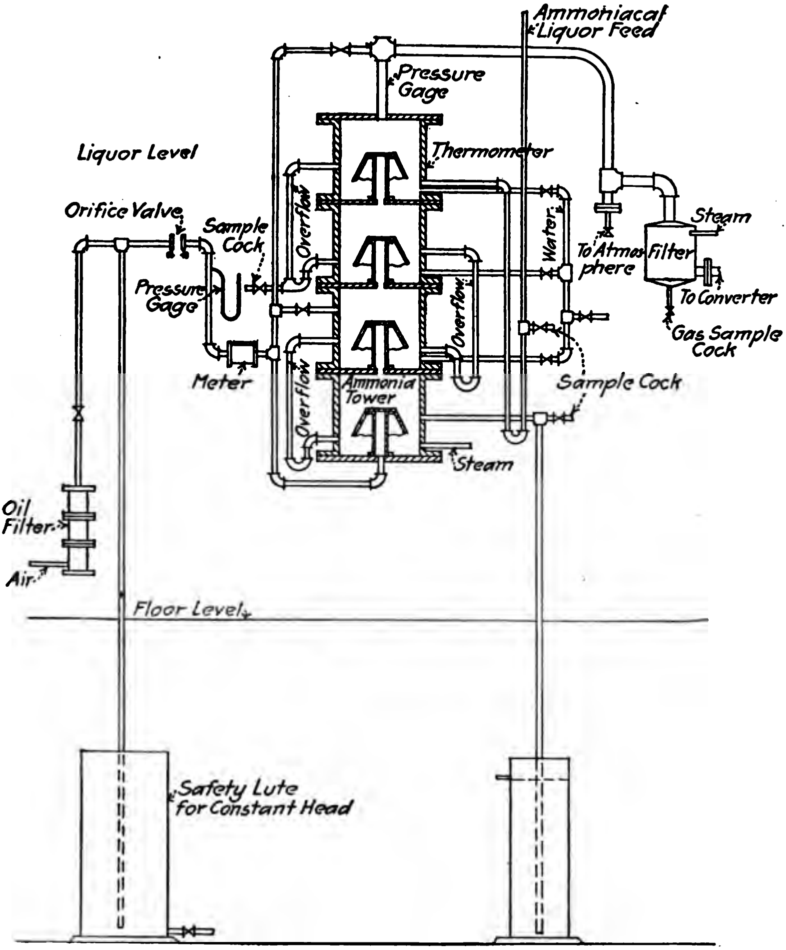

Fig. 49.

that the top compartment is kept at 8 per cent to 9 per cent ammonia, and 20° to 22°C. The bottom compartment is heated to 95° to 100°C. to exhaust the ammonia. Air is passed at the proper rate, and the mixture through a slag-wool or glass-wool

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filter. A little steam is necessary in the filter before the converter to avoid condensation.

The United Alkali Co. replaces the bubbling tower with a tall coke tower. Steam and air are introduced as before, but ammonia liquor is introduced at a point two-thirds up the tower. The upper portion of the tower thus acts as a cooler and gas filter, and no further filtration is necessary. This is also shown (Fig. 50).

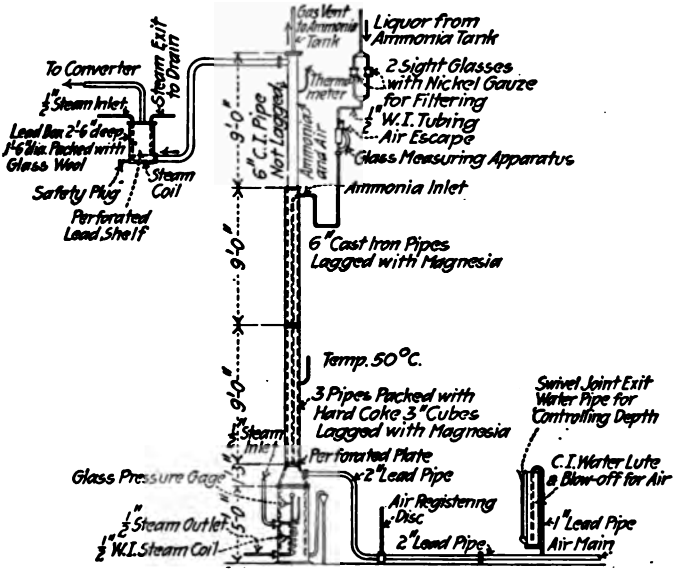

Fig. 50.

Air pressure depends upon the type of apparatus used, but should not fall below 5 lb. per sq. in. The air must be pure and free from dust; if the plant is near sulphur burners of any kind the air must be purified by passing through a lime box. There must be an oil trap after the blower. The air must be metered—the Builders' Iron Foundry, Providence, Rhode Island, furnishes good meters. After filtration iron pipes must *not* be used—aluminum, stoneware, or glass. The glass-wool filtering medium will probably need renewing every month, as it fills up with dust. Moisture can be kept out by introducing a little steam to prevent condensation.

The apparatus is started by switching on the current and heating up the gauze to visible redness. The mixture of air and

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ammonia is then admitted at a slow rate, until the catalyzer is uniformly dull red hot (650°C.), then the rate is increased to the maximum, the current being reduced as necessary. Very little further attention is required for weeks of running. If the gauze gets too hot the heating current, or the proportion of ammonia in the mixture, or both, should be reduced.

When electric heating is not used the plant is started by heating the gauze to redness with a hydrogen flame, turning on the air and ammonia mixture full, and removing the flame, after which the window is bolted into place.

New platinum gauzes are somewhat inactive, and should first be "activated" by passing at a fairly slow rate a mixture with an excess of oxygen, say, 1 vol. NH_3 to ten vols. air, and putting on full current till the gauzes are heated BRIGHT red (800° to 900°C.). After an hour or two the platinum becomes activated, and the white fumes of ammonium nitrite and nitrate leaving the converter (after cooling) change into clear red fumes of oxides of nitrogen. When this occurs the current is reduced and the ammonia brought up to the ratio of one to 7.5 air.

If electrical heating is not used, start with the ordinary gas mixture.

If spots show on the heated gauze and do not disappear rapidly, the catalyzer must be taken to pieces, the gauze boiled in pure hydrochloric acid, and the catalyzer reassembled. If the gauzes heat up unevenly it is usually a sign that the wire is too small, and the unit must be replaced. If in the activation any unevenly heated places are left they will take a long time to finally become active.

The gases leave the converter at about 400°C.. They consist of NO, steam, nitrogen, and a slight excess of air. The converter reaction is as follows:

$$4NH_3 + 5O_2 = 4NO + 6H_2O.$$

At this temperature the gas is colorless, as the secondary oxidation of NO to NO_2 has not begun.

The gases may be used with or without cooling.

Without cooling, the gas is conveyed through a lagged aluminum pipe, or if slightly cooled through a stone-ware pipe, to the Glover tower, chamber, or dust catcher of the system. The temperature must stay high enough to prevent water condensation in the main. There must be no pressure possibilities that burner gas could back up, in case of breakdown.

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If the burner gas does back up to the gauze it will rapidly become poisoned, and will have to be removed and boiled in hydrochloric acid. Therefore it is better to have the gas enter at a point where there is a slight suction, as in the Glover tower.

If the gas is cooled it is passed to a condensing cooler, where about 70 per cent of the water produced in the reaction is separated. If the cooling is performed sufficiently rapidly the condensate will contain from 1 per cent to 5 per cent of the total oxides of nitrogen as nitrous and nitric acid, and any trace of ammonia (0.05 per cent to 0.25 per cent) which may have escaped oxidation. This is the result from a very efficient cooler-up to 25 per cent of the oxides of nitrogen may be in the condensate. The cooler may consist of a silica spiral, connected directly with the bend on the converter hood, by suitable asbestos packing, and cooled by water. A spiral of 10 turns of fused silica S-pipes, the turns 2′–0″ in diameter, the pipe 3⁄16-in. thick and 1½-in. in diameter, will do the work. The condensate may be collected in a stoneware Woulff's bottle, and then drawn off to the Glover's; or it may run direct to the Glover.

The cooled gases, at about 30° to 50°C., now brown with oxidation from NO to NO_2, pass through stoneware pipes with a stoneware stop cock if desired, and with down pitch towards the point of entry, to the chamber system.

Remember that hot gases may cause warping at the point of entry, and provision must be made for it.

An advantage of using a cooler is the better analytical check on the process. Tests on the condensate for unconverted ammonia should be made from time to time to cheek up the working of the converter.

If there is more than one Glover to be supplied it is better to have a small independent converter for each, rather than have one larger one try to supply several, as uniform distribution is very difficult to get.

The accompanying table shows the quantity of ammonia that must be oxidized to replace any given quantity of nitre ($NaNO_3$). If the consumption of nitre varies the converter may be run below capacity—it may be run down to 25 per cent of capacity at 100 per cent efficiency, and will run well at 15 per cent. One of the great advantages of this system is its uniform running, and this should be taken advantage of if possible, by keeping the rest of the plant going at a uniform rate.

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Table 5

Sulphur burned	Metric tons of H_2SO_4 (100%) produced per day of 24 hours		Grams of ammonia required per hour, if nitre consumption be taken as per cent of the sulphur burned, per cent				
Tons per day	95% plant efficiency	98% plant efficiency	0.5%	1%	2%	2.5%	3%
.265	.77	.792	10	20	40	50	60
.53	1.55	1.584	20	40	80	100	120
1.06	3.1	3.17	40	80	160	200	240
2.12	6.2	6.35	80	160	320	400	480
6.6	19.25	19.8	250	500	1,000	1,250	1,500
15.85	46.2	47.5	600	1,200	2,400	3,000	3,600
26.4	77.0	79.2	1,000	2,000	4,000	5,000	6,000

Up to 3,000 g. NH_3 per hour, use 1–4-in. × 6-in. converter.
Above 3,000 g. NH_3 per hour, use 2–4-in. × 6-in. converter.

ANALYSIS

The analytical control of oxidization of ammonia is of the utmost importance, and considerable difficulty. With the methods here given the efficiency of any particular converter cannot be determined closer than 3 per cent. This is sufficiently accurate for works operations.

Determination of Ratio NH_3:Air before oxidation

The method consists in aspirating a known volume of the air-ammonia mixture through a sufficient quantity of standard sulphuric acid colored with methyl orange or cochineal, contained in a wash bottle connected with an aspirator. A Winchester bottle of water is placed between this and the aspirator, just to equalize the gas pressure in the inlet tubes to the converter, so that no gas bubbles through the acid until the aspirator is started.

The quantity of acid is sufficient to neutralize exactly 0.1 g. of NH_3. The indicator end point is quite sharp, and experiments show that the absorption of ammonia is complete with a single wash bottle. Each experiment should be conducted at such a rate as to last about 10 minutes, and be repeated every 20 minutes. An alternative method is to use a larger volume of standard acid in two wash bottles, to aspirate for a longer time, say half an hour, and titrate back with standard alkali.

A typical experiment gave 1.13 liters of water aspirated (*i.e.*, 1.13 l. of air in the air-ammonia mixture) to 0.1 g. of NH_3. This gives a ratio vol. NH_3:vol. air of 0.116, which is about the ratio for conversion of ammonia to NO_2 (0.114).

Determination of ratio oxidized NH_3:Air, after oxidation.

An aliquot part of the oxides of nitrogen and air, from the converter, taken from a T-tube after the cooler (see Fig. 51) is aspirated through:

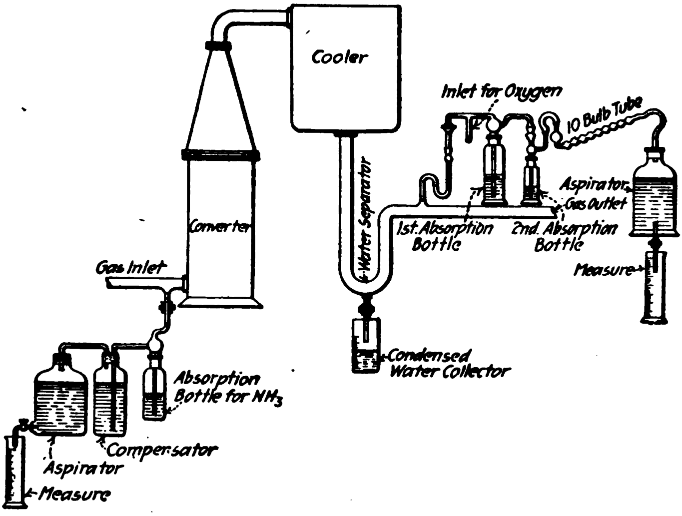

FIG. 51.

1. A Drechsel wash-bottle containing:
   100 c.c. distilled water,
   20 c.c. N/Na_2O_2 solution,
   20 c.c. H_2O_2 solution (20 volumes).
2. A Drechsel wash-bottle containing:
   50 c.c. distilled water,
   10 c.c. N/Na_2O_2 solution,
   10 c.c. H_2O_2 solution (20 volumes).

The N/Na_2O_2 is prepared by adding 78 g. Na_2O_2 to 1 kg. powdered ice in small quantities at a time, with stirring: then adding 1 liter distilled water and filtering through glass-wool.

It is kept in a bottle with a capillary tube through the cork to allow the traces of O_2 to escape.

3. A 10-bulb tube containing:
   5 c.c. N/10 potassium permanganate solution.
   10 c.c. 50 per cent H_2SO_4.

All connections are made with ground joints, a stopcock being inserted at the point where the gas sample is taken from the T-tube, as shown in the Fig. 51. The aspiration is effected by means of water dropping slowly from an aspirator bottle (about 1 liter per hour) into a measuring cylinder, and 1,500 c.c. of water are collected; the experiment thus lasts 90 min.

The two drechsel wash-bottles (1) and (2) are then emptied into two 250 c. c. Erlenmeyer flasks, the bottles being then washed. out with distilled water and the liquid in the flasks titrated separately with standard H_2SO_4, using litmus as indicator, and boiling if necessary. The end point is taken at the change blue to purple, and not blue to red, on account of the hydrolysis of the nitrous acid. This end point is easily recognized with a little practice. Methyl orange is useless on account of the action upon it of the nitrous acid, but Sodium Alizarine Sulphonate ("Alizarin Red. I. W. S., Hochst") has been used with very satisfactory results. The contents of the permanganate bubbler are washed out into an Erlenmeyer flask, treated with a slight excess of N/10 oxalic acid, warming if necessary, and the excess of oxalic acid titrated back with permanganate. It is assumed that the reduction of the permanganate is due to NO, and the NH_3 equivalent of this is calculated as follows:

$$2NO + 3O = N_2O_5,$$

that is, 2NO (calculated as NH_3) requires 3 atoms or 6 equivalents of oxygen, *i.e.*, 60,000 c.c. $N/10KMnO_4$: *i.e.*, 34 g. NH_3 = 60,000 c.c. $KMnO_4$.

$$\therefore 1 \text{ c.c. } N/10KMnO_4 = 0.000566 \text{ g. } NH_3.$$

Examples of calculations.

It was found in one experiment that the oxides of nitrogen had neutralized a quantity of the alkali in the two vessels corresponding to 0.159 g. NH_3, reckoning equivalents in nitrogen contents.

$$1 \text{ c.c. N alkali neutralized} = \frac{HNO_3}{1,000} = \frac{HNO_2}{1,000} = \frac{NH_3}{1,000} = 0.017 \text{ g. } NH_3.$$

The permanganate in estimation (3) was titrated with N/10 oxalic acid. It was found that 3.5 c.c. of N/10$KMnO_4$ had been used up. This corresponds with 0.0035 g. NO, and this is equivalent to 0.002 g. NH_3.

After the converter and the cooler, all the unconverted NH_3 will have been removed and the oxides of nitrogen are then totally absorbed in the absorption bottles. Now in the estimation of the ratio of NH_3 to air in the gas entering the converter, we have determined the weight of NH_3 associated with a given volume of air (the latter being simply equal to the volume of the water run out of the aspirator bottle). If there were no change of volume of the air after the converter, we should be able to make a direct comparison of the weight of the oxides of nitrogen, corresponding with 1.5 litres aspirated (these oxides being calculated as NH_3) with the weight of NH_3 associated with the same volume (1.5 litres) of air in the mixture of air and NH_3 entering the converter.

The aspirated volume after the converter, however, does not represent the volume of air which was associated with the ammonia corresponding to the oxides of nitrogen collected, because a portion of this air has been used up in the oxidation. This consumed oxygen consists of two parts:

1. A portion used in burning the NH_3 to NO in the converter.
2. A further portion used in oxidizing the NO to higher oxides, which are then absorbed.

The first portion is the same in all cases, and is calculated as follows:

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

25 volumes of air become 20 volumes of N_2:

i.e., the contraction of the air volume is here

$$\frac{(25 - 20) \times 22.4}{4 \times 17} = 1.647 \text{ litres per g. } NH_3 \text{ burnt.}$$

(Since the NH_3 is completely absorbed from the gas in the aspirator, before the converter, and the oxides of nitrogen from the gas in the aspirator after the converter, it is only necessary to consider the volumes of air.)

The further contraction, due to secondary oxidation, will depend upon the particular higher oxide of nitrogen produced. Of these, only two, namely, N_2O_3 and N_2O_4, can possibly be produced by the oxidation of NO by atmospheric oxygen, and

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it is therefore, necessary to calculate the contractions for these two cases only.

(a) $4NH_3$ becomes $4NO + O_2 = 2N_2O_3$

that 5 volumes air becomes 4 volumes N_2:

that is, there is a contraction of 1 volume, *i.e.*,

$\frac{22.4}{4 \times 17}$ litres = 0.329 litre per g. NH_3

(b) $4NH_3$ becomes $4NO + 2O_2 = 2N_2O_4$

10 volumes of air becomes 8 volumes N_2

that is, a contraction of 2 volumes, *i.e.*,

$\frac{2 \times 22.4}{4 \times 17}$ litres = 0.658 litre per g. NH_3

The aspirated volume, 1.5 litres, must therefore be increased in the ratios:

(a) (Weight of oxides of N expressed as NH_3) × (1.647 + 0.329) : 1, when these oxides are absorbed as N_2O_3;

(b) (Weight of oxides of N expressed as NH_3) × (1.647 + 0.658) : 1, when these oxides are absorbed as N_2O_4.

The volume of air so corrected is then directly comparable with the volume of air associated with the ammonia in the aspiration before the converter, and if equal volumes are compared, the weights of NH_3 in each (that after the converter being calculated from the titrations, as described) will give an immediate figure for the efficiency:

$$\frac{\text{wt. } NH_3 \text{ after conversion (as oxides)}}{\text{wt. } NH_3 \text{ before conversion}} \times 100 = \text{efficiency},$$

the weights being referred to equal volumes, as described.

AIR VOLUME CORRECTION

In the experiment described above, the weights of NH_3 corresponding with the oxides of nitrogen collected in the alkaline peroxide and permanganate, respectively, were 0.159 g. and 0.002 g. Since in a good experiment the permanganate figure should always be very small, it is only necessary to use the first figure, namely, 0.159 g. in correcting the air figure. This correction will be as follows:

(a) Gas assumed to be absorbed as N_2O_3:

corrected volume of air = 1.5 + 0.159 × (1.647 + 0.329) litres = 1.5 + 0.314 = 1.814 litres.

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Now in the aspiration before the converter, it was found that 0.1 g. NH_3 was contained in 1.13 litres.

$$\therefore NH_3 \text{ in } 1.814 \text{ litres before conversion } = \frac{1.814 \times 0.1}{1.13} = 0.1605 \text{ g.}$$

Oxidized NH_3 after conversion $= 0.159 + 0.002 = 0.161$ g.

$$\therefore \text{Efficiency} = \frac{0.161}{0.1605} \times 100 = 100.1 \text{ per cent.}$$

(b) Gas assumed to be absorbed as N_2O_4:
corrected volume of air $= 1.5 + 0.159 \times (1.647 + 0.658)$ litres $= 1.867$ litres.

$$NH_3 \text{ in } 1.867 \text{ litres air before conversion } = \frac{1.867 \times 0.1}{1.13} = 0.1650 \text{ g.}$$

$$\therefore \text{Efficiency} = \frac{0.161 \times 100}{0.165} = 97.6 \text{ per cent.}$$

The difference between the two values is thus seen to be only about 2.5 per cent, which is within the limits of experimental error. The true value lies between the two, and nearer the N_2O_3 figure, since experiments have shown that about four-fifths of the oxides are absorbed as N_2O_3 when no oxidizing agent is present in the liquid, and this ratio, therefore, represents the composition of the gas before absorption.

To the amounts of oxides of nitrogen collected in the absorption bottles must be added that present in the condensed water separated from the cooler. The analysis of this condensate is of value in estimating the unconverted ammonia, all of which separates in the condensed water in the form of nitrite and nitrate. The condensed water is collected throughout the whole experiment and its volume measured.

An aliquot part is titrated with N alkali and litmus for acidity, and the acidity of the total expressed as NH_3 (1 c.c. N/NaOH = 0.017 g. NH_3). Another aliquot part is distilled with NaOH and the ammonia collected in a measured volume of N/H_2SO_4. This ammonia was combined with an equivalent amount of acid, and its value must therefore be added to that found in the previous titration, to obtain the total OXIDIZED NH_3 in the condensed water. This is divided by the total weight of NH_3 passed through the converter during the run, and the result, multiplied by 100, gives the term which must be added to the efficiency

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calculated from the absorption bottles, to give the true efficiency. In the experiment described the values were:

Unoxidized NH_3 = 0.3 per cent
Oxidized NH_3 = 0.1 per cent
$\therefore$ Total efficiency = 100.1 + 0.4 = 100.5 or 97.6 + 0.4 = 98.0

If the proportion of air and ammonia entering the converter is such as to form NO, this could not be absorbed in the alkaline peroxide, and in this case it is necessary to add a measured volume of oxygen slowly to the gases aspirated from the converter. This is done by connecting a graduated gas-holder containing oxygen to a T-piece on the connection of the first bottle, the rate of addition of oxygen being controlled by passing it through a small wash-bottle containing water. About 300 c.c. of oxygen are added during the whole run of 90 min. This volume (300 c.c.) is subtracted from the volume of water collected and the usual correction for contraction applied to the remaining volume:

1,500 c.c. − 300 c.c. = 1,200 c.c. = 1.2 litres.

GENERAL REMARKS

In the estimation of the ammonia, the balancing water column in the Winchester bottle should be such that the gas pressure before the converter is just sufficient to bubble through the water. As soon as the aspirator is started bubbles will pass, and the rate should be adjusted so that the color of the indicator changes in about 10 min. When indications of a color change appear, the rate of aspiration should be reduced so that about one bubble per second passes, and the absorption bottle should be shaken. The connecting tubes and the upper part of the tube in the wash-bottle should, of course, be dry.

The alkaline peroxide bottles should be carefully fitted together, so that on opening the tap connecting with the outlet from the converter, on bubbles (or at most one or two) pass before the aspirator is started. **The rate of aspiraton must be slow, as stated. If white fumes appear in the second bottle, or the permanganate is discolored, or deposits much MnO_2, the experiment will usually be found to give an incorrect result.**

If oxygen is added it should be let in slowly, as stated, in order to insure that the whole of it passes through the aspirator bottles, and not backwards into the converter main.

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To insure that the pressures are equalized in the aspirator bottles, these may be provided with gauges, consisting of U-tubes containing water.

Hydrogen peroxide solution is usually acid, and allowance must be made for this in the titrations.

(*b*) *Determination Without the Use of Cooler.*—If the hot gases from the converter are utilized without previous cooling it has been found that a short length of aluminum tubing, inserted as a T-tube in the main from the converter, is generally sufficient in itself to cool the aliquot part of the gases which are slowly passing through it to the absorption system. It has been usual to neglect the small portion of unoxidized ammonia in this case. As alternatives the following suggestions are based upon information from those who have had occasion to carry out control tests on hot converter gases:

1. The converter gas is drawn slowly through a capillary tube to an absorption system similar to that described above.
2. The first absorption bottle contains N/10 alkali without peroxide. This, according to Fox (*Journal of Industrial and Engineering Chemistry*, August, 1917), retains all the unoxidized ammonia coming over, the amount of which is estimated after the titration by treatment with caustic soda and sodium hypobromite, when nitrogen is liberated and is measured (cf., Treadwell and Hall, Quantitative Analysis, p. 622). A correction must be applied to this volume of nitrogen, since the reaction is not quite complete (cf., Fox).
3. The second absorption bottle contains the same solution as the first bottle in the method described above.
4. The permanganate tube is retained unchanged.

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CHAPTER XIII

DRAFT

Early chamber plants depended upon natural draft for the movement of gases through the apparatus, but all modern plants use fans. In this way larger volumes can be moved and the control is much more positive.

Fans are of two classes, viz., iron fans which are used at some point preceding the Glover Tower, and lead fans, used at some point following the Glover Tower. Sometimes both kinds are used in the same system. It must be understood that if a fan is placed between the sulphur burners or roasters and the Glover Tower, high temperature, dry gases are to be handled and iron is the only suitable material for the service. If the fan is placed at any point beyond the Glover Tower, comparatively low temperature gases laden with sulphuric acid mist are to be propelled. For this service lead, usually stiffened by alloying with antimony, is the most suitable material. Iron of course would be quickly destroyed by the acid. Lead fans are more often used than iron though the latter certainly deserve much consideration as they have many advantages.

The arrangement most common for units of moderate size is to use a single lead fan between the Glover Tower and the first chamber. Very often a second lead fan is used between the last chamber and the Gay Lussacs. A less frequent plan is to use a single iron fan just in front of the Glover or an iron fan, with a lead fan between the last chamber and the Gay Lussacs. Any of these arrangements of suitable size and with the other features of the plant in conformity may give good results. It is well to consider that the fans are of very vital importance to continuous operation and that they have to be repaired and parts replaced at times. If there are two fans in a system with proper by-passes one of them may be cut out and worked on without causing a shutdown. To be sure a diminished production will probably result but that is not nearly so serious as cooling off furnaces and discontinuing the acid making process. A further important advantage of having a fan at each end of the system is that repairs

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may be made on the chambers more readily by producing a slight inward suction by varying the fan speeds. This is appreciated after chambers become several years old.

Iron fans suitable for this work are similar in general design to those used for many other purposes, such as ventilation of mines, buildings, etc. They must of course be quite tight, able to stand temperatures up to 1,000°F. and be of simple construction to avoid catching dust. The housing should be of cast iron as plate housings will warp badly in the heat encountered. The shaft will be course be very hot for some distance outside the housing and so the bearings must be water cooled. The rotor can be of cast iron or of steel plate with a cast hub spider. It may be overhung or may have a bearing on each side of the housing. The former method is perhaps more convenient as the inlet flue is not complicated by having a shaft and bearing on that side.

The speed of iron fans should be from 500 to 1,000 r.p.m. in order that they may blow the dust out and keep themselves clean. It must also be considered that due to its high temperature the volume of the gas is more than twice what it is after it passes through the Glover Tower. Consequently, the range of speed specified is advisable in order to move the gas with a fan not unduly large.

Several manufacturers in this country have stock designs which with slight modifications are entirely satisfactory for acid plant service. These fans are very much less expensive than the lead fans and over a period of years require less repairs. Why they are not used more is hard to understand.

Lead fans are in general much like the iron fans in design. It is necessary on account of the low strength of lead to make the metal much thicker than corresponding parts of iron. The shaft which carries the rotor is necessarily of steel, but it is entirely covered by lead until it leaves the housing. Usually the lead of the spider is poured around a cast iron hub which latter is keyed to the shaft. This is a detail which has given trouble in many fans, but if the cast iron hub is generous in size and made with dovetail grooves so that the lead can take hold of it well, no slipping or working loose will occur.

There are several lead fans specially designed for acid plant work on the market, and most of the manufacturers of blowers, will alter their designs of iron fans and make them of lead if

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desired. Two widely used specially designed fans are the Pratt and the Heinz-Skinner.

The Pratt fan, shown in Fig. 52, is made with both bearings on one side, *i.e.*, with rotor overhung. The gas enters on one side only. The housing is of cast hard lead made in two pieces and is self-supporting. It is so arranged that the top casting can be lifted off to allow removal of the rotor. This is a well-designed fan with the details perfected over a period of several years. This fan is designed to run at rather high speeds up to 800 or 900 r.p.m. It is therefore small comparatively and uses more power than the large low speed fan.

FIG. 52.

The Heinz-Skinner, Fig. 53, has several novel features though the principle upon which it works is the usual one. This fan has its shaft extending clear through the housing with a bearing on each side. The inlet pipe branches just before it reaches the fan and goes to an inlet on each side of the rotor. The housing is in two parts with a horizontal joint at the level of the shaft. The joint itself is a lute made tight by an acid seal. The upper part of the housing can be lifted off to change or work at the runner. This fan both as to housing and runner is largely built up by burning together rolled hard lead plates. It is entirely of hard lead excepting, of course, the shaft. This fan is also very well

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designed and if properly handled gives good service. It runs at speeds up to 500 or 600 r.p.m.

The Wedge fan which has been used in several large acid units built of late years is something of a departure from the above types in the matter of size and speed. This fan so far as I know is not made regularly by any manufacturer. The fans so far made have all had runners 8 ft. in diameter and 4 ft. wide. They run at speeds not over 200 r.p.m. They are enormously heavy and costly but they run with surprisingly little power and give very little trouble. Some of them have been in practically continuous use for more than 4 years without being opened. The housing of this fan is built up of ordinary sheet lead (15-lb.) supported by angle iron framework. There is a gas inlet on one

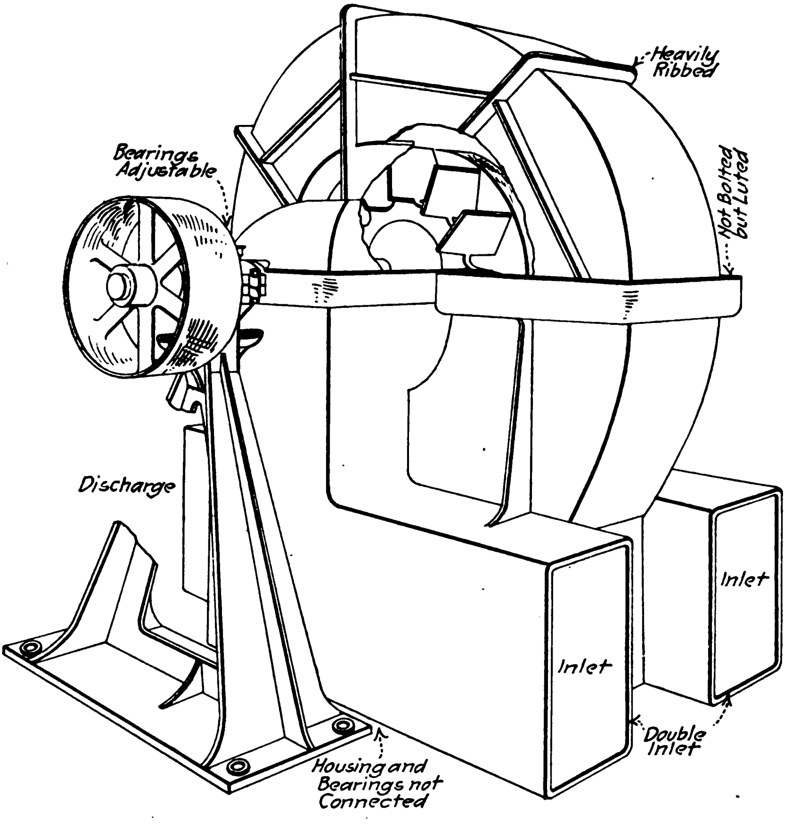

FIG. 53.

side only. The shaft runs in a bearing on each side of the housing. One fan of this size will provide draft for a properly designed plant to make 125 to 150 tons of 60° acid per day. It consumes only 12 to 15 H.P. at 200 r.p.m.

These fans are mentioned specifically not so much because they are more satisfactory than many others, but because they represent types and because they are specially designed for acid plant service.

FLUES

As the parts of the chamber system are enclosed in sheet lead considerable areas of which are unsupported, it is essential that flues, tower packing, etc., be so proportioned that no very great resistances shall be offered to the passage of the gas. Of course, the towers can stand somewhat higher differences between internal and atmospheric pressures, than can the chambers, because they are of heavier lead and the internal masonry lends them stability.

It is well to so design the plant that pressures corresponding to 1-in. of water shall not be exceeded in any tower and 0.75 in. as a maximum for any chamber. Of course, higher pressures will be found in many plants and it should not be inferred that they are particularly dangerous; however, the fact is that lead at a temperature of 200°F. is not very stiff and in the course of some years high pressures cause distortions which make trouble.

Calculations for flue areas must be made for individual cases, but the following statements will give an idea of proper areas which should be provided in a simple one-fan system. If the gas entering the acid system contains an average of 7 per cent SO_2 by volume, it will be necessary to put through the plant about 80,000 cu. ft. per 24 hours per ton of 60° acid made, at 0°C. and 760 m.m. This will be increased somewhat by the reaction temperature and decreased as SO_2 and O go to make liquid H_2SO_4. In the early parts of the system for example, the gas temperature may be 100°C. which would make 80,000 cu. ft. at 0° = 109,000 cu. ft. = 1.26 cu. ft. per sec. If we wish the gas velocity to be 10 ft. per sec. our flue area in this part of the system would be .126 sq. ft. per ton of 60° acid made. For a 100 ton unit the flue area should then be 12.6 sq. ft. which is almost exactly that of a 48-in. diameter flue.

In the back part of the system where the gas temperature is

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perhaps 45°C., the volume will have decreased on this account to about 86,000 cu. ft. The reaction and condensation of SO_2 and O to liquid acid will have removed about 10 per cent by volume or 8,600 cu. ft. so that the volume of gas per ton of acid will be about 77,400 cu. ft. per 24 hours = .9 cu. ft. per sec. and the necessary flue area will be 9.0 sq. ft. which is the area of a pipe about 41 in. diameter.

If several small flues are to be used instead of one large one, or if there are many bends or very long distances between parts of the apparatus which the flues connect, some allowances to compensate for increased friction should be made. The basis of 10 ft. per sec. is a safe one however for the flue connections found in most plants.

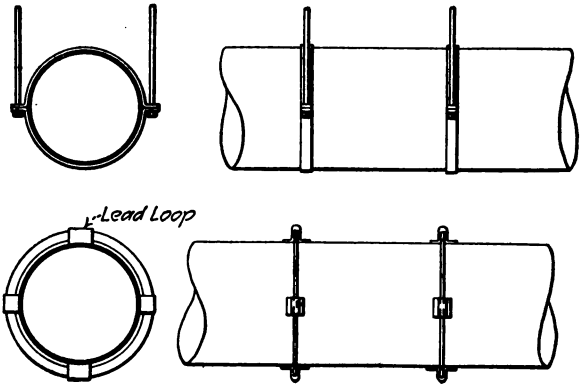

Fig. 54.

For tower packing, no very definite figure can be given as a minimum of necessary open area, experience and data on different types of packing are necessary. It is also necessary to consider the length of the column of packing through which the gas must pass. It is well in a Glover tower having a packed column 25 or 30 ft. high to provide a gross horizontal packed area of not under 2 sq. ft. per ton of 60° acid made. For Gay Lussacs, where combined packed heights amount to 75 ft. or more, 2 to 2.5 sq. ft. per ton of 60° acid made should be provided. Considerable divergences from these specimen figures may be made with entire propriety by using fans at various points of the system.

Circular lead flues are to be preferred to rectangular sections.

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They are stronger from the nature of their section and are simpler to support. Sharp angles are to be avoided, in general, in lead construction. Circular flues are best made of 10-lb. lead. The supports are flat or edge bands of iron as shown in Fig. 54. The edge bands are slightly more expensive to apply but are distinctly better in the long run. Bands should be frequent as in the later years of the life of a plant insufficient support of flues causes much trouble.

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CHAPTER XIV

TESTING

The control tests made about an acid plant are largely performed by men who have little knowledge of the refinements of chemical and physical measurements and consequently no high degree of accuracy is customary. Nor is a high degree of accuracy necessary. The tests and instruments to be described are intended only to represent such work. They are for the operator rather than for the chemist.

THERMOMETERS AND PYROMETERS

It is desirable in many parts of the plant to know the temperatures of the gases and acids involved in the process and for obtaining these, thermometers and pyrometers are used. Everyone is familiar with thermometers and little need be said concerning them. In the United States the Fahrenheit scale is almost universally used. For taking acid temperatures, straight stem thermometers with inclosed paper scales reading up to 220°F. are best. They are less expensive and more easily read than the engraved instruments. It is well to have a few thermometers reading up to 400° for testing the acid issuing from the Glover tower. Chamber thermometers having stems bent at 45° or 90° from the graduated portion are regularly made by the manufacturers of chemical apparatus. The stems are inserted into the chambers through rubber stoppers. In reading a thermometer it is important that a line from the eye to the end of the mercury column be at a right angle to the latter.

For ascertaining high temperatures such as those of the gases entering the Glover Tower, the pyrometer is used. When certain dissimilar metals or alloys are placed in contact with each other and heated, an electric current is set up which can be measured by a galvanometer and the corresponding degree of heat shown by a needle on a graduated scale. For the purposes of the chamber-acid plant what are known as base metal couples for insertion into the flue are most suitable. This form of couple, shown in Fig. 55 consists of a pipe or tube of one metal and a rod of a different metal inside it and insulated from

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it except at one end where the tube and the rod are welded together. This welded end constitutes the couple and is inserted into the gas whose temperature is desired. Couples made of platinum, and platinum alloyed with rhodium or iridium, are excellent but far more expensive. The only precautions necessary to be observed in using pyrometers are to have all the wire connections clean and tight and to keep the couple reasonably free from dust.

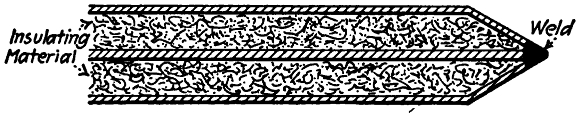

FIG. 55.

Several couples may lead through switches to one galvanometer. Temperatures exceeding 1,200°F. are not often encountered in flues so that an instrument graduated to 1,500° or 1,600°F. is suitable.

HYDROMETERS

The hydrometer is an instrument used for showing the concentration of sulphuric acid. It is made of glass and consists of a cylindrical float weighted at its lower end and with mercury, or shot, and surmounted by a thin stem containing a graduated paper scale.

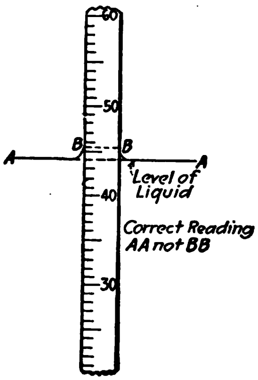

FIG. 56.

The acid to be tested is placed in a tall jar and the hydrometer allowed to sink in it until it comes to rest. On account of surface tension, the acid will curve up against the stem as shown in Fig. 56. The reading should be taken across the surface of the acid on line AA, not at the top of the curve line, BB.

The hydrometer universally used in chamber-acid plants in this country is called the American Beaumé. This is an arbitrary scale originally devised by making up a solution of pure salt, NaCl, 15 parts and pure water 85 parts by weight; immersing a hydrometer in it and calling the mark 15°. The point to which the hydrometer sunk in pure water was called 0°. The distance between these marks was divided into 15 equal parts, thus establishing the degree Beaumé. After many years of disagreement over the exact details of

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obtaining the degree and as to its relation to specific gravity, the U. S. Bureau of Standards adopted as the official American standard the relation expressed thus:

$$\text{Degrees Beaumé} = 145 - \frac{145}{\text{Sp. G.}}$$

In England Twaddles Hydrometer is most used. It is based strictly upon a specific gravity relation. Specific gravity 1.0 = 0° Tw— and each succeeding degree represents an increase of .005 in specific gravity, *e.g.*, 5° Tw = 1.025 sp. g. This scale is very little used in the United States.

Standard hydrometers are made for use in liquids at 60°F. If the liquid is warmer than 60°F. the hydrometer will read low and vice versa, if the liquid is colder than 60°F. Where sulphuric acid is said to be so many degrees Beaumé it is understood that the statement refers to the hydrometer reading at 60°F. When it is desired to determine what the hydrometer would read at 60°F. in acid which is warmer or cooler than 60°F., the hydrometer is read at the existing temperature and the temperature of the acid taken with a thermometer. The hydrometer reading is then corrected, increased if the acid is warmer than 60° and decreased if colder.

If the acid is near 40°Bé. .031°Bé. for each 1°F. above or below 60°
If the acid is near 50°Bé. .028°Bé. for each 1°F. above or below 60°
If the acid is near 60°Bé. .026°Bé. for each 1°F. above or below 60°

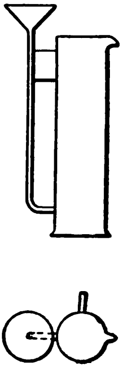

Fig. 57.

The Manufacturing Chemists Association of the United States has adopted the tables of Ferguson and Talbot as a standard for the relationships between specific gravity, degrees Beaumé, degrees Twaddel and per cent H_2SO_4. This table is very generally used in the United States. It can be found in Chapter XXIII, Table 1.

Hydrometers most useful in the chamber acid plant are the long 12-in. form with a range from 50° to 70° graduated to tenths of each degree and the short chamber 5-in. hydrometer with a range of 40 to 60° graduated in degrees. The former is used for testing the tower acids and the latter for the chamber drips.

Hydrometer jars for control testing are made of glass or lead in the form shown in Fig. 57. The acid enters the main jar from the bottom and assures the jar being full of the current flow.

GAS TESTING

The constituents of the gases regularly determined are SO_2 and oxygen. The Orsat apparatus is very generally used for determining both of these in the gases entering the system. In the latter parts of the plant where the SO_2 percentage of the gas is very low the Orsat is not suitable.

The Orsat apparatus consists essentially of a measuring burette graduated to 100 c.c., two absorption pipettes, connecting capillary tubes with stop cocks, and a levelling bottle. One pipette is charged with 30°Bé. caustic soda solution which absorbs SO_2 and the other with a solution of pyrogallic acid in caustic soda, which absorbs oxygen. This is shown in Fig. 58. To operate the Orsat apparatus the end of the glass capillary is connected with the vessel containing the gas to be analyzed by a rubber tube. Three-way cock E is turned to open from burette B to waste. Bottle A is raised to expel air from B and fill B with water. Cock E is turned so that B communicates with V, bottle A is lowered and the burette drawn full of gas. In order to be sure of a fresh complete gas sample the cock is turned to the waste position and the gas in burette expelled. A second sample is drawn and the bottle manipulated so that the water in the burette stands at O when bottle A is held so that water in A and B are level, with cock E closed. Cock to C is now opened, bottle is raised and gas all forced into C. The gas is drawn back and forth between B and C five times, then with level of liquor in C at original mark and cock closed a reading is taken in B with water in A and B held level. This reading is noted. The gas is again drawn back and forth between B and C twice and the

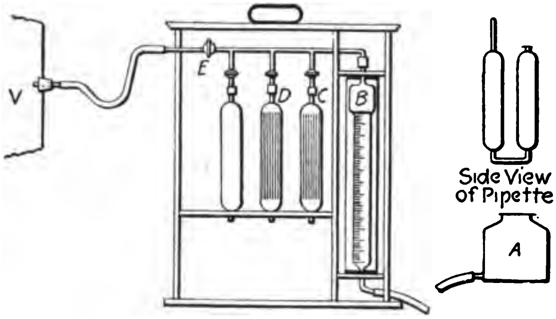

FIG. 58.

reading in B taken as before. If the two readings check, all the SO_2 is considered to have been absorbed in C. If the second reading is greater than the first the gas is sent into C again and until two readings do check. The final reading in cubic centimeters represents the per cent SO_2 by volume. Next the gas is manipulated into D and the same procedure gone through as with C. The difference between the reading obtained from absorption in C and that in D indicates the per cent of oxygen by volume. It is well to keep a thin rubber bulb on the back limb of D so that fresh air is not drawn in on the pyrogallic acid solution with each test, otherwise the absorbing power of the solution is quickly destroyed.

In gases free from CO_2 and which contain several per cent of SO_2 the Orsat test will answer very well for testing in connection with chamber control work. The accuracy is perhaps not high, but the test can be reliably performed by any reasonably intelligent person and it gives a good basis for estimating necessary changes in nitric feed and working the SO_2 furnaces.

The caustic soda solution used is made by dissolving about 300 g. pure caustic soda in a litre of water. It is not necessary to have these proportions exact.

The pyrogallic acid solution is made by dissolving about 12 to 15 g. pyrogallic acid in 125–150 c.c. of the above caustic soda solution. This amount is a suitable volume for charging the customary Orsat pipette. The caustic solution can be made up in any volume desired and kept indefinitely in a glass-stoppered bottle. The pyrogallic acid solution is best made up as it is wanted to charge the pipettes. It is well systematically to change the solutions once a week or at sufficient intervals to assure that the solutions do not become sluggish.

A direct test for SO_2 suitable for any gas found in chamber work is the Reich Test. This depends upon the reaction between iodine and SO_2 – $2I + SO_2 + 2H_2O = 2HI + H_2SO_4$, and upon the fact that a solution of cooked starch produces a deep blue color in a solution containing free iodine, and that the color disappears as soon as all free iodine has been reduced to HI.

The test is performed in apparatus shown in Fig. 59. Bottle A is charged with a definite weight of iodine dissolved in KI solution and colored with starch. Syphon tube C is opened and the gas under observation is drawn through the iodine solution until the color just disappears. The amount of water drawn

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from B is noted and it represents the amount of gas drawn through the iodine solution, less the SO_2 absorbed. Knowing the amount of iodine used and the volume of gas drawn, the per cent SO_2 by volume is readily calculated.

As a rule tests are made in a chamber plant at a point near the Glover tower where the SO_2 percentage is from 5 to 8, and at a point near the Gay Lussacs where the SO_2 percentage is under $\frac{1}{10}$. For the former it is convenient to use a $\frac{1}{10}$ normal iodine solution, *i.e.*, one which contains 12.7 g. iodine per litre. For each test 10 c.c. of this solution is used and a table is made up in the following way.

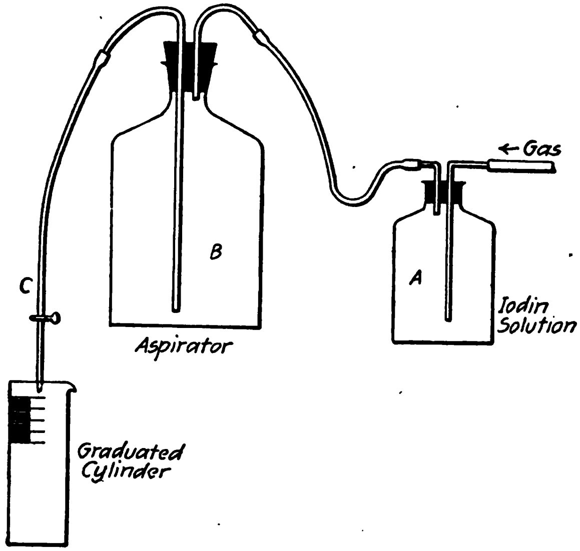

FIG. 59.

Ten cubic centimeters of $\frac{1}{10}$ normal iodine contains .127 g. iodine. According to the reaction above this amount of iodine will react with .032 g. SO_2.

$$
\begin{aligned}
2I : SO_2 &= 10 \text{ c.c. } N/10 \text{ I} : \text{wt, } SO_2 \\
2 \times 127 : 64 &= .127 \text{ g.} \qquad : .032 \text{ g.} \\
.032 \text{ g. } SO_2 &= 11.184 \text{ c.c. } SO_2 \text{ at } 0°\text{C. and } 760 \text{ m.m.}
\end{aligned}
$$

The total volume of gas drawn into the iodine solution in any test is then the amount of water syphoned from the bottle B plus

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11.184 c.c. which is the volume of SO_2 absorbed. Therefore

$$\text{per cent. } SO_2 = \frac{11.184}{\text{c.c. water} + 11.184}$$

$$\text{and c.c. water} = \frac{11.184}{\text{per cent. } SO_2} - 11.184$$

From this equation Table 6 is constructed.

In the rear of the system a 1/500 normal iodine solution is suitable. This contains .254 g. per litre. Table 7 is constructed for this solution in the same way as described for 6.

In using the Reich test, at any point in the chamber system following the Glover tower, a modification is necessary. The nitrogen oxids contained in the gas mixture render the test as described above worthless in that they reoxidize the HI formed and prevent decolorization of the solution. This can be prevented and the test made fairly accurate by adding to the iodine solution just before making the test, 10 or 15 c.c. of a solution containing 100 g. sodium acetate and 100 g. acetic acid per litre.

In Fig. 59 bottle A should be a 12 oz. salt mouth bottle fitted with a two hole rubber stopper carrying two tubes. One of these extends to within a short distance of the bottom. Its end is drawn down so that the opening is only 1 or 1½ mm. in diameter in order that the gas bubbles shall be small. The second tube goes barely through the stopper. This arrangement is for all practical purposes as good as the expensive and elaborate absorption bottles and when it is broken, it is quickly and cheaply replaced. The syphon bottle B should be at least two or three litres. Two graduated cylinders, a 500 c.c. and a 1000 c.c. should be provided.

The 1/10 normal iodine solution is made by dissolving 15 or 20 c.c. of potassium iodide crystals in 25 c.c. of water. Into this solution dissolve 12.7 g. iodine crystals. It is important that the KI solution be very concentrated or else the iodine will be slow to dissolve. When solution is perfect, make up to one litre with water.

The 1/500 normal solution is made by making up 20 c.c. of the 1/10 normal solution to one litre with water.

Starch solution is made by mixing 5 or 6 g. soluble starch to a thin paste and pouring into 500 c.c. of boiling water and allowing to boil for 5 min. The addition of a few drops of chloroform or

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TABLE 6.—STANDARD SO_2 TABLE

10 c.c. N/10 Iodine. 0°C.–760 mm.

Per cent SO_2	C.c. water	Per cent SO_2	C.c. water	Per cent SO_2	C.c. water
.1	11,173	4.1	262	8.1	127
.2	5,581	4.2	255	8.2	125
.3	3,717	4.3	249	8.3	124
.4	2,785	4.4	243	8.4	122
.5	2,226	4.5	237	8.5	120
.6	1,853	4.6	232	8.6	119
.7	1,587	4.7	227	8.7	117
.8	1,387	4.8	222	8.8	116
.9	1,231	4.9	217	8.9	114
1.0	1,107	5.0	212	9.0	113
1.1	1,006	5.1	208	9.1	112
1.2	921	5.2	204	9.2	110
1.3	849	5.3	200	9.3	109
1.4	788	5.4	196	9.4	108
1.5	734	5.5	192	9.5	107
1.6	688	5.6	189	9.6	105
1.7	647	5.7	185	9.7	104
1.8	610	5.8	182	9.8	103
1.9	577	5.9	178	9.9	102
2.0	548	6.0	175	10.0	101
2.1	521	6.1	172	10.1	99.5
2.2	497	6.2	169	10.2	98.5
2.3	475	6.3	166	10.3	97.4
2.4	455	6.4	164	10.4	96.4
2.5	436	6.5	161	10.5	95.3
2.6	419	6.6	158	10.6	94.3
2.7	403	6.7	156	10.7	93.3
2.8	388	6.8	153	10.8	92.3
2.9	374	6.9	151	10.9	91.4
3.0	362	7.0	149	11.0	90.5
3.1	350	7.1	146	11.1	89.6
3.2	338	7.2	144	11.2	88.7
3.3	328	7.3	142	11.3	87.8
3.4	318	7.4	140	11.4	86.9
3.5	308	7.5	138	11.5	86.1
3.6	299	7.6	136	11.6	85.2
3.7	291	7.7	134	11.7	84.4
3.8	283	7.8	132	11.8	83.6
3.9	276	7.9	130	11.9	82.8
4.0	268	8.0	129	12.0	82.0

This table is calculated using 2.8611 g. as the weight of the litre of SO_2.

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TABLE 7.—SO_2 BY REICH TEST

10 C.c. N/500 Iodine

Per cent SO_2	C.c. water	Per cent SO_2	C.c. water
.010	2,236	.060	373
.015	1,491	.065	343
.020	1,118	.070	319
.025	894	.075	298
.030	745	.080	279
.035	639	.085	263
.040	559	.090	248
.045	497	.095	235
.050	447	.100	224
.055	406		

oil of cinnamon to the cooled solution prevents souring. Only a few drops are used for each test.

The acetate solution is made by dissolving about 100 g. sodium acetate crystals in water, adding 100 c.c. acetic acid and making up to one litre with water. About 10 c.c. of this is used for each test.

TESTING FOR NITROGEN OXIDES

There are several materials about a chamber plant to be tested for their content of nitrogen oxides. The nitrometer method is suitable for any of them and every plant should have one in use. This instrument can be had in several different forms with compensating attachments but for the control work about a chamber plant the simplest form, consisting of a simple graduated burette with thistle top and two-way stop cock, and a plain levelling tube, is quite satisfactory. Figure 60 illustrates this.

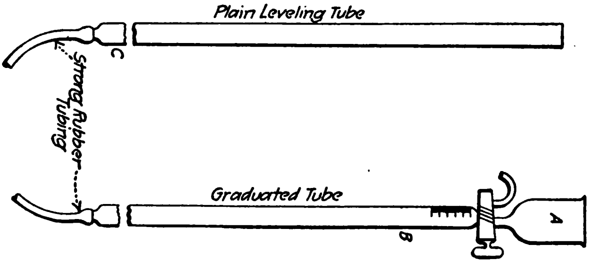

FIG. 60.

The nitrometer method depends upon the fact that in the presence of sulphuric acid mercury will react with nitric acid or any of the nitrogen oxides above N_2O, to form Hg_2SO_4 and NO, a colorless gas. By observing the volume of gas derived from a known weight of the compound to be examined, its nitric acid or sodium nitrate content, or equivalent, can be calculated at 0°C. and 760 mm.

$$1 \text{ c.c. NO} = .00281 \text{ g. } HNO_3$$
$$1 \text{ c.c. NO} = .00379 \text{ g. } NaNO_3$$

In performing a nitrometer test one should know in a general way the amount of nitrogen oxides contained in the material under examination and should figure out a suitable quantity for introduction into the nitrometer. If the graduated tube is of 50 c.c. capacity, a quantity of material should be used which will evolve a volume of gas preferably between 25 and 50 c.c. of NO.

The nitrometer is prepared by opening the stop cock into the reservoir A and raising the levelling tube until the mercury barely appears in the bottom of A. An accurately weighed or measured amount of the material under examination (in solution if a solid) is put into A. The cock is slightly opened and A is almost but not quite drained. Next about 10 c.c. of concentrated pure sulphuric acid is put into A, the cock opened slightly and the acid drawn into B as completely as possible without drawing in air. Tube B is now well shaken for about two minutes to bring the mercury and the solution into thorough contact. When one is assured that complete reaction has taken place a reading is taken of the volume of NO which has been evolved. The acid in B has a specific gravity about $\frac{1}{7}$ that of mercury so to observe the gas volume under atmospheric pressure the reading is taken with the mercury surface in C held at a point above the mercury surface in B equal to $\frac{1}{7}$ of the length of the acid column. For example, if the acid column is 14 c.c. the mercury in C will be held 2 c.c. above the mercury surface in B when the reading of gas volume is taken. A correction for temperature and pressure must be made in most cases. It is sufficient for the class of work under discussion to determine a correction factor for the usual room temperature and the normal barometer and to use this factor in all cases. This factor is determined by the following formula:

$$\text{Factor} = \frac{B}{760} \times \frac{273}{T+273}$$

B = Normal barometer in m.m.
T = Normal temperature in degrees Centigrade.

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The observed gas volume is multiplied by this factor and the result is the gas volume at 0°C. and 760 mm. pressure. The materials about a chamber plant to which the nitrometer test will be applied are nitrate of soda, nitre cake, nitrous vitriol and mixed acids.

To test nitrate of soda, dissolve 50 g. in water and make up to one litre. With a pipette introduce 2 c.c. into the nitrometer and perform the test as described.

$$\text{Per cent } NaNO_3 = \text{c.c. } NO \times 3.79$$

To test nitre cake, dissolve 5 g. in water and make up to 25 c.c. With a pipette introduce 5 c.c. into nitrometer and perform test as described.

$$\text{Per cent } NaNO_3 = \text{c.c. } NO \times .379$$

To test nitrous vitriol containing not over 70 oz. $NaNO_3$ per cu. ft., introduce 2 c.c. with a pipette into nitrometer and proceed as described.

$$\text{Oz. } NaNO_3 \text{ per cu. ft.} = \text{c.c. } NO \times 1.91$$

To test mixed nitric-sulphuric acids, it is usually necessary to dilute with concentrated sulphuric acid in order to avoid having to measure an exceedingly small quantity for use in the nitrometer. It is not well to try to use less than 2 c.c. of a solution for test as pipettes smaller than that are not very accurate.

A quick method of estimating the amount of nitrogen oxides in nitrous vitriol is by a titration with potassium permanganate solution. This assumes that all the nitrogen oxide exists as N_2O_3 and reacts thus:

$$5N_2O_3 + 4KMnO_4 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 \\ + 10HNO_3 + H_2O$$

Lunge and other writers on this subject recommend performing this test by measuring a known amount of permanganate into a dish and running in nitrous vitriol from a burette until the permanganate is decolorized. This is perhaps slightly more accurate than the way which will now be described.

Fill a 50 c.c. burette with standard permanganate solution. Draw a little water into a porcelain evaporating dish or casserole and run into it, from the burette, an amount of permanganate slightly less than needed. Now measure into the dish with a

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pipette 5 c.c. of nitrous vitriol. This should decolorize the permanganate. If it does not, repeat, using less permanganate. Next add permanganate from the burette until a faint color, which remains on stirring, appears in the dish.

This plan is much more convenient than the first described in that it is not necessary to fill, empty and clean a burette for nitrous vitriol for each test. It very closely checks the first method also. It is convenient to use a permanganate solution of such strength that 1 c.c. indicates 2 oz. $NaNO_3$ per cu. ft. of nitrous vitriol when using 5 c.c. nitrous vitriol for each test. In this, if the nitrous vitriol carries 50 to 60 oz. per cu. ft., there will be drawn 25 or 30 c.c. of permanganate for each test and a 50 c.c. burette is suitable for measuring it. Such a permanganate solution is made by dissolving 7.44 g. $KMnO_4$ crystals in water and making up to one litre.

EXIT GAS

A useful though rather rough test to determine if the Gay Lussac towers are functioning well mechanically is made by drawing several cubic feet of exit stack gas through a bulb tube, partly filled with 60° sulphuric acid. The bulb tube is shown in Fig. 61. It is charged with 100 c.c. of 60° sulphuric acid and the gas is bubbled through it for several hours. Its content of nitrogen oxides is then determined by the nitrometer. This test will show approximately how much nitre loss is being suffered by reason of insufficient contact between the gas and the acid in the Gay Lussac towers. Its results will often point out poor distribution of gas or acid or the need for further Gay Lussac towers.

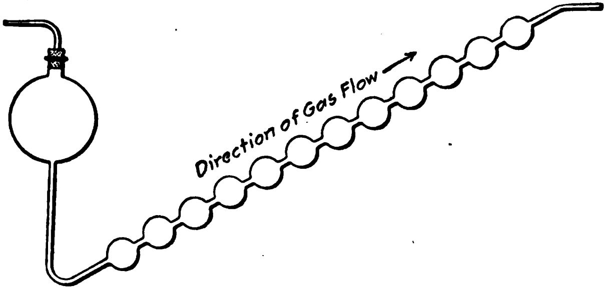

FIG. 61.

DRAFT MEASUREMENTS

It is desirable to observe daily the gas pressures at several points in the chamber system to be certain that fans are working properly and that no obstructions exist. The following points certainly should be examined; entering and leaving the Glover tower, before and after each fan and entering and leaving the Gay Lussac towers. In some plants further observations may be necessary. Two instruments are most useful for this work, viz., the small diameter U tube and the Ellison gage. The U tube is simply a glass tube of ½ to 1 cm. bore bent to a U shape with the limbs about 1 in. apart. This need not be more than 6 in. long. Behind this is placed a graduated paper scale marked in inches and tenths or in millimeters. One limb of this tube is connected to the flue or chamber whose pressure is to be determined, and the other left open to the atmosphere. The difference between the level of water in the two limbs shows the difference between atmospheric pressure and that in the flue. Figure 62 illustrates this.

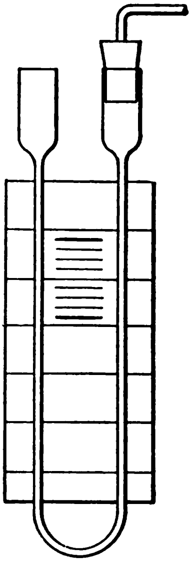

Fig. 62.

A much more sensitive instrument is the Ellison gauge, shown in Fig. 63. It is suitable for measuring very small differences of pressure as well as measuring considerable pressures with accuracy. In this instrument as shown, one limb is vertical and the other at a small angle with the horizontal. Any movement of the liquid in the vertical limb is accompanied by a movement about ten times as long in the sloping limb behind

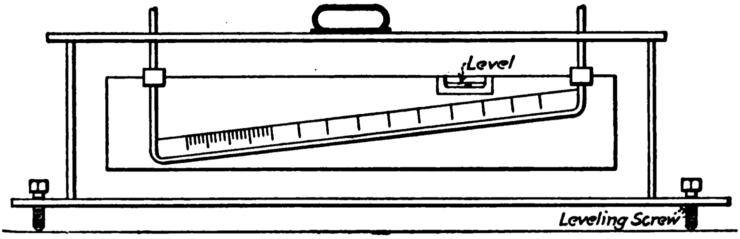

Fig. 63.

which the graduated scale is placed. The Ellison gauge is filled with a special oil colored red and the scale with which it is equipped is graduated to show directly hundredths of an inch of water and thousandths can be fairly accurately estimated by the eye. There is a levelling tube on the case and the base is equipped with levelling screws. This is a very practical and satisfactory instrument.

The application of the tests described will be taken up in the chapter on operation.

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CHAPTER XV

OPERATION

To successfully operate a chamber acid plant one should get clearly in mind the chemical and physical changes undergone by the gas mixture in its course through the plant. One must know what the ideal attainable conditions are in each part of the plant and make such observations as are necessary to know that they are being closely approximated.

First, to state the process briefly and simply, we have in the normally operating plant a steady uniform amount of SO_2 coming into the chambers and moving through them at such a rate that say 90 min. are occupied in the passage from one end to the other. Such an amount of nitric oxide is introduced into the gas by nitre pots and in the Glover tower as will oxidize substantially all of the SO_2 to sulphuric acid in that 90 min. This amount of nitre must be very accurately proportioned or results will be bad. A sufficient amount of water or steam must be introduced into the chambers at various points to make the acid formed therein have a concentration of approximately 50°Bé. The Gay Lussac towers through which the residual gas from the chambers is passed must be fed with a suitable uniform amount of cold 60°Bé. sulphuric acid to take into solution 85 to 90 per cent of the nitrogen compounds existing in the gas. This solution, the "nitrous vitriol," must be fed back uniformly into the Glover tower and there diluted to such an extent that the hot incoming gas will remove and carry on with it in gaseous form all of the nitrogen compounds. This is, of course, the main source of the nitric oxide to the process, constituting by simple inference 85 to 90 per cent of the amount required. The other 10 to 15 per cent is supplied by potting new nitre or adding nitric acid.

The chemical reactions which take place in the chamber process have been subjects of much controversy and there is still much difference of opinion concerning some of them. Without attempting any discussion of the various theories, a brief statement of the ideas of Lunge will be given. These may or may not

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be correctly representative of the chamber process, but they give a good basis for reasoning and are very well borne out by the phenomena of the chambers.

The reactions which take place in the nitre pots or the retorts of the nitric acid plant are:

(1) $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$

(2) $NaHSO_4 + NaNO_3 = Na_2SO_4 + HNO_3$

The first reaction takes place at low temperatures and the latter at higher temperatures. Nitre cake as usually made is a mixture of Na_2SO_4 and $NaHSO_4$.

In the Glover tower, nitric acid is reacted upon thus:

(3) $2HNO_3 + 3SO_2 + 2H_2O\cancel{_4} = 3H_2SO_4 + 2NO$

In the Glover tower, nitrous vitriol is reacted upon thus "(denitration"):

(4) $2HSNO_5 + SO_2 + 2H_2O = 3H_2SO_4 + 2NO$

In the Glover tower this reaction probably also takes place:

(5) $2NO + 2SO_2 + H_2O + 3O = 2HSNO_5$

In the Glover tower and the first chambers these two reactions 4 and 5 are the predominating ones. The only oxide of nitrogen which exists in quantity is NO. This is a colorless gas which explains the fact that front chamber gases show little red color.

As the gas mixture becomes leaner in SO_2 the following reactions take place:

(6) $2HSNO_5 + H_2O = 2H_2SO_4 + N_2O_3$

(7) $N_2O_3 + 2SO_2 + 2O + H_2O = 2HSNO_5$

These two reactions take place more and more as the gas approaches the last chamber. The predominating oxide of nitrogen is N_2O_3 (probably a mixture of NO and NO_2), which is a red gas and which gives the gas mixture its red color.

If conditions are ideal, the gas mixture entering the Gay Lussac tower contains substantially all its nitrogen oxide as N_2O_3 or equal parts of NO and NO_2. This is absorbed by the sulphuric acid in the Gay Lussac packing thus:

(8) $N_2O_3 + 2H_2SO_4 = 2HSNO_5 + H_2O$

If an excess of NO exists it is not absorbed by the Gay Lussacs. This condition exists when there is a considerable amount of SO_2

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in the gas mixture entering the Gay Lussacs. If an excess of NO_2 exists, it partly reacts with the sulphuric acid in the Gay Lussacs thus:

$$(9) \qquad 2NO_2 + H_2SO_4 = HNO_3 + HSNO_5$$

This reaction is not complete and some NO_2 goes through and shows as a red cloud at the stack. This condition exists when an undue amount of nitre is introduced with the entering gas and the SO_2 is completely converted to sulphuric acid sometime before the gas reaches the Gay Lussacs.

The time of passage of the gas through the chambers is something which varies in different plants and which depends upon the style of work done. In some chamber plants the period is as short as 1 hour and in others more than 2 hours. It is simple to calculate from the SO_2 analyses, the make of acid and the volume of the chambers what the period is. This should be known by the operator. The amount of nitre necessary to be introduced for normal work is also dependent on the individual characteristics of the plant and upon the style of work. In modern American plants, an average amount is probably 25 to 30 parts sodium nitrate for each 100 parts sulphur. For example, if 100 tons 60° acid is made per day, the sulphur in the SO_2 used is approximately 25 tons or 50,000 lb. The sodium nitrate equivalent of the nitrous vitriol plus the new nitre will amount to 25 or 30 per cent of 50,000 lb., or 12,500 to 15,000 lb.

If absolute uniformity of all the factors of the process could be maintained, the operation would be very simple. Involving as it does high temperature, dusty, corrosive gas and sulphuric and nitric acids, many irregularities occur and it is in meeting them properly that the skill in operating lies. It is of course, much simpler to operate a plant deriving its gas from brimstone burning than to operate one on blast furnace gas or some of the other metallurgical by-product gases.

In years gone by, chamber acid plants were almost entirely operated by rule of thumb methods. Operators by considerable periods of experience became often very skilled in handling the process, depending upon such observations as color of the gas mixture in the chambers, effervescence of nitrous vitriol on dilution with warm water and various other equally inexact phenomena. The old hand at the business did well sometimes but several years were necessary to make an old hand. In recent

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years, particularly since metallurgical gases have come to be used to a considerable extent, more exact methods are being employed, for control of the acid process. It is true that there are plants still operated by the old plan, but certainly better work can be done in any plant by making accurate observations and records.

The thing of chief importance in the chamber process is the proper proportioning of nitre to SO_2. The amount of nitre derived from the nitrous vitriol and from the nitre pots or fresh nitric acid must at any given time be precisely enough and not too much, to convert substantially all of the SO_2 coming in at that time to sulphuric acid during the period of passage of that gas through the chambers. If the amount of nitre is not sufficient all of the SO_2 will not be converted to sulphuric acid. The SO_2 remaining unconverted will pass out and be lost. The nitrogen compounds will exist as NO_2 and NO with NO in excess and as NO is not absorbed by the Gay Lussac towers, that excess will be lost. There will be loss of both sulphur and nitre. If the amount of nitre introduced be too much, there will be no loss of SO_2.

The SO_2 will all be converted to sulphuric acid some time before the gas mixture finishes its passage through the chambers and during that time, oxidation of the NO present will proceed and the gas entering the Gay Lussacs will contain NO_2 and NO with NO_2 in excess. NO_2 is partly but not completely absorbed by the Gay Lussac towers and the part that is not absorbed passes out into the atmosphere as a red cloud. In the absorption some nitric acid is formed which is not particularly good for the lead. From these statements it can be understood that nitre loss occurs if the amount of nitre originally introduced be either too large or too small to completely convert its accompanying SO_2 in just the proper time.

The original establishment of these conditions is done by trial. To maintain them, the modern acid maker depends mainly upon periodical observation and recording of the temperatures in the chambers at many points throughout the system, and upon periodical determinations of SO_2 in the gas mixture at a point just preceding or following the Glover tower, and at another point just preceding the Gay Lussac tower. There are other indications which are made of use to some extent such as the concentration and appearance of the chamber drips, the color of the gas,

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the appearance of the exit stack, the nitrous vitriol determinations, etc., but these are used more to confirm the temperature and SO_2 knowledge than anything else.

To illustrate in a concrete way how these observations are used, we will assume that hourly observations and records are made of

1. Temperature and °Bé. of drip on each chamber.
2. SO_2 in gas entering Glover tower.
3. SO_2 in gas entering Gay Lussac towers.
4. Nitrous vitriol.
5. Atmospheric temperature.

The operator comes on and immediately makes a set of records as above. If the percentage of SO_2 in the gas entering the Gay Lussac towers is correct he knows that 90 min. before, the nitre was properly proportioned to the SO_2. He looks back on his record sheets and observes that at that time the SO_2 entering the Glover was say 8.0 per cent and that the temperature of the front chamber was 195°F. If the gas entering the Glover is still 8.0 SO_2 he can reasonably assume that the front chamber temperature should be within a degree of 195°F. If it is much under 195°F. the amount of nitre entering is deficient and if much over 195°F. the nitre feed is more than necessary. If the SO_2 in the gas entering the Glover has decreased to say 7.6 per cent the operator will know by experience that his front chamber temperature should be somewhat less than 195°F., say 190°F. If on the other hand, the gas entering the Glover has increased to say 8.2 per cent he will know that his front chamber temperature should be perhaps 197° or 198°F. He will in the one case decrease the nitrous vitriol stream slightly and continue such adjustments until the desired temperature is attained. The correctness of the operators adjustments will be shown by the SO_2 determination at the Gay Lussacs 90 min. later. This system of observation and adjustment is carried out constantly and if faithfully attended to, produces excellent results.

A further elaboration of the plan of control by SO_2 tests has been proposed and carried out successfully by A. M. Fairlie. This plan is as follows: An SO_2 test is made at a point near the Glover tower. A short time later an SO_2 test is made at another point some little distance along say at the end of the leading chamber. The time between the tests is approximately that occupied by the gas in passing between the two test points. As-

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suming uniform gas velocity, for any given SO_2 percentage at the first point there is a certain proper SO_2 percentage at the second point to assure perfect conditions at the entrance to the Gay Lussacs. If the SO_2 at the second point is not correct, an adjustment in the nitre feed is made. This is a most excellent method of control and in certain cases where the gas supply fluctuates widely, its practical value is high.

Control of the nitre feed lies in two things, the nitrous vitriol and the nitre pots, or the nitric acid. Of the total the nitre derived from the nitrous vitriol amounts to between 85 and 90 per cent, and the added or new nitre to 10 to 15 per cent. It is a very good plan to decide upon a suitable amount of new nitre to be used at the beginning of each shift and to maintain it constant throughout the shift, barring, of course, large irregularities. The minor changes necessary, such as the ones specified above are taken care of by changing the flow of nitrous vitriol. This can be accomplished readily by means of a long distance control arrangement. If the frequent small changes desirable are made by varying the amount of nitre potted, the potting schedule becomes very intricate. If it is done by varying the flow of new nitric acid, many trips to the top of the Glover tower are necessary as it is hardly feasible to make nice changes in a stream of liquid ranging from knitting needle to pencil size with any long distance methods. The nitrous vitriol, on the other hand, is a rather ample flow, and its nitre content is low so that its control is very convenient.

To illustrate by an example, suppose a system running normally with 8 per cent gas and proper nitre feed of which 87 per cent is from the nitrous vitriol and 13 per cent new nitre. The gas decreases to 7.6 per cent, *i.e.*, 5 per cent. The nitre feed should be decreased 5 per cent. This can be done by decreasing the nitrous vitriol flow by 5.75 per cent (since 5 per cent is 5.75 per cent of 87). If the change is made by varying the new nitre, this will have to be decreased by 38.5 per cent(since 5 is 38.5 per cent of 13). With suitable tank space for nitrous vitriol, these minor changes are not often reflected back to the Gay Lussac towers which go on running with constant flows.

To decide upon the amount of new nitre to be used for a shift, the operator will observe the stock of nitrous vitriol in the tanks and whether the nitrous vitriol is of normal grade. If the stock is right and the nitrous vitriol normal he will establish or con-

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tinue the introduction of the normal amount of new nitre. If the stock is low or the nitrous vitriol below normal in nitre content, he will establish a rate of introduction of new nitre somewhat above normal in order to bring the nitrous vitriol stock and grade back where it belongs. If, on the other hand, stock or grade of nitrous vitriol are above normal, he will have an opportunity to run with less than the normal feed of new nitre.

The drips on the chambers are tested hourly. They should be kept between 48° and 50°Bé.—not higher, because the nitrogen compounds begin to be taken into solution, and not lower, because concentration capacity of the Glover tower will be overtaxed. The control of the acid strength lies in the amount of water or steam admitted to the chambers. Ordinarily the hydrometer readings are taken without correcting for temperature, although for strict accuracy, corrections up to .5°Bé. should be added. The bottom acid in a chamber is always slightly higher in strength than the drip.

The acid issuing from the Glover tower coolers should be observed several times a day for strength and temperature. It should ordinarily be kept between 59° and 61° after applying the temperature correction. The minimum represents the lowest proper strength for Gay Lussac feed. Above 61° there exists danger of incomplete denitration in the Glover unless the burner gas is very hot. The temperature of the acid issuing from the cooler should be not over 80°F. and preferably less. From time to time, the coils in the cooler become encrusted and when the acid temperature rises above 80°F. the cooler should be drained and washed out with a hose. It is well to test this acid from time to time by the nitrometer to be certain that no nitre is being retained by the acid. If denitration is not complete, the feed of weak acid on the Glover must be increased.

The nitrous vitriol issuing from the first Gay Lussac tower is tested with potassium permanganate once an hour. Any great variation from the normal should be accounted for. This normal nitrous vitriol is something which will be decided upon for each system. It is right in one plant to run with perhaps 35 oz. $NaNO_3$ per cubic foot and in another with 70 oz. or more. Several considerations enter. The amount of absorbable nitre entering the Gay Lussacs in a given system will be fairly constant. The nitre content of the nitrous vitriol will then depend upon the amount of acid fed to the Gay Lussac tower. The

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smallest permissible amount is that which can be divided and distributed over the packing with sufficient thoroughness to assure wetting the entire area. If any of the packing remains dry, or nearly so, the nitre laden gas will pass through that part of the tower without having the nitre recovered from it. A good safe quantity to assure wetting is one ton of acid per square foot of horizontal area per 24 hours. If the tower has for example, an area of 200 sq. ft., about 200 tons per day should be put over it. This quantity may be exceeded and assurance of complete wetting made doubly sure, but a greater amount than that mentioned is not necessary. If the plant served by this tower makes 100 tons 60° acid, the nitre entering the Gay Lussac tower will amount to about 12,500 lb. $NaNO_3$ and if 87 per cent recovery is made, the normal nitrous vitriol will be 45 to 46 oz. per cubic foot.

If, as in many plants, the horizontal area of the Gay Lussac towers is proportionally less, a smaller acid circulation will be used and nitrous vitriol of higher nitre content produced.

In any event, a proper normal will be established and any wide variation from it indicates an irregularity in process, or acid flow.

An observation and record of drafts should be made once a day by the instruments already described. Any important variation from normal should be investigated. Sometimes in a Glover tower, for example, there will be a very gradual increase in the packing resistance indicated by an increase in the difference between the pressures at bottom and top. This indicates usually, the accumulation of sediment or dust in the packing, and when it reaches a certain point, flushing out is necessary.

LABOR FORCE

The number of men required to operate a chamber plant is small, but care and reliability are absolutely essential. In order to give an idea of the normal labor force required, assume a 100-ton unit having mechanical burners, flue nitre pots and acid eggs for pumping. There will be, on each shift, one furnaceman, one nitreman, one pumpman and a chamberman who exercises general supervision. On the day shift will be a repairman and two laborers. This force may be reduced in certain small plants by having the furnaceman attend the nitre potting

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as well as the furnaces. In case a nitric-acid or mixed acid plant is used instead of flue pots, one man will produce enough nitric acid in one shift to run the plant 24 hours.

The whole operation should be supervised by a man of experience and judgment. It is a false economy to run even a modest sized plant without such a man.

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CHAPTER XVI

CONCENTRATION

Sulphuric acid made in the chambers is only, at its best, 52° to 53°Bé., and where an acid of greater concentration is required it is necessary to concentrate this chamber acid. There are various methods of doing this.

Before the introduction of the Glover tower, chamber acid was concentrated in lead pans, up to 60° or 61°Bé. Since the Glover's introduction it has been an easy matter for manufacturers to bring their chamber acid up to 61°Bé. in the tower, as described under that subject.

Lead pans are still used in old works that have no Glover tower, and in concentrating waste acid.

The vapor from boiling, dilute sulphuric acid consists almost entirely of water vapor: therefore, the acid will become more and more concentrated, as the boiling proceeds, as long as 60°Bé. is not exceeded.

In pan concentration lead pans are almost universally used for the concentration of acid up to 60°Bé. Above this point, lead is acted upon, necessitating the use of other material.

Pans may be heated by direct flame, either from the top or bottom, by steam, or by the waste heat from pyrites or sulphur burners.

When the purity or appearance of the acid is of less importance than the saving in fuel, or in labor, top firing is generally used. The pans are generally 30 ft. long, 4 ft. 11 in. wide, with sides 17 in. high. They are built from heavy lead, 15 to 30 lb. to the sq. ft., and always in one piece; the corners are never cut, but are folded over.

It is necessary to protect the lead from the direct action of the fire. The fire box is always built separate from the pan, and is only connected to it by an arch which extends the length of the pan, and a fire-proof clay slab at the bottom. The pan inside is protected by acid-proof bricks or slabs. At the long side these extend up to the arch, while on the short, or fire side, they only reach to the top of the pan, and there is placed the fire-proof

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slab to the fire box. There are openings left in the bottom of the partition slabs, so the acid can circulate freely. The pan is always raised 3 ft. or more above the ground.

The acid is introduced at the end nearest the fire box, and drawn out at the far end. Evaporation is very rapid, both because the hot gases come into direct contact with the acid, and because the chimney draught carries away the water formed. The damage to the pans is very slight, as the brick lining protects the lead from direct heat, and up to 60°, or even 61°Bé. the acid has very little effect upon lead. But above that degree of concentration not only does the acid act upon lead, but its boiling point gets close to the temperature at which lead begins to soften.

Keeping the acid at a constant level also protects the pans. Except for repairs the acid is never drawn off entirely, but as the concentrated acid sinks and is drawn off from the bottom fresh weak acid is added at the top. Efforts at water cooling have not been successful, as lead pipes or jackets start leaking easily, and cause trouble.

The greatest destructive effect is at the fire end of the pan, and to keep it as cool as possible the weak acid is added here, through a pipe through the arch. The syphon to withdraw concentrated acid is at the cool end of the pan, but even then the acid is too hot to use, and is run into shallow lead cooling pans, stayed with wood or iron frames.

If the pans need staying it should be done by cast-iron or pressed-steel grids, as their large radiating surface will help keep the lead cool.

Coal used will vary from 2 per cent to 10 per cent by weight of the acid concentrated, varying with quality of coal and size of pan. A long pan is most economical.

One square foot of pan surface will concentrate 150 lb. of chamber acid to 61°Bé. per 24 hours.

The strength of concentrate is regulated by the fire and the weak acid fed.

No data is available as to the loss of acid in this method of concentration, but it is probably more than for bottom-heated pans, as the stream of hot gases carries away acid in minute drops, that are very hard to condense. We meet this same mist in the contact process, and it gives us the same trouble.

The spray of acid from the stacks is not only a loss, but a

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nuisance, and sometimes the basis of suits by neighboring property owners. Gas, instead of coal, firing has been tried as a remedy, without much success, and the only relief has come from the use of higher stacks, causing a better diffusion in the air.

Lead pans heated from below are always smaller than those using "top fire," and are built in sets. The reason for this is that the pans nearer the fire are worn out first, and it is cheaper to have a small pan to replace. The concentration is very regular, the weak acid flowing in at one end, and running from one pan to the next, until it runs off sufficiently strong at the other end.

The pans are rectangular, 5 to 7 ft. on a side, and about 15 in. deep. There are four to six in a set. The acid is carried from pan to pan by overflow pipes, so that it takes the acid from the bottom of one pan to the top of the next, as the acid is stronger at the bottom. The flow of weak acid is so regulated that the proper concentration of acid is obtained at the last pan.

The pan bottoms are protected from the fire by iron plates, these plates being heavier at the fire end. The iron, being a good conductor of heat, also assists the heat distribution. Sometimes copper plates are placed between the pan bottom and the iron plate to prevent, by their good conducting qualities, local overheating and buckling of the pan.

The general plan is to place the fire under the weak pan. In this way the strong pan does not receive much more damage than the others, and evaporation goes on satisfactorily as well. The old practice was to place the fire under the strong pan, because the boiling point of the strong acid is the highest, but on account of the wear on the pan it has been found more economical to reverse the operation.

Bode gives the following table, where the fact that the greatest heating takes place at the third pan shows that the fire is badly utilized:

Acid running in....	......	1st pan	2nd pan	3rd pan	4th pan	5th pan	6th pan
Temperature.......	25°	112°	150°	160°	148°	145°	143°C.
Strength...........	110°	113°	120°	128°	134°	140°	144° Tw.
Temperature.......	24°	110°	145°	156°	145°	142°	142°C.
Strength...........	110°	113°	118°	126°	134°	140°	144° Tw.

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He estimates, for English practice (1910), that a set of six pans will cost $500, and the maintenance will be 12 per cent. Total cost of concentration 55¢ to 65¢ per ton.

Coal required is about 15 per cent of the weight of the acid concentrated, and each squae foot of pan area will produce 85 lb. of 60° acid every 24 hours.

Pans for utilizing waste heat from pyrites or brimstone burners must be designed for each special case, the principles being the same as for bottom-heated pans. Sometimes the pans are placed over the dust flue, but protected from the direct action of the burner gases by brick, or often over the burners themselves. This method of concentrating is very cheap, requiring only part of a man's time, and the maintenance charges, Bode says, 10¢ to 18¢ per ton (1910).

Steam pans are of many forms, all depending upon slow evaporation far below the boiling point of the pan acid. Steam is introduced through a lead coil, which lies on the bottom of the pan, the condensation returning from it to the boiler. There is no acid mist escaping, so no injury to vegetation is possible; but steam coil concentration is so expensive that the writer does not know of a single installation in the United States.

QUALITY OF LEAD

Lead as heavy as that used for concentrating pans is difficult to bend cold, so a light fire of shavings is made on the part of the lead plate to be bent, and the lead softened sufficiently to be easily manipulated.

W. B. Hart, *Journal of the Chemical Society*, 1907, writes as follows:

Lead may fail from either or both chemical or physical faults: The effects of impurities are as follows:

(*a*) With bismuth and tin, lead forms alloys of low fusibility, causing local perforation. Acid may concentrate in these leaks, and become strong enough to attack the lead itself.

(*b*) Aluminum, tin, or zinc may cause sudden failure at certain stages of the concentration.

(*c*) The physical condition of zinc will sometimes increase the chemical action of acid upon lead.

(*d*) Electrolytic action may be set up between deposits of impurities and the lead.

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(*e*) Antimony may have a strong and harmful chemical effect, and copper, arsenic, and silver very little. Copper may even be helpful under certain conditions. By constant use copper may be entirely dissolved out, and its corrosive effect upon other impurities lost. This will sometimes explain the sudden failure of a pan that has been in good condition for a long time.

(*f*) Pure lead, under normal pan conditions, is undoubtedly less affected than the impure metal.

Faulty physical conditions may be due to bad remelting, use of unsuitable casting temperatures, and too severe pressure in the rolling operation.

(*a*) Production of a loose crystalline structure, by casting the metal at too high a temperature, causing leakage.

(*b*) Production of a surface more susceptible to attack, by too severe pressure during rolling.

(*c*) Strong acid action in the temporarily physically altered form of lead, before the annealing effect can take effect, explains the failure of pans that have been in use a very short time.

(*d*) Altered physical condition can make unsuitable even a lead of exceptionally pure chemical composition.

CONCENTRATION FROM 60° TO 66°

Concentration of sulphuric acid naturally resolves itself into three divisions—first, chamber to 60°Bé.; second, 60° to 66°Bé., or "93.19" (per cent), as it is often called, and from 93.19 per cent H_2SO_4 up to 97.50 or 98 per cent H_2SO_4.

Ordinary pan concentration, as just described, is the usual first step. For the second several methods are used, and are presented in what the writer considers their order of merit.

First, because very simple and efficient, comes the "heat exchanger." As applied at one large works, this is a continuation of the lead pans.

A series of five lead pans concentrates the acid to 62°Bé., and the acid leaves the last lead pan at a temperature of from 285° to 320°F., practically the temperature of the first pan. The highest temperature usually comes in the third pan.

From the last lead pan the acid flows to a pulsometer, or air lift, which raises it to the top of the heat exchanger. The heat exchanger is a lead-lined steel tower, further lined with three courses of acid-resisting brick, and filled with broken quartz. It

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is 12 ft. high, and 21 in. in diameter inside the brick. The acid trickles down through the broken quartz packing, and meets the ascending gases, rich in SO_3, from the covered iron pan, which is set directly over the flame. The falling acid is cool enough to absorb practically all of the SO_3 in the ascending gas, and while it does take up some of the moisture driven off too, it is not enough to hinder the concentrating operation. The unabsorbed gas, now almost entirely steam, passes from the top of the heat exchanger to two lead-lined condensing towers, filled with coke, which catches any drops of acid. The passage of the gases through the heat exchanger and condensing towers is induced by a steam jet, attached to the exit flue of the second tower.

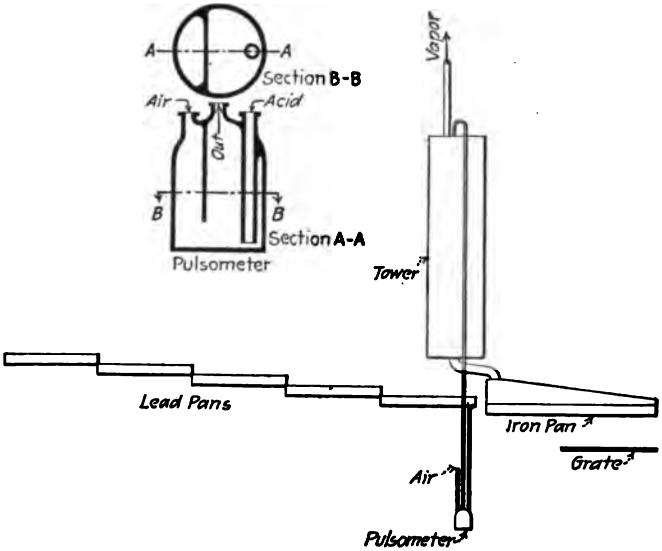

FIG. 64.

From the bottom of the heat exchanger the acid, enriched by the SO_3 absorbed, flows to the iron pan, where it is concentrated to 66°Bé., and is then syphoned off to a tant-iron box, equipped with cooling coils of lead, where it is cooled down to 80°F. Thence it goes to storage.

The temperature of the iron pan is unheeded. The first lead pan is kept at 285° to 310°F., and upon the fire necessary to accomplish this depends the degree of heat of the iron pan.

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The lead pans hold the following temperatures:

No. 1 about 320°F
No. 2 about 330
No. 3 about 360
No. 4 about 345
No. 5 about 330

The **Kessler apparatus** really covers two steps of the concentrating field, as it will bring chamber acid up to 98 per cent H_2SO_4 in one operation. In this apparatus hot air is used to concentrate the acid. The operation requires that a current of hot air shall be brought into contact with the liquid, to immediately reduce its temperature. The air must become thoroughly saturated with steam and acid vapor. The apparatus must be so constructed that it will stand the action of hot acid, and that the deposits do not give any trouble. Under these conditions the acid may be concentrated at a temperature far below its boiling point, for instance, to concentrate acid to 95 per cent H_2SO_4, boiling at 280°C., the temperature needs to be only 180° to 190°C.

The part of the apparatus where the gases are saturated with acid vapors, and the temperature greatly reduced, is called the "saturator." Immediately above it is placed the "recuperator," where the acid vapors are caught. This recuperator resembles the dephlegmating columns used in the rectification of spirits.

The saturator is a trough built of acid-proof slabs, surrounded by a thick lead jacket, both of which must resist hot acid and gases. Between the bottom and cover of the saturator there are placed several partitions, to force the hot gases into immediate contact with the acid. In this way the gases are quickly reduced to 150°C., and the acid as quickly gives off its water and some acid vapor. The acid is run off from the saturator in the concentrated state, at the end furthest from the fire box.

The recuperator consists of a tower, lined with acid-proof brick, and containing 5 horizontal plates, dividing the tower up into 6 equal parts; each plate, however, is perforated by 100 holes with raised edges, so that there is always a film of acid on the plates. The holes are covered by inverted porcelain cups with jagged edges, forming an hydraulic seal, so that ascending gases must bubble up through the acid on the plates. The chamber acid runs to the top plate first, and then by overflow piping to the other lower ones, and finally to the saturator. The gases from

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the saturator are drawn up through the holes, and so through the descending acid, by an injector, and SO_3 is absorbed, and a little water given up, as in the tower of the just described heat exchanger.

A thermometer is placed at both top and bottom of the recuperator, for temperature control. The lower one should stand at 300°F., the upper a little under 200°F.

After leaving the recuperator the gases pass through a coke tower, to recover any acid spray.

Ninety-eight per cent H_2SO_4 can be made in one operation, from chamber acid. Gas firing is most satisfactory, and requires 8 per cent coke, on the acid concentrated. The injector requires 2 per cent steam, also figured on the concentrate.

The Benker system is a third modification of the heat exchanger, all being based upon the principle of the Glover Tower, although I do not know who first applied this system in this way. The Benker system uses a cascade instead of a pan, however, for the final heating.

Two parallel rows of duriron or tantiron plates, are arranged in cascade form, with the flue running up between the two rows. On account of the great fire space, and the thin film of acid, evaporation is very rapid. The cascades are covered, and the gases are lead to a packed tower, which removes the SO_3, the draught being provided by a fan. A cooling box is necessary, between the cascades and the tower, as the gases, owing to the intimate contact with the heat, due to the thin film of acid, are too hot for good working of the tower. The gas passes through a coke tower after the tower.

The acid leaves the tower at the bottom, at a concentration of 61° to 62°Bé., and a temperature of 300°F., running direct to the cascades.

Such a plant, to cost, in 1916, $3,500, will furnish 9 to 10 tons of 92 to 93 per cent H_2SO_4, clear as water, in 24 hours, with a coke (for gas) consumption of 12 to 15 per cent on the acid made. At this concentration losses will run about 3 per cent, and higher on 98 per cent acid.

Because of the thin film of acid on the plates, the temperature of the acid will get higher than in either of the two previously mentioned systems, giving this method greater capacity, but driving off more SO_3: and as the tower acid is less efficient, the higher the SO_3 content of the ascending gases, the losses are consid-

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erably greater. Of the three, the writer prefers the "heat exchanger."

The objection to the use of direct heat in all concentrating systems is that at the high temperatures, up to 800°C., from direct flame there is considerable dissociation of the acid into H_2O and SO_3, requiring very large spaces, usually coke boxes, to give room and thus time to assist in reassociation. For instance, in a Kessler system, concentrating 5 tons of 66°Bé. acid per 24 hours, a coke box 24 ft. long, 8 ft. wide and 6 ft. high is needed: and this coke box, with its supports, constitutes a large proportion of the cost of plant.

The Buffalo Foundry and Machine Co. system gets away from this by combining outside and direct heating, as follows:

The hot gases pass from the fire around the acid pot at a temperature of approximately 800°C.; thence to a heat exchanger, where they heat air that is under 5 lb. pressure and then pass into the tee that is at the bottom of the concentrating tower, at a temperature of approximately 300°C. This tower, of four 2-ft. 6-in. sections of cast iron, 36 in. in diameter inside of lining, is lined with sheet lead and acid-resisting brick, discharges the vapors, now well cooled down, through a 12-in. I.D. lead pipe, to a 6-ft. × 6-ft. × 3-ft. scrubber, where any acid carried over is condensed. There is very little dissociation at the temperatures employed, and this small scrubber, is ample in size.

The weak acid feed is to the heat exchanger, which is heated by the concentrated acid, hot from the pot. From the heat exchanger the weak acid goes to the top of the tower, trickling down over the tower packing meeting the ascending gases from the tee, and runs off into the acid pot. The final concentration takes place in this pot, and the overflow from it is 66°Bé. and plus acid, which is cooled for storage by heating the feed acid.

This pot, in addition to its acid feed from the tower, receives the heated air under pressure, from the heat exchanger, near the bottom. A small removable liner is placed to receive the impingment of the air and protects the pot. A collar of high-silicon iron, carried on lugs, and outside of which is the outlet, prevents the weaker acid from reaching and attacking the pot itself. The arrows in the sketch show the course of the acid within the pot.

The air introduces heat and agitation, furnishing, in effect, "direct flame," but at a low enough temperature to avoid acid

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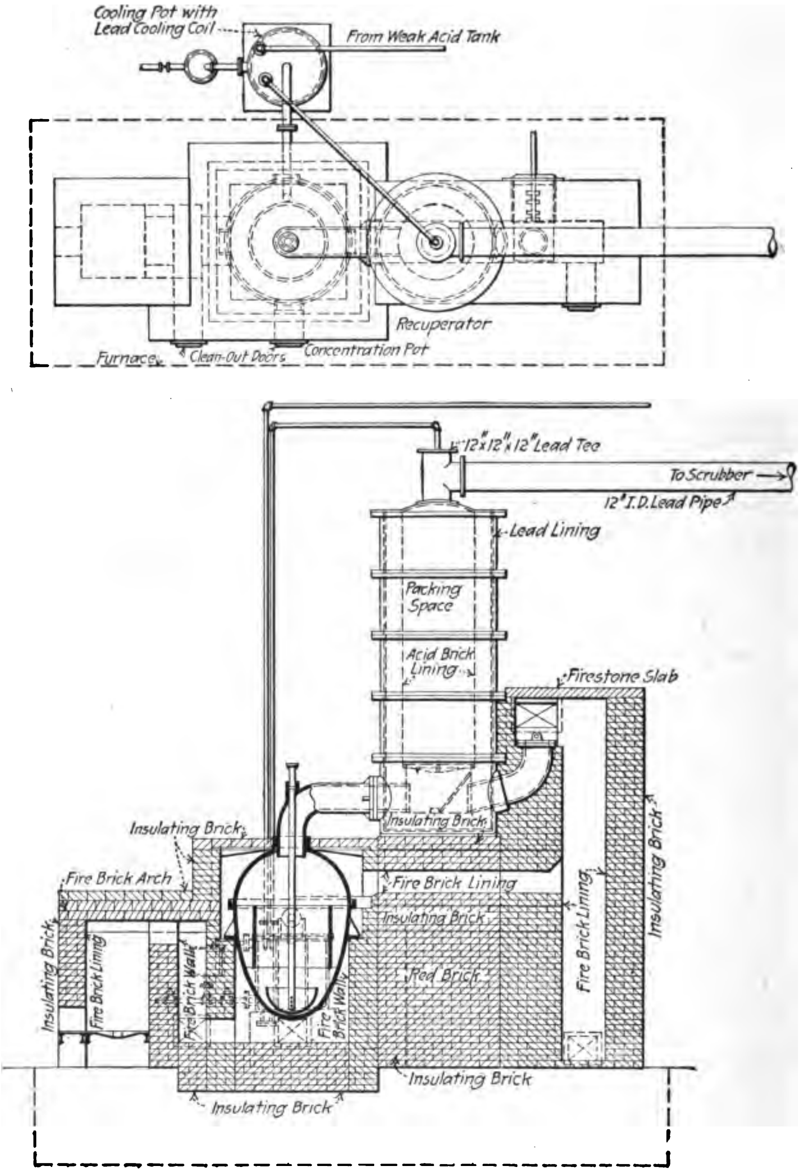

Fig. 65.

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dissociation and, of course the heat outside the pot is similar to that applied to the bottom of a pan.

The vapors rising from the pot pass to one leg of the tee, the other one of which receives the gases from the heat exchanger, and up through the tower.

The same number of heat units is applied as sometimes give a dissociation up to 25 per cent, at a concentration to 97.5 per cent in a direct heated pan system, but the distribution is better.

Tubes and small castings are made of high-silicon iron-larger ones, such as the pot and tower sections, are close grained semi-steel.

This system uses 8 per cent to 10 per cent of coke on the acid made depending upon the strength of the feed, and final concentration of the acid.

PLATINUM STILLS

The concentration of sulphuric acid in platinum dishes is still carried on to a small extent in this country, when very pure acid is required, as for laboratory use. But with platinum at $145 an ounce (1920), the contact process can use it more economically.

In the platinum still of today only the pan is platinum, the bell being a lead water jacket. The size of the still depends upon the production—roughly 75 oz. of platinum per ton of 95 per cent acid produced per 24 hours. A dish to turn out seven tons of 95 per cent acid daily would weigh 45 lb., be 3½ ft. in diameter, and cost $78,300. The rim of the dish has a groove in which the lead bell sets loosely, condensation forming an hydraulic seal. There is an overflow pipe from this seal, to remove the weak acid condensed.

A large pipe runs over from the top of the bell, and dips down into a condenser, through which the vapors pass, the weak condensate from here and the seal being added to the feed. Two or three stills make up a set, the acid from the first one going by gravity to the next, for further concentration.

The still is carried upon a cast-iron frame.

Acid fed to platinum stills is first concentrated in bottom-fired lead pans, to furnish it as pure and clean as possible. Glover tower acid contains too much dissolved iron sulphate, which settles out to form "crusts" in the platinum stills. The stills are cleaned by running them as nearly dry as possible, and washing them out with hot water or weak acid, which dissolves the

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crusts. The frequency of cleaning depends entirely upon the acid fed, it may be every day, it may be every three months.

The acid is kept very shallow in the still, from 2 to 3 in. only, and even comparatively small heat fluctuations cause large variations in the concentration of acid produced. Coal firing is not sufficiently steady, so gas, usually from a producer, is used, and gives excellent results.

The lead work on such a set of stills has to be renewed in two years. The platinum is also slowly dissolved, losses running from .2 to .3 g. per ton of 98 per cent acid made.

VITREOSIL CASCADE CONCENTRATORS

The continuous cascade concentrator was originated in England, and at first consisted of four or five glass retorts arranged in cascade over a coal- or a gas-fired furnace. Porcelain dishes set in an acid-proof brick chamber were later substituted for glass retorts. One of the most serious drawbacks to this system, whether using glass or porcelain, was the heavy breakage of the pans and the difficulty of getting high fuel efficiency; hence the system was not generally adopted.

With the development of vitreosil (fused silica) in 1906, there was a more general adoption of the use of cascade systems, and several were installed in this country. The largest is at the plant of the Davison Chemical Co., at Baltimore, Md.

Plant for full range of concentration (50° to 66°Bé.) is composed of rectangular trays and circular basins. The trays measure 24 × 12 × 6 in. and are used only in the operation of the plant covering the range from 50° to 60°Bé. This portion of the plant is uncovered, as the fume from acid below 60°Bé. is practically acid free. The basins are used on the range 60° to 66°Bé. and may be either 12 in. or 16 in. in diameter. This portion of the plant must be covered, as the fumes from acid of higher strength than 60°Bé. carry sulphuric acid and it is essential that these fumes be scrubbed of their acid content before allowing them to pass out into the air. If higher strengths than 66°Bé. are required, the acid from the cascade may be run directly into iron pans, which would be so set up as to be fired from the same firebox as the basin cascade, and the fumes from this acid recovered by one of the systems previously described.

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In the full range plant, the tray and basin cascades are set up so as to allow a continuous flow from one to the other and to allow a fire from a single firebox.

There is but slight loss of acid in the concentration up to 66°Bé., this usually amounting to about 2 per cent, based on the weight of finished acid, and usually running in strength from 10° to 12°Bé. for the entire distillate. For the fuel efficiency of the cascade concentrator, it is usual practice to concentrate over the range 60° to 66°Bé. with a fuel consumption of about 14 per cent, while over the range 50° to 66°Bé., the fuel consumption is usually about 17 per cent. The above percentage figures are based on the weight of finished acid and figuring on soft coal as a fuel running about 13,000 B.T.U. Breakage in usual operation amounts to about 5 per cent on the basins and about 1 per cent on the trays per annum.

The cascade concentrator is applicable to the concentration of sulphuric acid from either a brimstone or pyrites set. Sludge acid may be recovered in the cascade plant if free from high percentages of mineral or organic matter, which will cause excessive frothing due to evolution of SO_2. Sludge acids carrying only small amounts of organic matter, and in which the frothing would not be excessive, may be readily carried on in this type of plant by using a specially designed basin.

The cascade type of concentrator, using vitreosil dishes is especially recommended where freedom from contamination during concentration is desired.

Vitreosil is unaffected by sulphuric acid of any strength or at any temperature. Its melting point is about 1,750°C., although there is slight softening around a temperature of 1,400°C. Vitreosil due to its extremely low coefficient of expansion .00000054 per degree centigrade, over the range 0° to 1,000°C., about $\frac{1}{17}$ that of glass, is applicable to high temperature operations.

The process of the Kalbperry Corporation, worked out from the tower developed at the plants of the Franklin H. Kalbfleisch Co., cannot be described, as it is a trade secret, unpatented, licenses being issued for its use. One important feature is that it will give a high degree of efficiency on concentrating very dirty acid, the concentrate being perfectly clean. Operating cost is low, in 1916, it being 50 cts. per ton of 97 per cent acid produced. Exclusive of building and license, this tower cost, in 1916, about $4,000.

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The license charge is a flat fee of \$3,500, in return for which the client receives complete detail working drawings, bills of material, flow sheets, and can obtain the service of a skilled operator for a time to demonstrate and put the tower on a working basis.

RECOVERING SULPHURIC ACID FROM A MIXTURE WITH NITRIC ACID

Nitric acid alone cannot be handled in steel or iron containers, because of its corrosive action, unless it is sufficiently dilute. As in most nitrating operations water is liberated, and must be cared for, sulphuric acid fulfills the double function of diluting nitric acid to a point where it will not attack iron containers too energetically, and of absorbing the water liberated.

It is impracticable to remove this water without separating the two acids and reconcentrating them, and a brief description of the most successful method of separation is in order.

Nitric acid boils at 188°F., water at 212°F., but a mixture below 91 per cent acid boils at a higher point still. 68.5 per cent HNO_3 boils at 251.5°F., which is the highest boiling point of nitric acid of any concentration, and nitric acid of any concentration, if boiled alone, will approach that concentration, by the loss of HNO_3 if above that concentration, of water if below 68.5 per cent. It will then evaporate to dryness, remaining at 68.5 per cent.

So it is necessary to use something to retain the water, letting the HNO_3 fumes pass to the condensers, and sulphuric acid is an ideal substance.

A tower 21 ft. high, 3 ft. in diameter, packed with quartz, with openings for steam at the bottom and for the concentrating mixture at the top, with sulphuric acid opening at the bottom and fume (HNO_3), outlet at the top, is the apparatus required.

The concentratng mixture, strong H_2SO_4 and weak HNO_3, is derived from the formula $\dfrac{\text{per cent } H_2SO_4}{\text{per cent } H_2SO_4 + \text{per cent } HNO_3} = S$

or,

$H = $ per cent HNO_3 in mixture,
$h = $ per cent H_2SO_4 in mixture,

then,

$$S = \frac{100H}{100 - h}$$

S is therefore directly proportional to H_2SO_4, and inversely proportional to H_2O, and is a direct measure of the heat-develop-ing capacity of the mixture: and since a definite amount of HNO_3 requires a definite amount of heat to volatilize it, it must be high for high HNO_3, low for low.

With H_2SO_4 about 84 per cent the mixture automatically falls about right for complete denitration.

The addition of water, in the form of steam, is the one weak point. It takes about a pound of steam to distill a pound of HNO_3.

The concentrating mixture is fed in at the top and trickles down over the quartz, meeting the steam blowing in at the bottom. The heat from the steam, and that from its reaction with the H_2SO_4, volatilize all the HNO_3, which rises, being pulled through by suction.

As it approaches the top the steam begins to condense, and having greater affinity for the H_2SO_4 than for the HNO_3, unites with it, leaving the vapors practically water free. The reverse of this process takes place in the decending mixtures, more and more HNO_3 is driven off in its downward passage, until at the bottom there is no HNO_3, the mixture being only H_2SO_4 and H_2O. A top temperature of under 200°F, is excellent operation, and that at the bottom should run 300 to 330°F.

The rate of feed mixture and steam must be correct, or immediate trouble insues. Too little mixture means too little H_2SO_4 to unite with the steam, the excess of which escapes at the top, raising the top temperature, and giving weak nitric acid. Also, too much steam may first liberate, and then condense and reabsorb HNO_3.

If too much concentrating mixture is used, there will not be heat enough to vaporize all the HNO_3.

The weak sulphuric acid is then concentrated in lead and iron pans and the heat exchanger, up to 66°Bé.

The vapors from the concentrating towers are almost entirely HNO_3, with a little H_2O, NO and NO_2, and traces of N_2, N_2O, and CO_2. All the water, and practically all the HNO_3, are condensed, a little HNO_3 going over as a spray into the absorbtion towers, where it condenses. The NO is oxidized to NO_2 by the air present, and then reacts as follows with water:

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

The HNO_3 is absorbed, and the HNO_2 reacts as follows:

$$3HNO_2 = 2NO + H_2O + HNO_3,$$

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the NO being oxidized and the product decomposed over and over again, until it is practically all acid.

Spent acids from the nitration of nitro-cellulose, nitro-glycerine, or similar substances contain so small an amount of low oxides of Nitrogen actually in chemical combination with H_2SO_4, that whilst dilution of the spent acid in the denitrating tower is necessary, such dilution need not be carried to anything like the extent that is necessary when handling spent acid from nitration of hydrocarbons: and in the case of spent acid from glycerine it may be regarded as more of a distilling process than dinitration; the principal function of the tower in this case (nitro-glycerine) is to remove the nitric acid as such from S/A in a most highly concentrated state, and decompose traces of N.G. in S/A.

But "spent" from the nitration of hydrocarbons, in the manufacture of T.N.T., picric acid, etc., usually contains about 2 per cent nitric acid and 4 per cent of the lower oxides: in the case of one large T.N.T. plant in Canada it was the equivalent of 7 per cent of 100 per cent HNO_3—certainly well worth recovering.

These lower oxides are in large part not free, but are combined as definite compounds with sulphuric acid, and the Buffalo Foundry & Machine Co. has worked out a plant which will make a 98 per cent recovery at low cost.

Their process for handling S/A from nitro-glycerine or nitro-cellulose is based upon careful heat control: and this includes the superheating of the steam introduced, furnishing the amount of heat required with the minimum of water, thus keeping down the amount of water which must be removed by, and later from, the sulphuric acid.

A 12-in. column of high silicon metal lagged with 4 in. of asbestos, or acid proof lined C.I., 35 ft. high, is fed at the top with heated acid, the temperature being controlled within approximately 1°C., automatically. This top temperature is kept under 100°C., the exact point depending upon local conditions (Fig. 66).

If it is at 100°C., the recovery will be in 93% HNO_3
If it is at 95°C., the recovery will be in 97% HNO_3

The steam, carrying 100° of super-heat, is introduced through high-silicon iron tubes, full of small holes, 6 in. below the surface of the liquid in the bottom. The bottom temperature is maintained at approximately 300°C. The amount of steam introduced being kept down, the H_2SO_4, absolutely denitrated, runs

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out 78 per cent–80 per cent, instead of the customary 60 per cent that obtains from the ordinary denitrating system. At this strength iron pans may be used for concentrating, eliminating lead pans entirely.

The fume leaves the tower at the top, and is carried down through a condenser, from which the condensate flows to a receiver. From this receiver the non-condensible gases are sucked through oxidizing towers, in series, similar in construction to the denitrating tower, but of greater diameter and less height. In these towers good construction, low velocity, plenty of air, and good atomizing of the absorber make the oxidation good enough to make a 98 per cent recovery.

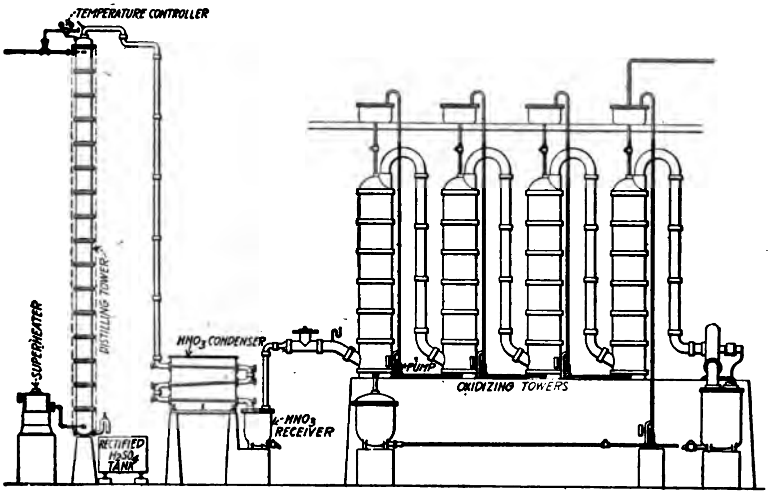

Fig. 66.

The absorbing liquid fed to each tower is from the base of the succeeding tower, raised to a receiving tank above the tower, and fed through an atomizer, with valve control. The fume is fed at the bottom of each tower, and drawn off at the top.

Mr Authur Hough, the designer of the apparatus, stated that the increased operating efficiency of a modern dynamite plant, of 10 tons per day capacity, using the improved acid recovery system, amounts to many thousands of dollars per year.

Corrosive liquids, like strong mineral acids, cannot be handled by pumps, so the pulsometer has been developed. It is shown in section in Fig. 64; is made of chemical stone ware, and operates

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as follows: Up from the three openings shown lead tubes, not over an inch and a quarter in diameter. The inlet, indicated by "acid" comes from a raised supply, which, flowing in, of course rises to an equal height in the two other tubes. Sufficient pressure of air is then blown in at the appropriate opening, to overcome the head of liquid. This air blows all the liquid out of the air inlet, blows down and under the partition, and of course rises through the liquid, up through the "out" tube. It is kept from entering the incoming tube by that tube being extended near to the bottom of the pulsometer than the bottom of the partition.

The air, rising through the outgoing tube, carries up with it bubbles and regular "slugs" of liquid, these slugs being sometimes two inches thick. If the tubes are too large in diameter the slugs will not form, the air just blowing up through, and agitating the liquid.

The heighth to which a liquid can be raised by this apparatus depends upon the hydrostatic head of the entering liquid, air pressure, diameter of tubes, and liquid itself—nitric acid can be raised to four times the hydrostatic head.

BATTERY ACID

Battery acid is *pure* sulphuric acid, from 1.118 sp. g. to 1.125 sp. g.

As the fume from the concentration of acid from 60° to 66°Bé. runs about 1.1 sp. g., and is usually clean, and of good purity, it is an easy matter to condense this fume, and concentrate it, using Vitreosil, as platinum is not necessary for this work.

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CHAPTER XVII

OUTLINE OF THE CONTACT PROCESS

The "Contact Process" takes its name from the fact upon which it depends—that SO_2 and O will combine to form SO_3, under proper conditions of temperature, concentration, and purity of gas, **In Contact ~~With Platinum.~~** vanadium (V) oxide

Catalytic action has been known since 1834, when Mitsherlich concluded that the formation of ethyl ether and water from ethyl alcohol, in the presence of sulphuric acid did not depend upon the dehydrating power of the acid, nor upon any intermediate product being formed, but that the mere presence of the acid facilitated the reaction, although it did not in any way enter into it.

Mitsherlich suggested calling this contact action, but the next year Berzilius called it catalysis, and the latter name, while certainly no better nor more descriptive, is the better known.

SCOPE

While from its great affinity for sulphur tri-oxide, water would seem the logical "absorber" in this process, thus rendering possible by this one method the production of any and all degrees of concentration, with practically no change of apparatus for different concentrations, from the very weakest to 100 per cent SO_3, we are practically limited to the making of fuming acid, because water will *not* do.

When SO_3 comes into contact with water vapor a white mist is formed. As to its character, two opposing views are held. One is that it is minute drops of H_2SO_4, the other is that in the presence of the water vapor a double molecule, S_2O_6, is formed, and that this molecule is not easily absorbed.

Whatever the actual reason for, or character of, this mist, it resists all attempts to condense it, passing through as many as six scrubbers, with sulphuric acid as the scrubbing agent. It is, however, partly removed by condensation, when filtered through fine coke or asbestos fibre. It causes trouble when present before the conversion by its activity as an arsenic or

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lead carrier, and in the absorber house, because it passes, in apparently undiminished volume, right through the absorbers and out of the fume stacks, simply throwing away that much good SO_3.

This mist is, of course, what limits our product.

Sulphuric acid of 98.3 per cent concentration, or more, holds very firmly to its small percentage of water, but as concentration drops below that point the space above the acid contains water vapor, and especially where the temperatures are at all high, as in the first scrubber or absorber tower.

So we are in practice limited to sulphuric acid of not less than 98.3 per cent concentration as an absorbing medium, which in turn means that we must make an acid of higher concentration than that: in other words, "fuming." For this reason the hopes of the pioneers in the industry, that this process, requiring a smaller, more compact plant, would ultimately entirely supercede the older process, have not been realized. It has, however, entirely eliminated the Starck process of distillation of Bohemian shales, and the "cracking" of sulphuric acid into SO_3 and H_2O, the sulphur tri-oxide being absorbed as in our process.

TECHNOLOGY

There are three steps in the production of sulphuric acid by the contact process.

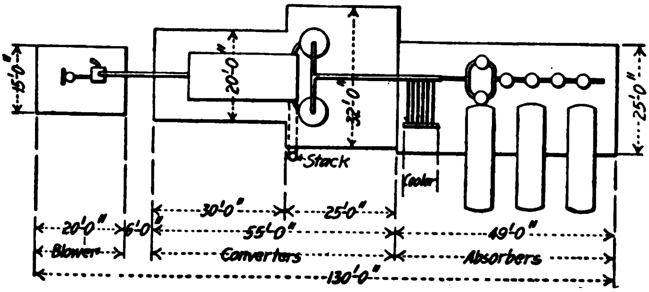

FIG. 67.—Layout for contact plant.

(a) Production of SO_2 from some sulphur bearing material, as pyrites or brimstone. (While this process has not yet been adapted to the utilization of metallurgical gases, as the Anaconda Company, for instance, is doing with the chamber process, the

Davison Chemical Co. silica gel promises great things in this direction.)

(b) Oxidation of the SO_2 to SO_3.

(c) Absorbtion of the SO_3 formed by a weaker acid, until the desired concentration is reached.

There are two processes used extensively in this country, the Badische, the rights for which are controlled by the General Chemical Co., and the Schroder-Grillo, controlled by the New Jersey Zinc Co. The methods of cooling the burner gas, the contact mass, and the means of bringing the purified gas up to the temperature necessary for conversion are fundamentally different in the two processes.

But they are alike in that both require a clean gas for the conversion of SO_2 into SO_3, and that the same underlying principles control their absorbtion systems.

The production of SO_2 has already been covered in Chapter V, the methods in use being common to both the chamber and contact processes. After this the gas must be

Cooled;

Freed from dust, moisture, small quantities of SO_3 formed in the burners, and other impurities;

Freed from any mechanically carried sulphuric acid;

Filtered to remove any last traces of liquids, which at this point is usually a sulphuric acid mist;

Heated to the conversion temperature;

Converted;

Cooled;

Absorbed;

The acid weighed and delivered.

Lunge says, ironically, in his "Sulphuric Acid and Alkali:" "There are 279 sulphuric acid plants in the United States today, of which 44 employ chemists." Working within the comparatively narrow limits that we must in this process, a well equipped laboratory is a necessity—even more than in the chamber process—for this must be controlled all the way through by analysis. If the acid in either the scrubbers or absorbers gets too low in concentration we will soon be face to face with a badly corroded system; if the absorber acid gets too high, its absorbing properties fall off very fast, and we loose SO_3 out of the stacks. Acid is bought and sold on analysis, both as to concentration and purity.

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The "strength" of the gas is determined at regular (every two-hour) intervals, by the Reich starch-iodine test: it is most important that this test be made frequently and regularly, because in a well conducted plant the loss due to imperfect conversion is the largest loss, and the gas strengths, both relative and absolute, give us all our information upon this important point.

The method used is that of Reich for the estimation of sulphurous acid in gas, and while of no higher degree of accuracy than any other color test, is sufficiently accurate to control the process. This test, and the pyrometers for reading the converter temperatures are our only guides, but with a properly made mass and clean gas, are enough to insure a satisfactory conversion.

FIG. 68.

This is of course occasionally checked by the laboratory, using the K_2CO_3 method.

The early investigators worked along serenely at this process in the belief that SO_2 and O must be present in stoichometrical proportions, and many believed that nitrogen had a distinctly bad effect, aside from its diluting the gas; which means, of course, more gas to move, heat, and cool. Those who were working to put it upon a commercial basis, and saw in the air the natural supply of oxygen, tried to get a burner gas that ran 20.3 per cent SO_2, which left just enough oxygen to oxidize the SO_2 to SO_3. But the rate of conversion was low; the process would not become a success.

In 1878 Winkler, realizing that reactions do not go to conclusion but rather to a state of equilibrium, showed that there must be an excess of air to get a good rate of conversion, and while he never reached 100 per cent efficiency, he frequently was able to get up to 99 per cent. This is high for general practice, as the production suffers when conditions that will allow so high a conversion are maintained.

This discovery of Winkler's put the contact process upon a commercial basis.

Suppose that the plant is burning 1,000 lb. of sulphur an hour, with an 8 per cent entrance gas. If the SO_2 content is increased to 9 per cent the amount of sulphur must be 1,130 lb. per hour and correspondingly more acid made, without any increase of expense except in the one item of raw material-less than 50 per cent of the cost anyway. The same labor and overhead pay for the increased production.

Acid production may be figured as follows:

Let a = available SO_3 = sulphur burned × 2.5 × per cent yield,
b = pounds water made per 1,000 lb. fuming acid,
x = weight of weak acid used per day,
y = weight of fuming acid produced per day,
c = per cent strength of weak acid,
d = per cent strength of fuming acid,

Then

$$y = \frac{by}{1000} + a + x = \frac{1000\,(a + x)}{1000 - b}$$

and

$$d = \frac{cx + a.}{y}$$

But as the SO_2 content of the gas goes up, above a certain point, the rate of conversion goes down. This point is not the same for all plants, nor is it a constant for any one plant, varying with the contact mass and the purity of the gas, which in itself varies with the weather, etc. Seven per cent may be taken as a safe starting point, however, and the best working conditions for the individual plant then determined. It is impossible to draw a curve showing per cent conversion plotted against per cent SO_2

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in the gas—and it is equally impossible to show, except for the individual plant, at what point the decreased conversion ceases to be overbalanced by the increased production.

Gases leave the converters around 350°C.; much too hot to make possible any high degree of absorbtion, which should be conducted not far from 40°C. (104°F.). The methods of removing this heat used by the Badische and the Schroder processes are fundamentally different—the former uses it to heat the incoming gases, the latter wastes it by radiation. The net result is a gas of the proper temperature, which is brought into intimate contact with sulphuric acid, not less than 98.3 per cent, by towers and tanks, such as are described in the chapter on absorbtion, the SO_3 absorbed, and the remaining gases passed out through the stack. This remainder consists of N, O, the minor gases contained in the air, and practically all the unconverted SO_2—this latter constituting by far the greater part of the loss in the system. The SO_2 absorbed by the acid, either in the scrubbers or absorbers, and slowly oxidized to SO_3, thus becoming part of the acid, is not only inconsiderable, but is not a loss.

The degree of concentration of the finished product must depend upon the market to which it goes. Higher acid is made more slowly, as the absorbing power of any acid varies directly as its vapor pressure, and reference to the curve of vapor pressures in Chapter XXIII will show the very rapid increase in vapor pressure with concentration, of "fuming." While acid of 80.5 per cent SO_3 will absorb practically 100 per cent of the SO_3 in any gas passed through it, at 88 per cent SO_3 it will only take up 23 per cent.

The freezing point must be considered very carefully in deciding what concentration of acid to make. A glance of the curve of freezing points, Chapter XXIII, shows a wide range of choice. Eighty-four and five tenth per cent SO_3 will remain liquid at the lowest temperature of any really concentrated acid. The addition of a few per cent of nitric acid drops the freezing point many degrees, but spoils the acid for some purposes.

COSTS

A thousand pounds of 100 per cent sulphuric acid made by the contact process cost, in 1914, from $7.50 to $8.50. A plant to burn 1000 lb. of brimstone an hour cost then $150,000. This

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does not include power house, sulphur storage, shops, office, laboratory, or any auxiliary buildings. Operating labor will be 1¼ to 1½ man hours per 1000 lb. acid. Capital expense must of course be figured for each case.

Where depreciation leaves off and maintenance begins is a difficult question to answer. The usual practice is to take a figure gained by experience for depreciation, and all renewals above that are charged to maintenance. Maintenance will vary so with the management that it is not possible to give any figure that could serve as a guide.

An industry handling corrosive material expects very rapid depreciation. Weak sulphuric acid, and nitric acid, even in small quantities, destroy iron and steel very rapidly. The usual method of handling sulphuric acid, by compressed air, puts serious strains upon parts of the apparatus. When acid mixtures are made a great deal of heat is evolved and high temperatures result, producing expansion that will have serious results unless the design of the plant provides for expansion bends as liberally as on steam lines. Expansion joints are not practicable for pipe work to handle corrosive liquors.

Fuming sulphuric acid does not destroy cast iron by dissolving it, but by bursting. Cracks appear, in no particular direction, and sometimes the fitting actually suddenly explodes with a considerable report. Examination of the broken pieces rarely shows a flaw. Dr. Kneitsch suggests that the acid enters into the pores of the iron and becomes vaporized, producing sufficient pressure to burst it. At any rate, steel castings are far less liable to rupture, and as the pores are smaller would seem to bear out this theory.

Acid is moved by "blow cases"—horizontal air tight tanks of steel—with the acid outlet pipe running down almost to the bottom of the tank. When air pressure is put on the tank the acid rises in the pipe, and is thus forced around without the use of pumps, upon which acid is very hard.

All iron gate valves should be used. The writer prefers sheet asbestos packing, although sheet lead is widely used; this is open to two objections—the direct action of the acid upon lead, and the additional corrosive effect of the electrolytic action, between two metals, in the presence of an acid. Brass valves have a very short life where there are any acid fumes in the air, in spite of which they are frequently used on air lines. Any valve that is

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exposed to sulphuric acid and is not frequently eased by opening and closing will soon become useless.

The use of rising spindle valves is not to be thought of. A valve left open by mistake can be attended with very serious consequences, and the only safe way is to try each valve each time: any type of valve that indicates whether it is open or shut without actual trial tends to promote carelessness in this respect.

Shower baths, where the full stream is released by one turn of the handle, frequently inspected, should be placed at convenient intervals. When a man gets any acid on himself he wants water, and he wants it in a hurry.

The first aid boxes should contain a bottle of a solution of bicarbonate of soda, boracic acid, an eye cup, vasoline, absorbent cotton, and surgical tape. This will care for any probable injury until medical aid can arrive.

LABOR

Such a plant requires on each shift a foreman, burner man, engineer, fireman, and absorber-house man, who also attends to the scrubbers. Three men, a millwright, a pipe fitter, and an electrician, can attend to all maintenance, and the outside help, unskilled labor, will bring in sulphur or ore, coal, pack filters, remove ashes and cinder, help the maintenance crew, and keep the outside clean. The size of this crew depends upon local conditions.

The operation of a well-designed contact plant is easy and pleasant, and it is always possible to get a good grade of labor. The writer prefers Americans, and likes them young enough to be easily trained.

In any continuous process coöperation between the shifts is an absolute essential. Rivalry is to be discouraged, as it tends towards evils such as trying to burn more sulphur on one shift than the condition of the burners warrant, leaving the following shift to pull the plant out of the hole. Try above everything else to make the men realize that the DAY, not the SHIFT, is the unit of time, and that to gain an apparent temporary advantage, such as the burning of a couple of thousand pounds more sulphur than the shift before, and leaving the plant in such condition that the following shift cannot come within four thousand pounds of the required amount, is not a victory at all. Have a meeting that all three foremen MUST attend, every week. Post your monthly

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yields on a plant bulletin board. Let all the men know what the results are. Success of all kinds appeals to all men, and when the figures are posted the men will forget all about the Athletics or the White Sox, while they digest—and more important, discuss—the comparisons. Where there are few men employed they come to know each other well, and as friends will get along better together than enemies, an unpopular man has no place in such an organization.

SHUTDOWN

Because of the corrosive effect of sulphuric acid upon iron, a plant making or handling it must be very carefully prepared for a shutdown, either temporary or permanent. If the work is done as outlined below the plant will be in good condition to start up at any time on short notice, and at small expense.

It is a good plan to start in at the burners and work through, as in this way nothing is likely to be overlooked.

All traces of sulphur must be burned, the burners thoroughly cleaned, and then painted, inside and out. The outlook will dictate the extent of repairs and replacements of arms, etc. All bearings must be well greased.

Get the preheaters going, and run the blowers for several hours, thus forcing hot air through the converters and absorbers, which will remove most of the SO_3.

All gas lines must be washed out thoroughly with a little soda ash and water, then rinsed out with water and allowed to dry, and then blanked off into convenient sections, the blanks being air tight. Fittings at low points in the lines must be removed, putting on the blanks there.

Pump tanks are filled up with soda ash and water, rinsed, and allowed to drain. The pumps should be washed, greased, assembled, and painted, and put back into the tank again.

The soda solution from the tanks should be pumped over the towers for 2 hours, when the interior will be neutral. If the shutdown is to be long, the packing and lining should be removed, the inside of the tower washed, dried, and painted, and then the tower sealed tight.

The acid-soaked coke in the coke filters may disintegrate in time—it does not always do so. The most thorough way is to remove the coke, neutralize it with lime water, wash it, wash the filters, paint them, and replace the same coke. Then seal up

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the filters tight. Or the filters may be simply sealed up, taking a chance on the coke standing up.

The blower must be washed out with soda water, dried, and painted. All bearings must be greased. The cylinder head of the engines must be removed, and the inside of the cylinder greased.

The converter mass is safer inside the converter than anywhere else, and as there should be no SO_2 nor SO_3 nor moisture left inside after the blowing out with hot air, simply blanking off the preheaters and converters is the best thing to do.

The absorber house can be treated as was the scrubber house, with the addition that the brick linings of the pump tanks should be removed.

All acid lines should be washed out with soda, dried, and blanked off in sections, all valves being greased.

All iron work, such as on the buildings, should be carefully painted.

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CHAPTER XVIII

PURIFICATION OF GASES

In the Contact Process, to get any reasonable degree of conversion, the gas must be of a certain concentration, certain temperature, and CLEAN.

Impurities in the gas are both mechanical and chemical, and each class of treatment is necessary.

A distinction must be drawn between an impurity that is merely a diluant, and one that has in itself a bad effect upon the result, either from its effects upon the system or upon the contact mass.

The first class is well represented by atmospheric nitrogen, present to the extent of 77 per cent (by weight) in the air drawn into the system. This means that about four-fifths of the gas handled, cooled, and heated, is worthless; but this handling is more economical than the use of pure oxygen would be. The nitrogen, also the minor gases of the atmosphere, have no effect upon the contact mass nor upon the life of the system, and leave the stacks as inert as they were upon entering the burners.

Mechanically-carried dust will finally stop the contact action simply by covering the mass and preventing its coming in contact with the gas. If in sufficient quantity it might clog the system.

Moisture dilutes acid, and the action of dilute acid is well shown in Table 21, Chapter XXIII, covering the action of sulphuric acid of various concentrations upon iron.

Sulphur as a sublimate will crystalize out somewhere in the system, possibly causing a complete block.

Sulphur trioxide unites with water vapor to cause the mist spoken of in the last chapter.

Arsenic, antimony, lead, mercury, selenium, tellurium, and silicon tetra-fluoride are all enemies of the contact process, chemically, and the greatest of these is arsenic. They destroy almost entirely the catalytic action of the platinum; they "poison" it; and the action cannot be reobtained in any known way, short of removing the mass, recovering the platinum in the form of platinic chloride, and making up the mass again.

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Arsenic can be partly, and some authorities say completely, removed from the mass by passing chlorine, or, better, hydrochloric acid gas through the mass, and then removing the gas by blowing heated air through. But at ordinary converting temperatures part of the platinum is converted into chloride, carried off, and deposited somewhere in the system.

Lead, mercury, and their salts form compounds, or perhaps alloys, with platinum, which destroy the catalytic properties of the platinum. It is theoretically, but not practically, possible to volatilize the lead.

Nitric acid rapidly destroys iron work.

Silicon tetra-fluoride, chlorine, and hydrochloric acid stop the catalytic action of platinum while actually present: but as soon as the impurity has passed by the action goes on without any bad effect. In this respect these impurities differ from arsenic and antimony.

The gas, under suction, leaves the burners not far from 500°C., carrying with it all or any of the impurities mentioned above.

The order usually observed in purifying the gas is to remove first the sulphur vapor, then dust, excess heat, SO_3, arsenic and the other contact "poisons," moisture, and the sulphuric acid "mist." The arsenic may be partly removed, but a fuel containing much of it will soon destroy the usefulness of the mass, so great care must be exercised in the purchase of ores or sulphur.

Although SO_2 begins to form at 109°C., and sulphur melts 2° higher, there is probably always some unburned sulphur escaping from the burner, due to incomplete mixing with air. The temperature is high enough to burn this sulphur vapor, if sufficient oxygen is present, as is always the case after dilution with air at the back end of the burner. This results in combustion in the combustion chamber, and in cases where very hot burners produce large quantities of unburned, vaporized sulphur, even back into the cooling flue. This of course cuts down the cooling surface, and throws an additional load upon the cooling system, whatever form it may take, which follows.

Dust recovery is a mechanical problem, the dust being carried slowly through brick dust chambers, sometimes depending solely upon the very slowly moving gas to afford an opportunity for the dust to settle out, and sometimes equipped with baffle plates. These chambers have a bottom sloping to one side, and at the bottom of the slope iron clean-out doors. One of the many

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advantages of brimstone over pyrites is the absence of dust; no provision at all need be made for it.

As the bulk of the dust carried over comes from the iron oxides left after roasting pyrites, and as Fe_2O_3 is an active catalytic agent, particularly at the temperature of the dust flue, some SO_3 is produced at this part of the line.

This dust is so fine that without some method of agglutination it is practically impossible to smelt it. It is free enough from sulphur to be a welcome addition to a blast furnace charge, when properly agglutinated—for a fair sized plant a sintering machine of the type described in Chapter V is the best from every angle, but briquetting will make a salable product, under most conditions. Large lumps usually have "green" cores, but the dust is roasted through and through. I speak of iron furnaces as possible customers, but frequently the cinder is valuable for other metals, as copper or zinc, and if the pyrite carries gold or silver there is almost certain to be a concentration of the precious metals in the dust chamber, due to their votility.

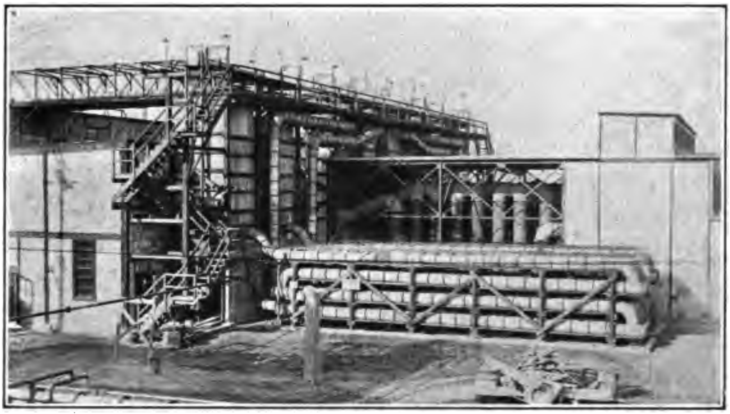

Fig. 69.—Cooling coils.

The brick walls of the dust chamber are very poor conductors of heat, so there is little cooling effect felt in the chamber.

The first fundamental difference between the Badische and the Schroder-Grillo processes is in the method of cooling the gases.

The Badische process effects the cooling by evaporating water. A large tower, usually 8 ft. in diameter, by 12 ft. high, receives the gas: and within that tower, where, owing to the ample space,

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the gas travels slowly, 55°Bé. acid trickles down over broken quartz, making an intimate contact with the gas. At this concentration of acid, the gas, at its temperature of 500°C., simply distills off water, great clouds of steam being formed: but as there is no decomposition of the acid, and consequently no SO_3 formed, there is no mist. Because of the large amount of water removed as steam, it is constantly necessary to "butt down" this cooling acid.

This cooling tower must not have any exposed iron work, as acid of such low concentration attacks it very rapidly. The towers are usually lead, and the piping and tanks lead-lined. The pumps are hard lead, on an iron frame. Towers are sometimes built of iron, chemical brick-lined, but any leak through the lining will soon let through enough acid to attack the metal.

Passage through this cooling tower lowers the temperature of the gas to 250°C.; below the decomposition point of the real scrubber acid. The gas enters the second tower, which is much smaller in diameter than the first, or cooling, tower, and rises through 99 per cent H_2SO_4. There is so much moisture in the gas that the acid, in absorbing this moisture, drops 1 per cent in its passage down the 12 ft. of the tower. This of course necessitates constant "butting up," as 99 per cent is at the top of the curve of vapor pressures, which corresponds almost exactly with the absorbing properties of sulphuric acid. The gas leaving the tower is free from moisture.

Experiments with the use of 88 per cent H_2SO_4 for cooling, showed that the temperature of the entering gas was sufficient to decompose acid of that concentration, forming a large amount of mist. Eighty-eight per cent was chosen, as it is the lowest concentration that is safe to apply hot to iron and steel.

The Schroeder process removes heat by radiation. The gas is passed through a long iron flue, which is water cooled, usually by passing it through a tank of water, and delivered to the first scrubber at 250°C. This temperature is low enough so that the scrubber acid is not decomposed. When running on pyrites lead must be used in the construction of this flue, because enough H_2SO_4, formed from the moisture in the air and the SO_3 formed by the catalytic action of the iron oxides, is condensed, to destroy any iron work. Only if the temperature of the gas is kept up to 400°C. is it safe to use iron, and at that temperature the scrubber acid is decomposed.

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After passing the scrubber towers what little acid condenses is cool enough and strong enough not to be harmful to cast iron.

In the writer's experience it has been necessary to keep the temperature of the acid in the first scrubber down to 95°F. to prevent dissociation of acid, and consequent formation of mist. twenty cubic feet of 98 per cent acid, at 95°F., will cool a thousand feet of gas at 450° to 500°C., to below the dissociation temperature, and at the same time dry it thoroughly, leaving it entirely free from moisture or mist.

It is difficult to give any figures on the amount of water necessary to cool the acid, owing to local conditions. Water in the South, particularly if from shallow rivers or ponds, gets warm enough in summer to seriously complicate the cooling.

It may be assumed that no fuel having over a trace arsenic would ever be used for the contact process, so that no company that makes lower concentration acid by diluting fuming with water need ever fear getting any arsenic into its mass, which should last indefinitely. So much chamber acid carries arsenic in relatively large quantities that the plant that depends upon purchased acid for the weak acid it requires must exercise the greatest and most constant care. If the gas is properly cooled, so that no mist is formed, there is no need for concern, even with a considerable amount of arsenic in the scrubber acid: but if any mist forms, and there is over 0.02 per cent arsenic in the scrubber acid, trouble may be looked for with confidence, as that mist is the arsenic carrier par excellence, and it will go through any kind of filter or scrubber that the writer has ever seen.

Too much stress cannot be laid upon proper cooling, for only by keeping the temperature down can this mist be prevented. Its formation *must* be prevented, because after once forming we do not know how to remove it from the gas.

To prevent spashing of acid, and the consequent spray that the draught will carry over, two devises are in use. The acid may be introduced onto a cast iron plate, through a funnel. The plate, covering the entire inside diameter of the tower, is as shown in Fig. 79. Normally the acid goes through the many ½-in. holes onto the filler inside the tower: the gas rises through the 2-in. holes, which are guarded against the entry of acid by the surrounding cast iron nipples, and thus the gas gets into the space above the plate with a minimum of splashing. When the small holes become clogged, as sometimes happens, the acid rises

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high enough upon the plate to relieve itself through the large holes.

The other method is to pump the acid to a reservoir, from which it flows gently through porcelain tubes to the surface of the filler.

The acid must be delivered at the top of the tower, as it flows down by gravity, but the gas may pass in either direction that plant convenience dictates.

The cooling coils, filled by gravity from the tower are cast iron pipe, usually 6 in., laid horizontally. The acid is admitted into the lower section of pipe, so that water dropping first upon the top pipe and then on to the lower one will reach the coolest acid first, and reserve its greatest cooling action, by evaporation, for the hot acid at the bottom.

Figure 78, in Chapter XIX, showing an absorber tower, tank, and equipment, illustrates equally well an ideal scrubber tower.

As the hot gasses direct from the burner have greater volume than those later on, it is customary to use a larger tower, or two small ones in parallel, for the first tower.

The amount of moisture taken out of the air drawn through it by the scrubber system is large. I have seen a plant handling 150,000 cu. ft. air per hour remove 3,500 lbs. of water, in 24 hours, on a damp day in winter from the air, and over 6,000 lbs. in summer.

The unit of a scrubber system is a tower, set of water cooled cooling pipes, and a tank with a turbine pump. For our ideal plant a tank holding 100,000 lbs. of acid is a good size. This tank should be horizontal, 6 ft. × 24 ft. of 5/8-in. boiler plate, unlined, with a cleanout hole in the bottom, turbine pump of 20 cu. ft. a minute capacity, set through a manhole in the top, manhole for cleaning out, proper connections to receive and discharge acid, and a gauge glass in the end. The acid is pumped to the top of the tower, and is spread by a distributer, so that in its passage down through the tower it comes into very intimate contact with the gas, flows from the towers to the coolers by gravity, and thence back to the tank.

Do not depend upon the gauge glass reading for accurate information about the quantity of acid in the tank. The acid that passes up into the gauge glass when the tank is filled is practically withdrawn from circulation, and retains its original specific gravity. So as that in the tank becomes diluted by scrubbing, or stronger by absorbing, that in the glass will float upon, or, sink

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into, this acid of different strength, and will not stand at the level of that inside. The writer has found 5 in. difference between a gauge glass and a stick measurement.

Each tank should have a 1-in. vent pipe, leading outside the building, to relieve the pressure caused by incoming acid. For sampling, a 2½-in. gate valve, or a 2½-in. nipple and cap should be set in the top. Do not use a tapped hole and plug, as plugs stick badly, rough handling with a wrench makes them loose their corners quickly, and then they are very hard to get out. A cap on a nipple is much better, and a gate valve best of all.

Types of pumps are discussed in Chapter XIX.

The towers of different designers vary greatly, although all have the same function: to bring into intimate contact the scrubber acid and the gas. Twelve feet high seems to be the only common dimension. The internal diameter varies from 3 ft. 6 in. to 8 ft., they may be lined with lead or acid-resisting brick, set in Pecora or other acid-resisting cement, and filled with broken quartz, chemical-ware rings, or cast-iron filling pieces.

The cooler pipes, always warm, afford excellent opportunities for the growth of any water plants, particularly those of a slimy nature, and slime and mud collect upon them very quickly. Any foreign matter acts as an insulator, and should be removed at once. Rubbing with a piece of burlap is the best way to clean these pipes, although a broom will do a fine job.

The current of gas carries some acid along with it mechanically, and some method of mechanical condensation and filteration is necessary to remove it. A large tower filled with pea coke, followed by another filled with buckwheat size, each tower having a trapped drain in the bottom, will remove most of the spray, and a good part of the mist that forms. These towers should be large enough (not under 10 ft. in diameter) to permit a slow movement of the gas, and should have a depth of at least 10 ft. of coke, with ample space at the top and bottom, for entrance and exit of gas. In practice about as many plants take the gas in at the top and release it at the bottom as do it the other way. The writer prefers to remove the gas from the top, believing that in the open space at the bottom, with acid dripping from the coke above, some new spray is formed, which is carried along by the suction. When a tower is newly packed there is undoubtedly some dust taken along from the top, but the coke soon becomes damp enough to prevent this.

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The quantity of spray caught will vary, but will be sufficient to make the installation of a small blow case to save the drip well worth while. It should be so piped that all the coke towers, or "spray catchers," run into it, and can run to a storage tank.

While much mist is condensed by the coke, enough is still left in the gas to make further filtration necessary. While cotton is occasionally recommended as a filtering medium, I have never known it to last a week. The condensed acid is strong enough to carbonize the cotton rapidly, even in the cold, causing it to turn to a black dust—of course worthless for filtering.

So asbestos fibre has come to be the one material used. It is picked over, usually by hand, to break up the lumps it packs into during handling and storage, and is then blown by a light current of air, which "fluffs" it. The apparatus required is a covered wooden trough, with air, controlled, by a hand valve, admitted at one end through a ⅛-in. pipe. The fibre is blown down the trough to a large box, with one side made of burlap, through which the air escapes. The longest staple asbestos possible should be procured. Grade 201A of the H. W. Johns Manville Co. is an excellent product. On account of the lightness of the asbestos fibre it is necessary to bring the gas in at the top, driving it down through the filter: otherwise the strength of the draught will carry it away. A good form of filter is a set of cylindrical tanks, three or four in number, 6 ft. in diameter by 4 ft. high, in parallel, with a screen of ⅜-in. boiler plate, punched with ½-in. holes, set on lugs 12 in. from the bottom. There are usually two sets of these filters, in series.

The fibre is spread smoothly over this screen, to a depth of 15 in.; 7.5 sq. ft. filtering surface, per hundred pounds of sulphur burned per hour, in each series will do good work, and will require a little over a pound of fibre per square foot every time they are packed.

These filters work better when moist, so moisture in itself is harmless. But where there is arsenic in the mist the filters will rapidly become impregnated with it and must be cleaned to prevent the arsenic from reaching the converter mass. When the filters are drained constantly there is less necessity for frequent cleaning than where the condensate is allowed to accumulate in the bottom, to be removed at intervals.

Cleaning simply consists in removing the manhole cover and

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taking out the old asbestos with a fork, then spreading the new. The blower must be stopped while the work is under way. Only experience can tell how often it is necessary to repack filters—one plant may need it every 3 weeks, another every 6 months. When the asbestos is soggy it is time to repack it, but being damp will do no harm at all.

All attempts to regenerate the asbestos have failed, not that it is hard to wash out the acid, but that wet asbestos packs into a cement.

Unslacked lime, nut or pea size, has been tried as a filtering material, and does its work well, but is hard to keep open, as the calcium sulphate formed crumbles, and the dust packs. Also, the condensed acid is lost.

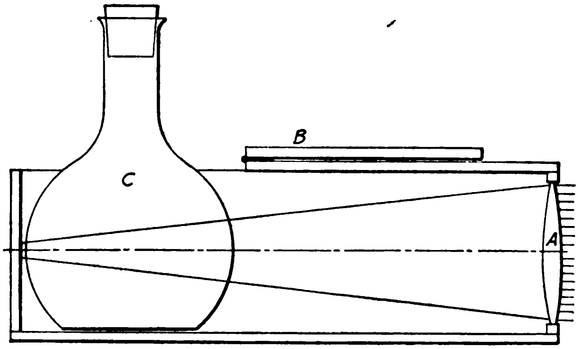

FIG. 70.

The Tetelow Chemical Co. uses, on gases that contain a little chlorine, a weak milk of lime wash, where first a bisulphite is formed with the SO_2, which reacts with and retains the chlorine.

The Tyndall test shows any mist in the gas that is invisible to the naked eye. An apparatus, shown in Fig. 70, consists of C, a small flask with a rubber stopper, through which two glass tubes pass, and A, a lens, the focus of which is just beyond the flask: all enclosed in a wooden box, painted black inside. The flask is filled with the gas to be tested, either by direct pressure, or, if on the suction end of the system, by an aspirator bottle, the ends of the tubes corked, the flask replaced in the box, and a beam of sunlight directed through the gas in the flask, via the lens. If there is any mist it will show in the path of the beam as the motes dance in a beam of sunlight in the old dusty

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attic. But if the gas is dry a disk of light shows on the side of the flask where it passes through the glass, and that is all.

If, through faulty design, it is impossible to prevent the formation of this mist, this arsenic carrier, the greatest efforts must be made to remove as much of it as possible, because arsenic is more liable to get into the system via the scrubber acid than through the fuel burned, and if there is no mist this arsenic will not be taken from the acid, ultimately getting to the converter mass.

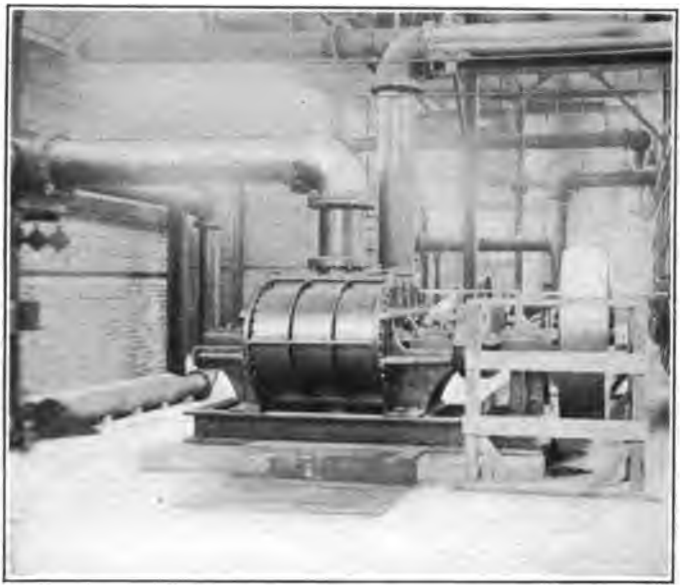

Fig. 71.—Roots blower.

Without proper provision for cooling mist will form. One of the plants built in a hurry to respond to the demand for fuming acid at the beginning of the European War, in 1915, was not provided with sufficient cooling area, and although operated with great skill, and giving in all respects but this very satisfactory results, showed all the bad effects of insufficient cooling—the filters had to be cleaned very frequently, arsenic went through to the converter mass, and the exit stacks were always fogging.

The blower is placed at the end of the scrubber system, so that the maximum pressure may be available to force the gas

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through the converter mass. This blower is always a valveless, direct-acting blower, of the Roots type. These engines are so well known that any extended description is unnecessary. They may be built either direct connected to a steam engine, or to be belted to shafting or a motor, and act over a very wide range of speeds very efficiently. The usual guarantee is that the slip will not exceed 15 per cent. As the rotors have 1/128-in. clearance, and no sliding surfaces, these engines have a very long life. The small clearance is not sufficient to cause much slip. If a sudden stop in the suction line occurs the partial vacuum formed will cause the blower to reverse itself for several revolutions, against the steam pressure.

If arranged this way, the pressure at the engine is almost twice the suction, mainly because of the resistence offered by the converter mass: but also because there are usually more showers in the absorber house than in the scrubber house. Our ideal unit will show, for normal running, about 12 in. of water suction at the blowers.

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CHAPTER XIX

CONVERTING

The second step in making Sulphuric Acid by the Contact Process is the conversion of SO_2 to SO_3, by bringing it into intimate contact, at a suitable temperature with finely divided platinum.

A mixture of SO_2 with air will slowly oxidize to SO_3, but so slowly that this action is valueless from a commercial standpoint. Many substances have a catalytic action upon this chemical reaction, that of Fe_2O_3 and Fe_3O_4, among the common substances, being very marked. All the metals of the platinum group posses this activity, but none other to the extent that platinum itself, in a finely divided state, does.

The catalyzer itself is entirely unacted upon, and its simple presence is all that is necessary. The effect is without doubt **adsorbtion,** or condensation of gas upon the surface of the catalyzer. When glass is wet by water the water is not absorbed —it is held however by the force we call adsorbtion—and some solids have this effect upon some gases. It is probable that there is a concentration of gas in a condition to react, and by the law of Mass Action the reaction must be hastened. Reasoning along these lines, the plan of the Davison Chemical Co. to use liquid SO_2, recovered from fume stacks by their new silica gel process, should give high yields and capacity, because of the "strong" gas used.

Six factors enter into the conversion: catalytic agent, which is always finely divided platinum; sulphur dioxide; air, supplying oxygen; temperature; time, and impurities.

The Badische process, worked out mainly by Rudolf Knietsch, uses platinized asbestos as a catalizer, a solution of platinic chloride being sprayed over the asbestos fibre, which is then put into the converters and dried. The mass then looks like wool died a lemon yellow, is soft and fluffy, and is not subjected to any furnacing at all. It dries out very rapidly in the converter, the chlorine of the platinic chloride is driven off, and metallic platinum left in an extreme state of division.

The Badische conversion unit is made up of a preheater, used

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for starting up and in emergencies, two converters and three transfers. The drawing shows the general arrangement of the converter—the gas enters at I, filling the space A, goes up the closed bottom tubes B, and down through C containing the converter mass, into D, and through the outlet O to the absorption system. C is made about three inches in diameter, to provide for uniform cooling of the mass by the incoming stream of cold SO_2 and air. It is this form of converter that gives the Knietsch process its economy of fuel, and is patented in this country under United States patents 652,119, 688,020, and 823,472, dated respectively, June 19, 1900, December 3, 1901, and June 12, 1906. Of these 652,119 is the fundamental one, the others being modifications thereof. See fig. 70.

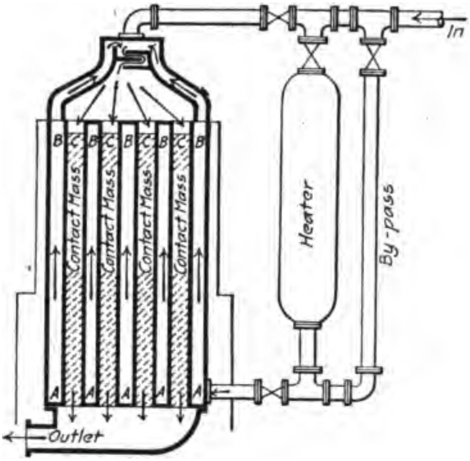

FIG. 72.

The Schroeder-Grillo process uses platinum deposited upon magnesium sulphate for the mass.

Pure magnesium sulphate, with the water of crystalization driven off, is coated, not impregnated, with platinum to the extent of 0.3 per cent of its weight. This gives a very large surface, as the salt in this state is very porous, and the platinum is spread out thin over a wide area. The magnesium sulphate is spread out upon a flat surface, 6 in. thick, and the platinic chloride is sprayed on through glass nozzles connected by rubber tubing to the bottles of solution, the bottles being supplied with air under pressure. At intervals the mass is turned over with

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wooden shovels, as it is of the utmost importance to get the platinum on evenly.

The sprayed mass is then put into the furnace previously used to dry the magnesium sulphate, and heated to redness for half an hour. By this time all the chlorine has been driven off, leaving the platinum in an extreme state of division.

The mass is then allowed to cool and is put into tight cans, weighed, and put away until needed, as it will keep indefinitely.

Usual practice is 4.5 per cent of platinum on the weight of SO_2 per hour. This will give a 97 per cent conversion with good handling. A smaller proportion of platinum will give a lower conversion, and in each case it must be determined whether it is better to have a smaller investment, and loose more SO_2 out of the stacks. For instance, ½ the platinum investment will about double the stack loss—2¼ per cent platinum on the hourly SO_2 will give about 95½ per cent conversion, other conditions being equal to the 97 per cent conversion with 5 per cent platinum.

The sulphur dioxide and air are intimately mixed in their passage through the burners, scrubbers, and blowing engines, and are freed from impurities as much as possible, so that the gas entering the converters contains SO_2 and O as active agents, and the nitrogen and other inert gases of the air as diluants.

Dr. C. L. Reese has proved experimentally that moisture present will not affect the mass, but as of course acid would be formed the plant would suffer. CO_2 is harmless. The worst of the impurities liable to be encountered is arsenic, which "poisons" the mass by forming a glassy coating of a salt of arsenic and platinum, as little as 2 per cent of As on the weight of platinum being sufficient to render the mass inert. Dr. C. L. Reese says that As can be removed from the mass by passing HCl in with the gas mixture, but my advise is not to let any get into the mass—the action seems to be that the As coating simply encloses the platinum so that it cannot come into contact with the gas mixture.

Dust of all kinds has a purely mechanical covering action. which is just as effective as the arsenic in preventing contact, H_2SO_4 "gums up" the mass, making it difficult to penetrate.

TEMPERATURE

$2SO_2 + O_2 = 2(SO_3 + 40250$ B.T.U.), on the authority of Prof. J. W. Richards. The reaction proceeds slowly at low

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temperatures, really beginning at about 200°C., and continuing to increase in velocity with rising temperature. However, the reaction is reversible and above 420°C., decomposition of SO_3 sets in, becoming more marked with further increase of temperature, until at 1,000°C. SO_3 cannot exist, in the presence of the catalizer.

The best temperature to carry is entirely dependent upon the condition of the mass and the "strength" of the entering gas, and it will vary with variations in these two, and therefore is a purely local condition. From 375°C. to 425°C. is about right.

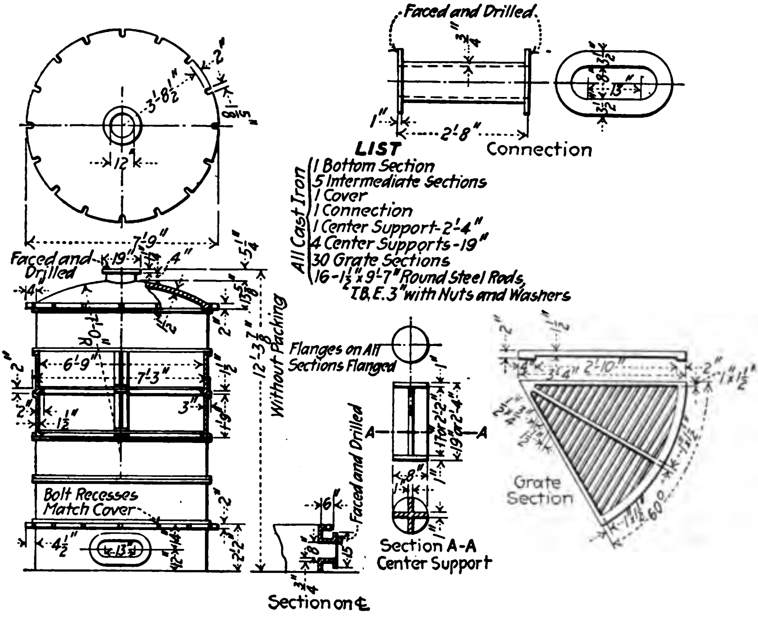

FIG. 73.

The entering gases must be heated sufficiently to start the reaction, as they have been well cooled by the scrubbing, and the converted SO_3 must be cooled before absorbtion.

Here lies the fundamental difference between the Badische and the Schroeder-Grillo processes—the former makes its converter into a heat exchanger, and heats its entering gases by taking the excess heat from its SO_3, where the latter uses fuel to heat up, and then wastes the heat generated in the converter.

The Badische conversion unit has been described. The

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Schroeder-Grillo unit is a vertical cylinder of cast iron, 5 to 8 ft. in diameter, built up in 18 in. to 2 ft. sections, flanged, joints packed with asbestos wicking, all held together by stay bolts from the top to the bottom flanges. Each section contains a perforated cast iron floor, upon which lies ¼-in. mesh iron wire screen, and upon this the mass. There are usually 5 sections to a converter, and 4 converters to a unit. For a converter 7 ft. outside diameter the normal amount of mass is 7500 lbs. evenly divided among the 5 trays, and carrying 0.3 per cent Pt. That means about $190,000 worth of platinum at today's (November, 1919) prices, of $145 per ounce. Such a plant will burn 1000 lbs. of sulphur an hour.

Fig. 74.

During the war, at one large plant, the quantity of mass was cut in half, concentration (per cent of Pt) remaining the same. This dropped the conversion from 97 per cent to between 94 per cent and 95 per cent—this brings up the question of the balance between stack losses, which represent raw material, power, and labor, and the investment in platinum. This will be considered in the chapter on accounting.

Good recording pyrometers are absolutely necessary for conducting this operation. Leeds & Northrup, Philadelphia; Industrial Instrument Co., Foxboro, Mass.; and the Taylor Instrument Co., Rochester, N. Y., can be depended upon to furnish good ones.

The Schroeder-Grillo preheater is a brick box, full of 6-in.

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boiler tube pipe, vertically set, flanged, connected by return bends, through which the gas passes to the converters, all heated by coal or oil fires, flue gases passing around the outside of the pipes. For a plant burning 1,000 lb. sulphur per hour, 4 converters, each 5 sections high, will be used, and the preheater to each one will contain 250 ft. of 6-in. pipe, plus the return bends. The pipe is set vertically to prevent flue dust from settling on it, insulating the gas inside. Such a plant will use 6 tons of steam coal daily in summer, 7 to 8 in winter. On 1919 coal prices, that is, over 50 cts. per 1,000 lb., 100 per cent acid produced—well worth saving. But even with this high fuel cost, the writer prefers this system to that of the Badische because of its simpler operation.

Fig. 75.

The gases from the Schroeder-Grillo converters, consisting of N, SO_3, unconverted SO_2, and impurities (mighty few of these however) are at a temperature around 350°C., much too hot for

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absorption; so they are cooled by passing through 250 ft. of cast iron pipe, set horizontally, between headers, and arranged to have a spray of water drip over them in warm weather. These pipes must be equipped with drain cocks, because upon starting up there is always some moisture in the mass, which will come from the hot converters as sulphuric acid vapor, and will condense here, effectually trapping the system if not removed.

Time of contact is controlled by the blowing engine, and will vary so with the plant that no rule can be laid down. For the size of blowing engine figure the volume of gas necessary to provide a 7 per cent gas for the sulphur to be burned, at 80°F.

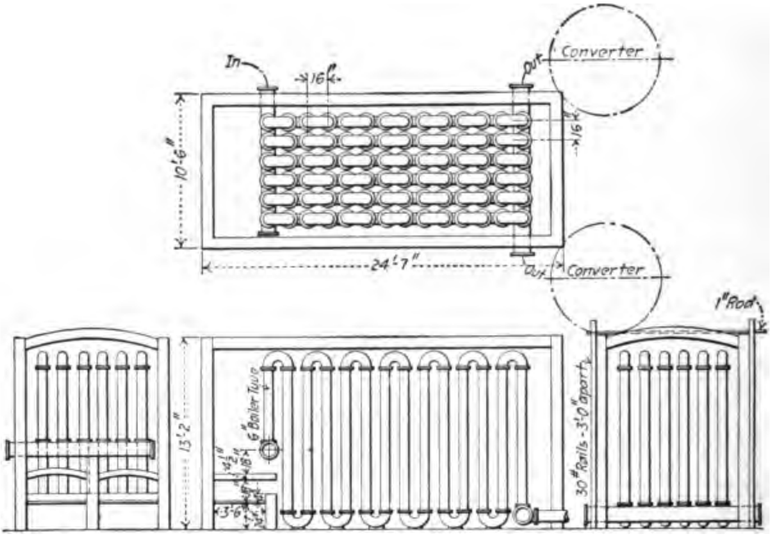

Fig. 76.

The only pressure is that of the blowing engines, sufficient to overcome the friction of the system, and keep the current of gas moving.

The early experimenters thought a stoicometric mixture of SO_2 and O necessary to get a good conversion, but were never able to convert over 77 per cent of their SO_2, and then only under laboratory conditions. The production of pure oxygen was expensive, and later proved a needless expense, as air was shown to give excellent results, the nitrogen having no deleterious effect whatever.

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Ferric oxide comes to its maximum as a catalytic agent at 675°C., at a point where the dissociation of SO_3 is very marked, which eliminates it as a possible contestant with platinum.

It is necessary to use a catalytic agent that will do maximum work at or under 450°C., and platinum is the only one known so far.

Some experimental work along the lines of colloidal precipitation of the platinum upon the mass have been done, notably by Botho Schwerin, in U. S. patent 1,098,176, owned by the Chemical Foundation, 81 Fulton St., New York. In view of the fact that the investment is the greatest part of the cost of contact acid, anything to increase the surface of platinum exposed will pay well, and should be followed up.

Kurt Albert, in U. S. patent 1,018,402, also owned by the Chemical foundation, claims to have reached a 94 per cent yield with iron and strontium oxides as a catalyzer. This with the Davison adsorption system on the exit stacks to prevent the loss of unconverted SO_2 offers a fertile field for research.

Dr. Knietsch formulated the law of mass action as follows:

$$\frac{SO_3}{SO_2} = \frac{100\sqrt{KO_2}}{1 + \sqrt{KO_2}}$$

when K = concentration in volume per cent. This shows the conversion we may obtain, but nothing about velocity of reaction or proper temperature.

Each plant must develop its own suitable working conditions, and adhere as closely as possible to them. If the operator starts out to make a 7 per cent "gas"—7 per cent by volume—he will not be far wrong.

Although it is necessary to dry the gas as much as possible, an absolutely dry gas will stop the reaction. It is not possible to remove the last traces of moisture with our scrubbing systems, but they remove all that might be dangerous, as an excess would be.

Uniformity of temperature is of the utmost importance—the control should be within 5°C. If the mass is injured in any way it is likely to require a higher temperature to get conversion, and that is about the only way there is of detecting mass "poisoning."

GAS CONTROL

The Reich test for SO_2 in gas, with the pyrometer readings, is our guide. This test is conducted as described in Chapter XIV.

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The laboratory should occasionally check this by the K_2CO_3. test.

This gas test should be made not less often than every 2 hours, on both the entrance and exit gases. Be sure the gas passes through the apparatus for a minute before each test, to make certain that it is the gas of the present, not of 2 hours ago, that is being tested. Quarter inch pipes, led off of the gas mains, and controlled by valves, bring the gas to the test.

In figuring conversion after the test, it must be borne in mind that the volume of gas is decreased by the amount of oxygen the SO_2 has taken in its oxidation.

SLIDE RULE FOR SO_2 TO SO_3 CONVERSION[1]

In general, if an equation can be written in the form

$$f(x) = f(y), f(z)$$

a slide rule may be so constructed that the value of any variable can be found if the others are known. As a simple illustration, consider the computation of conversion in the contact process for the manufacture of sulphuric acid.

Let a = per cent by volume of SO_2 in entrance gas,
b = per cent by volume of SO_2 in exit gas,
c = per cent conversion = per cent SO_2 converted to SO_3.

These quantities are related by the equation

$$c = \frac{10,000(a - b)}{100a - \frac{3ab}{2}}$$

This form of equation is not suitable for the construction of a slide rule, but it may be rewritten as

$$1 - \frac{c}{100} = \left(\frac{100}{a} - \frac{3}{2}\right) \div \left(\frac{100}{b} - \frac{3}{2}\right)$$

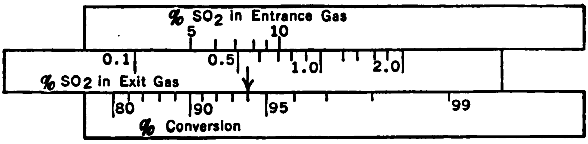

FIG. 76A.

$SO_2 - SO_3$ slide rule set, 10 per cent entrance, 0.7 per cent exit = 94 per cent conversion.

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[1] From *Chemical and Metallurgical Engineering*, September 15, 1919.

The slide rule scales for the solution of this equation are in the accompanying figure. The upper scale is laid off proportionally to log $\left(\frac{100}{a} - \frac{3}{2}\right)$, the slide to log $\left(\frac{100}{b} - \frac{3}{2}\right)$, and the lower scale to log $\left(1 - \frac{c}{100}\right)$. These scales are laid off from right to left so that the marked values a, b, c will increase from left to right, as this is the most natural method of reading scales. The proper values of SO_2 in burner gas and exit gas are set together, and the conversion read opposite the arrow. The zero point (*i.e.*, log1) of the lower scale is moved to the left relative to the upper one, to make the rule more compact, and the arrow displaced the same distance to give the correct reading.

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CHAPTER XX

ABSORBTION

As stated briefly in Chapter XII, water is not a satisfactory absorbing agent for SO_3, and as the water in diluted H_2SO_4 acts like water, it is necessary to use strong (not less than 98.3 per cent) sulphuric acid. You might say that the gas is scrubbed with the absorbing medium, for the apparatus used is a gas scrubber of some type, the object being to get as intimate an association as possible of the gas and the acid.

If sulphuric acid of less than 98.3 per cent is heated in an open pan at 350°C. water will distill off until this "critical" point, *i.e.*, 98.3 per cent is reached—if the original acid is of a higher concentration than the "critical" strength, SO_3 will come off until the strength drops to 98.3 per cent—after it has reached that point however it comes over at that strength until the end. Of course pan concentration cannot go to this point profitably, because the losses by entrainment increase very fast with the strength of the pan acid.

At 98.3 per cent and 100°C. sulphuric acid has a minimum vapor pressure in vacuo, and at this point its sp.g. is the highest. At this point absorbtion of SO_3 is practically 100 per cent.

The heat of combination of SO_3 and H_2O is 180,540 B.T.U., according to Richard's "Metallurgical Calculations," which runs the temperature in the absorbing apparatus up to the point where cooling is always necessary. This is usually done by circulating the absorbing acid, keeping a large volume in service, and cooling the storage tank and circulating system with water. The first tower will require, for a unit plant of 1000 lbs. S per hour, not less than 250 ft. of cooling pipe, aside from necessary connections.

As fuming acid is very hard on iron or steel, tanks and towers must be carefully lined with an acid-resisting material. The writer does not think much of any of the asphalt bitumens that are used for this purpose, prefering a good acid-proof tile, well laid in acid-proof cement. The cost of towers thus protected is high, but worth that cost.

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As the strength of the acid in the tower increases, so does the vapor tension, and the absorbing qualities fall: also the temperature being high works against good absorbtion, so it is usual to arrange 6 towers in series, fresh acid being added in the last one, at intervals, the towers nearer the first one being replenished from those behind, and the acid made being drawn from No. 1. The temperature in the later towers is progressively lower than in the first, and as the strength also gets nearer and nearer to that point where the vapor tension is negligable, the percentage absorbtion is increasingly great, and if the acid in all towers is above the dead line of 98.3 per cent, so that no "mist" is formed, the absorbtion will be practically complete.

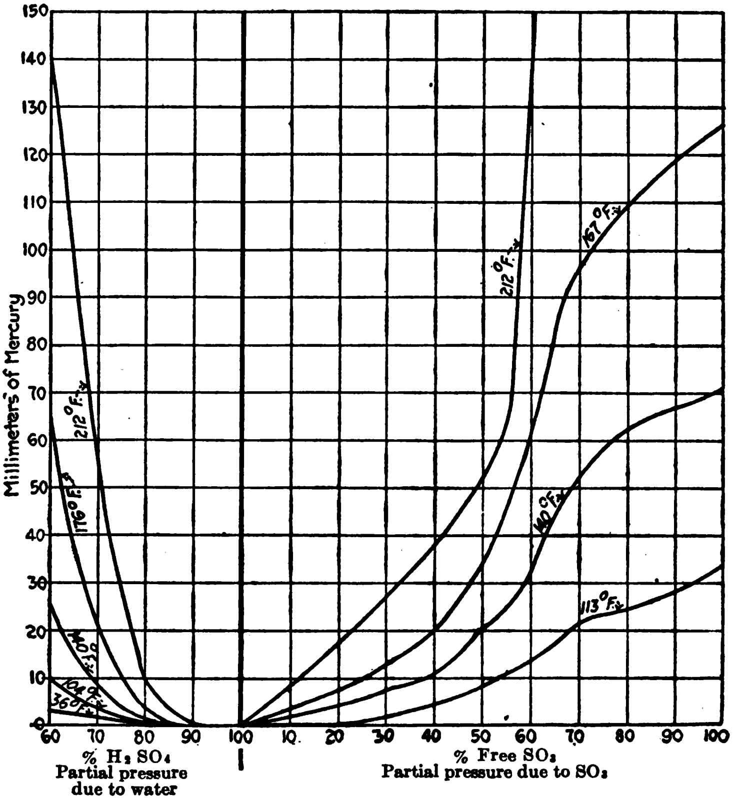

FIG. 77.

The use to which the acid is to be put of course determines the strength to be made, but the season of the year has an influence also: and a look at the freezing curve, in Chapter XXIII, will show why. Acid of about 103.6 per cent with a freezing point of 10°F. is a good winter strength to aim at.

While analysis is necessary to determine the strength of acid in the various towers, experience will soon teach the operator how often to sample: and while this system is very flexible, and will stand a lot of bad handling, it is easy to handle well.

If the Feld washer, made by the Bartlett-Hayward Co., of Baltimore, can be designed to stand fuming acid it will be an ideal piece of apparatus, and as the rotating part is hung from an overhead bearing, out of the acid, it seems reasonable to hope that it will. Of course there is bound to be some vibration, which in time is sure to open up the joints in the acid lining.

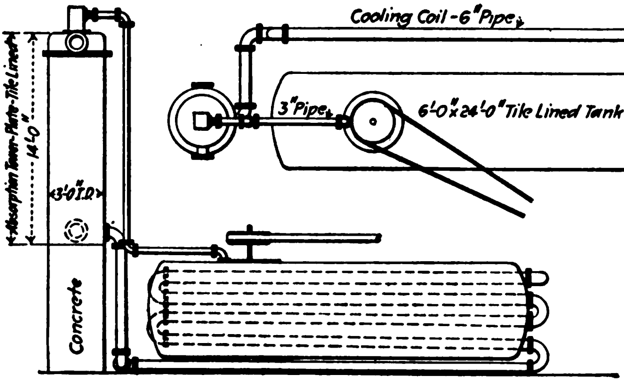

Fig. 78.

It has been proposed to build the tower of stone-ware, but this seems impracticable to the writer, because of the high temperatures in the first towers, which would be reasonably sure to crack the stone-ware if a draft of cold air struck the outside.

Apparatus of the type shown in the cut on this page is very satisfactory. The pump is a centrifugal, made by G. C. Bretting, Ashland, Wis., belt driven, 1700 R.P.M., delivering 40 cu.ft. of acid a minute, and requiring 7½ H.P. It is built with a manhole cover, so can be hoisted into place by a chain block on a mono-rail, and fastened with set screws. As the pump is about the only part of the system that is likely to get out of order, this ease in changing is very important. The pump made by the Kutztown Foundry & Machine Co., Kutztown, Pa., is also a good one.

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Failures of the wrought iron piping come apparently not from corrosion, but from bursting. These bursts are always longitudinal, and can be welded. The writer has seen many bursts, but never one on a welded pipe, either at the weld or anywhere else in that vicinity, which seems to show that when the internal strains have been relieved by the springing open of the pipe in the first burst, the acid alone cannot burst it.

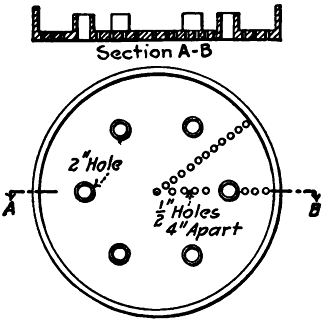

Fig. 79.—Distributor plate for tower.

Failure to provide for expansion in pipes handling the hot acid from the tanks is sure to result in broken fittings, as the acid is so hot that expansion is considerable.

There are more likely to be "spills" of acid in this department than in any other, so the floor must be one that will stand such acid. Common red brick, laid dry in sand, makes a splendid floor.

The gas coming from the converters is hot. The heat is used in the Badische system to heat up the incoming gases, but in the Schroeder-Grillo process the heat must be removed by some other means. The simplest means is a cast iron or steel header, with 6-in. wrought-iron pipe running to another header. For our standard unit 450 ft. of 6-in. pipe will do the work, without

Fig. 80.—Converters.

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help in winter, but will require the help of a spray of water in the summer.

Drainage must be allowed for in the bottom of the cooler, as no matter how well the mass is made up the magnesium sulphate is sure to contain some moisture, which of course will form acid and condense in the cooler. This blocks the system.

The "absorber man" has little to do but sample and shift his acid, as it increases in strength, and could easily handle four absorber units; so where the production is sufficient it is customary to house two units in the same building, in parallel. Weak acid is usually received, and strong delivered, at this end.

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CHAPTER XXI

CONVERTER MASS

The most costly part of a contact plant is the platinum, and every effort is being made to find a suitable substitute, and failing that, to reduce the amount necessary. As the catalytic action is undoubtedly a surface condensation, the logical thing to do is to spread the platinum out as thin as possible. Much research work has been done along these lines.

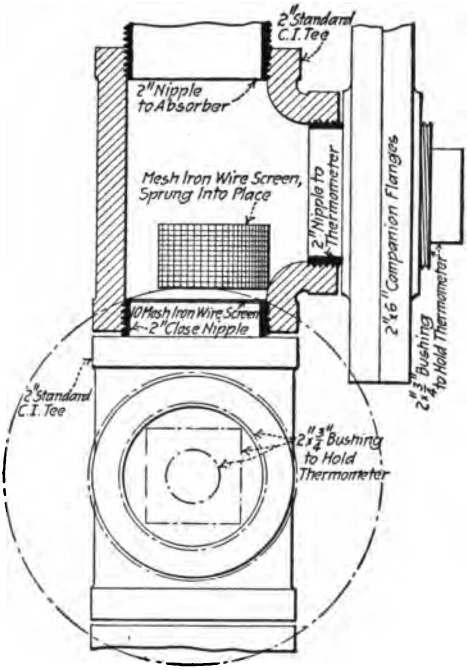

Fig. 81.

As with varying conditions it is not possible to use any standard plant, a simple laboratory converter is useful, and will be here described.

Five (5) 2-in. C.I. tees, connected by close nipples, and a 2 × 6-in. flange at the outlet, on another close nipple, the whole stood upright, and a circle of 10 mesh iron wire screen resting

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in the bottom of each tee, upon the upper end of the close nipple. The mass is put in through the outlet, held from running out by a piece of screen sprung in, the companion flange, in which there is a ¾ × 2-in. bushing, put on, the thermometer put in the bushing, connected up with the gas supply at the lower end, and started off. Plastic asbestos is the best covering, and such a system must be covered, as the area is large in proportion to the volume. (Fig. 81.)

Sodium free magnesium sulphate is melted in its water of crystalization (it contains 52 per cent) in a crucible, stirring continuously after it melts, both to prevent its sticking and to make it porous—the porosity depends directly upon the amount of stirring. In about 35 min. the mass will be free from water and solidifies, when it is heated to a dull red, and poured out to cool. After cooling it is broken to pass a ⅜-in. screen, but to stay on a ⅛-in. one. The platinic chloride is then sprayed on with a glass nozzle, from a solution made up as later described in this chapter, the mass put back in the furnace in the crucible and heated to a dull red, when the chloride is reduced to metallic platinum and the mass turns black. It is then ready for use.

Such a plant will enable the research laboratory to work out any problems in connection with the gas to be used.

PREPARATION OF MASS

Platinum has increased in price within the last eight years, up to 1920, from $12 to $145 a Troy ounce, and as the quantity necessary to get a 97 per cent conversion, in a plant burning 12 tons of sulphur a day of 24 hours, is about 1,300 oz.—$188,500—every effort must be made to spread it out very thin.

The logical thing to do is to deposit it upon a base of such uneven surface that a very large area is exposed in a relatively small volume. This base must also be unaffected by the gases passing through, by the temperature, and by the chemicals used in depositing the platinum. It should also be of such a nature that the platinum can be easily recovered.

Asbestos fibre fulfills perfectly the first four requirements, and is largely used. It has the fault of packing under any considerable weight, so the converter must have shelves only a few inches apart, thus having comparitively shallow layers of platinized asbestos.

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Dehydrated magnesium sulphate answers all five requirements, plus the fact that it does not pack.

The base is coated by spraying with a solution of platinic chloride, made by dissolving platinum at the rate of 125 gr. Pt per liter beaker in twice the theoretical amount of aqua regia. This is heated over a sand bath. The beaker should stand in a porcelain dish containing water, large enough to hold the entire contents of the beaker, in case of accident.

About 80 per cent of the platinum will dissolve readily. This solution is poured into a porcelain dish, which, for safety's sake, stands inside a larger dish, and is concentrated. More aqua regia is added to the undissolved portion, until all has gone into solution.

The solution is then analyzed and diluted to contain 7 gr. per c.c.* Because of the high atomic weight of solutions containing platinum, they diffuse slowly, so mixing must be very carefully and thoroughly done. This is diluted to 1/10 before using.

The asbestos fibre must be very carefully "fluffed," and the solution sprayed on from glass bottles, through a rubber tube with a glass nozzle, drawn to a fine opening, using low-pressure air to drive the solution out. The asbestos must be turned over continually, to get as even a distribution as possible: a pitchfork makes a good tool.

This mass is put right into the converters, where the heat of starting up reduces the platinic chloride to metallic platinum before the first SO_2 arrives for conversion.

The magnesium sulphate used must be pure. The New Jersey Zinc Co. supplies a very high grade.

A small reverberatory furnace is used for calcining the "mag. sulph." lots of 250 lb. to 500 lb. being a charge. Thirty-five to 40 min. is sufficient time to melt the salt in its own water of crystallization and drive the water off. The furnace should be at a dull red heat, and the charge rabbled continuously, as otherwise it will harden and stick to the hearth. The more it is rabbled the more porous it becomes.

* The Avoirdupois pound is the usual unit of weight in the sulphuric acid industry, but platinum is weighed in the Troy (or Jewelers') scale. The following comparisons of the two scales are helpful:

1 pound Avoirdupois = 7,000 grains = 16 Avoirdupois ounces,
1 pound Troy = 5,760 grains = 12 Troy ounces.
1 pound Troy = .8229 pounds Avoirdupois.

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After the charge is drawn it is broken and screened, pieces above 5/8 in. being broken, and below 1/8 in. rejected.

Various plants use varying amounts of platinum per unit of mass—0.2 per cent to 0.3 per cent are the most usual.

The spraying is done the same as with asbestos fibre, but the mass is put back into the furnace for 20 or 30 min., at a dull red heat, and rapidly turns black, from the reduction of platinic chloride.

REGENERATION

Asbestos is difficult to dissolve, so when it is necessary to recover the platinum it is simpler to dissolve the platinum in aqua regia, filter, purify the solution, and make new mass, than to try to dissolve the asbestos.

A spraying with a solution containing 20 per cent HCl, 7 per cent HNO_3, and a little soluble organic matter, such as starch or sugar, and returning the mass to the converter, will serve for regeneration if the mass is not in very bad shape. The effect is to dissolve (partially) and redistribute the platinum, and dissolve the impurities and have them carried off in the gases from the burning organic matter.

If the mass from magnesium sulphate to be regenerated contains a large proportion of fines it should be put into a wooden tub, with a solution similar to that used for ordinary regeneration, and water added as the solution boils down from the heat of the reactions; and finally, after perhaps 10 to 24 hours, a smooth paste results. It should be more or less sloppy. The finer the material the less time required.

The result is a semi-solution of crystalline magnesium sulphate, with platinum, which is furnaced as was the new salt, and the mass is then ready for use.

Of course this treatment results in some platinum being shut up within the pieces of magnesium sulphate, and the action of such quantities lost, so it is good practice to spray on 5 per cent of the original quantity, after regeneration. After several regenerations the salt should be dissolved in a weak sulphuric acid solution, the platinum recovered, and new mass made.

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CHAPTER XXII

ACCOUNTING

BY W. M. LE CLEAR

All well organized concerns recognize the advantages of Cost Sheets which reflect the costs to a very accurate degree, and it is not considered necessary to dwell or argue upon this point, because it is a conceded fact that without these records the management cannot follow the destinies of its operations.

The usual factors entering into the cost of any product are appraised here—*i.e.*

Labor, direct,
Labor, indirect,
Materials, direct,
Materials, indirect,
Repairs and Maintainance,
Insurance, Taxes, etc.,
Overhead,
Depreciation.

These various charges reflected in the cost sheets may come through sub-cost sheets, such as Power House cost sheets, or they may be charged direct to the Sulphuric Acid cost sheet, depending entirely upon what basis the managment wishes the cost data to be prepared. In either case the final result should be identical.

The Direct Labor represents the labor actually employed in obtaining the product. The Indirect Labor is labor that is necessary to the operation, but which does not go directly into the product, as for instance, foremans' time, laboratory time, sweepers, oilers, etc.,

Direct and Indirect Materials are classified along lines similar to the Direct and Indirect Labor. Direct Materials represent such items as sulphur, pyrites, etc., while the Indirect Materials would be Nitric acid in some form (usually Chile saltpeter), fuel etc.

The Repair and Maintainance charges should represent the labor and materials expended which keep the apparatus in operating condition, and do not add perceptably to the life of the

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equipment. Charges falling into the latter classification should be capitalized.

The Charges, for Taxes, Insurance, etc., should be determined as nearly as is possible to estimate them. It may not be amiss to state that accounting authorities do not consider the United States Government Income and Excess Profits Taxes to be a part of the manufacturing cost, and are in reality a division of profits with the Government.

The charge for Depreciation should represent the diminishment in value due to wear, tear, and obsolesence, as nearly as it can be estimated. With proper care the buildings will last a long time, while the chambers, the most costly part of a chamber plant, should be amortized on an 8-year basis, although they will frequently go 10. Other parts of the plant must be taken care of with regard to their varying life. The thought I wish to bring out is that no one figure will do for a plant making corrosive chemicals. Buildings at 4 per cent and Power House Equipment at 10 per cent, will fit in very well.

The charges for Overhead should represent General Office salaries, etc., which are not charged under the classifications previously discussed. If desired the details on the cost sheets may be carried out to the minutest details, but ordinarially this is not considered necessary.

The basic feature to be borne in mind in the preparation of the Cost Sheet is, that EVERY CHARGE that has any bearing upon costs is reflected therein. The details of these items and their arrangement is of course important, but only secondarily so.

It is probably unnecessary to add that the costs should be reflected upon the pounds of 100 per cent acid produced.

It is difficult to lay down any specific rules or instructions regarding the cost information which should be furnished daily, as this feature depends entirely upon what the management considers necessary for its information. It is very important however that the management know the number of men, cost of labor and materials used, and the production daily. The author's opinion is that all elements of cost should be calculated daily, some factors must of necessity be estimated, which by the preparation of a monthly progressive sheet would at the end of each month very closely tie up with the monthly cost sheet.

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Per 1,000 lb. H_2SO_4

Labor	1.3 hr. @ 48c.
(Production roughly 3,825,000 lb. per mo.)	
Say $275,000.00 investment per line.	
Interest 6 per cent	16,500
Dep. 25 per cent	68,750
Insurance 3 per cent	8,250
Taxes 1.5 per cent	4,125
	$97,625
Labor	.624
Materials, 330 lb. S	3.03
Coal	.50
Superintendence	.16
Office and labor including supplies	.075
Capital	2.12
	$6.509

Repairs not included.
Steam not included.

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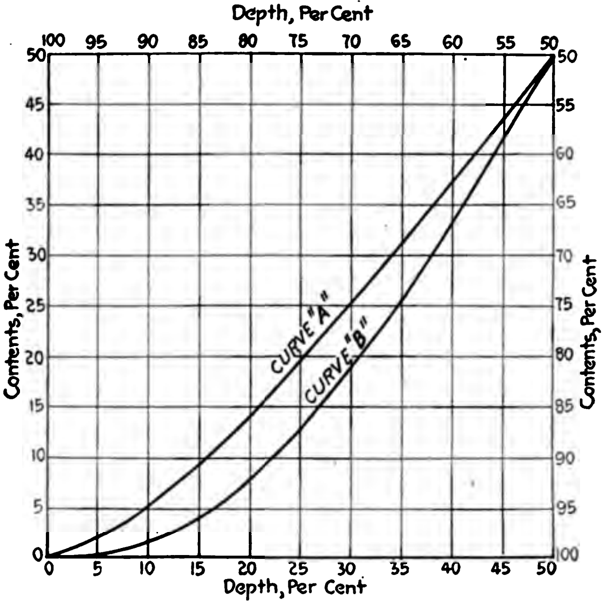
APPENDIX

TANK CAR TABLE

The Standard Tank Car for acid is 78 in. in diameter, and the length of the side is 27 ft. 6 in. The two ends are dished outwards, the radius of the dish always being the same as the diameter of the tank itself.



NOTE

Curve "A" = % Depth vs. % Contents Curve for Plain Cylinder, Longitudinal Axis Horizontal

Curve "B" - % Depth vs. % Contents Curve for Dished End

Total Volume of Cylinder Referred to in Curve "A" = $0.7854D^2L$

Total Volume of 2 Ends Referred to in Curve "B" = $2\pi h^2(D-\frac{h}{3})$

In Which: $= .10774D^3$

D = Inside Diameter of Tank, and Radius of Dished End

L = Length of Plain Cylindrical Part of Tank

h = Total Depth of Dished End

h = 0.134 D

FIG. 82.

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Other sizes of "tanks" are used for acid—so many in fact that it would be out of the question to give a gaugeing table for all sized tanks. However, with the tank curve a table for any sized tank can be quickly prepared.

To prepare such a table, first find the area of the vertical section of the car in feet: then multiply this by the length of the straight side of the tank—this will give you the number of cubic feet in the cylindrical part of the tank. Then prepare a table giving the per cent of height for every inch of height—then set down opposite each inch the per cent of the capacity of the tank that is represented at that height—for instance, in the table given, at 16 in. the per cent of the total is 20.54. Then multiply this by 913+, which is what the cylinder holds full, and you get 135.55 cu. ft. Then figure from the formula given how much the dished ends hold full, look on the "end curve" to see how much the ends hold at 20.54 per cent, and you will find it is about 8.4 per cent. From the formula the ends hold about 37 cu. ft., and you get 3.08 cu. ft., which added to the 135.55 cu. ft. of the cylinder gives you the amount of acid in the tank: 138.63 cu. ft.

Because of the varying relations between the length and diameter, it is not possible to work it all out in one formula, so a table must be prepared as above.

From a hydrometer the density of the acid is then determined, its weight per cu. ft. looked up, and the total weight calculated.

While there may be some errors in the last place of decimals, it is not possible to read a stick to within one-hundredth of an inch, and after a tank car has been in service a very short time it will be distorted more than any error in this curve.

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Table for Standard Tank Car

Height of acid in tank, inches	Per cent of depth	No. of cu. ft.	Height of acid in tank, inches	Per cent of depth	No. of cu. ft.
1	1.28	2.24	40	51.28	491.02
2	2.56	6.09	41	52.56	506.96
3	3.84	11.67	42	53.84	523.58
4	5.13	17.88	43	55.13	538.10
5	6.41	24.81	44	56.41	553.55
6	7.69	32.49	45	57.69	569.00
7	8.98	40.93	46	58.98	584.42
8	10.26	49.85	47	60.26	599.73
9	11.54	59.36	48	61.54	615.17
10	12.83	68.52	49	62.83	630.28
11	14.11	79.23	50	64.11	645.33
12	15.38	90.65	51	65.38	660.29
13	16.69	102.32	52	66.69	675.20
14	17.97	114.07	53	67.97	689.72
15	19.25	126.24	54	69.25	704.14
16	20.53	138.63	55	70.54	718.71
17	21.82	150.97	56	71.82	732.95
18	23.10	163.31	57	73.10	746.74
19	24.39	176.43	58	74.39	760.22
20	25.67	189.78	59	75.67	773.57
21	26.95	203.26	60	76.95	786.69
22	28.24	217.05	61	78.24	799.03
23	29.52	231.29	62	79.52	811.37
24	30.80	245.86	63	80.80	823.76
25	32.09	260.28	64	82.09	835.93
26	33.37	274.80	65	83.37	847.68
27	34.65	289.71	66	84.65	859.35
28	35.93	304.67	67	85.93	870.77
29	37.21	319.72	68	87.21	881.48
30	38.49	334.83	69	88.49	890.64
31	39.77	350.27	70	89.77	900.15
32	41.05	365.58	71	91.05	909.07
33	42.33	381.00	72	92.33	917.51
34	43.62	396.45	73	93.61	925.19
35	44.89	411.90	74	94.89	932.12
36	46.17	427.42	75	96.17	938.33
37	47.45	443.04	76	97.45	943.91
38	48.72	458.98	77	98.73	947.46
39	50.00	475.00 half full	78	100.00	950.00

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Tables and General Information

SPECIFIC GRAVITY

Manufacturing Chemists Association of the United States

°Bé.	Sp. gr.	Per cent H_2SO_4	Weight of 1 cu. ft. in pounds, av.	Freezing (melting) point, °F.
0	1.0000	0.00	62.37	32.0
1	1.0069	1.02	62.80	31.2
2	1.0140	2.08	63.24	30.5
3	1.0211	3.13	63.69	29.8
4	1.0284	4.21	64.14	28.9
5	1.0357	5.28	64.60	28.1
6	1.0432	6.37	65.06	27.2
7	1.0507	7.45	65.53	26.3
8	1.0584	8.55	66.01	25.1
9	1.0662	9.66	66.50	24.0
10	1.0741	10.77	66.99	22.8
11	1.0821	11.89	67.49	21.5
12	1.0902	13.01	68.00	20.0
13	1.0985	14.13	68.51	18.3
14	1.1069	15.25	69.04	16.6
15	1.1154	16.38	69.57	14.7
16	1.1240	17.53	70.10	12.6
17	1.1328	18.71	70.65	10.2
18	1.1417	19.89	71.21	7.7
19	1.1508	21.07	71.78	4.8
20	1.1600	22.25	72.35	1.6
21	1.1694	23.43	72.94	− 1.8
22	1.1789	24.61	73.53	− 6.0
23	1.1885	25.81	74.13	−11.0
24	1.1983	27.03	74.74	−16.0
25	1.2083	28.28	75.36	−23.0
26	1.2185	29.53	76.00	−30.0
27	1.2288	30.79	76.64	−39.0
28	1.2393	32.05	77.30	−49.0
29	1.2500	33.33	77.96	−61.0
30	1.2609	34.63	78.64	−74.0
31	1.2719	35.93	79.33	−82.0
32	1.2832	37.26	80.03	−96.0
33	1.2946	38.58	80.74	−97.0
34	1.3063	39.92	81.47	−91.0
35	1.3182	41.27	82.22	−81.0
36	1.3303	42.63	82.97	−70.0
37	1.3426	43.99	83.74	−60.0

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SPECIFIC GRAVITY

Manufacturing Chemists Association of the United States

°Bé.	Sp. gr.	Per cent H_2SO_4	Weight of 1 cu. ft. in pounds, av.	Freezing (melting) point, °F.
38	1.3551	45.35	84.52	−53
39	1.3679	46.72	85.32	−47
40	1.3810	48.10	86.13	−41
41	1.3942	49.47	86.96	−35
42	1.4078	50.87	87.80	−31
43	1.4216	52.26	88.67	−27
44	1.4356	53.66	89.54	−23
45	1.4500	55.07	90.44	−20
46	1.4646	56.48	91.35	−14
47	1.4796	57.90	92.28	−15
48	1.4948	59.32	93.23	−18
49	1.5104	60.75	94.20	−22
50	1.5263	62.18	95.20	−27
51	1.5426	63.66	96.21	−33
52	1.5591	65.13	97.24	−39
53	1.5761	66.33	98.30	−49
54	1.5934	68.13	99.38	−59
55	1.6111	69.65	100.48	Below −40
56	1.6292	71.17	101.61	Below −40
57	1.6477	72.75	102.77	Below −40
58	1.6667	74.36	103.95	Below −40
59	1.6860	75.99	105.16	− 7
60	1.7059	77.67	106.40	+12.6
61	1.7262	79.43	107.66	27.3
62	1.7470	81.30	108.96	39.1
63	1.7683	83.34	110.29	46.1
64	1.7901	85.66	111.65	46.4
64¼	1.7057	86.33	112.00	43.6
64½	1.8012	87.04	112.34	41.1
64¾	1.8068	87.81	112.69	37.9
65	1.8125	88.65	113.05	33.1
65¼	1.8182	89.55	113.40	24.6
65½	1.8239	90.60	113.76	+13.4
65¾	1.8297	91.80	114.12	− 1.0
66	1.8354	93.19	114.47	−29.0

Allowance for Temperature

At 10°Bé., .039°Bé. or .00023 sp. gr. = 1°F.
At 20°Bé., .036°Bé. or .00034 sp. gr. = 1°F.
At 30°Bé., .035°Bé. or .00039 sp. gr. = 1°F.
At 40°Bé., .031°Bé. or .00041 sp. gr. = 1°F.
At 50°Bé., .028°Bé. or .00045 sp. gr. = 1°F.
At 60°Bé., .026°Bé. or .00053 sp. gr. = 1°F.
At 63°Bé., .026°Bé. or .00057 sp. gr. = 1°F.
At 66°Bé., .0235°Bé. or .00054 sp. gr. = 1°F.

Approximate Boiling Points

50°Bé	295°F.	63°Bé	432°F.
60°Bé	386°F.	64°Bé	451°F.
61°Bé	400°F.	65°Bé	485°F.
62°Bé	415°F.	66°Bé	538°F.

Theoretical Production Figure

$\frac{\mathrm{H2SO4}}{\mathrm{S}} = 3.0585$ Log of 3.0585 = .485508

Specific Gravity (at 95°F.) and Melting Point (Freezing Point) of Fuming Sulphuric Acid

Total SO_3	Free SO_3	Sp. gr.	Melting (freezing) point, °F.
81.63	0.00	1.8136	50.0
82	2.05	1.8300	46.7
83	7.50	1.8480	31.5
84	12.95	1.8657	14.5
85	18.38	1.8847	12.2
86	23.84	1.9086	28.1
87	29.27	1.9258	56.3
88	34.70	1.9429	78.8
89	40.17	1.9607	93.6
90	45.63	1.9667	93.6

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Per cent Total SO_3	when free SO_3 =	Per cent Total SO_3	when free SO_3 =
81.63	00	87.87	34
81.99	2	88.24	36
82.36	4	88.60	38
82.73	6	88.97	40
83.09	8	89.33	42
83.46	10	89.70	44
83.82	12	90.07	46
84.20	14	90.44	48
84.66	16	90.81	50
84.93	18	91.18	52
85.30	20	91.55	54
85.66	22	91.91	56
86.03	24	92.28	58
86.40	26	92.65	60
86.76	28	93.02	62
87.14	30	93.38	64
87.50	32	93.75	66

Specific Heat

Total SO_3 Per cent	Spec. heat	Total SO_3 Per cent	Spec. heat
80	.3500	92	.4000
82	.3450	94	.4550
84	.3400	96	.5350
86	.3390	98	.6500
88	.3500	100	.7700
90	.3600		

Vapor Tension

Per cent H_2SO_4	36°F. M.M.	104°F. M.M.	140°F. M.M.	176°F. M.M.	212°F. M.M.
61.7	3	10	25	68	143
70.0	2	3	8	22	57
81.5	1	1	1.5	3	10
89.0	0	0	0	0	1
Above 90.0	0 at all temperatures.				

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VAPOR PRESSURES OF SOME QUALITIES OF OLEUM

¾ volume oleum. ¼ volume air.

Temp. °C.	Pressure of oleum, 30% atm.	Pressure of oleum, 40% atm.	Pressure of oleum, 50% atm.	Pressure of oleum, 60% atm.	Pressure of oleum, 70% atm.	Pressure of oleum, 80% atm.	Pressure of oleum, 100% atm.
35	.....	.....	.....	.....	.....	0.150	0.40
40	.....	0.075	.....	0.225	0.375	0.500	0.65
45	0.050	0.125	.....	0.350	0.575	0.650	0.87
50	0.100	0.175	0.350	0.525	0.775	0.875	1.20
55	0.140	0.225	0.450	0.675	1.025	1.200	1.60
60	0.200	0.275	0.550	0.825	1.400	1.500	1.85
65	0.225	0.350	0.700	1.025	1.650	1.900	2.25
70	0.275	0.400	0.825	1.275	2.050	2.300	2.75
75	0.340	0.475	1.000	1.570	2.525	2.800	3.30
80	0.400	0.575	1.150	1.850	3.100	3.500	4.00
85	0.450	0.675	1.400	2.150	3.700	4.175	4.90
90	0.530	0.825	1.700	2.575	4.400	5.050	5.90
95	0.625	0.950	2.050	3.150	5.000	6.000	....
100	0.730	1.100	2.400	3.700	6.000	.....	....

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Heat of Solution. (Dr. Kneitche)

Determined Values

H_2SO_4 Per cent	SO_3 Per cent	Free SO_3 Per cent	Calories
50.32	41.07	.....	40.45
60.18	49.12	.....	65.46
63.86	52.13	.....	79.05
70.24	57.33	.....	110.05
73.76	60.21	.....	132.3
76.86	62.74	.....	151.4
71.41	64.82	.....	171.7
99.88	81.62	0.0	194.06
.....	83.49	10.12	221.4
.....	85.26	19.75	245.27
.....	87.31	30.91	277.6
.....	89.08	40.55	299.05
.....	91.05	51.28	327.9
.....	92.67	60.10	361.4
.....	94.72	71.26	393.6
.....	96.62	81.60	433.5
.....	98.48	97.81	470.6
.....	99.64	99.48	491.1

Heat of Solution of Solid Oleum. (Dr. Kneitche)

Determined Values

Total SO_3 Per cent	Free SO_3 Per cent	Calories
89.4	42.3	271.0
90.73	49.53	303.2
92.5	59.2	330.4
94.5	70.1	369.2
96.28	79.75	408.8
98.14	97.32	436.1
98.54	99.34	481.4
99.84	99.77	486.0

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Heat of Solution of Sulphuric Acid and Oleum. (Dr. Kneitche)

Graphically Determined

Sulphuric acid			Oleum			
SO_3, %	H_2SO_4, %	Cal.	SO_3, %	Free SO_3, %	Cal.	Heat of solution of solid oleum, cal.
50	61.25	39	82	2	199	...
51	62.48	41	83	7.5	210	...
52	63.70	44	84	12.9	223.5	...
53	64.93	46.5	85	18.3	237.5	...
54	66.15	49	86	23.8	250	...
55	67.38	51.5	87	29.2	265	...
56	68.60	54	88	34.7	278	...
57	69.83	57	89	40.1	292	...
58	71.05	59.5	90	45.6	308	286
59	72.28	62	91	51.0	325	304
60	73.50	65	92	56.4	344	322
61	74.73	68	93	61.9	363	340
62	75.95	72	94	67.3	381	360
63	77.18	75	95	72.8	401	380
64	78.40	79	96	78.3	421	402
65	79.63	83.5	97	83.7	442	423
66	80.85	88	98	89.1	465	442
67	82.08	93	99	94.6	490	463
68	83.30	98	100	100	515	486
69	84.53	103				
70	85.75	108				
71	86.98	113				
72	88.20	119				
73	89.43	126				
74	90.65	133				
75	91.88	139				
76	93.10	146				
77	94.33	152				
78	95.55	160				
79	96.78	168				
80	98.00	178				
81	99.23	188				
81.63	100.00	193				

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Electrical Resistance of Sulphuric Acid at 25°C.
(Dr. Kneitche)

SO_3, %	H_2SO_4, %	Ohm	SO_3, %	H_2SO_4, %	Ohm
40.19	49.23	0.235	75.19	92.01	0.70
48.80	59.79	0.29	76.73	94.00	0.72
53.27	65.14	0.245	78.45	96.11	0.795
57.54	70.55	0.345	78.52	96.20	0.79
60.28	73.85	0.475	79.55	97.46	0.80
61.07	74.82	0.525	80.22	98.27	1.10
64.00	78.40	0.60	80.98	99.21	1.95
65.14	79.80	0.67	81.27	99.55	2.2
67.04	82.14	0.74	81.345	99.64	2.7
68.53	83.97	0.75	81.425	99.74	3.5
69.12	84.68	0.76 max.	81.455	99.78	4.2
70.23	86.03	0.745	81.53	99.87	5.7
70.84	86.79	0.74	81.535	99.88	5.7
73.40	89.92	0.705	81.59	99.95 monohydrate	7.45 max.

Electrical Resistance of Oleum at 25°C.

Total SO_3, %	Free SO_3, %	Ohms	Total SO_3, %	Free SO_3, %	Ohms
81.695	0.34	6.15	90.5	45.0	23.4
81.74	0.5	5.35	90.8	50.0	53.0
82.4	4.0	2.43	91.6	54.0	88.0
83.44	9.8	2.20	92.7	60.3	222.0
84.2	14.0	2.15 minimum	93.4	64.0	287.0
84.7	16.7	2.15	94.6	69.6	759.0
85.2	19.4	2.23	95.4	75.0	1,265.0
86.3	25.5	2.95	96.35	80.0	4,000.0 at 27
87.05	29.5	4.05	96.87	83.0	6,650.0 at 32
88.3	36.3	6.65	98.16	90.0	61,850.0 at 36
89.0	40.2	15.2			

ATTACKING ACTION UPON IRON

Decrease per square meter per hour in grams after 72 hours action of acid acid at 18°–20°C. [65°–68°F.]. (Dr. Kneitche.)

H_2SO_4, %	SO_3, %	Cast iron	Ingot iron	Welding iron
48.8	39.9	0.2177	......	......
61.2	50.0	0.1510	......	0.3032
67.7	55.3	0.0847	......	0.0789
73.4	59.9	0.0662	......	0.0623
79.7	65.0	0.1560	......	0.1159
83.7	68.4	0.1388	......	0.1052
85.1	69.5	0.1306	......	0.1034
88.2	72.0	0.1636	......	0.1417
90.6	73.9	0.1750	......	0.1339
92.0	75.2	0.0983	......	0.1040
93.0	75.9	0.0736	0.0987	0.0855
94.1	77.0	0.0723	0.0933	0.0708
95.4	77.9	0.1274	0.1471	0.1209
96.8	79.0	0.1013	0.0815	0.0988
98.4	80.3	0.0681	0.0533	0.0655
98.7	80.6	0.0583	0.0509	0.0570
99.2	81.0	0.0568	0.0418	0.0504
99.3	81.07	0.057	0.042	0.050
99.5	81.25	0.060	0.038	0.049
99.77	81.45	0.066	0.042	0.049
100.0	81.63	0.087	0.088	0.076
Total SO_3	Free SO_3			
81.8	0.91	0.201	0.393	0.323
82.02	2.00	0.190	0.285	0.514
82.28	3.64	0.132	0.441	0.687
82.54	4.73	0.154	0.956	1.075
82.80	7.45	0.151	0.566	1.321
83.50	10.17	0.079	0.758	1.540
84.20	12.89	0.270	1.024	0.892
84.62	16.16	0.271	1.300	0.758
85.05	18.34	0.076	1.988	1.530
86.00	23.78	0.070	0.245	0.471
88.24	34.67	0.043	0.033	0.053
90.07	45.56	0.040	0.018	0.019

COMPOSITION	CARBON	GRAPHITE
Cast iron	3.55 per cent,	2.787 per cent.
Ingot iron..................	0.115	....
Welding iron................	0.076	....

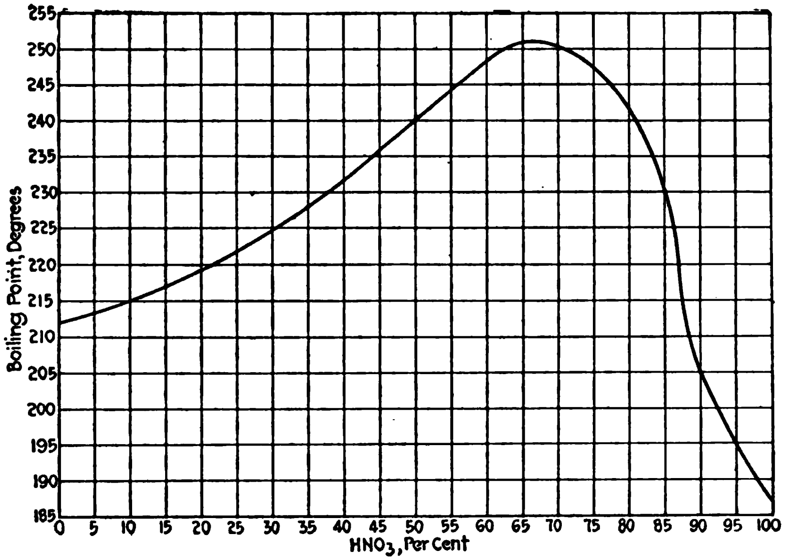

FIG. 83.—Boiling points of nitric acid.

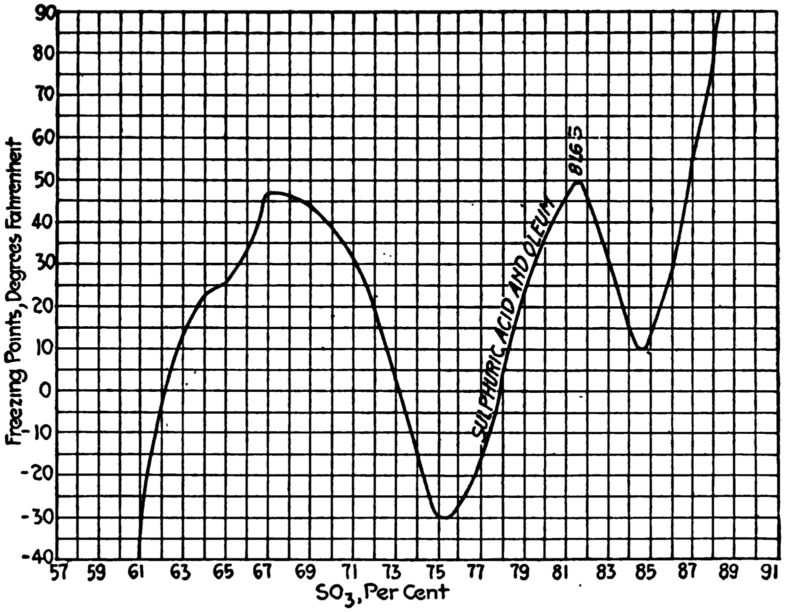

FIG. 84.—Freezing (melting) points of sulphuric acid.

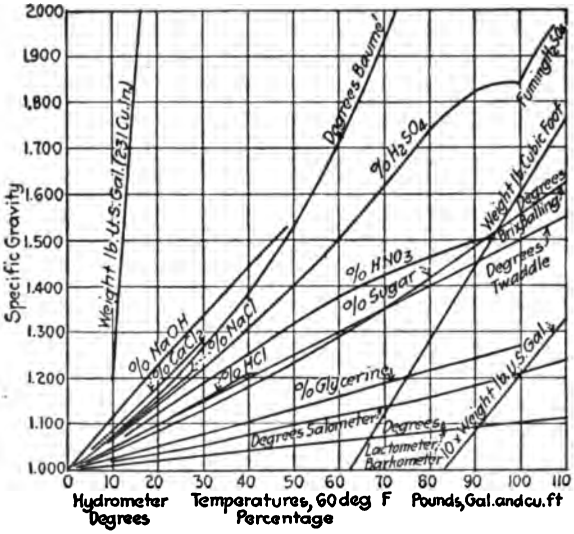

FIG. 85.

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