ON TWO NEW

Electrochemical Processes

FOR THE

Extraction of Silver and Gold from Their Ores

THESIS

Presented in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in the College of Chemistry
of the University of California

BY

MOOSHEGH VAYGOUNY

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CONTENTS

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INTRODUCTORY

Some two years ago, Mr. Gilbert Gurney, a practical mining man, came to this University with some of the now well-known Tonopah gold and silver ores, with a view to finding out "what could be done with them in the line of a remunerative treatment of the same." As Mr. Gurney, upon the writer coming to know him, admitted frankly to have very limited command of the knowledge of chemistry or metallurgy necessary to cope with the problem in question, the latter, by common consent, soon devolved upon the present writer, while Mr. Gurney himself kindly offered to purvey certain facilities whereby the necessary investigations were to be carried out.

The following is an account of the results of the various experiments and studies that were undertaken in this line during the academic year '03-'04, and continued throughout the year '04-'05.

It is necessary to state here that nearly all the assays made in connection with the first part (Chloridation method) of this study were made by Thomas Price & Sons, professional assayers of San Francisco, through the courtesy of Mr. Gurney. On the other hand, the writer assumes responsibility for the remaining assays, all of which were made at the chemical laboratories of this University.

HISTORICAL

It seems to be an admitted fact in mining circles that, in spite of the goodly number of the various methods proposed, some in journal and mostly in patent literature, in the last half century or so, the desideratum of an economic, wet process for the simultaneous extraction of the precious metals gold and silver from their sulphide ores is still keenly felt. Indeed, the methods in vogue, even at present, are still some one form or another of smelting, amalgamation, Augustin, or hypo-sulphite processes, all of which entail, at some point or other in the course of their operations, certain costly treatments, now in the form of a preliminary roasting, and now in form of constant consumption or rejection of the reacting chemicals, such as salt, copper sulphate, and mercury or its salts, while all, except smelting, are none too efficient, even irrespective of the cost of treatment.

Although at the time the writer began the studies which form the subject of this paper, and for some time later, he was quite unaware of the various attempts and suggestions made in patent literature in the line of improved methods of handling such precious sulphide ores, and though such patent literature, at best, could constitute anything but reliable information to guide one's steps by, it is none the less of interest to first give here a cursory account of the most important methods having any direct bearing on those to be advanced in these pages, as far as they have come under the writer's notice.

While the use of purely "wet" or chemical-reaction methods had been introduced as early as the sixteenth century by the adoption of the well-known Patio process—where silver sulphides are decomposed by means of a solution of copper sulphate and salt, and amalgamated—it seems, however, that Becquerel* was the first to realize (in 1835) the importance of the introduction of some neat and less empirical methods

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*Becquerel, *Comptes Rendus,* vol. 38, p. 109; also, *Elements d'Electrochimie,* chap. VI.

in the process of silver and gold ore treatment. Becquerel's idea was an entirely new departure in the metallurgical methods then known. He suggested to first oxidize the ores, either by a roasting or by means of a solution of $CuSO_4$ in presence of a concentrated solution of common salt, and then to recover the metals thus dissolved by using voltaic couples of zinc and iron, for instance. To do this, the less electro-positive metals were dipped in the solution containing the metals to be recovered, while the more electro-positive metals were immersed in an ordinary solution of salt, separated from the first by means of a porous membrane.

Although this process has long since been left out of serious consideration, and for obvious reasons, still, if we remember that not only was this method proposed in those early days when dynamos were unknown things, but that Becquerel had the patience to actually treat many tons of ore in this way, we cannot but admire the insight and courage of that great man.

The next mention of an improved method of treating sulphide ores is that of Body, who, in a United States patent issued in 1886, proposed to use a solution of a mixture of ferric salts and common salt as the agent to react upon the sulphides in general, such as those of Ag, Cu, Pb, etc., and the electric current from a dynamo machine as the agent to recover the dissolved metals. For this purpose Body advocated the use of a cement tank provided with two quadrangular compartments, one within the other, and separated from each other by means of a porous diaphragm. Towards the upper part of the cell these compartments communicated with each other freely, as the diaphragms did not stand high enough to separate them completely. The inner one of these two compartments was provided with a carbon floor serving as anode, while the cathodes stood upright in the outer compartment. The ore—previously roasted or otherwise oxidized, if necessary—being put in the anode or inner compartment, the solution was admitted from below and made to ascend through it, while the entire mass was being kept constantly stirred. During its stay in this compartment, the solution was to dissolve the desired metals by acting upon their sulphides, thus being itself reduced to a solution of ferrous salts, but soon oxidized again to the ferric condition by virtue of the chlorine here generated simultaneously with the deposition of the metals on the cathodes outside under the influence of the electric current. To facilitate the deposition of the metals, the solution was not allowed to remain long in this same compartment, but was continuously forced upward and made to overflow into the next or cathode department, and there be directly electrolized and freed from its metals. This done, the solution, which must not only have now been impoverished of its metals, but also have its iron salts largely reduced to the ferrous condition, was next returned to the anode compartment again, there to have first oxidized the latter to the ferric condition and then to have resumed the attack of the remaining sulphides.

Needless to say that, in spite of the fact that this process seems to have been widely discussed in those days, it does not seem to have as yet taken a practical form anywhere, and for obvious reasons. Indeed, even if the chemical principles involved left nothing to be desired, the idea of burying an electrode under tons of non-conducting ore-masses could certainly not stand the test of any practical operation.

In the same year that Body's patent was issued, Endlich and Muhlenberg* secured a patent claiming the use of "chlorine solutions in presence of other metallic chlorides, such as those of iron and copper, with or without the addition of common salt." These inventors, however, did not specify by what means they intended to recover the metals brought into solution; so that their suggestion does not even stand the test of a fair criticism.

Soon after this, also in the same year, a patent was issued to Cassell,§ who proposed to use a diaphragm cell, the ores being kept in the anode compartment, somewhat on Body's principle, but using merely a solution of common salt as the lixiviating agent. It was claimed that during the passage of an electric current the chlorine generated at the anode and there held in the solution impregnating the ore, would act upon the metallic compounds and bring about their attack

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*United States Patent Office Gazette, October, 1886.

§United States Patent Office Gazette, October, 1886.

and dissolution. This done, the same electric current was then merely to carry the desired metals over into the cathode compartment, through the diaphragm, and there deposit them.

It will be seen that in this process the chief defects are, unlike that of Body, in the chemical principles involved more than in practical considerations, since, not to speak of other difficulties, aquous chlorine, upon whose presence the oxidation of the sulphides is supposed to depend, is neither an active oxidant of such sulphides nor can it be got in any practically useful concentrations, this gas being only slightly soluble in concentrated brines.

Some two years later there appeared the patents of Dr. Hoepfner,* whose process seems to have caused much more excitement in certain mining circles than perhaps any of the other similar electro-chemical processes advanced before or since then. Dr. Hoepfner proposed to use solutions of $CuCl_2$ in conjunction with common salt or $CaCl_2$ and their subsequent electrolysis. Although his chief aim was to treat ores of the sulphides of copper, his process was also expected to extract any silver and nickel which may accompany the copper in the ores.

In this process the ores were finely crushed and leached with the above solution, in order to decompose the sulphides present and take up their corresponding metals. The solution was then continuously passed through special diaphragm cells, where the silver was either to be deposited on special cathodes by means of a current, or it was simply to be precipitated by copper shot. This done, and the other foreign metals being thrown out by chemical methods, such as by the use of CuO, CaO, KOH, etc., the solution was then electrolyzed with a proper voltage so as to recover the excess of copper brought into solution during the extraction of the ore. During this latter operation the remaining cuprous salts were oxidized to cupric salts, and could therefore be used over again to leach the ores with.

It has been pointed out in all the accounts on this process—which has been given a more thoroughgoing, practical test than perhaps any of the others, though without success—that

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*Borchers, *Electric Smelting and Refining.*

one of the principal drawbacks in the method lies in the necessity of having to use diaphragms. Be the case as it may, however, it only stands to reason that such a process could not be used for exclusively silver ores for reasons economical and practical, as will be indicated further on.

Besides the above-enumerated more prominent methods, the writer has, through the kindness of Dr. W. J. Sharwood, been able to come to know of a list of not less than fifteen to twenty different patents, issued in this country or abroad, all relating to the extraction of silver and gold by the use of solutions of copper or iron salts, now in the form of sulphates, now as chlorides; sometimes in conjunction with the use of a strong solution of common salt, sometimes without it; now by introducing some free acids, and now none, while nearly all prescribe a preliminary roasting and some form or other of a diaphragm cell whenever electrical methods are explicitly stated to be employed in recovering the metals brought into solution.

Such was found to be the status of the problem of the chemical, wet methods of extracting the precious metals from their ores when the writer first took cognizance of them. It needs no special argument to show that, in face of such accounts of "suggested," but "unhatched," "patent" methods of various degrees of theoretical soundness, but of no positive reliability, the problem could still be fairly considered one awaiting a special study, and a solution, if possible. Indeed, it is a recognized fact that not a few of the patents granted every year in such chemical or metallurgical lines represent mere hastily conceived ideas, unbacked by any sound experimental data, and that the few methods which have found their way into text-books can be called anything but of unquestionable authenticity, they being more or less the results of hearsay or gathered from patent accounts.

Owing to the above considerations, it will therefore not be improper, in the following pages, to carry on the discussion entirely without reference to these patent suggestions. This will be the more logical as the first and essential steps in these studies had been taken, as was mentioned above, long before the writer was aware of the existence of the methods sketched or alluded to.

THEORETICAL

On first venturing to develop any chemico-metallurgical method of treating ores of the type here under consideration, the first points to be considered are, naturally, relative to the requirements to be fulfilled by the process to be worked out. In the case on hand, what are these requirements? They are obviously that the method should be economical; it should be a lixiviation process pure and simple, as far as possible; and, if the method is at all to be of wide applicability, it should be capable of extracting both the metals in question—silver and gold—as they occur so frequently together. Further, it must do away with any preliminary roasting, which is more or less troublesome and expensive. On the other hand, the solution used must neither be costly nor have any properties deleterious to health; the metals dissolved thereby must admit of being readily recovered; and, finally, the solution should lend itself to being regenerated by some appropriate and ready means, so as to avoid the necessity of its being constantly renewed; in other words, the method should be "cyclic."

Now, given the fact that in the entire field of chemistry there is no solution of a known compound that will dissolve the sulphides in question, as such, sufficiently and economically, without the necessary oxidation of the latter, it becomes forced upon the investigator—in view of the above conditioning factor that all roasting operations should be avoided, as far as possible—that he choose only such solutions as have naturally oxidizing properties. But all oxidation reactions involve concomitantly a reduction on part of the oxidizing agents which may be employed; hence, if these agents are to be used cyclically, they must necessarily admit of being readily oxidized back into their original conditions. Further, since economic operation requires that there should be no decomposition products arising, not only during the attack of the sulphides, but also during such regenerating operations, the compound or compounds to be selected as the solvent agent desired must be fairly stable and be very "labile," or capable of taking up first a higher, then a lower stage of oxidation. Then, too, since the best and neatest method of recovering the metals dissolved would be, beyond doubt, one depending upon the use of the electric current, it would be highly desirable that the compounds selected should be capable of being oxidized by means of this same current, best concurrently with the electro-deposition of the metals.

If now, with these data on hand, we inquire as to which compound or compounds will meet the requirements imposed, we will notice that there are only two groups of salts that will answer for the purpose at issue, and which are at the same time sufficiently cheap and available. We have:

I. THE SULPHATES AND THE CHLORIDES

of those common elements, with varying valencies or degrees of oxidation, as are also sufficiently soluble in water, namely, those of iron, copper, and manganese.

II. THE SO-CALLED PERSULPHATES

A comparative view of the desirabilities of the salts of iron, copper, and manganese will, however, show that not all these three classes of bodies are equally desirable. For while a moderately acid solution of the above iron salts may well be electrolyzed without any of the metal separating at the electrodes, those of copper and manganese, on the other hand, cannot be so treated with advantage. For, with solutions of copper salts, not only would we have economic difficulties to meet with in the line of the large amounts of copper which would have to be locked up in the stock solutions to be used, but, what is more, such solutions could only be freed from undesirable base metals, such as Sb, As, etc., which would accumulate in them and foul them in time, with both complicated and costly chemical methods of precipitation of these impurities. This would be the more unavoidable, as it would certainly be difficult to avail one's self of the neater methods of simple electrolysis with higher voltages to remove these base metals, lest, in doing so, copper should also be deposited on the cathodes, and thereby cause much trouble. Again, with the salts of manganese, the oxide MnO_2 is likely to appear at one or both electrodes during the electrolytic winning of the metals, and thus give rise to many unnecessary difficulties.

It thus becomes clear that, of the salts of the above three commoner elements, those of iron, when used in conjunction with some free acids, are much to be preferred, since, besides presenting none of the above difficulties, they are also the cheapest and most readily got.

Leaving the study of the persulphates for the second part of this paper, we may then first consider here the application of the iron salts to the extraction of the precious metals.

* * *

I. CHLORIDATION OR SULPHATATION

If we attempt to study, in a preliminary way, the relative adaptations of the chloride and the sulphate of iron by carrying out some qualitative experiments with artificially prepared silver sulphide, and with two separate solutions, one made up of about 1 to 2% $FeCl_3$ and HCl, the other consisting of about the same amount of $Fe_2(SO_4)_3$ and H_2SO_4, we observe that, so far as their efficiencies in oxidizing the silver sulphide is concerned, whether in the cold or in the warm, there is no appreciable difference to be noticed in favor of one or the other of these solutions.

Now, seeing that it is a matter of no small economic importance whether one deals, in practice, with sulphates or with chlorides, it might seem here, *a priori,* that a sulphuric acid solution of ferric sulphate should be preferable to one of HCl and $FeCl_3$. This would be especially so, inasmuch as, in practice, such a solution would be expected to form the more soluble Ag_2SO_4, instead of the insoluble AgCl, on reacting with the sulphides of this metal, and that, therefore, it would lend itself better to the subsequent leaching out of the values from the ore masses.

Such a choice, however, would be objectionable for two main reasons. In the first place, $Fe_2(SO_4)_3$ having no appreciable solvent action on free gold, its exclusive use would not be in conformity with the desideratum set previously, namely, the simultaneous extraction, as far as possible, of both the silver and the gold contained in ores. In the second place, the use of such simple sulphate solutions would be amiss, even with ores that contain no appreciable amounts of gold but are more exclusively silver ores, because, there being no natural ore, nor a method of ore treatment possible that could avoid sufficiently the introduction of some chlorine compounds during such treatments, there would always be a liability for the conversion into AgCl of much of the dissolved Ag_2SO_4 formed under the oxidizing influence of the ferric sulphate upon the silver sulphides. In fact, such a change would be undesirable not merely owing to the impracticability thus arising of the removal of the silver values by a simple leaching, but also because the formation of the insoluble AgCl would tend to hinder the complete oxidation of the silver sulphides, owing to a protective coating which this compound would form and envelop the particles of the sulphides unless it be dissolved away and removed as fast as it is formed.

If, therefore, ferric sulphate is at all to be chosen as the oxidizing agent desired, it is essential to use concurrently with it, on the one hand, some simple, appropriate solvent of AgCl, and, on the other, one of free gold.

Unfortunately, of all the simpler solvents of AgCl or of gold, there seems to be none known capable of co-existing in solution with ferric salts, let alone the consideration of their cheapness. Thus, cyanides could not be used because of the liability of their giving rise to insoluble ferro or ferri cyanides, thus resulting in loss and in general nuisances. On the other hand, thiosulphates and bisulphites could not be used owing to their being decomposed in presence of ferric salts; nor, for obvious reasons, could NH_4OH be used for the purpose under consideration.

There is, however, but one possible solution to this problem, and that lies in the use of high concentrations of some suitable, soluble chloride, such as common salt, in conjunction with these sulphates. Such chloride solutions, indeed, are especially appropriate, as by their use not only is it possible to bring about the solution of gold readily under the influence of the free chlorine which can be generated and made to saturate the main solution simultaneously with the electro-deposition of the dissolved metals, but particularly because they also afford a ready means for the dissolution and removal of the silver values concurrently with the gold. It seems, indeed, a peculiarity of silver chloride that it will go into solution quite appreciably in presence of other chlorides, especially those of the alkali and alkaline-earth metals, and more particularly in free HCl. No doubt the secret and the sole function of the use of such large amounts of common salt in conjunction with $CuSO_4$ in the old Patio amalgamation process lies in just this effect of the salt being capable of holding in solution the silver chloride which is formed under the oxidizing effect of the $CuSO_4$ on the sulphides of this metal, so that the mercury may with readiness first reduce this latter from its solution to the metallic state and then amalgamate with it.

But now, if such high concentrations of chlorides are to be used, as they needs must, with a solution of ferric sulphate and sulphuric acid, it at once becomes evident that there remains no serious advantage in favor of such a solution over one of ferric chloride and either HCl or H_2SO_4. Indeed, so far as economic differences in the use of one or the other of these compounds are concerned, none can exist worth being called serious, inasmuch as, once the necessary supply of either salt is secured and the stock solution made up, the process being cyclic, the concentration of the iron in solution will not diminish sufficiently to necessitate any continued supply of such salts, if, indeed, it be ever necessary to buy these, even in long-continued practice, rather than depend upon the iron contents of the ores themselves to furnish what little amount of iron salt be requisite at any time.

On the other hand, though there is certainly an apparently decided difference in the cost of the two acids HCl and H_2SO_4, still, it being true that to whatever extent SO_4 radicals are substituted by Cl radicals to that extent will the solvent power of the solution on AgCl be enhanced—a fact which alone is of nature to counterbalance what slight difference there may be in original outlays in securing these acids—even the use of one or the other of these compounds becomes more or less a matter of choice in a cyclic process like that in question. Indeed, should even a given ore be too alkaline to stand the cost of the HCl necessary to first neutralize it, it may be treated with H_2SO_4 in a preliminary way; or one may even use HCl itself in such extreme cases, allowing this acid to percolate through the mass, and subsequently treating the collected solutions—now containing all the calcium as $CaCl_2$—with H_2SO_4, thus rejecting this metal as $CaSO_4$ by a simple filtration and at the same time regenerating the HCl which had combined with the calcium.

On the whole, therefore, it seems quite immaterial, for the purpose on hand, whether one uses a solution made up of $Fe_2(SO_4)_3$ and H_2SO_4 in presence of a cheap chloride, such as NaCl, or whether one chooses a solution of $FeCl_3$ and HCl or H_2SO_4, with the same cheap salt, or of $CaCl_2$, to furnish the necessary concentration of chlorine radicals. As for the concentration of the reagent solution in these various compounds, one need not diverge materially from the approximate composition given on a previous page, though the concentration of the common salt (NaCl) or of $CaCl_2$ may best be made as high as 20%.

But it may be objected here that such strong solutions as the above may not be the best that could be wished from the standpoint of facilities in commercial handling. However, considering the fact that these solutions can be cheaply got, readily recovered, and regenerated indefinitely, coupled with the fact that they possess high electric conductivities, and therefore require less expenditure of power for the electrolytic work, than were they more dilute, these facts are certainly of a nature to more than counterbalance what little disadvantage this high concentration may offer.

Reactions Involved.—Before giving quantitative data to show to what extent the use of ferric salts, under proper conditions, can be regarded satisfactory for the extraction of the precious metals from their ores, it is of interest to consider here first the mechanisms of the reactions involved in their use.

In carrying out qualitative experiments with the above solutions under the proper conditions, namely, in presence of much NaCl, for instance, we observe, especially if the solutions be warmed, that the Ag_2S is rapidly decomposed. At the same time silver goes into solution and much of the ferric iron present is reduced to the ferrous condition, while a grayish scum of sulphur appears floating on the surface of the solution. The reaction taking place seems therefore to be, with the sulphate of iron:

$$Ag_2\overset{S}{_\wedge}+Fe_2(SO_4)_3=Ag_2SO_4+2FeSO_4+\underline{S}\quad X$$
$$Ag_2SO_4+2NaCl=2AgCl+Na_2SO_4$$

and with the chloride of iron:

$$Ag_2S+2FeCl_3+NaCl=2AgCl+2FeCl_2+S+NaCl$$

Now while this seems to be the simplest way for representing the facts observed—and it is indeed the one commonly accepted—still it is a question whether the reaction involved is as direct as that shown above. For the same facts may be represented equally as well by the following equations, considering exclusively chloride solutions alone for clearness' sake:

$$Ag_2S+2HCl=2AgCl+H_2S$$

and then:

$$H_2S+2FeCl_3=2HCl\overset{2}{+}FeCl_2+S$$

The mere fact that, ordinarily, acids alone have no appreciable effect upon the sulphide of silver is certainly no criterion against such a view. For if this preceding reaction be regarded as a reversible equilibrium reaction—as all reactions may be so looked upon—only with its equilibrium point towards the extreme left, namely, toward the formation of Ag_2S, it becomes clear that if we only remove the disturbing reaction product, H_2S, by some appropriate method, the point of equilibrium could be readily shifted to the right, so that AgCl could form freely. The function of the ferric salt would therefore be, in this light, only a secondary one, namely, one of removing this disturbing reaction product, H_2S, as fast as it is formed under the direct influence of the acids. That this view is more than a mere supposition is evidenced by the fact that when a mixture of Ag_2S and HCl, for instance, is boiled, even in absence of any oxidizing agents, there is a slight decomposition of the sulphide taking place, especially if the acid used be concentrated. It being permissible to regard the effect of boiling as merely facilitating the expulsion of H_2S, this phenomenon may well be taken as an indirect evidence in favor of the above view. The very fact, indeed, that, even in commercial practice, Ag_2S is decomposed by concentrated H_2SO_4 in the absence of oxidants may here be adduced as even a more tangible evidence.

Again, the fact that a solution of a ferric salt, free from any surplus foreign acids, decomposes Ag_2S cannot be adduced as necessarily favoring the existence of a direct action between these two compounds, inasmuch as all ferric salts are hydrolyzed freely, and are therefore apt to play the role both of acids and of oxidizing agents.

In view of these considerations, it seems that the reactions whereby the oxidation of Ag_2S takes place may best be explained in the light of the second view, unless, indeed, it be admitted that both the direct and the indirect reactions take place concurrently.

As regards the mechanism whereby the AgCl goes into solution in presence of the foreign chlorides, there seems to be conclusive evidence that this takes place by virtue of a tendency the former compound has to give rise, with these chlorides, to double salts analogous to double iodides and double cyanides. Such a combination of AgCl and NaCl is readily obtained in crystalline form whenever the conditions are such that NaCl will begin to separate, such as by concentrating a solution containing these two compounds, by evaporation, or by adding concentrated acids to it, especially HCl, In either case, the first crop of crystals that separate will contain practically all the silver chloride. These crystals are visibly cubic and look exactly like so many crystals of pure NaCl, and, strange enough, they do not even seem to be affected by light. They are, however, readily decomposed into flocculent AgCl and NaCl when thrown into pure water.

Unfortunately it is very difficult to form a definite idea as to the exact composition of the double salt represented in these crystals, as they do not seem to be of any fixed composition, but rather individuals produced by the simultaneous and isomorphous crystallization of both a double salt and of independent molecules of NaCl. Although treatises on chemistry* do not seem to make specific mention of a double salt of silver and sodium chlorides, still, as they allude in a general way that AgCl can form double salts of the composition AgClMCl, it seems that the compound here under consideration may best be represented as

$$AgCl.NaCl + xNaCl$$

If this be correct, and it seems to be strengthened by the fact that several attempts to obtain this compound in a form sufficiently free from extra NaCl for analysis have resulted in failure, then the salt here under consideration would rep-

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*Watt's *Dictionary of Chemistry* (Muir and Morley); Ladenburg's *Handwoerterbuch der Chemie.*

resent a definite case of crystallization where double salt formation and isomorphism may coexist.

There remains now to consider the mechanism of the oxidation of gold.

It must be admitted here that, in spite of the assertions of certain authorities,* no appreciable solution of gold can take place in solutions of ferric iron, whether in form of chloride or sulphate, except in presence of some foreign oxidizing agent, such as chlorine, nitrates, and even ordinary atmospheric oxygen.§ This is certainly not surprising, seeing that such an attack of gold by a ferric salt would give rise concomitantly to so much of a ferrous salt, and that this latter would naturally tend to react backwards and cause the re-precipitation of gold by virtue of the well-known effects of ferrous salts on solutions of gold.

It is evident, therefore, that the essential condition for the successful attack of free gold, along with the oxidation of the sulphides of silver and other metals, lies in the removal of the ferrous salts formed during such reactions, as represented on a previous page.

Such an oxidation of ferrous salts can of course be brought about best by means of the chlorine which will tend to be liberated at the anodes during the electro-deposition of metals, and with which the main solution may be made to be saturated in actual practice. The reactions here involved would then be:

$$FeCl_2 + Cl = FeCl_3$$
$$3FeSO_4 + Cl_3 = Fe_2(SO_4)_3 + FeCl_3$$

in both of which cases the ferric salts regenerated can then react upon gold to the extent that there is free chlorine left on hand in the solution, and on the sulphides to the extent that there is any iron left in the ferric condition.

Now a critical consideration of the above reactions involved in this alternate oxidation and reduction of the iron salts will reveal the fact that while in purely chloride solutions the iron will always remain combined with chlorine—that is, it will be present as chloride—with solutions, on the other hand,

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*Comey's Dictionary.

§McIlhiney, *Am. Jour. of Science,* '96, vol. 152, p. 293.

where the iron may have been originally introduced as a sulphate there will be a continuous tendency for them to have this sulphate of iron converted into the chloride form. It is, indeed, clear that every time $Fe_2(SO_4)_3$ is reduced to $FeSO_4$, the subsequent oxidation of this latter by means of chlorine will convert part of the iron present into $FeCl_3$, as is shown in the second reaction above; so that when this process is repeated many times there will be more and more sulphate of iron disappearing, while chloride of iron will take its place.

Owing to this consideration, it is important to note here that the method of ore treatment here discussed should be properly regarded as a "chloridation" method, at least for clearness' sake, even though the iron originally introduced may have been in the sulphate form, or the acid in the stock solution may be H_2SO_4, and not HCl.

We may now pass to a quantitative study of the extent of suitability of such chloride solutions of iron salts to the treatment of some actual ores and the conditions of operation.

EXPERIMENTAL

EXPERIMENTS WITH ORE NO. I

In the following experiments the ore used was obtained from Tonopah, Nevada. Ore No. 1 was a grayish quartzose ore, containing some galena, pyrite, calcite, silver sulphides, and gold, with a gangue consisting mainly of quartz. It also contained a notable proportion of metallic iron, introduced into the ore owing to improper grinding.

Experiment I.—In this experiment the ore was ground to 80 mesh to start with, owing to its reputation of being very refractory, and, instead of treating it with a stock solution already made up, it was thought best to utilize the metallic iron in the ore by dissolving it in an acid. As it was of importance to first study the effect of sulphate solutions, the acid chosen here was H_2SO_4. When the action had ceased, an excess of this acid and NaCl was added, so that the resulting solution contained about .5% metallic iron, 2% H_2SO_4, and 20% NaCl, with a total volume of 1 liter for an ore mass of 1 kilo. The mixture was put into a large flask, chlorine was introduced into it so as to oxidize the $FeSO_4$ formed under the influence of the H_2SO_4 upon the metallic iron in the ore, and a mixture of ferric sulphate and chloride was thus obtained in the ratio of 5:2.

In order to facilitate the reactions and shorten the time of treatment, heat was then applied to the mass, which was kept nearly boiling for three hours, care being taken that there was always an abundance of chlorine on hand in the solution throughout this period. At the end of this time the mass was filtered and well washed with a strong solution of common salt until a few drops of fresh leachings showed no turbidity on being diluted with water, which meant, of course, that all the silver chloride held in the solution wetting the ore mass had been washed out. (It is hardly necessary to say here that it was essential to use a concentrated solution of salt for this operation, because, had ordinary water or even a very dilute solution of salt been used, the liquors impregnating the ore mass would be diluted thereby, and thus much silver chloride might be precipitated and left back in the ore.)

When this was done, the mass was further washed with pure water to remove the excess of salt solution wetting it, and lastly it was dried and sent to professional assayers as tailings.

The following are the results of the assays of the sample before and after treatment:

RESULTS OF ASSAY, EXPERIMENT I. ORE NO. I

	Au.	Ag.
Sample	Oz. per ton.	Oz. per ton.
Original	.8	84.7
Tailings	.35	4.8

This corresponds to about: 56% extraction of gold
and 94.4% extraction of silver.

It will be seen from these data that there was much room for improvement as regards the extraction of the gold values.

Having, however, obtained similar results in a second test, under similar conditions, it was then thought interesting to study the effect of the finer crushing of the ore upon the extraction of the values.

Experiment II.—Another lot of the same ore was therefore crushed to 120 mesh and assayed for the second time. The treatment carried out in this experiment was identical to the above in details as to the composition of solution, length of time of boiling or treatment, and, of course, as to care in the method of washing the tailings. Only it was carried out on a lot of ½ pound, with the corresponding amount of solution, instead of 1 kilo. of ore, as was done in the first experiment.

RESULTS OF ASSAY. EXPERIMENT II. ORE NO. 1

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Original	1.03	86.2
Tailings	.125	1.1

This corresponds to about: 88% extraction of gold
and 98.7% extraction of silver.

It will now be noticed, on comparing the results of these two experiments, that a good deal of the gold values of *this ore* are very closely locked up in the ore gangue, thus necessitating very fine crushing, and that, so far as the silver values are concerned, 80-mesh crushing is practically as good as 120-mesh.

Experiment III.—Since in the above experiments the solution had to be kept boiling during the treatment, and since the keeping warm of a mass of ore is quite an item in large-scale practice, the necessity of some experiments to study the effect of treatment in the cold became now quite evident. The following test was therefore carried out to elucidate this point.

The ore treated was ½ pound of the 120-mesh sample. The details of treatment were identical to those in the above tests, except that they were carried out in the cold, and the time of treatment was prolonged to two days, with occasional shaking.

RESULTS OF ASSAY. EXPERIMENT III. ORE NO. 1

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Original	1.03	86.2
Tailings	.575	18.7

This corresponds to: 44% extraction of the gold
and 79% extraction of the silver.

These data clearly showed the necessity of further prolongation of time of cold treatment, and consequently the following test was then made:

Experiment IV.—The conditions in this experiment, too, were identical to those of the preceding experiment, except that hydrochloric acid, instead of sulphuric, was used to dissolve the free iron in the ore mass, whereby all the iron was put in the chloride form on chlorinating it, instead of part of it staying in the sulphate condition. The time of treatment was extended to three days instead of two, as in the preceding test.

RESULTS OF ASSAY. EXPERIMENT IV. ORE NO. I

	Au.	Ag.
Sample	Oz. per ton.	Oz. per ton.
Original	1.03	86.2
Tailings	.325	6.6

This corresponds to: 69% extraction of gold
and 92.4% extraction of silver.

From these results it can be seen that a three days' treatment of the ore with a cold solution will extract highly satisfactory percentages of silver values.

It might be argued here that the favorable difference obtained by this last test might have been due not to the prolongation of the time of treatment, but rather to the fact that in using hydrochloric acid instead of sulphuric, more ferric chloride, and therefore more chlorides, were introduced into the solution than in the first case.

Experiment V.—In order to determine to what extent such may have been the case, a special experiment was carried out subsequently under the same conditions as with the preceding test, only substituting H_2SO_4 for HCl. The following were the results obtained:

EXPERIMENT V.

	Au.	Ag.
Sample	Oz. per ton.	Oz. per ton.
Original	1.03	86.2
Tailings	.39	5.6

Corresponding to about: 93.5% silver extraction
62.1% gold extraction.

It becomes evident from these results that the divergence between the results of the two preceding tests must in reality have been chiefly due to the difference in the length of time of treatments rather than to the influence of the increase in the percentage of iron present as chloride in the testing solution.

In order to further test this method of extraction of precious metals, another ore was now taken up and experimented with.

EXPERIMENTS WITH ORE NO. 2

This ore, also obtained from Tonopah, was a reddish, oxidized ore, containing much ferric oxide, some silver sulphides, and gold, but very little galena or lime. It was crushed to 80-mesh before the following tests were made with it.

Experiment VI.—This experiment was carried out under conditions similar to those of Experiment 1, only 500 grams of ore being taken instead of 1 kilo.

Although in this ore there was practically no metallic iron to depend upon to furnish the ferric salt required for the attack of the sulphides, there was, however, a sufficiency of Fe_2O_3, occurring as such in the ore, to serve for that purpose by going into solution when the mixture of H_2SO_4 and NaCl was added. The iron thus brought into solution amounted to about .4% by weight of the solution.

RESULTS OF EXPERIMENT VI

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Original	·55	49·45
Tailings (hot treatment)	.18	5·5

These correspond to an extraction of about: 89% silver
and 67.3% gold.

Experiment VII.—In order to determine to what extent these results could be affected by adopting the conditions of Experiment IV, namely, by a cold, three-day treatment in presence of chlorides alone, a second test was made under the latter conditions, with the following results:

EXPERIMENT VII

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Original	·55	49·45
Tailings (cold treatment)	.075	7·3

Corresponding to an extraction of: 85.7% silver
86.4% gold.

Although no further experiments were carried out with this ore to study the effect of a finer crushing than 80-mesh, or of a more prolonged treatment, it is safe to say, however, that had these measures been resorted to, the above results would probably have been much improved upon, especially in view of the fact that it was noticed, after the above tests were made, that the ore experimented with was not quite of 80-mesh crushing, but that fully 15% would not pass through such a sieve.

It may have been noticed, from the descriptions of the above ores, that they were both remarkably free from any large amounts of the sulphides of "base" metals, such as antimony, lead, etc. The question may therefore arise here as to whether the method of ore treatment under consideration would at all successfully apply to ores containing much base sulphides, and, if so, to what extent and under what conditions.

To answer this question, the following experiments, undertaken with the above point in view, may be cited.

EXPERIMENTS WITH ORE NO. 3

This ore was obtained from Idaho. It was a dark gray, almost black, mass, chiefly made up of sulphides of antimony and lead, with much silver, but very little gold. The gangue was silicious, with practically no lime or iron oxide. Besides the above sulphides, there was a small amount of chalcopyrite and pyrite seen scattered through the mass. The ore was coarsely crushed when received. An assay gave the following results:

Original ore: 161.8 ounces silver and .12 ounces gold per ton.

Experiment VIII.—Although difficulties in treating this ore in the cold might have been expected *a priori,* still it was thought of interest to carry out some preliminary experiments with it under conditions as nearly economic as possible, namely, in the cold and with ordinary crushing.

First Treatment.—The ore was crushed only to 40-mesh to start with, and, knowing it to contain not much iron to depend upon to supply the necessary amount of oxidant by going into solution during the treatment, the mass was treated with a stock solution containing 2% $FeCl_3$, and H_2SO_4 and NaCl to the extent of 3 and 20% respectively. The weight of ore taken being 300 grams, the volume of solution used was therefore 300 c. c., that is, in the same relative proportion as in all the previous experiments. The resulting mixture of ore and solution was kept in an open vessel for three days at room temperature, but without introducing any free chlorine into it.

Twice during this period, however, part of the solution was decanted off and replaced with an equal volume of the fresh stock solution so as to facilitate the reactions by keeping a good supply of ferric iron on hand and, at the same time, by removing the reaction products, especially the ferrous iron, which would form and accumulate in the solution to a great extent.

After this period the mass was thrown on a filter paper in a funnel, leached, washed first with strong salt solution, then with pure water, and finally carefully dried and assayed. The following were the results thus obtained:

Tailings, ore No. 3, first treatment { 100.1 oz. silver per ton
.06 oz. gold per ton

If we compare these results with those of the assay of the original ore, we see that this corresponds to an extraction of only about 38.2% of the silver and 50% of the gold present.

Second Treatment.—To see to what extent a prolongation of treatment could improve matters, the above tailings were treated with a fresh lot of the stock solution and allowed to remain in contact with this latter for three days more, part of the solution being again decanted off and renewed twice during this period. The results obtained were:

Above tailings, after second treatment { 82.5 oz. silver per ton
Traces of gold per ton

Which corresponds to an extraction of about 49% of the silver present and practically all the gold.

It is to be noted here that while thus far the extraction of the silver cannot be called satisfactory, yet that of the gold is strikingly good. To what was the latter fact due?

Although it is not known what was the exact state of combination of the gold originally present in the ore, it is not unlikely, however, that this metal was found there in some readily soluble form, such that it was gradually removed during the successive renewals of the solution by decantation or filtration. The fact that the ferrous iron—which was always present in the solutions during the treatments, in larger or smaller amounts—did not hinder such a removal of the gold must have been due first to the extreme smallness of the amount of this metal present in the ore, and then to the fact that the precipitation of gold by means of ferrous salts is not quantitative when other oxidizing agents, such as ferric salts or atmospheric oxygen, are also at hand.

Third and Fourth Treatments.—In order to discover whether finer crushing would help the extraction of the remaining silver materially, the above (second) tailings were now crushed down to a fineness of 70 meshes and then subjected to a third treatment with the same stock solution for three more days.

However, as even the tailings thus resulting assayed 63 ounces of silver per ton (corresponding to a total extraction of 61%), a fourth treatment of the same tailings, covering three more days, was next undertaken, this time crushing the ore down to 100 meshes and increasing the percentage of ferric chloride in the solution to 5%. This last treatment, however, did not materially alter the preceding results, as the tailings now indicated a total extraction of only 63% of the silver, originally in the ore, during the four treatments, covering a total period of twelve days.

This naturally rendered it necessary to use the agency of heat so as to accelerate the reactions, and thereby determine whether the fault lay in the process itself or was due to the character of the ore.

Before doing this, however, it was thought interesting to decide first whether it was the length of time of treatment that governed the degree of extraction of the silver in the above experiment, or whether the latter depended mainly upon the fineness of division of the ore.

Experiment IX.—To answer this question, another experiment was therefore undertaken, this time with a fresh lot of ore, crushed to 100-mesh to start with, and with a solution containing $FeCl_3$ to the extent of 5%, as in the preceding test. The results obtained after a four days' treatment in the cold, with a daily decantation and partial renewal of the solution, showed almost exactly the percentage of extraction arrived at at the end of the twelve days in the above-repeated tests with coarser crushing.

This proved definitely that the ore was of an exceptionally refractory character, so far as the silver contents were concerned.

The necessity of "forcing" the decomposition of the sulphides in this ore by carrying the treatment in the warm, especially if finer crushing was to be avoided, became the more apparent at this juncture, as it was noticed at the end of the fourth day, even in the preceding test, that the further action of the solution upon the ore became extremely weak.

Experiment X.—A fresh 300-gram lot of the 40-mesh ore was now taken and a series of tests made with it, by boiling the mass in a flask in presence of a solution of 3% H_2SO_4, 20% NaCl, and 5% $FeCl_3$, for the total period of 22 hours. The treatments lasted from three to six hours each, the solutions being, of course, renewed for each new test. The following is a tabular statement of the data thus obtained:

EXPERIMENT X. HOT TREATMENT OF ORE NO. 3

	Ag. oz. per ton.	Au. oz. per ton.	Per cent extr. silver
Original ore	161.8	.12	
Tailings, 1st treatment, lasting 5 hrs.*	55.2	—	65.9
Tailings, 2nd treatment, lasting 3 hrs.	36.1	—	77.7
Tailings, 3rd treatment, lasting 3 hrs.	30.0	—	81.5
Tailings, 4th treatment, lasting 6 hrs.	12.2	—	92.5
Tailings, 5th treatment, lasting 5 hrs.	9.0	—	94.5

At the end of these 22 hours of treatment, the solutions collected were analyzed (approximately) and found to have

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*The solution was once decanted and renewed at the end of the first 2 hours.

extracted antimony to the extent of 3% of the weight of the ore, and as much as 2% of lead, besides some copper, and silver as shown above.

From these results it appears clearly that "Chloridation" will succeed even with ores as refractory and "base" as that under consideration, provided the agency of heat is introduced to accelerate the decomposition of the sulphides.*

It is now of interest to consider what results may be expected of this method of ore extraction as applied to very poor ores or tailings.

EXPERIMENTS WITH ORE NO. 4

This ore was a reddish, oxidized mass containing much limestone, ferric oxide, copper carbonate to the extent of .5%, some silver, and some gold.

Experiment XI.—As the ore contained much $CaCO_3$ and Fe_2O_3, it was thought to utilize these by using a rather strong solution of HCl alone for the lixiviating agent, and thereby omitting the introduction of the chlorides of sodium and iron.

Two hundred grams of the ore were therefore taken and treated with the above acid, so that when all the carbonates had been completely decomposed, there was an excess of 10% HCl left free in the total volume of 200 c.cs. of solution.

Although the ore contained a small percentage of MnO_2, which, reacting upon the HCl present, gave some free chlorine, nevertheless, in order to insure the attack of the gold, the mass was gently chlorinated and kept at room temperature for three days, with occasional shaking. The following are the results thus obtained:

EXPERIMENT XI

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Original	.09	4.2
Tailings	.02	1.4

Which correpsonds to about: 66.6% silver extraction
and 77.8% gold extraction.

In order to ascertain whether or not these low results were

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*The possibility of giving a preliminary roasting to such ores in lieu of heating the solution has not yet been considered.

referable merely to the conditions of experimentation, several other experiments were carried out under varying conditions as to the composition of the solution, using H_2SO_4 and NaCl, etc., but it was found that in nowise could the above results be improved. Of course, the possibility of using heat in connection with the treatment of such low-grade ores in practice being out of the question, no attempt was made to test the ore with hot solutions. It is well to say here, however, that just as it is likely that such hot treatments would give better extractions with the above ore, as with the others, by disintegrating the coarser grains in it—to whose presence these low results are probably due—just so it is probable that, had these coarser particles been ground finer, the extraction would have been improved, even with ordinary cold treatments. Nevertheless, it seems doubtful if *tailings* of the type of the above, namely, those rich in Fe_2O_3, can ever be totally deprived of the precious metals, owing to the fact that such ores are likely to retain by occlusion, as is well known, considerable amounts of chlorides, those of silver and gold among others, in a manner difficult, if not impossible, to obviate.

Besides the above ores, others were experimented with, some mere tailings, others fairly rich in silver and gold. Without going into a detailed account of these various experiments, the following conclusions, based upon the experience thus far gained by the writer, may be safely drawn:

1. The Chloridation method, as above described, may well be depended upon to extract the precious metals from their ordinary ores of good grade in a very satisfactory manner, especially as regards the extraction of the silver values.
2. The thoroughness of extraction of the gold values depends entirely upon the degree of oxidation of the reacting solution by means of chlorine.
3. In many cases, with silver ores carrying gold, a sufficient percentage of this latter metal is also extracted, besides the silver, to pay a large share, if not the whole, of the expenses of treatment, and this with no more care than is to be given for the extraction of silver alone.
4. With very low-grade ores, or tailings rich in oxide of iron, the highest extractions can only be had economically by fine crushing.

5. With very base ores of good grade the process is too slow to be paying if carried out in the cold. In such cases, unlike with ordinary ores, the agency of heat must be resorted to, either by way of warming the solutions or by giving a preliminary roasting to the ores.

6. In practice the solution used in any case may be either salt and sulphuric acid, or salt (or calcium chloride) and hydrochloric acid, or hydrochloric acid alone, or any other suitable combination, according to local economic facilities. As to the supply of iron salts needed, it is probable that it will seldom be necessary to introduce such salts into the main solution from without, since ordinarily ores will be found to contain enough of the compound of this metal in a soluble form to furnish all the oxidizing agents necessary to enable the solution to do its work properly, once these salts of iron are brought to the ferric condition.

ELECTROLYSIS

There remains now to consider the electrolysis of the solutions, with a view to recovering the precious metals dissolved thereby, oxidizing the ferrous salts, and therefore regenerating the ferric salts and the solution as a whole.

So far as the recovery of the metals is concerned, it seems to be safe to say that, in view of the many vain attempts made by the writer to obtain good adherent deposits on the cathodes, it is useless to trouble one's self by trying to get any such deposits in large-scale practice.

Without going into any unnecessary accounts as to the details of these various attempts, it is sufficient to say here that if the solution be kept in motion during the electrolysis, which is a necessity for continuous work, it is found that a current density of .1 ampere per square decimeter, with a voltage of 1.5 to 2 volts, and with platinum electrodes, will not deposit the values on the cathode at all; whereas this same current will succeed in precipitating all the values if the solution be kept quiescent. The reason for this peculiarity lies, undoubtedly, in that the deposit being slimy or spongy and easily rubbed off the surfaces of the cathodes by the solution in motion, this latter thus has a stronger tendency to re-dissolve the values than has a current of the given density to precipitate them. By increasing the current density, however, the deposition is carried to completion, although as slimy as ever.

If, however, a very small percentage (the fraction of a per cent) of glue or any mucilaginous substance is added to the solution, the character of the deposit obtained is wholly changed. Instead of the loose and black precipitate on the cathode, one now gets, as a rule, especially if the solution be warmed, a good, firm, and whitish gray deposit, which takes a high polish when rubbed with the handle or back of a knife. Moreover, it now matters no longer whether the solution is left quiescent or stirred vigorously or even kept boiling. The deposit is always good, provided the current density is proper. Thus, by reason of the very fact that this deposit sticks firmly to the cathode, it would seem as if with a small "trick" like this one might get good and firm deposits and thus stop the values, once deposited on the cathodes, from falling off into the solution and there being subject to redissolution.

Unfortunately, however, sometimes, in spite of the best intentions and care on the part of the operator, the solution refuses to give good deposits, even with the addition of glue. And then the deposit is again slimy and black. For these and other reasons liable to cause possible hitches in the work of electrolysis, in practice it might be better to have recourse to some mechanical device whereby the slimy metals on the cathodes may be continuously removed before they have any chance to fall off into the solution.

A handy method in point is one described by Tomassi.* Briefly described, it lies in that the cathodes are made of circular plates, only half of each of which dips into the solution. They are, further, so arranged that they can rotate at a slow rate, say once or twice a minute. In consequence of this rotation there is always some new surface being covered with slimy metal deposit, while other portions emerge from the solution already so charged. In its motion the external part of a plate comes to rub itself against some rubber

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**Comptes Rendus*, Académie des Sciences de Paris, vol. 122, p. 1476.

pads provided with long grooves leading to a suitable receptacle near by. Along these grooves, serving as channels, the slimes, loosened by the friction between rubber pads and cathode plates, are drifted by means of small jets of a dilute solution of salt, and thus carried into the receptacle where the values are thus collected.

As for the materials of which the electrodes may best be made in connection with this work, it is obvious that carbon or graphite would be the most suitable as regards durability, desirability, and cheapness, especially as no other cheap metal could stand unattacked in such solutions of ferric salts.

As regards the oxidation of the ferrous salts in solution or the regeneration of the ferric salts, the writer is in position to state here that, in order to bring this about by means of the electric current, there is absolutely no necessity of using any diaphragm cells of any sort. If the current density be properly adjusted and the metals deposited or satisfactorily removed from solution, whether by using glue or by means of the above, or any other, mechanical contrivance, the oxidation of the ferrous salts accumulated in the solution during the latter's passage through the ore mass can go on concurrently with the electro-deposition of the metals, so that ultimately there are not only no ferrous salts left unoxidized, but what is more, the solution will be found to be charged with free chlorine. It is important to call special attention to this fact, inasmuch as certain authorities and all the inventors of "patent" methods, who have so much as specified the use of the electric current for the regeneration of the solution, have persistently thought it to be impossible not only to thus reoxidize the iron salts in solution, but have actually feared that, instead, the higher oxides of this and other metals dissolved might be reduced to lower ones; and they have, therefore, advocated the use of some form or other of porous diaphragms to separate the cathodes from the anodes in the electrolytic cells.

When it is remembered that diaphragms are not the best things that could be wished for or even allowed in large-scale practice, and in solutions of the character here under consideration, the importance of the foregoing observation can scarcely be lost sight of.

In actual practice, what should be the mechanical and other arrangements to be adopted in treating ores on a serious scale by the electro-chemical "Chloridation" method here advanced?

It would certainly be idle to enter here into any details of the possible contrivances which might be devised and put into use under such circumstances. Large-scale practice alone will decide questions of that character.

Suffice it to say here, however, that in putting the method into practical use, the governing principles of operation will be the following:

The ores, suitably crushed, are to be kept in wooden vats and treated with the stock solution best by simple leaching.

The leachings thus collected are made to pass continuously through simple electrolytic vats where, on the one hand, the dissolved metals are recoverd and, on the other, the solution is reoxidized, or "regenerated," under the influence of the electric current. The number of cells and electrodes, the current strength, and the flow of the solution so arranged that, by the time the solution leaves the last cell, it is satisfactorily impoverished of its precipitable metals and completely oxidized, chlorinated, in other words, fully *regenerated;* which done, it is ready to be led over into the ore vats again, allowed to leach through the ore masses, then passed through the electrolytic cells, and finally returned to the ore vats over again, and so on, cycle after cycle.

When a given batch of ore is sufficiently impoverished of its metals, it is treated with pure water so as to displace and recover the stock solution impregnating the exhausted ore.

To what extent this latter operation may be economically carried out, and what other modifications, in the line of secondary treatments, may be introduced into the process as a whole, will be alluded to in the second part of this paper.

II. PERSULPHATATION

HISTORICAL

Unlike solutions of cupric and ferric salts, and in spite of the fact that they have come latterly to be regular articles of commerce, persulphates do not seem to have as yet been used, or even suggested, as direct agents for extracting metals from their ores. There seems to be one allusion made in the literature on the subject* to the effect that persulphates could be used in conjunction with cyaniding as a substitute for oxidation by aeration, which is well known to be essential for the hastening of the solvent action of the cyanides upon gold. Although it appears even that a patent has been issued to a German company§ to cover this particular use of persulphates along with cyaniding, yet nothing seems to be known, in practical mining circles, of this method of ore treatment having ever been put into actual, large-scale operations anywhere.

Considering the fact, however, that cyanides are decomposed by persulphates,‡ it is not at all unlikely that this "patent" suggestion, like so many others, has never as yet left the confines of patent specifications.

THEORETICAL

In the method of metal extraction here to be described, the chief point of interest lies in that both the oxidation of the sulphides of silver and of gold is brought about under the influence of one and the same compound, namely, the persulphate used, under proper conditions, but without any necessary dependence upon the generation of chlorine by electrolysis.

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*Elbs, *Ztsch. Angew. Chemie*, '97, p. 195.

§*Journal Am. Chem. Soc.*, '97, vol. 19, p. 900.

‡N. Tarugi, *Centrlbl.*, '03, p. 616.

In bringing this double effect about, advantage is taken of the fact that persulphates decompose chlorides, setting chlorine free, ready to attack gold, especially in presence of free acids, and that, on the other hand, they attack sulphides, readily converting them into sulphates, while they themselves break down to simple sulphates.

The reaction taking place in the first case seems to be of the type:

$$2NaCl+K_2S_2O_8+H_2SO_4=Na_2SO_4+K_2SO_4+H_2SO_4+Cl2$$

the decomposition of the chloride being referable to the formation, first, of free persulphuric acid, thus:

$$K_2S_2O_8+H_2SO_4=K_2SO_4+H_2S_2O_8$$

which then reacts upon the chlorides in a manner now well known:

$$2NaCl+H_2S_2O_8=Na_2SO_4+H_2SO_4+Cl_2$$

While with the ordinary concentrations of acids and persulphates the attack of chlorides can be called all but rapid at best—a fact which is rather fortunate from the practical standpoint, seeing that the nature of the work to be done by the chlorine thus liberated, namely, the solution of gold, requires only a slow but continued oxidizing effect—that of the sulphides, on the other hand, is much more readily accomplished. In fact, this decomposition goes on readily, even in neutral or slightly alkaline solutions, though it is certainly more vigorous in the presence of acids. The reactions here in question seem to take place as follows:

$$Ag_2S+K_2S_2O_8=Ag_2SO_4+K_2SO_4+S$$

though much of the sulphur forming the metallic sulphides is oxidized completely over to sulphuric acid.

These being the mechanisms and character of the reactions immediately involved in the use of solutions of persulphates for the dissolution and extraction of the precious metals, it is evident that, as with the chloridation method, so also here it is essential for the successful working of the present method in actual operations to have these solutions charged with a soluble chloride. The introduction of such chlorides is, indeed, important in this case, not merely because it is necessary to have some chloride present in the solution so as to react with the persulphates and liberate the chlorine necessary to dissolve the gold in the ore, but also because, AgCl being no more soluble in simple persulphate solutions than in ordinary solutions of iron salts, there is here the same danger of much silver being lost in consequence of the unavoidable presence of chlorine compounds occurring as impurities in ores, unless some appropriate solvent of AgCl is used here as with the chloridation method.

But there is even a more grave reason for which such a solvent of silver should be used in this connection, and that is that silver salts form an insoluble precipitate of peroxide of silver (Ag_2O), in presence of persulphates, which is only decomposed and dissolved satisfactorily by strong chloride solutions.

In endeavoring to select an appropriate solvent for these insoluble silver compounds, it was at first thought that, unlike with the previous method, ammonia would be a desirable substance to use in conjunction with the present method of ore extraction, inasmuch as it would act as a very efficient solvent of any silver chloride which might form in the course of the treatment, while, at the same time, the action of persulphates upon the sulphides would not thereby be impaired in any way. This belief had, however, soon to be abandoned. It was, indeed, observed that, far from being a suitable substance for the purpose, ammonia was decidedly objectionable, inasmuch as it was found to be rapidly decomposed into free nitrogen and water whenever any appreciable amount of silver and a persulphate were found in solution with it. This oxidation of ammonia under these circumstances is due, doubtlessly, to a catalytic reaction depending upon the formation, primarily, of the peroxide Ag_2O, which then attacks, more or less violently, any free ammonia which may be present in the solution, and causes its complete decomposition in a well-known manner.*

The reaction is, indeed, so characteristic that the writer has

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*Dammer's *Handbuch Anorganischen Chemie.*

found it to be a very handy way for detecting the presence of silver salts in chloride solutions, which is the more useful as it is oftentimes impossible to detect silver in such solutions, whether by any other simple precipitation method or by a mere dilution of the solution with the hope of thus diminishing the solvent power of the liquid on AgCl and thereby causing a turbidity of this compound to appear. In carrying out this test, a strong solution of a persulphate, preferably the ammonium salt, is added to the solution to be tested, and then this latter is made strongly alkaline with NH_4OH, when, if silver be present, a more or less rapid evolution of nitrogen gas will be observed to take place.*

The use of ammonia as a solvent of insoluble silver salts being thus out of the question, and none of the other non-chloride solvents being sufficiently stable in presence of persulphates, the choice of concentrated solutions of a chloride thus becomes a necessity.

Now, as it is remembered that the use of persulphates as reagents for treating ores of the precious metals was suggested, on an earlier page of this paper, on the ground that they were good oxidants, *capable of being regenerated by the electric current;* and, further, as it is realized here that, though a small percentage of a chloride in concentrated solutions of sulphates is very advantageous for the electrolytic formation or regeneration of persulphates,§ higher percentages of chlorides are quite injurious to such regeneration, the question may arise here as to whether the means above stated for holding silver salts in solution in actual practice would not render the process as a whole inoperative, at least as a "cyclic" method. It is, indeed, only too evident that, an essential condition for the formation of persulphates by means of the electric current being a high anodic current density, or better, a high rate of discharge, per unit of area and time, of SO_4 ions at the anodes, the introduction of unduly large proportions of a non-sulphate electrolyte, such as NaCl for instance, will tend to diminish the yield of the current in persulphate formation.

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*This catalytic reaction has also been studied lately and similarly explained by Hugh Marshall (*J. Chem. Soc.*, '01, Abstr. ii, p. 156).

§Elbs, *Ztschr. fur Elektrochemie,* '95, p. 245.

How such a serious difficulty may be overcome in practice will be discussed further on. Suffice it to say here only that, were there even no way of surmounting this difficulty, the fact that persulphates are becoming more and more readily available as regular chemicals of commerce, so that they could be economically secured for practical usage, this fact justifies the study here of their suitability for the extraction of the precious metals from their ores.

As for the question which may arise here regarding the advantages such a method may have, at best, over the chloridation method previously described, the following points may be cited in answer:

1. Theoretically the use of a persulphate should be preferable to that of ferric salts alone, because, unlike the latter, whose reaction products, namely, the ferrous salts, are notorious for their tendency to reprecepitate the precious metals from their dissolved state, persulphates break down merely to sulphates, that is, salts having no such injurious effects upon the solutions of these metals.

2. For this reason principally, simple gold ores could be treated by persulphatation to a better advantage than by chloridation, or perhaps by any other wet method.

3. In practice one may have to treat ores that are too rich in limestone to be economically handled by the chloridation process, inasmuch as they would first have to receive a preliminary acid treatment before they could be subjected to the action of ferric salts, lest these latter should be precipitated out and the process rendered more or less inoperative. Such ores should be amenable to persulphatation to a better advantage, seeing that persulphates can decompose sulphides of silver, as was stated above, in neutral or slightly alkaline media as well as in acid.

On the other hand, it is only fair to admit here that, with very "base" ores, persulphatation cannot be expected to be nearly as useful a method as chloridation, owing to the fact that the satisfactory oxidation of such ores by wet methods such as these, requiring, as they do, the heating of the reacting solutions, persulphates would be rapidly decomposed under these conditions and hence be useless as economic agents for treating this type of ores.

To what extent the above premises may be justified will now be studied in a quantitative way.

In the following experiments the persulphate worked with has been the potassium salt throughout. This choice was made for two chief reasons. In the first place because sodium persulphate, whose use would suggest itself first, is unfortunately not to be had on the market here, nor can it be made readily in the *solid* condition. In the second place because the ammonium salt, though it is of all the persulphates the one most readily made or got, is not adapted for experiments of this kind, let alone for large-scale use, owing to the fact that it is rather unstable and easily decomposed into free nitrogen or its oxides by auto-oxidation,* and especially under the influence of the chlorine, which would tend to be liberated, whether during the treatment of the ores or during the electrodeposition of the metals.

As none of these disadvantages is seriously shared with by potassium persulphate, hence its selection for the following study.

EXPERIMENTAL

EXPERIMENTS WITH NON-ALKALINE ORES

As both the decomposition of sulphides and the solution of gold can be best brought about by persulphates when some free acid is present, it is obvious that whenever the use of acid solutions is permissible they should be resorted to in practice. In fact, there is a second advantage gained in such a practice, namely, that under these conditions there are also more or less ferric salts introduced into the solution through the agency of the acidity of the liquids upon the compounds of iron which may be in the ores, and hence the oxidizing power of the solution is thereby enhanced.

The following experiments were carried out with a view to studying the effect of persulphates under these conditions:

ORE NO. 2

This ore was that already described on a previous page. As it represented more nearly the average type of good ores

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*Marshall, *J. Chem. Soc.* (London), '01, abstr. ii, p. 156.

ordinarily met with, it was thought best to study it first in this connection.

In order to form an idea as to the possibilities of the method in a general way as a means of precious metal extraction, a set of experiments was undertaken in a preliminary way.

Experiment XII.—The solution used in these tests was made up of 10% H_2SO_4, 20% NaCl, and 2% $K_2S_2O_8$. The tests were carried out on a lot of 300 grams of ore, with the usual corresponding bulk of solution, namely, 300 c.cs. in the present case. The mass was put into a bottle and left standing in the cold during a period of 3 days, with frequent shaking. At the end of each 24 hours, however, it was thrown on a filter, leached, washed, and dried, exactly as with the tests previously described in connection with the chloridation method, and finally a sample was taken and assayed. This done, the remaining tailings were treated with a solution of the same concentration as above mentioned, for a second and third time, only using a fresh solution each time.

The following were the results obtained:

EXPERIMENT XII

	Au.	Ag.	Per cent Extr.	
Sample	oz. per ton.	oz. per ton.	Gold.	Silver.
Original	·55	49·45		
Tailings after 1st day's treatment	.092	7·5	83·3	84·9
Tailings after a 2nd day's treatment	.032	4·5	94·2	90·9
Tailings after a 3rd day's treatment	.031	3·9	94·2	92.1

These results clearly show a decided improvement over those obtained previously by chloridation alone.

As it is stated here that during these treatments there was a strong odor of chlorine evolved by the solution, it may be lightly thought *a priori* that the thoroughness of the extraction of gold is due to the presence of this gas in solution. As it is remembered, however, that this same gas was also present in the solution with the chloridation tests carried out with the same ore, and even in larger amounts, it becomes evident that the present remarkably high degree of extraction of the gold is due to more than the mere presence of chlorine in solution. It seems, indeed, that the chlorine on hand in the solution in the present experiments being nascent, while that in the chloridation tests was molecular, the favorable difference here observed should be referred to this particular fact of the chlorine being here in a nascent state. If so, this would constitute another advantage of persulphatation over chloridation proper, or perhaps any other form of chlorination, especially as a method of gold extraction.

Now, since the percentage of free acid used in the above preliminary tests was somewhat unduly too high from the practical standpoint, it was of interest to study the effect of varying the amount of the free acid in the solution on the extraction of the metals, with a view to using lower percentages in practice.

Experiment XIII.—A new set of tests was therefore undertaken, using two solutions, one containing 3%, the other 5% H_2SO_4, with 2% of $K_2S_2O_8$ and the normal amount (20%) of NaCl in each. The treatment, carried out as before in all other respects, lasted only 24 hours, and gave the following results for the tailings assayed:

EXPERIMENT XIII

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Tailings (3% H_2SO_4)	·3	5·75
Tailings (5% H_2SO_4)	.22	5·1

From these results it would appear that the chief function of the acid lies in that it improves the extraction of gold alone, while that of silver is left practically constant.

Experiment XIV.—In order to decide whether this relationship was merely fortuitous or not, another set of experiments was carried out, this time using a solution of only 1% $K_2S_2O_8$, but extending the time of treatment to 48 hours, with a daily decantation and renewal of the solutions, the acidity in the latter being again 3% and 5% respectively.

EXPERIMENT XIV

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Tailings (3% H_2SO_4)	·30	9.0
Tailings (5% H_2SO_4)	.163	8.4

Whence it is clearly seen that in reality the chief function of the acid in these solutions lies in that it facilitates the dissolution or extraction of the gold rather than that of the silver values. In other words, the alteration of the concentration of the acidity in these solutions affects the extraction of the first metal rather than that of the second. And the general results of these experiments have been corroborated in a third set of tests.

This point having been thus definitely ascertained, it became next important to see what effect the variation of the concentration of the persulphate would have upon the extraction of these precious metals.

Experiment XV.—For this purpose two tests were made, using two solutions of 1% and 2% $K_2S_2O_8$ respectively, while both were acidified to the extent of 3% H_2SO_4.* The results, after 24 hours' contact of the ore with the solutions, were:

EXPERIMENT XV

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Tailings (1% $K_2S_2O_8$)	.30	13.3
Tailings (2% $K_2S_2O_8$)	.30	5.7

Strange as it may seem, these results clearly indicate that the variation in the concentration of the persulphate in solution affects especially the extraction of silver alone. In other words, the function of the persulphate would seem to be especially one of oxidation of the silver compounds.

Experiment XVI.—In order to ascertain that this was not either a mere fortuitous coincidence, a new test was carried out using a solution containing 3% H_2SO_4 and 2% $K_2S_2O_8$, but extending the time of treatment to 48 hours. This was done so as to be able to compare it with the results of a previous test (given in table preceding the last), where only 1% $K_2S_2O_8$ was used, with also 3% H_2SO_4 and a 48-hour treatment. The following is a statement of the results of these two tests:

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*In this and in all the subsequent experiments, as in those preceding, the treatment was carried out in the cold, and the solution used contained the normal amount (20 per cent) of salt, unless otherwise stated.

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Tailings (1% $K_2S_2O_8$)	.3	9.0
Tailings (2% $K_2S_2O_8$)	.27	4.8

Whence it is clearly seen that in reality the concentration of the persulphate affects principally the oxidation of the silver sulphides.

From these various experiments, then, it becomes unmistakably evident that the best conditions of operation in treating such ores would be to use higher concentrations of both acids and of persulphate as far as practicable, say 5% of the former and 2% of the latter, since solutions containing larger amounts of the one would be inconvenient and uneconomical, while with the other difficult to obtain, $K_2S_2O_8$ being only slightly soluble in aquous media.

In order to determine how favorably the present method would compare, under such average conditions as to the concentration of the acid and persulphate in solution, with the chloridation method in extracting the precious metals from the ore under consideration, another experiment was now undertaken.

Experiment XVII.—In this test the concentration of the solution in acid and persulphate was 5% H_2SO_4 and 2% $K_2S_2O_8$ respectively, with the usual percentage of common salt. Since at no time during the treatment with such a percentage of acid in solution would there be the large excess of chlorine on hand which was the case with the chloridation test of the same ore as previously described, it was thought best to equalize the conditions by having recourse to a continuous percolation of the solution through the ore mass, as would be the case in actual, large-scale practice. To do this, the ore (200 grams) was put in a cylindrical funnel, the lower (inner) orifice of which was covered with a small piece of filter paper, and the solution was poured on the mass and let leach gradually until one charge had entirely disappeared. When this was done, a lot of fresh solution of the same percentage composition as the above was poured on the mass and again allowed to leach, the charge of solution being then renewed as before, and so on. It must be noted here, however, that the first lot of solution passing through the ore mass having been analyzed and found to have extracted iron from the ore to the extent of .4%, all subsequent, newer additions of solutions were treated with the corresponding amount of $FeCl_3$, so as to render the conditions more nearly as they would be in actual practice.

When ten such additions of solution and thorough percolation of same were completed, which required about a week in all, the last leachings were tested for silver, and they being found free of this metal, the extraction was called complete. Fresh water was now added to the mass to displace the saline solutions impregnating the ore before assaying it.* This done, the ore was taken out, dried, and assayed, giving the following results:

EXPERIMENT XVII

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Original	·55	49·45
Tailings	.04	2.7

These correspond to an extraction of about: 94.6% silver
and 92.7% gold.

These results make it clear, therefore, that, as compared with the chloridation method—at least as applied to this particular ore—the persulphatation method is far more efficient.

Having obtained such encouraging results with this ore, it was thought of interest to extend this study to richer and more exceptional ores.

ORE NO. I

Experiment XVIII.—300 grams of ore No. 1, described on a former page, was taken, and, after attacking it first with a simple solution of H_2SO_4 to dissolve the metallic iron contained

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*It is of great importance, from the practical standpoint, to note here that when a weight of solution one-half that of the ore used was collected, it was noticed that the leachings now became remarkably free from acid or salt, so much so, indeed, that silver nitrate would give but a slight turbidity with the percolating liquid, while tasting could not at all detect the presence of any saline matter in solution.

in it, enough of $K_2S_2O_8$ was added to oxidize completely the ferrous sulphate thus formed to the ferric condition, which done, common salt, more H_2SO_4 and $K_2S_2O_8$ were added to the resulting solution, so that the latter now contained 20% NaCl, 10% H_2SO_4, and 2% $K_2S_2O_8$. The experiment was carried out exactly as was done with the first persulphatation tests with ore No. 2 (page 42), that is, the ore was treated first for 24 hours, then it was filtered, washed, dried, and assayed as usual, after which it was again treated for a second 24 hours and assayed, and then treated for a third 24 hours and assayed for a third and last time.

The following is a statement of the results obtained:

EXPERIMENT XVIII

	Au.	Ag.	Per cent Extr.	
Sample	oz. per ton.	oz. per ton.	Gold.	Silver.
Original	1.03	86.2		
Tailings after 1st 24 hrs.' treatment	.66	32.00	36.0	62.9
Tailings after a 2nd 24 hrs'. treatment	.4	13.2	61.2	84.7
Tailings after a 3d 24 hrs'. treatment	.4	7.5	61.2	91.3

Experiment XIX.—These results not being quite satisfactory, a second set of experiments was undertaken, this time working with three separate lots of the ore. These were treated with a solution and in a manner identical to the above, only one being assayed at the end of the first 24 hours, a second at the end of 48 hours, and the third at the end of 72 hours, the solutions, with the last two, being merely decanted off and renewed once every 24 hours, instead of filtering, drying, and re-treating them, as was done in the preceding experiment. The results now obtained were as follows:

EXPERIMENT XIX

	Au.	Ag.	Per cent Extr.	
Sample	oz. per ton.	oz. per ton.	Gold.	Silver.
Original	1.03	86.2		
1st tailings (24 hrs'. treatment)	.57	34.5	44.7	60.0
2nd tailings (48 hrs'. treatment)	—	31.2	—	63.8
3d tailings (72 hrs'. treatment)	.4	25.5	61.2	70.7

Leaving the low figures of the first and second tests aside, that the third test, lasting three days, should also thus fall so far below the degree of extraction previously obtained with the chloridation method (page 24) with this same ore becomes now quite unaccountable. The difficulty grew more mysterious, indeed, as it was especially noticed during the lapse of the experiment that in all these tests the solutions were always kept well oxidized, as was evidenced by the weak, but distinct, odor of chlorine which evolved from them.

Experiment XX.—Thinking that matters might perhaps improve if the solution were left in contact with the ore during the three days without changing it, or again, perhaps by prolonging the time of treatment, two more tests were carried out under these new conditions, keeping the percentage composition of the solutions used as that in the preceding experiments. These, however, gave no better results, as can be seen from the following data:

EXPERIMENT XX

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Tailings (3 days' treatment)	.6	21.75
Tailings (4 days' treatment)	.5	21.00

In order to see how far the use of HCl, instead of H_2SO_4, would improve the results, another experiment was now undertaken, which was also prolonged for 4 days, with the following results:

EXPERIMENT XXI

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Tailings (with HCl, 4 days)	.6	14.7

These results were certainly not very much better, as they still left the high extractions obtained with the Chloridation method unattained.

Experiment XXII.—It was finally thought that perhaps a treatment under the conditions of Experiment XVII (page 46), namely, resorting to a continuous percolation of the solution through the ore mass for a long period, would give better results. A new test was therefore started under these conditions, using a solution of about the same percentage composition, in every respect, as that of the preceding experiments, the total duration of the treatment being 7 days. Unfortunately, however, even the results thus arrived at were still far from being satisfactory, as can be seen from the following:

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Tailings (by percolation)	.33	14.1

Having thus studied all the various conditions as to the concentration of the reagents in the solution, the modes and the durations of treatment, with a view to attaining more satisfactory results, and having thereby ascertained that none of these could have been responsible for the low extractions obtained by the present method, as against those obtained by chloridation, it was now thought that perhaps the sole explanation of the difficulty might lie in the relative abundance of chlorine held in solution in these two methods. It is indeed a matter of fact that while in the experiments with ferric salts alone there was always used a large abundance of chlorine in solution, in the present tests, on the other hand, there was, comparatively speaking, only a small excess of chlorine on hand at any time. Now since when sulphides are decomposed and oxidized by means of chlorine, the oxidation of the sulphur in combination takes place more completely, resulting in the formation of H_2SO_4, when a large excess of this gas is on hand, whilst it only results in the separation of spongy sulphur when the chlorine on hand is not sufficiently abundant, it naturally seemed that the low extraction of the precious metals with the persulphatation method, as applied to this ore, may have perhaps been due to the formation of notable amounts of just such spongy sulphur, which might then have coated the particles of the sulphides in the ore, and thus prevented their further decomposition.

Now, if this were so, it is clear that the question would be to remove this sulphur by some appropriate method, and in some appropriate manner, whether by a complete oxidation or by a mere dissolution and removal of this element from the ore mass.

However, as the complete oxidation of sulphur to sulphuric acid could best be brought about, from the practical standpoint, by the introduction of sufficiently large excesses of chlorine gas into the solution, and as even such a procedure could not always be brought about in large-scale work, it becomes clearly desirable to adopt some lixiviation method whereby the sulphur may be removed from the ore mass by the use of a simple, convenient solvent of that element, and subsequently got rid of or recovered therefrom as far as possible.

Now, of all the simple solvents of sulphur, the one which would lend itself best to this purpose is certainly a solution of a fixed alkali, such as NaOH, and for good reasons. Indeed, not only could such a solution be economically made by a simple electrolysis of a sulphate, say Na_2SO_4, in a diaphragm cell, but, what is of special value, after the formation of the desired amount and concentration of the free alkali, and the subsequent use of the latter to dissolve the sulphur in ores as desired, the impure, sulphuretted alkaline solution thus resulting could then be treated with the acid solution which had formed and accumulated in the anode compartment of the electrolytic cell during the electrolysis of the Na_2SO_4, and thus made to yield the sulphur it had extracted from the ore either as H_2S or as free, precipitated sulphur, and at the same time to regenerate the original Na_2SO_4, which can then be electrolyzed again and used as desired.

How well would such alkaline solutions answer for the purpose on hand?

Experiment XXIII.—In order to determine this point, the first tailings (3-day treatment) of Experiment XX were taken up, treated with a 10% NaOH solution, and left over night. The following day the mass of ore and solution was filtered off and washed with pure water till it was free from alkali. This done, it was now treated with the ordinary stock solution of acid, salt, and 2% $K_2S_2O_8$, and left stand 2 days in the cold, with occasional shaking.

At the expiration of this period, the mass was filtered, washed, dried, and assayed, giving the following results.

EXPERIMENT XXIII

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Original ore	1.03	86.2
Original tailings (Exp. XX)	.6	21.75
Tailings after second treatment, subsequent to the treatment with NaOH	.11	3.00

Which corresponds to an extraction of about: 96.9% silver
89.3% gold.

It thus becomes strikingly evident that the use of NaOH in facilitating the further attack of an ore by oxidizing agents is of a great and undeniable value. On the other hand, that it is no less undeniable that the action of NaOH in bringing about this remarkable condition of affairs is in reality due to its power to merely dissolve considerable amounts of spongy sulphur and help to remove it out of the ore mass, thus laying bare the remaining particles of sulphides subject to the further attack of the main oxidizing solution, is proven by the fact that the now impure, brownish solution of NaOH, recovered after the treatment of the ore with it and filtration of same, gave a decided precipitate of yellow, flocculent sulphur, when neutralized with H_2SO_4, along with a little H_2S.

In fine, then, it is evident that even such extreme ores as the one under consideration may be treated by the use of a persulphate alone, irrespective of the introduction of any chlorine gas from without, provided the use of an alkaline solution is resorted to.*

EXPERIMENTS WITH OTHER ORES

Besides the above, two new samples of high-grade ores were treated similarly so as to give a rigorous test to the method here advanced.

Ore No. 5.—This ore was obtained from Mexico, and represented a specimen sample of very high grade, consisting chiefly of the simple sulphide of silver or Argentite (Ag_2S), a little ruby silver (Ag_3SbS_4), gold (not free milling), and a gangue of quartz, with some chalco-pyrite disseminated through it.

Experiment XXIV.—In order to form an idea as to the degree of extraction which could be obtained with coarser crushing, the ore was first ground to 50-mesh only. The test was carried out on a 200-gram lot by the continuous percolation method, as previously described, using a solution made up of 12% HCl, 1% $FeCl_3$, and 2% $K_2S_2O_8$, but with no NaCl

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*It is scarcely necessary to note here that this same modification in the method of ore extraction may be introduced also, if necessary, in connection with the chloridation method, described in Part I of this paper.

whatever, as it was intended to have the large percentage of HCl used take its place.

The ore being unusually rich in silver, the complete removal of this metal required fully 15 days, when the final washing with pure water was given and the mass dried and assayed. The following were the results obtained:

EXPERIMENT XXIV

	Au.	Ag.
Sample	Oz. per ton.	Oz. per ton.
Original	3.00	680.00
Tailings (50-mesh)	1.32	102.00

Corresponding to an extraction of about: 85% silver
and 57% gold.

Experiment XXV.—In order to ascertain to what extent finer crushing would help matters, these tailings were now ground down to 70 meshes, and again percolated with the solution.

Although this new treatment showed some more extraction of values, as could be seen by a dilution of the percolates, yet as the effect stopped being noticeable within less than even 24 hours, and in a manner which could not well be taken to mean that all the remaining 102 ounces of silver per ton, for instance, had so soon been extracted from the mass, it was then washed with water, and a 10% solution of NaOH was next allowed to percolate through it so as to dissolve the sulphur, which must have accumulated in the ore, and thus to free the particles of the ore from this encumbrance and facilitate their further decomposition by the solution of persulphate. This done, the ore was again washed with water, and then treated anew with the stock solution, when a large abundance of silver and gold was immediately observed to have gone into solution again. When this action (lasting over 3 days) was also over, the ore was washed, dried, and assayed, as usual, with the following results:

EXPERIMENT XXV

	Au.	Ag.
Sample	Oz. per ton.	Oz. per ton.
Tailings, after second treatment (subsequent to treatment with NaOH)	.72	34.8

These correspond to an extraction of about: 95% silver
76% gold.

Although, as it is here seen, the silver extraction was very satisfactory considering the extremely rich character of the original ore, there was still room for improvement as regards the extraction of the gold values.

Experiment XXVI.—A third experiment was now undertaken, using the same solution as in the above tests and with the above tailings crushed down to 100 meshes. The results arrived at were:

EXPERIMENT XXVI

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Tailings (third treatment)	.48	24.0

Corresponding to an extraction of about: 96.5% silver
and 84% gold.

No further experiments were carried out with this ore, as a further extraction of the precious metals was now becoming increasingly difficult.

Ore No. 6.—This ore was an average one, also obtained from Mexico, consisting chiefly of argentite, galena, chalcopyrite, and some gold, with a gangue of quartz.

Experiment XXVII.—Knowing it to be an ore of the same type as the preceding one, this sample was crushed to 70 meshes to start with, and the experiment carried out under the same conditions, in all respects, as with the above ore.

Owing to its being more of an average type, the extraction of this ore was complete within a week (3 days prior to treatment with NaOH and 3 days subsequent to it), when an assay gave the following results:

EXPERIMENT XXVII

Sample	Au. Oz. per ton.	Ag. Oz. per ton.
Original	1.9	106.00
Tailings	·5	5·3

Which corresponds to an extraction of about: 95% silver
and 73% gold.

Although the extraction of gold is still thus seen to leave much to be desired, no attempts were made to repeat the experiment with a finer crushing of the ore, as it was rather certain that better results could thus be obtained, seeing that the ore represented, as was alluded to, the same type of ore as the preceding one.

EXPERIMENTS WITH ALKALINE ORES

There remains now to consider the treatment of alkaline ores by means of a persulphate in neutral solutions, so as to determine to what extent such ores may be amenable to a treatment without necessitating the preliminary neutralization of their carbonates with correspondingly large amounts of acids.

Ore No. 1.—As ore No. 1, previously described, contained a large percentage of $CaCo_3$, corresponding to as much as 15% H_2SO_4, it was thought proper to study it in this connection first.

One hundred grams of this ore, powdered, as in all the preceding experiments with the same ore, to 120-mesh, was put in a percolating cylinder and the mass treated with a solution of 20% NaCl and 2% $K_2S_2O_8$ alone.

After 10 days of continuous percolation, necessitating ten renewals of solution, the mass was leached with pure water, dried, and assayed, giving the following results:

EXPERIMENT XXVIII

	Au.	Ag.
Sample	Oz. per ton.	Oz. per ton.
Original	1.03	86.2
Tailings	.52	7.4

Which corresponds to an extraction of about: 91.4% silver
and 49.6% gold.

From these results it will be seen that, as might have been expected, the silver values of the ore are satisfactorily extracted by such a treatment with a neutral solution of potassium persulphate, although the extraction of the gold values leaves still much to be desired. Was this latter due to the extremely fine state of division of this metal in the ore, or was it merely due to the extreme slowness of the liberation of chlorine in such a neutral solution of a persulphate?

Unfortunately, as the writer has been unable to obtain other alkaline, but fairly good, ores to test by this modified method, he is not in a position to answer the foregoing question definitely. It may, nevertheless, be well to note here that ore No. 4, which was almost as rich in carbonates as the above ore, was also thus treated and found to give an extraction of about the same order as when treated with the Chloridation method, a fact which, considering the inherently difficult character and extremely low grade of the ore, would seem to speak quite favorably of the feasibility of economically treating certain excessively alkaline ores of the precious metals by means of a neutral solution of a mixture of salt and a persulphate, as against their treatment by the chloridation method, which would necessarily require a preliminary treatment of such ores with an acid, a necessity which might not always be trifling.

ELECTROLYSIS

So far as the electrolytic recovery of the precious metals from these persulphate solutions is concerned, no detailed mention need be made here of the various steps to be followed in this operation, as it is, in all essential details, identical with that mentioned in the first part of this paper in connection with the chloridation method.

As regards the electrolytic regeneration of the main reagent, the persulphate, however, things are unfortunately not quite as simple. Indeed, the essential conditions for the electrolytic formation of persulphates being principally dependent upon the concentration of SO_4 ions transferred to the anodes (platinum) per unit of time, the unavoidable introduction of *large* amounts of a non-sulphate, such as NaCl or HCl, into the solution is quite incongruous with the purpose at issue. For, as has been mentioned on a former page, though a little amount of a chloride is highly favorable to persulphate formation, yet when higher concentrations of such a non-sulphate salt are used, the yield of the electric current in persulphate formation decreases very rapidly, owing chiefly to the fact that these foreign compounds also take part in the transfer of electricity through the solution, thus decreasing the rate of discharge of SO_4 ions at the anodes, and consequently the yield to the current in persulphates.

In view of this fact, it becomes apparent that, in order to obtain satisfactory yields in the formation of persulphates, either the current density at the anodes must be increased proportionately; or some method must be resorted to whereby the bulk of the chlorides may be removed from the solution before attempting to regenerate, or rather, reform the persulphate consumed during the treatment of the ore; or, again, one must strive to separate some of the sulphate in solution by some appropriate means, convert it into a persulphate, and then return it to the main solutions.

Now a consideration of these possible methods of arriving at the goal set forth will show that the first method, or that depending upon the increase of anodic current density with solutions of a mixture of sulphates and chlorides, is not the best that could be desired, from the practical standpoint, and for two reasons. First, this is so because the current densities used in ordinary practice, even with pure sulphate solutions (namely, 50 to 500 amperes per square dm.), requiring, as they do, voltages not below 5 volts, sometimes even as high as 7 or 8 volts,* any further increase of the current densities, which would be necessary to offset the injurious effect of the presence of chlorides, would perhaps mean doubling or even trebling the latter figures for the potentials required for the purpose on hand, thus resulting in the decrease of the rendement in persulphates per unit of power. In the second place, the regeneration of the persulphates needed by direct electrolysis of a solution of sulphates in presence of much chlorides is not desirable, because, the only metal admissible to serve as anodes for such a purpose being the costly platinum, and this metal being far from unattacked when used as anodes in chloride solutions, an economic difficulty thus looms up in the way of any continued practical operations in such a line of work.

Further, owing to the fact that no special, economical method can be devised whereby the dissolved chlorides could be adequately removed from at least a part of the stock solu-

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*Friedberger and Muller, *Ztsch. fur Elektrochemie,* '02, p. 231.

tion before the electrolysis of this latter is carried out in attempting to reform the persulphate consumed, this second method must also be considered impracticable, if not impossible, for large-scale practice.

This leaves only the third method above suggested as a means of regenerating the necessary persulphate, namely, that consisting in the removal of part of the sulphate in solution from an aliquot part of the latter, converting it into a persulphate in a special electrolytic cell, and finally returning it to the main solution as needed.

A careful consideration of this possibility will show that not only could such a method be the most rational and feasible, but that the question thus viewed admits of more than one solution. Indeed, since the problem is one of separating a part of the sulphate from the stock solutions by crystallization, it is clear that this may be brought about in two ways, to wit: either by concentrating, by evaporation, an aliquot part of the solution until the sulphate alone begins to separate—the original solution being more nearly saturated with respect to this salt than with respect to the chloride in solution—or by taking advantage of the decrease in the solubility of certain sulphates by lowering the temperature of their solutions.

Thus, if the sulphate worked with in practice be the potassium salt,* part of the liquors holding this latter in solution may be shunted off—best directly after the recovery of the precious metals therefrom—and a desired amount of the sulphate made to separate out in the solid form, either by concentrating the solution with respect to this salt by evaporation, or by cooling it sufficiently, according to practical facilities. In either case, the solution being more nearly saturated with respect to the sulphate than the chloride present, the former salt will naturally separate out first, in form sufficiently pure and free from admixed chlorides to be redissolved in a fresh, sufficiently chloride-free solution of the same sulphate, and electrolyzed in special electrolytic cells, with a view to converting it, at least in part, to a persulphate, which may then be removed from the solution and returned to the stock liquors.

While, with potassium sulphate chosen as the starting material to work with in practice, the evaporation method

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*Same would be true with $(NH_4)_2SO_4$.

seems to be much more likely to be practicable, with the sodium salt (Na_2SO_4), on the other hand, the separation of the solid Na_2SO_4 from the shunted solutions by cooling seems to be equally likely to meet with success in practical operations. Indeed, the very *rapid* decrease of solubility of the Na_2SO_4 with the lowering of the temperature of its solutions, and the very *slight* decrease under the same conditions of the solubility of NaCl which may be present in the same solution, render this method highly useful as a means of bringing about the separation of the former salt from a concentrated solution of both these compounds in a form sufficiently free from the latter for all purposes concerned, and that with only a slight lowering of the temperature of the solution.

But to what extent can this happy coincidence be turned into practical use, supposing Na_2SO_4 to be chosen as the starting material to be converted into the corresponding persulphate? Would not the difficulty of preparing the persulphate of sodium in solid form—owing to its excessive solubility—stand in the way of the sulphate of this element being used, in actual commercial practice, as the starting material needed?

While not prepared to make light of this difficulty, the writer is of the opinion that it is not absolutely necessary to prepare this persulphate in the solid form, but that the sulphate of sodium (whether original or recovered from the shunted parts of the stock solutions) may be dissolved in water and then converted, to any desired extent, into a solution of the corresponding persulphate, which solution may then be returned, in body, to the main or stock liquids. Nor is it, perhaps, true that sodium persulphate cannot be obtained in the solid form, although all authentic accounts of the authorities who have dealt with the subject from a *purely scientific standpoint* either seem to categorically deny its feasibility,* or at least make no mention of any one having met with success in that line. Indeed, according to Lowenherz,§ the persulphate of sodium can be obtained without any special difficulty, provided the current density is increased to unusually high limits.

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*Marshall, *J. Soc. Chem. Industry,* '97, p. 396; Elbs, *Ztsch. fur Elektrochemie,* '95, p. 245.

§Lowenherz, *Wagner's Jahrsbr. Chem. Technol.,* '95, p. 366.

As the account of Lowenherz's work is got from his patent specification, however, and as no other authority seems to have thus far proven it to be false or correct, it would be unsafe to draw any foregone conclusions, in positive terms, for or against such a possibility. Personally, the writer regrets that he has had no opportunity, as yet, to verify or disprove the contentions of the patent.*

Just what should be the exact form of the cells and other appliances to be used in this operation of regenerating the persulphates it would be unnecessary to discuss here. The question belongs, strictly, to the domain of practical, large-scale operation, and could therefore be best studied and decided upon under such conditions. Suffice it to say in this connection, however, that the contrivances and methods to be used in practice need be neither complicated, involved, nor costly, since one has to deal with only a rather limited volume of solutions at a time, from which to crystallize the needed amount of the sulphate, and then to "persulphate" the latter by electrolysis. In other words, these contrivances need not be materially different from those made use of in the ordinary commercial method of the preparation of persulphates.§

RÉSUMÉ

Two independent cyclic methods have been studied and advanced, in the present work, for the simultaneous winning of the precious metals from their sulphide ores.

The first, or "chloridation," process depends upon the use of acid solutions of ferric chloride or sulphate, in presence of high concentrations of soluble chlorides, especially hydrochloric acid or sodium chloride, which act as solvents of silver chloride. With sodium chloride used as a solvent, it was observed that, under certain conditions, an insoluble complex salt of silver and sodium chlorides would separate in form

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*It is important to note here further that besides the above alkali sulphates, that of iron, and *especially* of aluminum, could also be used in this connection in converting them to their corresponding persulphates.

§See foregoing references.

of definite isometric (cubic) crystals. Attempts were made to obtain this salt in condition sufficiently free from extra sodium chloride for analysis, but without success. This salt seems to be best represented by the formula $AgCl.NaCl+xNaCl$, where x represents the number of molecules of extra sodium chloride which will unavoidably crystallize isomorphously with the double salt $AgCl.NaCl$. This may therefore be regarded as an interesting case where double salt formation and isomorphism may coexist.

Various ores were treated by this process, and quantitative data obtained showing an average extraction, under proper conditions, of over 95% silver and from 60% to 88% gold, varying with the character of the ore.

The metals dissolved were recovered by electrolysis. It was found that, under proper conditions, the reoxidation of the ferrous salts formed during the decomposition of the sulphides, and the consequent regeneration of the ferric salts, could be readily accomplished without the use of any diaphragms whatever. This is of special interest, as in all the electro-chemical processes heretofore suggested for this purpose the use of some diaphragm has been thought to be an unavoidable, though troublesome, necessity. It was further found that there was no difficulty in carrying the reoxidation of the solution so far as to even charge the latter with much free chlorine, which could then act as an efficient solvent of gold.

A very small percentage of glue added to the solution was found to give good, coherent deposits of the metals.

The second, or "persulphatation," method studied depends upon the use of persulphates, also in conjunction with concentrated solutions of chlorides. Various experiments were carried out to study the effects of varying the concentration of acids and persulphate in solution. The best results were obtained with about 2% persulphate of potassium and 5% sulphuric acid. The extractions correspond to over 95% silver and from 70% to 92% gold.

It was observed that an intermediate leaching of the ore masses with a solution of an alkali, such as sodium hydrate, would facilitate the further attack of the sulphides. This was found to be due to the fact that such alkalies dissolve away the sulphur and help to remove this element, which otherwise forms a coating around the particles of the sulphides and thus hinders their further decomposition. The reaction giving rise to the formation of free sulphur may be represented thus:

$$Ag_2S + K_2S_2O_8 = Ag_2SO_4 + K_2SO_4 + S$$

One important advantage of this second process was found to lie in the fact that it could be used with ores that are too highly alkaline with carbonates to admit of the expenses of a preliminary neutralization of the ore masses with acids, which would be necessary if the first process were to be used.

A test has been suggested, in this connection, to detect small amounts of silver held in solution by virtue of the presence of chlorides. This test depends upon the use of a persulphate in presence of free ammonium hydrate, when, if silver is present, an abundant evolution of free nitrogen gas takes place. This is due to a catalytic action depending upon the intermediate formation of peroxide of silver and its immediate action upon the free ammonia present.

ACKNOWLEDGEMENTS

The writer wishes to extend here his grateful thanks to Professors Edmond O'Neill and W. B. Rising, and to Dr. F. G. Cottrell and all the members of the Faculty of this Department, for assistance, advice, and kind considerations shown to him while engaged in the foregoing studies.