GAS REPLACEMENT OF METAL SULFIDES

Ore Concentrate (Fe, Cu, Ni, Co, Zn, Mn) → LEACHING SYSTEM → Acidic leach liquor

Iron Sulfide (or Ore) → PRIMARY REPLACEMENT → Reducing Gas

Iron Sulfate plus Sulfate of metals, the sulfides of which are more soluble than FeS (i.e., Fe, Mn)

Gangue (to waste)

FeS, Cu, Co, Ni, Zn, Mn

Mixed Sulfides less soluble than FeS (i.e., Cu, Co, Ni, Zn) plus unreacted FeS

Figs. 1.

Sulfates Solution

Iron Sulfide (or Ore) slight deficiency → PRIMARY REPLACEMENT → Reducing Gas

FeS-free mixture, major portion all sulfides less soluble than FeS

FeS

Iron Sulfide slight excess

Iron Sulfate plus Sulfates of metals, the sulfides of which are more soluble than FeS (i.e., Fe, Mn)

Excess FeS plus minor residual portion all sulfides less soluble than FeS

Figs. 2.
Mixed Slurry of Metal Sulfides less Soluble than FeS (Cu, Ni, Co, Zn) plus Unreacted FeS

Air and/or O₂ → OXIDIZER → Acid

Sulfates solution → FILTER → Residue (to discard or leaching)

Iron Sulfide

Cu₅S REPLACEMENT (pH 3 to about 15% acid)

FILTER → CoSO₄ (to discard)

Cu₅

Equivalent Fe to Cu → Lime → FILTER

Co₅S REPLACEMENT (pH about 3-5) → Reducing Gas

FILTER → CoSO₄ (to discard)

Co₅

Equivalent Fe to Co → Lime → FILTER

Ni₅S REPLACEMENT (pH about 5-6) → Reducing Gas

FILTER → CoSO₄ (to discard)

Ni₅

Equivalent Fe to Ni → Lime → FILTER

Zn₅S REPLACEMENT (pH above 6+) → Reducing Gas

FILTER → CoSO₄ (to discard)

Zn₅

Equivalent Fe to Zn → Lime → FILTER → CoSO₄ (to discard)

Iron Sulfate Liquor (discard)

Figt. 3.

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Attorney
Iron Sulfide

slight deficiency  Fe to Cu  

Cus Replacement #1

Slurry

FILTER

Residue

Cus

slight excess  Fe to Cu  

Cus Replacement #2

Slurry

FILTER

CuS + FeS
Residue

NH4 OH

FILTER

slight deficiency  Fe to Co  

CoS Replacement #1

Reducing Gas

Slurry

FILTER

Residue

CoS

slight excess  Fe to Co  

CoS Replacement #2

Reducing Gas

Slurry

FILTER

CoS + FeS
Residue

Filtrate
to further treatment  (NiS and ZnS recovery)

Fig. 4.

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This invention is concerned with the production of non-ferrous metals broadly, but specifically with the production and separation of their sulfides. It deals with ores which are mixtures of metal-values minerals and diluents, particularly those which contain copper and at least one other metal value and have iron-bearing minerals and acid-insolubles as diluents and gangue. These ores are treated to convert the metal values content thereof to a solution of soluble salts. From such solutions, the corresponding sulfides of the metal values and/or the metals per se are subsequently recovered.

With the increasing utilization, over the past fifty years, of non-ferrous metals, particularly copper, there has steadily grown a demand for improved procedures whereby such metals can be more efficiently recovered from their ores. Particularly throughout the latter half of this period, repeated attempts have been made to devise processes for carrying out this operation chemically.

Roughly, the overall problem may be broken down into two parts. First, the mineral values must be extracted from the ore by some successful leaching system. Second, pure metals must be economically and efficiently recovered from the solutions obtained in the leaching operations. Whether considered as part of the leaching problem, or as part of the metal-recovery problem, there is the additional difficulty, which must be overcome, in that the mixture of metals or their minerals or salts must be separated each from the other.

In the past, largely with respect to the treatment of copper minerals, a number of proposals for such chemical extraction procedures have been presented. Unfortunately, all these operations suffered from one or more serious defects. As a result, none have been capable of commercial development on a scale commensurate with the possibilities of a suitable process of this type.

When the wide variety of problems presented by the copper industry alone are considered, this failure is not particularly surprising. For example, it is desirable to be able to treat many varieties of copper minerals by the same process, including those of oxidized and sulfide copper minerals. When this problem is complicated by the presence of other minerals, which not only must be removed therefrom, but also recovered, the complexities of the problem and the previous failures to provide successful solutions there to become even more readily appreciated.

Nevertheless, a demand remains in the industry for a process capable of easily and economically treating a minerals mixture. It must be adaptable to separate and to recover the copper and other metal values from the gangue and/or diluents. It is, therefore, a principal object of the present invention to provide such a process. It is with the combination of leaching and mineral separation that the present invention is concerned. In general, it deals with the treatment of ores which are mixtures of metal-values minerals to obtain one or more enriched concentrates of metal sulfides. These may be either mixtures freed from gangue and diluent metals, or individual selected sulfides.

Still more specifically, leach solutions, preferably obtained by acid leaching of the minerals mixture, containing dissolved salts of the metal values, are treated by a replacement reaction. In the latter are employed an additional metal sulfide or metallic sulfides and a reducing agent. The metal-values sulfides are thus precipitated in a mixture of all the sulfides whose solubility is less than that of the added metal sulfide. The mother liquor will contain, as dissolved salts, all the remaining metal-values, i.e., salts of those sulfides of which are of equal or greater solubility than that of the added sulfide. In addition, it will contain an amount of dissolved acid salt equivalent to the added metal sulfide reacted in replacing the desired sulfides. The desired sulfides, as precipitated by the reaction, are recovered and treated to convert the sulfides to solutions of soluble salts. The latter may then be treated further to separate selected sulfides.

Of the previously-proposed processes, perhaps the best is that disclosed in the application for United States Letters Patent, Serial No. 97,224, filed June 4, 1949, now Patent No. 2,568,963 issued September 25, 1951. This is by two of the present inventors, P. J. McGauley and E. S. Roberts. In that application, copper is separately removed as equivalents of crystallized copper sulfate from liquors obtained by acid leaching of minerals mixtures containing iron and other metal minerals.

In that application, an effective industrial method of separating soluble copper salts from iron and other metal salts, in an acid leach solution containing the copper and other metal sulfates, is disclosed. The process involves treatment of the copper-bearing leach solution by replacement with iron sulfides, usually that in the ore. When this operation is properly conducted, it results in the complete precipitation of copper from the solution as copper sulfides. It is
accompanied by the simultaneous dissolution of an equivalent amount of iron sulfides which is converted to ferrous sulfate. The copper sulfides are collected by filtration and the filtrate is discarded. The collected copper sulfides are oxidized to copper sulfate in solution; and so much of the latter as can be crystallized as pure copper sulfate is separated out and collected. By recirculation, all copper is eventually thus recovered.

This device was found to be very useful as a method of discarding iron and acid-insoluble diluent metals from a leaching-reduction system without causing loss of copper. However, when the ore being treated contains other valuable metals, such as cobalt, nickel, zinc, manganese and molybdenum, these metals are also dissolved during leaching but are not recovered. They remain in the leach solution and are removed from the system in the ferrous sulfate liquor. Since these metals are valuable and are often present in amounts sufficient to be profitably recovered, they cannot be discarded with the ferrous sulfate without economic loss. The problem of devising a suitable recovery system, which would also recover these additional non-ferrous metals, thus remained unsolved. Preferably, each metal should be recovered as a separate product, if possible.

It is, therefore, a further object of the present invention to devise a separation and recovery system which is capable of recovering these additional non-ferrous metals, as their sulfides, with the copper sulfides fraction, rather than losing them in the ferrous sulfate solution. In addition, the process should also permit a simple separation of the resultant sulfide mixture into its separate components.

These objects, as well as the primary object, are readily accomplished by the surprisingly effective process of the present invention. Broadly, the latter comprises carrying out a replacement reaction on the leach liquor in which the action of one or more replacement metal sulfides is supplemented by the action of a reducing agent, preferably a reducing gas.

In general, the process of the present invention is shown in simplified flow sheet form in the accompanying drawings, in which:

Figure 1 is a representation of a simple flowscheme, showing separation of a mixture of the majority of the valuable metals in an ore as their sulfides, in a mixture substantially free from the other metals and gangue;

Figure 2 is a modification thereof to obtain the mixture of sulfides completely free from sulfides of diluent metals;

Figure 3 is the development of a flowscheme for separating the metal sulfides mixture obtained by the processes of Figures 1 and 2 into its components;

Figure 4 is a drawing of a modification of the process of Figure 3; and

Figure 5 is a development of a process in which the flowschemes of Figures 3 and 4 are adjusted to handle different requirements.

Several general considerations, applicable to the present invention, should be noted at this point. In the present application, where the relative solubility of a sulfide is discussed, it is taken as indicated by the solubility product "K", i.e., the product obtained by dividing the product of the metal ion concentration and the sulfide ion concentration by the concentration of the un-ionized sulfide in solution. For purposes of comparison, several values of the solubility product "K" for various metal sulfides, in water at 18°C, are listed in the following table:

<table>
<thead>
<tr>
<th>Metal sulfide</th>
<th>Solubility product &quot;K&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnS</td>
<td>1.4 x 10^-11</td>
</tr>
<tr>
<td>FeS</td>
<td>3.3 x 10^-10</td>
</tr>
<tr>
<td>ZnS</td>
<td>1.2 x 10^-10</td>
</tr>
<tr>
<td>CuS</td>
<td>1.2 x 10^-12</td>
</tr>
<tr>
<td>PbS</td>
<td>3.9 x 10^-12</td>
</tr>
<tr>
<td>CdS</td>
<td>2.4 x 10^-12</td>
</tr>
<tr>
<td>Bi2S4</td>
<td>6.8 x 10^-13</td>
</tr>
<tr>
<td>CuS</td>
<td>2.5 x 10^-13</td>
</tr>
<tr>
<td>CoS</td>
<td>2.5 x 10^-13</td>
</tr>
<tr>
<td>Ag2S</td>
<td>1.6 x 10^-13</td>
</tr>
</tbody>
</table>

From the foregoing table, it will be readily seen that FeS is more soluble than any of the other sulfides listed, with the exception of that of MnS. This fact is utilized in the present invention in the following way. While MnS is more soluble than FeS, it is not present in most sulfide ores of non-ferrous metals in appreciable quantities, and economically, the content present therein may usually be discarded in the ferrous sulfate liquor without appreciable loss. Further, manganese sulfide per se is neither common nor cheap. It is, therefore, not a desirable sulfide for use in the replacement reaction of the present invention. Iron sulfides are both common and cheap. Therefore, naturally-occurring sulfides such as FeS, FeS2 and mixtures thereof make excellent sulfides to replace other sulfides from solution in the present process.

If sulfide minerals, containing available iron sulfides, are added to the hot pregnant leach liquor containing sulfates of such metals as copper, nickel, or zinc, whose sulfides are less soluble than FeS, iron goes into solution as ferrous sulfate. At the same time, replacement and precipitation of an equivalent amount of one of the other metals occurs. This metal is always found to be preferentially that which has the next most insoluble sulfide.

By way of further illustration, it may be assumed that an ore containing copper and iron sulfides is to be leached with acid-ferric sulfate solution, with oxidation. Such a case is shown in the above-noted McGauley and Roberts application. A pregnant leach liquor, containing copper and iron sulfates, is obtained. If this solution is then treated with additional amounts of the ore concentrate, similar reactions to the following will be expected to take place:

1. CuFeS2 + H2SO4 = H2S + FeSO4 + CuS
2. CuS + H2SO4 = H2S + CuSO4
3. 2CuSO4 + H2S = 2H2SO4 + CuS
4. Fe2(SO4)3 + H2S = 2FeSO4 + sulfur + H2SO4

Thus, when CuFeS2 is added to a hot acid solution of copper sulfate, H2S is produced according to (1). The first of this H2S is used up according to (4). After all of the Fe2(SO4)3 has been converted to FeSO4, the additional H2S is used to precipitate copper according to (2). These or similar reactions will continue until all of the copper is precipitated from solution as CuS or CuS2. Further, if other metal salts, such as nickel, cobalt, zinc, lead, or cadmium and the like, the equivalent metal sulfides of which are more soluble than CuS, are also present in the solution, substantially none of their sulfides will be precipitated under equilibrium conditions.
unless and until all the copper is replaced and precipitated as its sulfide. In the above-noted McCauley and Roberts application, this device is used to separate and purify copper from all the remaining metals. Accordingly, as was noted, these metals are lost from the system in solution with the ferrous sulfate.

Although the present invention is not intended to be limited to a particular theory of operation, it is believed that the complete precipitation of sulfides other than copper is due to the fact that oxidation reactions, such as that of Equation 4 above, destroys the \( S^{2-} \) ions before their concentration becomes great enough to permit the solubility product for one of the other metal sulfides to exceed its solubility constant. For example, in the case of nickel sulfide, the sulfide ions are destroyed before the product of their concentration, multiplied by the concentration of the nickel ions, and the product divided by the concentration of the NIS ions in solution, becomes great enough to exceed the above-noted value, \( 1.4 \times 10^{-24} \). Above this value of this constant, NiS will precipitate as a solid. In the process of the present invention, precipitation of all metal sulfides less soluble than the replacing sulfides is caused, rather than prevented, as was previously done.

It is also a principal feature of the present invention that an added reducing agent is used, with the added metal sulfide, in the replacement reactions. Thus, an acid salt solution being treated with an added metal sulfide, such as iron sulfide, is simultaneously subjected to the action of a reducing agent. It is believed, although once again not intending to limit the invention to any particular theory of operation, that this tends to reverse the oxidation reactions, such as that of Equation 4 above, and thereby increases the sulfides ion concentration in solution. In this way, by suitably controlling additions, the replacement reactions may be controlled to completely precipitate sulfides of any, or all, of those metals the sulfates of which are in solution, but the sulfides of which are less soluble than the replacing metal sulfide, i.e., FeS, i.e., have a lower \( K \) value than does the latter.

The application of these principles of the process of the present invention is believed to be well illustrated in Figure 1. As shown therein, an ore concentrate is treated. Such concentrates, ordinarily, form the feed material for the process of the present invention. They may have been obtained by froth flotation, gravity separation, or any other conventional method, wherein a bulk of the gangue constituents is eliminated.

For purposes of illustrative discussion, it may be considered that the representative ore concentrate is one which contains nickel, cobalt, zinc, and manganese only. Other constituents, such as silver, lead, molybdenum and the like, will no doubt be present, at least in small amounts. However, the amounts thereof are either small enough to be discarded economically or their treatment will be shown by one of the illustrative metals. This will depend on whether, like manganese, the sulfides are more soluble than FeS or, like copper and zinc, the sulfides are less soluble. These facts being true, it simplifies the further discussion of the present invention to consider the problem as if these additional metals were not present. After the discussion has been developed, it is believed that treatment for any one of these particular sulfides, if desirable, will have been clearly indicated.

An ore concentrate of the above-noted illustrative nature is first sent to some type of leaching system. The invention is not particularly concerned with the arrangement of the leaching operation and apparatus. It is quite possible to adapt the overall process to any of the various acid, sulfate and ammoniacal leaching systems or procedures which are now well known.

However, it will be brought out that the replacement reaction of the present process is initiated, and usually is carried out, in an acid solution. For other than acid leaching, therefore, adjustment of the pH of the leaching solution must be carried out before the replacement reaction is carried out. The latter must be done on a solution of soluble salts, preferably the sulfoates. Therefore, while sulfoates, or some other equivalent salt, are readily formed in solution after leaching, regardless of the exact leach liquor used, acid sulfate leaching is usually the most desirable and will be generally taken as being illustrative in the following discussion.

Whatever the leach liquor used, it is added to the ore concentrate in the leaching system. In Figure 1, as noted, this is shown as an acid leach liquor. Preferably, but not necessarily, air or oxygen or oxygen-enriched air is blown through the mass being leached. The acid sulfate leach liquor, the use of which is illustrated in Figure 1, is also preferably, because it is adapted to the treatment of a greater variety of non-ferrous metal ores, including both sulfides and oxidized metal minerals.

Specific details of the leaching operation are not an essential feature of the process of the present invention. Leaching is carried out in some known manner, according to conventional practice. Usually, but not necessarily, it is carried out at elevated temperatures. An acid leaching with concomitant oxidation is highly exothermic. Due to the preferred use of air or oxygen, it is therefore preferably carried out under increased pressure. Conventional apparatus is usually available for the purpose.

The discharge from the leaching system properly comprises a slurry. The latter will contain undissolved solids, principally gangue, and a solution of salts of the minerals values. As shown in Figure 1, this slurry is filtered to remove the residue. The latter is principally gangue and, in the case of Figure 1, an acid-insoluble gangue. If such metals as lead, whose sulfates are insoluble in the leaching solution, are also present in the ore concentrate, these will be removed with this residue. This residue, normally, is sent to waste. Various circulating systems, to insure against metal losses in the leaching steps, are conventional.

Although, as noted above, acid leaching is preferred, if a basic leaching system is to be used, the pregnant leach liquor, ordinarily, will be converted to the acid side of the leaching reaction. While a replacement reaction may be carried out in a basic circuit, such a procedure will, ordinarily, involve a considerable amount of additional apparatus, require additional reagents and very appreciably complicate filtration. Accordingly, replacement, as noted above, is preferably carried out in acid solution. Acidification for this or other reasons may be carried out, either before or after filtration. Since the illustrative case in Figure 1 is not in-
volved in basic leaching, this specific modification is not shown. It is believed that its operation and practice is clearly apparent from the foregoing.

Acidification, if necessary, may be accomplished by the direct addition of acid. Preferably, however, it should be done by using the basic pregnant leach liquor as a menstrum to carry out a supplementary leaching, with additional amounts of sulfide ore. In this way, neutralizing acid may be formed in situ. This latter process is shown in the copending application for United States Letters Patent, Serial No. 97,286, filed June 4, 1940, by Patrick J. McGauley, one of the present inventors, now Patent No. 2,647,822, issued August 4, 1953.

As shown in Figure 1, the metal values are now present in the filtrate as a solution of soluble sulfates. This solution is sent to the primary replacement reaction. Here, as noted, it is treated with the metal sulfide and a reducing agent. Replacement may be carried out in any suitable vessel, equipped to carry out chemical reactions under pressure. In the illustrative case, the solution of Cu, Co, Ni, Zn and Mn sulfates is treated with added iron sulfide. As shown in Figure 1, this is preferably from some separate source as fairly concentrated FeS. However, as also shown, if so desired an equivalent amount of the same ore concentrate fed to the leaching system may be used. In some cases, it may be desirable to use a mixture, partly ore concentrate and partly FeS from some such separate source, such as pyritic iron ore.

Whether used from a separate source of iron sulfides, or as part of the ore concentrate, or as a mixture, there must be available iron and available sulfur present. In the process of Figure 1, the total amount of added iron and sulfur must be at least slightly in excess of the theoretical equivalents required to precipitate sulfides of all the replaceable metals whose sulfates are in the pregnant leach liquor.

Ordinarily, the reaction will be carried out at elevated temperatures. Usually this will be in the range from about 275-750° F. While higher temperatures may be used, there is no particular advantage in so doing. While the lower temperature range places the least restrictions on the apparatus at the lower temperatures, considerably longer periods are required. If an oxidizing acid leach is used, the reaction is exothermic. Also, there is no trouble in obtaining the elevated temperature which is preferable in the replacement reaction. The sulfates solution, coming to the replacement reaction, is already hot. If additional heat is required for further temperature rise, it is readily available from the waste heat of the apparatus, that is ordinarily removed by blowing steam from the oxidizing leaching system, to prevent the temperature of the latter from becoming too high.

For the same reason that elevated temperatures are preferred, apparatus equipped for agitation is also desirable. It is not essential to successful operation. However, in general, a replacement vessel should be carried in one and one-half to two hours at about 450° F. Without violent agitation, can be carried out in about one-half hour, at the same temperature, if the pressure vessel is equipped for additional agitation of its contents.

Supplementing the action of the added solid sulfides is one of the critical features. For this purpose, as noted above, an additional reducing agent, preferably a gas, is used. Subsequently any available reducing gas may be made to serve the purpose. Carbon monoxide, sulfur dioxide and the like, may be used, for example. Hydrogen, is, perhaps, even better, as it is an excellent supplement to the hydrogen sulfide which is always liberated during the replacement reactions. Mixtures of carbon monoxide and hydrogen are found in various industrial gases, and are usually the most economical and the most readily utilized. Hydrocarbons, such as methane and ethane, may be used. However, their use alone is not too desirable, because, in some cases, they appear to form complex ions with some of the metals. Their presence, or interference of sulfur-bearing gases, as part of an otherwise desirable and available gas mixture, does not appear to be harmful, in this respect.

The actual consumption of reducing agent is comparatively small. It is necessary only to maintain sufficient concentration to retard or reverse the tendency toward completion of oxidation reactions, such as that discussed above. For this reason, if desirable, or necessary, other and less expensive reducing agents may be used. For example, methyl and ethyl alcohol may be used for the purpose. Formic acid, oxalic acid and the like, formaldehyde in its various commercial forms, and as its sulfoxylates, serve the purpose. Ordinarily, however, the use of a gas will be found more desirable, physically and economically.

Treatment with the added reducing gas, or other agent, and the iron or other metal sulfides is continued until substantially all of the precipitatable sulfides less soluble than the treating sulfide, i.e., the FeS, have been precipitated. The resultant slurry is filtered, as shown in Figure 1. The filtrate is ordinarily removed from the system as an iron discard. The iron, which will be principally present as ferrous sulfate, is, in the illustrative case, the principal diluent metal.

In addition, this solution will contain sulfates of those metals whose sulfides are equally, or more, soluble than FeS. In the illustrative case, these metals are represented by the manganese. When they are present in the ore, the filtrate, therefore, will also include such values as, for example, magnesium, aluminum, chromium and the like. These are minor constituents and are present in very small amounts. The current practice in treating these ores is to discard these minor fractions. There is no reason why this practice should not be continued in the operation of the present invention, unless an exceptional ore is found. In the latter case, the content of manganese or molybdenum or the like may be sufficiently high as to warrant special treatment.

The presscake from this filtration will contain any slight excess of iron sulfides over that required to precipitate the less soluble sulfides. In addition, it will contain sulfides of all the metals the sulfides of which are less soluble than FeS. In the illustrative case, these will be the sulfides of copper, nickel, cobalt and zinc. While this mixture of sulfides will contain some iron sulfide, as did the original ore concentrate, the proportions are entirely different. The small amount of iron remaining is readily removed.

One additional feature noted in Figure 1 may be considered. In some cases, the leaching operation may not produce a solution in which the ratio of other metal sulfates to iron sulfate is sufficient to meet the requirements of the process. If so, a part of the presscake from the filtration may be diverted and
returned to the leaching system to supplement the valuable metals content of the ore concentrate being fed thereto. In this way, the solution from the leaching operation may be given any desirable ratio of valuable metals to iron. It is found that from about 5:1 to about 20:1, as ratios in solution, is a good general practice.

As will be seen from the foregoing discussion, replacement by means of the added metal sulfide and the reducing agent can be used to separate the metal values sulfides substantially completely from the diluent metals and gangue in the original ore. In some cases, it may be desirable to insure complete precipitation without having present these slight excesses of the metal having a sulfide of sufficient solubility to be used in the replacement. In the process of Figure 1, if such complete precipitation is carried out, the concentrate will necessarily contain the excess unreacted replacement sulfide. However, instead of having a metal sulfide to precipitate metals with a ratio of 1:1 or lower, as frequently found in an original ore concentrate mixture, the product sulfides mixture is now substantially free from iron.

When, as noted, it is desirable to have this mixture completely free from replacement sulfides, this is accomplished by the flowscheme shown in Figure 2. As shown therein, the result is accomplished by using two replacement reactions. In the first, slightly less than the amount of added more soluble metal sulfides than is stoichiometrically required to replace all the other less soluble sulfides is used. Precipitation will then cease when the iron or other replacement sulfide is used up, rather than when the less soluble sulfides of the replaced metals are completely precipitated. The so-replaced sulfides, free from replacing sulfide, which, in the illustrative case means free from iron, may then be collected in any desired manner, as by filtration.

As shown in Figure 2, the remaining solution is then subjected to complete precipitation with an excess of added metal sulfide, i.e., iron sulfide. This second, or supplemental, replacement produces a sulfides concentrate which is small in amount and contains added metal sulfides as well as replaced metal sulfides. This concentrate is collected and is either recycled to the leaching operation, or added with the slurry coming into the primary replacement stage. The latter operation is, perhaps, simpler.

It might appear that, after stripping the sulfides with a deficiency of soluble metal sulfide, and removal of the desired sulfides concentrate, the residue could be returned directly to the replacement reaction which, in Figure 1, is designated as a primary operation. This cannot be done, because, except in special circumstances, such a practice would build up an excess of dissolved iron sulfate, or its equivalent, in the replacement circuit.

While the practice of the process of Figure 2 is practical, it is, of course, much simpler, and will presumably be considerably more valuable than the mixed sulfides by using a slight excess of iron sulfide, or its equivalent, as in Figure 1. The resultant small amount of iron sulfide contaminant is readily removed later. This was noted above and will be explained more fully below.

A second principal operation of the present invention operates in the separation of the sulfides mixture concentrate into its component sulfides. Commercially, of course, any process which cannot accomplish this result is not particularly useful. In the past, little helpful information has been available as to processes suitable for the purpose. In general, they were largely confined to two fields, fractional crystallization and selective leaching.

A substantially complete solution of all the recoverable metal values in a concentrate is almost a requisite for economical operation. Unfortunately, such a mixture of constituents, as is found in most sulfide flotation concentrates, is completely dissolved only by means of acid or acid-ferric sulfate leaching, generally with oxidation as an added requirement. This is the operation preferred in the present invention. Pregnant leach liquor so-obtained can, and often will, contain, for example, iron, copper, cobalt, nickel, manganese, zinc, molybdenum, silver, arsenic, tin, bismuth, calcium, magnesium, selenium, sodium chloride and other minor items.

Discounting the iron, which in copper recovery is usually a diluent, metal values of copper, nickel, cobalt, and possibly silver, zinc, and lead, are the only constituents likely to be present in amounts which warrant an attempt at their recovery by the present process. As noted above, the remainder is usually present in small amounts and, in general, may be discarded. If, occasionally, one or more of these constituents is present in industrially-recoverable amounts, a special circuit can be set up for it.

Otherwise, in the practice of the present invention, the custom used in the present industry of discarding these minor constituents is generally followed.

Reverting to the pregnant leach liquors, the illustrative valuable metal constituents are in solution as soluble salts, generally as sulfates. Unquestionably, the solubilities of these salts is such that little, if any, benefit can be obtained by attempting to separate them by fractional crystallization. Particularly is this true in the ratios in which they are usually present in the pregnant leach liquors. Industrially, very little has been accomplished in this field, principally because of the obvious limitations.

The other alternative, selective leaching, can be successfully carried out under certain conditions. Using very carefully controlled leaching on highly suitable ores, those ores containing only metals whose sulfides differ widely in solubility and in amount, selective leaching can be employed. Again, unfortunately, such suitable ores are not common. Further, the careful leaching conditions are difficult to establish and to maintain. Even more unsatisfactory, complete leaching of all the valuable metal constituents is seldom, if ever, possible.

It is, therefore, no small feature of the present invention that it may be readily employed to separate such a sulfides mixture as is produced by the processes of Figures 1 and 2, into its components. This is done by properly controlled replacement. An illustration of its use is shown in Figure 3 of the accompanying drawings. The reference to the procedure shown in Figure 3, as noted, indicates the operation being carried out on a mixed slurry. Since, in Figures 1 and 2, a specific mixture was discussed for illustrative purposes, the same mixture will be discussed throughout the remainder of this specification. The material to be treated, illustratively, according to the process of Figure 3, is the same mixed
slurry containing unreacted iron sulfide which is obtained by the preferred operation shown in Figure 1, above.

This slurry is subjected to an acid oxidation. For this purpose, the slurry is combined with a suitable acid, preferably sulfuric acid, since this sulfate is a desirable salt, and subjected to oxidation by blowing therethrough air, oxygen, or oxygen-enriched air. The reaction is carried out, preferably, in the manner used in the conventional oxidizing acid leaching process. It is carried out under pressure at an elevated temperature of about 250–750°F. Since the reaction is exothermic, there is no difficulty in obtaining either the pressure or the temperature. Usually, it may be necessary to bleed steam from the operation, in order to prevent excessive temperature and pressure loads upon the apparatus. The lowest practical temperatures and pressures are preferable, as they decrease corrosion problems in the apparatus. The resultant solution of soluble sulfates is also filtered to remove any insoluble residue. Ordinarily, this will only result in the removal of discardable waste material. In some cases, however, the preextraction may contain a small amount of the material which is desirable to recover. Usually, this is due to incomplete oxidation in the preceding step. In such cases, the residue is readily passed back to the oxidation step, or, as shown in Figure 3, to the leaching system.

The resultant filtrate is subjected to the first of the actual sulfide separating operations. In Figure 3, this is designated as the CuS replacement. It is accomplished, preferably at about 250–450°F, by treating the filtrate in a suitable vessel with some metal sulfide which is more soluble than copper sulfide. Again, for illustrative purposes, as shown in the drawing, this is considered to be iron sulfide. In the actual operation, it will be iron sulfide per se, in most cases, because of the large amounts readily available from pyritic iron ores. It may be one concentrate, if necessary or desirable. An amount stoichiometrically equivalent to the available copper in the filtrate is added thereto. Replacement continues until precipitation of the copper sulfide is substantially complete.

Solubilities of various metal sulfides is markedly affected by the acidity of the solution in which it is attempted to dissolve them. In the present case, it is desirable to completely precipitate copper sulfide, while maintaining in solution all the other metal sulfides. The resultant iron sulfide should also be retained. At a pH above about 2.7–3.0, other metal sulfides, such as cobalt and/or nickel sulfides, tend to precipitate with the copper, and a pH of about 2.7 is, therefore, about the maximum desirable limit and 3.0 is about the limit permissible for suitable operation. On the other extreme, too high a concentration of acid makes it difficult to precipitate copper sulfide. About 18% acid content in solution is approximately the highest acidity which is desirable in this circuit.

Since it is undesirable to precipitate additional sulfides in this particular step; in fact, to the contrary, it may be desirable, and it is quite feasible to remove small amounts of ferrie sulfide to prevent other metal sulfides from being precipitated with the copper; it is apparent, then, that in this one step, the added reducing agent is not necessary. However, added metal sulfide is used in usually substantially sufficient amount to insure, in and of itself, replacement and precipitation of all the copper as copper sulfide. This is collected as product, as shown in Figure 3.

The filtrate, remaining from the removal of the copper sulfide, is passed to the second of the sulfides separation operations. As shown in the table of the solubility products, above, the next least soluble sulfide, in the illustrative case, is that of cobalt. Accordingly, it is recommended to be removed. As discussed above, complete precipitation are in the pH range of about 3–5. Under favorable conditions, this range may be increased to 2–5 or 2–5.5.

Reduction in the acid content of the solution to the requisite pH may be carried out in any desired manner. Probably the most simple method is the addition of aqueous ammonia, or an equivalent base, which will not cause precipitation of insoluble metal salts. However, it is usually much more economical to use a solution of some similar alkaline-earth metal oxide or hydroxide. In the latter cases, however, the resultant insoluble alkaline-earth metal sulfate must be removed to prevent contamination of subsequently-precipitated metal sulfides. To illustrate this point, there is the operation shown in Figure 3. At the end of the copper precipitating period, the copper sulfide is filtered out, lime is added to the filtrate, and the resultant calcium sulfate precipitate is filtered out. The calcium sulfide may be discarded.

Iron sulfides, as the illustrative added sulfide, are then added in equivalents to the cobalt sulfide, the equivalent sulfide of which is to be precipitated. Replacement is carried out until precipitation substantially ceases. Again, the slurry is filtered and the cobalt sulfide is collected.

In a similar manner, subsequent replacement operations are carried out to successfully precipitate sulfides of the remaining dissolved metal salts, i.e., those of nickel and zinc, in the illustrative case. The most favorable pH conditions for replacement of the nickel sulfide is believed to be about 5.0–6.2. Zinc sulfide is most readily precipitated at a pH of from about 6.2 to approximate neutrality. Care should be taken not to pass the precipitation reaction at the basic side of the pH range at this stage. If such precaution is not taken, it will be found that iron sulfide is not soluble. The replacement, using iron sulfide therefore, is ineffective.

Because definite pH limits to be used in the present process have been specified, does not necessarily mean that a sulfide replacement for any one metal cannot be carried out at other pH ranges, particularly when other metals are not present. The ranges indicated here are those which have been found suitable for the separation operations. Also, it should be noted that the reaction is being carried out under reducing conditions. Therefore, where the metal sulfides or sulfides being precipitated are of a metal or metals commonly exhibiting differing valences, all or a part of the precipitated sulfides may be of the metal or metals in their reduced form.

The final filtrate, which may contain some small amounts of metal values, usually is of insufficient economic value to warrant further treatment. Air, oxygen, or air ordinarily, sent to discard, as shown in Figure 3.

Again, it should be noted that, as discussed above, the illustrative case is limited to certain metals. Others may possibly be present in sufficient amount to be economically recoverable. In
that case, a separate circuit, therefore, should be set up, utilizing the principles disclosed with respect to the illustrative metals.

In the above discussion of Figure 3, purity of the precipitated sulfide depended upon using stoichiometric quantities of iron sulfide. As a practical matter, this is somewhat difficult to control. A slight deficiency in the amount of iron sulfide to be used to precipitate a different, particular sulfide, such as that of copper, has two effects. Copper will be precipitated as pure copper sulfide; unfortunately, however, not all the copper is precipitated, and this residue is passed into the next stage and becomes a contaminant of the sulfide to be precipitated therein. This is shown in the illustrative case of the cobalt sulfide. Similarly, in each succeeding step, there is danger of carrying over unprecipitated, potentially precipitable, metal, which will become a contaminant in attempting to recover the next sulfide to be separated.

On the other hand, the use of a slight excess of added sulfide allows the theoretical equivalents required has an entirely different, but equally undesirable, effect. The excess metal sulfide, not being reacted, remains as a solid in the slurry, and reports as a contaminant in the same precipitation step. Either result is to be avoided, if possible.

By slight modification of the circuit, this difficulty is readily overcome. Such a modification, as it is to be applied to the illustrative case, is shown in Figure 4. As indicated therein, a mixed sulfates solution, such as that obtained from the oxidation and filtration at the outset of the process of Figure 3, serves as starting material. This solution is then subjected to the first of a plurality of copper sulfide precipitations. In the first, a deficiency of iron is used. As a result, incomplete precipitation of copper sulfide is obtained. However, the precipitated sulfide so obtained comprises substantially all the copper, and it is substantially pure, i.e., substantially free from other metal sulfides. This precipitate is filtered out and recovered as copper sulfide product.

The filtrate, containing the remaining metal values, and the small amount of unprecipitated copper, is then given a second treatment to precipitate the copper. In this second treatment, a slight excess of iron sulfide is used. This precipitates all the residual copper sulfide as copper sulfide which is contaminated with the unreacted excess iron sulfide. It does not, however, constitute loss, because, as shown, the solids can be recovered by filtration. The collected mixed sulfides, small in amount, are recirculated as part of the solids fed to the first copper sulfide precipitation.

As a result, the second filtrate is then reduced to a pH suitable for the precipitation of the next insoluble sulfide. As shown in the drawing, aqueous ammonia is used for this purpose, although, as discussed above, as a practical matter, it will usually be cheaper to use lime, burned dolomite, or the like, and a second filter. Ammoniacal matter in this drawing is introduced in order to simplify the discussion. The pH-increased solution is treated to obtain a first cobalt sulfide precipitate, using a slight deficiency of replacement sulfide over the theoretical requirements. At the same time, as in the foregoing discussion, a reducing agent is used. The resulting precipitate of pure cobalt sulfide is collected by filtration.

The filtrate, containing a small amount of cobalt, is given a second cobalt replacement; and, as in the case of copper, the remaining sulfide is precipitated and collected in a precipitate slightly contaminated with ferrous sulfide. As was the case with the second copper sulfide precipitate, this second cobalt precipitate is returned as part of the solids fed to the first cobalt sulfide replacement. In this way, as was the case of the copper, all the desired metal sulfides eventually report as a sulfide free from both different metals sulfides, sulfides of the metal values having a lower or a higher solubility than the desired sulfide, and from soluble salts.

While the succeeding steps, in which nickel sulfide and zinc sulfide, in the illustrative case, are not indicated in Figure 4, it is believed that their operation is apparent. These can be carried out in the same way, modifying the nickel sulfide replacement into two stages, and the zinc sulfide replacement into two stages. The final filtrate, after the zinc sulfide replacement, is again discarded.

In accordance with the present invention, sulfides other than iron, together with reducing gas, may be used to replace those metals whose sulfides are less soluble than that of the replacement metal. Illustrative examples may be found in the following representative equations:

\[
\begin{align*}
(5) & \quad \text{NiS} + \text{CuSO}_4 = \text{NiSO}_4 + \text{CuS} \\
(6) & \quad \text{ZnS} + \text{CuSO}_4 = \text{ZnSO}_4 + \text{CuS} \\
(7) & \quad \text{ZnS} + \text{CdSO}_4 = \text{ZnSO}_4 + \text{CdS}
\end{align*}
\]

Reactions such as those illustrated above may be employed to perform the replacement and separation of separate sulfide products from sulfate solutions, in accordance with the present invention. This may be done in one of several ways. The replacement, or replacements, may be carried out on solutions obtained in other processes, or they may be carried out on solutions made expressly for the purpose. Preparation of the latter has been fully illustrated above.

It should also be noted that, in the operations discussed above as illustrative, stoichiometric quantities of iron sulfide were reacted with the sulfates solution. Only the metal with the most insoluble metal sulfide is precipitated and filtered off. The acidic conditions were maintained at the most favorable range for the process. The solutions were then treated successively with additional quantities of iron sulfide and additional quantities of reducing agent, thereby successively separate metal sulfides were replaced. This is repeated until the desired separations are accomplished.

A differing, and in some cases preferable, procedure is shown in the drawings in Figure 5. In the latter procedure, the metal sulfides mixture, instead of being dissolved, as in Figure 3, is divided into two portions. Only one part is oxidized to convert the metal sulfides into dissolved soluble salts, as was done with the whole sulfides mixture in the process of Figure 3. The remaining portion is filtered and the presscake or residue is discarded, exactly as was done in Figure 3. The filtrate, however, receives a distinctly different treatment.

Rather than using iron sulfide to replace the valuable metal constituents, as mixed sulfides, the untreated portion of the sulfides mixture is used to treat the filtrate as the replacing metal sulfide. The filtrate, containing copper, nickel, and zinc, is sent to the first copper replacement. Therein, as shown in Figure 5, a
mixed metal sulfides portion, taken out as noted above, is taken of sufficient weight to have a cobalt plus nickel plus zinc content slightly deficient to the equivalents of available, replaceable copper in the filtrate. Replacement is carried out with these mixed sulfides, exactly as was done with iron sulfide, in Figures 3 and 4. The resultant slurry is filtered and the presscake from the filtration step is the substantially pure copper sulfide product.

Filtrate is then treated with enough more of the divided-up sulfides to provide a cobalt plus nickel plus zinc total slightly in excess of the remaining copper. In this reaction, the second copper sulfide replacement, the remaining available copper is precipitated. As in Figures 3 and 4, there will be precipitated therewith, the slight excess of mixed sulfides which are unreacted. Slurry is filtered, and the mixed sulfides are returned as part of the feed to the first copper replacement, exactly as was done in the process of Figure 4. In this way, eventually all the copper reports in the pure copper sulfide fraction, and all the other metals continue into the subsequent treatments.

The filtrate, after the removal of copper sulfide and the mixed sulfides, is divided into two portions. Each portion is treated in a manner analogous to that used in the copper precipitation. One portion is used to obtain the replacement sulfides to be used in the next step. The remainder is used as the solution, from which the next most insoluble sulfide is replaced. In the illustrative case, therefore, the next step, as was true in Figure 4, is the removal of cobalt.

The first portion of the divided filtrate is sent to a separate replacement operation. Here, it is treated with additional quantities of iron sulfide and a reducing agent, as shown in the drawing this is a gas, and enough is used to convert the total cobalt, nickel, and zinc in solution to insoluble sulfides. Iron sulfide, for example, is taken as illustrative, because it is usually the most readily-available cheap sulfide for the purpose. Any other available sulfide may be used. It must, however, be able to replace less soluble, but desirable, metal sulfides.

In general, it is best to use a very slight deficiency of the iron sulfide. This is done to insure freedom from excess iron sulfide in the replaced precipitate. If so desired, an arrangement such as that shown in Figure 4 may be used to prevent loss. Otherwise, the minor amount of unperturbed cobalt, nickel, and zinc, may be discarded with the iron sulfide. The resultant precipitate of cobalt, nickel, and zinc is collected by filtration. Being free of both iron and copper, it is used as a replacement sulfide in treating the other portion of the filtrate to precipitate the cobalt.

The amount of sulfides mixture used for this purpose should have a nickel plus zinc content at least equivalent to the cobalt in solution. The solution is reduced in pH acidity to the approximate value, as was discussed above. As was also noted above, this may be done most economically by using lime, or other alkali-earth oxide or hydroxide and an extra filter. However, to simplify the flowsheet, the extra filter has been omitted, and ammonium hydroxide has been used as the neutralizing agent. It is desirable to have the reducing agent at this stage, as was noted above, in connection with the process of Figure 3 and Figure 4. The resultant slurry so obtained is filtered. Due to the use of a slight deficiency of replacement sulfide, a substantially pure cobalt sulfide product is obtained. Again, the filtrate is treated with a slight excess of the mixed nickel and zinc sulfides. The resultant precipitate of cobalt sulfide, as was the second copper precipitate, is recycled to the first cobalt sulfide replacement.

The filtrate, which will then be cobalt and copper free, is passed to succeeding treatments, as shown in Figure 5. In each succeeding stage, the same general procedure is followed. The filtrate is divided into two portions. One is treated with an extraneous sulfide, such as that of iron, to obtain precipitating sulfides; and the remaining solution is treated to obtain the product sulfide. It is believed that these successive treatments are apparent from the foregoing discussion. There should be sufficient zinc available in this way to precipitate the nickel. This is indicated in the case of the mixture being taken as illustrative. Since the solution, after removal of the nickel, in the illustrative case, will contain only zinc, and zinc cannot be readily precipitated with zinc, some additional sulfide must be used for the removal and collection of the latter. Again we prefer the iron sulfide. However, it is not necessary that it be used. Especially at this stage, the solution is approaching neutrality. There is no reason why other sulfides, such as sodium sulfide, could not be used to replace the zinc sulfide.

As was noted above, replacement can be carried out in basic solution, if so desired. In such a case is sodium sulfide, potassium sulfide, or the like, which can be used as the replacement metal. By such a procedure, for example, it is possible to precipitate manganese sulfide from the ferrous sulfate liquor obtained in the earlier stages of the process. It is believed that, from the discussion of the principles of this case, there will be no difficulty in setting up a circuit for this purpose, if so desired. Such a circuit, for example, is highly convenient if it is necessary to recover a small amount of gold from the system. The gold sulfide is most readily precipitated from basic solution.

We claim:

1. A method of treating an ore concentrate, containing (a) a plurality of non-ferrous metal values, (b) acid-insoluble gangue and (c) at least one diluent metal, including the steps of subjecting the ore concentrate to a leaching operation, whereby substantially all the non-ferrous metal values and at least part of the diluent metal are dissolved as soluble salts in aqueous inorganic acid solution, removing the residual undissolved solids and precipitating from resultant solution at least one non-ferrous metal value as an insoluble sulfide thereof; the improvement which comprises: treating said slurry in a primary replacement under acid conditions simultaneously with (a) at least one replacement metal sulfide, the solubility of the least soluble replacement sulfide, at the replacement acidity, being not substantially greater than that of at least one non-ferrous metal value to be precipitated but not greater than that of the sulfide of any diluent metal, and (b) reducing agent in sufficient amount to insure substantially no oxidation of sulfide ions to free sulfur, whereby at least one dissolved non-ferrous metal is precipitated as metal sulfide; continuing treatment until non-ferrous metal sulfide precipitation substantially ceases and collecting resultant sulfide precipitate.
2. A process according to claim 1 in which said ore concentrate and resultant solution both contain at least one diluent metal and said replacement sulfide is added in slight stoichiometric deficiency to the dissolved non-ferrous metal to be precipitated.

3. A process according to claim 1 in which the reducing agent comprises a gas selected from the group consisting of hydrogen, carbon monoxide and mixtures thereof.

4. In a method of treating an ore concentrate containing (a) a plurality of non-ferrous metal values, including copper, (b) acid-insoluble gangue and (c) at least one iron sulfide, including the steps of subjecting the ore concentrate to a leaching operation whereby substantially all the non-ferrous metal values and at least part of iron are dissolved as soluble sulfates in aqueous sulfuric acid solution, removing the residual undissolved solids and precipitating from resultant solution at least one non-ferrous metal value as an insoluble sulfide thereof; the improvement which comprises: treating resultant clarified solution in a primary replacement under acid conditions simultaneously with (a) an iron sulfide and (b) a reducing agent in sufficient amount to insure substantially no oxidation of sulfide ions to free sulfur; continuing the treatment until non-ferrous metal sulfide precipitation substantially ceases and collecting resultant sulfide precipitate.

5. A process according to claim 4 in which said non-ferrous metal sulfide precipitation is carried out at a pH less than about 3 but an acid content of less than about 15% by weight.

6. A process according to claim 4 in which iron sulfide as the replacement sulfide is utilized in slight excess over the stoichiometric equivalents required to precipitate all the non-ferrous metal sulfides less soluble than FeS.

7. A process according to claim 4 in which the replacement iron sulfide is added in slight stoichiometric deficiency to the amount required to replace all the non-ferrous metal sulfides less soluble than FeS; treatment is continued until all the added iron sulfide is in solution; resultant iron-free precipitated solid sulfides are collected; residual solution is treated with a stoichiometric excess of added iron sulfide; treatment is continued until precipitation substantially ceases, whereby a second sulfides precipitate is obtained, and said second sulfides concentrate is collected.

8. A process according to claim 7 in which said second sulfides concentrate is recycled as feed to said primary replacement.

9. In a method of treating an ore concentrate, containing (a) a plurality of non-ferrous metal values, (b) acid-insoluble gangue and (c) at least one diluent metal, including the steps of subjecting the ore concentrate to a leaching operation whereby substantially all the non-ferrous metal values and at least part of the diluent metal are dissolved as soluble sulfates in aqueous sulfuric acid solution, removing the residual undissolved solids and precipitating from resultant solution at least one non-ferrous metal value as an insoluble sulfide thereof; the improvement which comprises: treating resultant clarified solution in a primary replacement under acid conditions simultaneously with (a) a stoichiometric equivalent to dissolved non-ferrous metal values of at least one replacement metal sulfide, the solubility of all replacement sulfides, at the replacement acidity, being greater than that of the sulfides of all non-ferrous metal values to be precipitated but not greater than that of any diluent metal, and (b) a reducing agent in sufficient amount to insure substantially no oxidation of sulfide ions to free sulfur, whereby substantially all dissolved non-ferrous metals are precipitated as mixed metal sulfides; continuing treatment until non-ferrous metal sulfide precipitation substantially ceases; collecting resultant mixed sulfides precipitate; and subjecting collected mixed sulfides to oxidation in the presence of free inorganic acid, whereby said sulfides are converted to a substantially diluent metal free solution of mixed dissolved non-ferrous metal salts.

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