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RECOVERY OF METAL VALUES FROM
COMPLEX ORES

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18 Claims. (Cl. 75-105)

This invention relates to the recovery of metal values from complex ores, and relates particularly to the recovery of copper, zinc, lead, iron, silver and gold metal values from complex ores.

The complex ores, here under discussion, are those that contain two or more metal values in chemical union or in such physical union as to prevent normal mechanical separation of the values. The complex ores include metal values such as copper-iron sulphide, zinc-iron polysulphide, zinc-copper polysulphide, zinc-copper-iron trisulphide, lead vanadate, lead chromate, lead molybdate, lead tungstate, lead silicate, and lead compounds combined with other acidic radicals, and also possibly other complex sulphides. The ores under discussion also include simple compounds such as zinc sulphide, copper sulphide, iron sulphide, and lead sulphide uncombined chemically with other sulphides, and include also gangue, dirt and other insolubles.

In the past, attempts have been made to extract copper, zinc and lead values from such complex ores by a selective concentration of one of the ores and a subsequent smelting to recover the particular value desired. Such a procedure has several major disadvantages. First, the ability to concentrate a complex ore by standard gravity or oil flotation methods does not meet with much success inasmuch as such processes are advantageous only in separating the simple sulphides from each other (such as copper sulphide from zinc sulphide), but cannot separate each of the metal values in the double sulphides, the triple sulphides or other complex compounds above mentioned. The concentrate, when shipped to the smelter, thus contains, in addition to the particular metal sought (for example, zinc), substantial amounts of other values such as copper and lead, and since the smelter is designed to process a particular metal, the shipper does not get paid for these other values (with the exception of gold and silver). In fact, if the lead or copper content in a zinc concentrate is above a certain point, penalties for their presence would be exacted by the smelter.

The average assay of so-called zinc and lead selective concentrates for the Western States in recent years, as produced by standard oil flotation methods, are given in Table I.

TABLE I
Average assay of selective concentrates

Element	2,000 lbs. of Zinc Concentrates	2,000 lbs. of Lead Concentrates
Gold.....oz.....	0.05	0.43
Silver.....oz.....	3.54	25.74
Copper.....percent.....	1.48	2.74
Lead.....do.....	1.69	41.
Zinc.....do.....	51.37	8.39

It will be seen by studying the above table that substantial amounts of copper and lead values are present

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in the zinc concentrates, while substantial amounts of copper and zinc values are present in the lead concentrates. In addition, generally both zinc and lead concentrates have approximately 10% of iron therein. It can thus be seen that because of the other metal values invariably present, a process which involves the steps of first "selectively" concentrating an ore for a particular value, and then smelting to obtain that particular value, is both inefficient and uneconomical.

The process of selectively concentrating such complex ores is in itself a relatively inefficient mode of recovery in comparison with that of making a collective concentrate of the values. Thus, it is found that a 15-20% increase in the recovery of lead, zinc, copper, gold and silver values is possible by collectively concentrating the ore for the various values, instead of attempting to selectively concentrate the ore for a particular value.

There are still other disadvantages to the smelting operation itself, chiefly those of the high cost of processing and the high investment per pound of metal recovered. For all of the above reasons, the winning of copper, zinc, lead, gold, silver, and iron values from such complex ores as above described, has, in general been commercially unsuccessful.

Complex ores treated by the orthodox method outlined above, that is, by smelting a selective concentrate of each of the metal values results, on the average, in approximately 40-50% recoveries of copper and approximately 60-70% zinc recoveries.

Attempts at achieving some measure of separation by other means, such as by grinding, have also been unsuccessful since the metal values are usually crystallized in such minute particles that grinding to the degree of fineness required to actually achieve separation, is very costly and economically prohibitive.

Wet processes, that is, those involving leaching operations after a roasting operation, have also not been successful recovering zinc, copper, lead values from such complex ores regardless of whether the ore is first selectively concentrated or collectively concentrated. Approximately 60-80% of the total amount of zinc and approximately 40-50% of the total amount of copper present in such complex ores can be recovered by orthodox wet processes.

The loss of zinc and copper in both smelting and wet processing appears to be due to the formation of certain highly insoluble zinc and copper compounds.

Bearing in mind the foregoing, it is a major object of the present invention to provide a process whereby substantially complete recovery of copper, lead, zinc, silver, gold and iron values from their complex ores can be obtained in a manner that is simple in operation and inexpensive in comparison with both wet and smelting processes of the prior art.

Another object of the present invention is to provide a process for the recovery of metal values from complex ores of the class described, wherein a bulk or collective concentrate of the metal values of the complex ores is first produced.

A further object of the present invention is to provide a wet process for the recovery of the above-named metal values from complex ores which includes steps for eliminating the formation of highly insoluble metal compounds whereby substantially complete recovery of the metals is obtainable.

A further object of the present invention is to provide a process for the substantially complete recovery of metal values from complex ores which comprises the steps of first collecting a bulk concentrate of the metal values to be recovered, second, preliminarily roasting the bulk concentrate at low temperatures to prevent formation of undesirable interfering compounds, third, leach-

ing certain of the metal values after the preliminary roasting step, fourth, conducting a high-temperature roast on the undissolved residue, and fifth, leaching other metal values from the re-roasted ore, the above combination of steps enabling the recovery of substantially all the zinc, copper, lead, iron, gold and silver values in the complex ore.

It is still another object of the present invention to provide a process for the recovery of metal values from complex ores wherein the values recovered are in an extremely pure state.

These and other objects of the present invention will become clearly understood by referring to the following description, and to the accompanying diagram, which is a diagrammatic flow sheet of a preferred form of my process for the treatment of complex ores of the class described.

In general, after the collective or bulk concentration of the metal values, the process comprises a first low-temperature preliminary roasting step whereby some or all of the copper values in the bulk concentrate are rendered acid-soluble and undesirable acid-insoluble compounds of the metal values are prevented from forming. Some or all of the copper is then leached from the roasted ore, along with other substances which would later form undesirable acid-insoluble compounds, the copper being thereafter obtained in elemental form by any one of a number of standard methods.

The leached residue is then roasted at a substantially higher temperature than the first roast, inasmuch as the undesirable substances which would form acid-insoluble compounds such as ferrites, have been removed by the first leaching step. The zinc is converted into the acid-soluble form by the second roasting step and leached out along with any remaining copper by an acid solution.

The lead is then recovered from the remaining residue by suitable conversions and leaching operations, as will be described. After the removal of the lead, copper and zinc values, the remaining residue is treated to recover the gold and silver by any standard method, such as by cyaniding to dissolve the silver and gold therefrom. Iron values are then removed from the remaining residue by standard reduction of ferric oxide contained therein.

Referring now to the flow sheet, complex ore as mined is first ground and sent to a bulk concentrating zone 10 along the line 12 where the ore is concentrated by standard oil flotation methods. That is to say, a concentrate of the complex zinc, copper, lead, iron, and precious metal sulphides, as well as all the simple sulphides of the metal, is separated from the gangue, rock and dirt, designated generally by the tailings 14. It is found that the bulk concentrate produced contains approximately 15-20% more of the metal values than are present in the combined totals of selective concentrates for each of the values. The reason for the increased recovery of the zinc, lead, or copper-zinc values is that standard oil flotation methods for selectively concentrating each of these values separate only the simple sulphides of each of the elements, and, of course, cannot separate or decompose the complex disulphides and trisulphides, which are present in substantial amounts. It is also possible to employ my process without any ore concentration, i.e. processing the ore directly as mined, but the collective concentration is found much more feasible.

The bulk concentrate, upon analysis, has been found to usually contain the following compounds:

Copper-zinc polysulphide
Copper-zinc-iron polysulphide
Copper-iron sulphide
Zinc-iron polysulphide
Copper sulphide
Silver sulphide
Zinc sulphide
Lead sulphide

Lead vanadate
Lead chromate
Lead molybdate
Lead tungstate
Lead silicate
Lead plus other acidic radicals
Ferrous sulphide, iron disulphides or sulphides of iron
Cadmium sulphide
Antimony sulphide
Arsenic sulphide
Bismuth sulphide
Gold (elemental)

Very small amounts or traces

The proportions of the metal values in the bulk concentrate, of course, vary a great deal. By way of illustration, however, an average assay of a bulk lead concentrate of an Arizona ore is given below.

Metal:

20	Zinc (Zn) -----percent--	9.95
	Copper (Cu) -----do----	1.16
	Lead (Pb) -----do----	28.8
	Iron (Fe) -----do----	21.0
	Silver (Ag) -----oz./ton--	38.3
	Gold (Au) -----oz./ton--	1.0
25	Cadmium (Cd) -----percent--	0.01
	Antimony (Sb) -----do----	0.1
	Silicon (Si) -----do----	2.0

The bulk concentrate is sent along a line 15 to a roasting zone 16, the temperature of which is preferably maintained between certain specified, relatively low limits. The primary purpose of this low-temperature roast is to prevent formation of ferrites which would otherwise combine with the zinc, copper and lead values in the ore concentrate to form acid-insoluble ferritic compounds. The term "roast," "roasting," and the like, used herein and in the claims are used to denote a heating in an oxidizing atmosphere.

Specifically, it has been discovered that the primary cause of formation of the ferritic compounds is due to the conversion of ferrous compounds, such as copper pyrite (Cu.FeS_2) and pyrite (FeS_2), into ferrites having the formula MFe_2O_4 , where M represents a particular metal such as zinc, copper, or lead. By maintaining the roasting zone 16 at a temperature above 340°C. , but below 400°C. , decomposition and oxidation of these ferrous compounds to ferric compounds is obtained without decomposition and oxidation of any of the other complex or simple sulphides of zinc, lead, silver, gold, and copper (with the exception of copper pyrite). It can thus be seen that there is no possibility of zinc and lead ferrite formation because the compounds in which these values are found are not decomposed and are not therefore susceptible to ferrite combination. Further, at these low temperatures, no copper ferrites are formed. Rather, the copper of the decomposed copper pyrite is converted primarily to cupric oxide (and some cupric sulphate). Hence, no ferrites can be formed at the low-temperature roast just described.

As mentioned, the ferrous compounds are readily oxidized to ferric oxide at these temperatures; some ferrosferric oxide (Fe_3O_4) is also usually formed. The ferrous portion of the ferrosferric oxide is acid-soluble and is removed prior to a high-temperature roasting of the concentrates to thereby eliminate any possibility of the formation of ferrites at the higher temperatures. The ferrous iron removal and high-temperature roasting operations will be described in detail hereafter.

Zinc sulphide, as well as the sulphides of cadmium, antimony, bismuth and arsenic and silver remain unchanged at low roasting temperatures. Lead sulphide is partially converted to the sulphate, but the major portion of this sulphide remains unchanged. The compounds of lead with an acidic radical, such as lead vanadate, lead chromate, lead molybdate, lead tungstate, etc., are

lead chromate, lead molybdate, lead tungstate, etc., are

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not converted to the oxide or sulphate form, to any appreciable extent, during the preliminary low-temperature roast and remain substantially unchanged.

The decomposition of the simple and complex sulphides of iron and copper (principally copper pyrite and pyrite) during the roasting operation in zone 16 produces sulphur dioxide, which is used as the basis for the making of sulphuric acid for the acid leaching operation to be described. The sulphuric dioxide gas leaves the roasting zone 16 along the line 18.

The roasted concentrate is sent to a leaching zone 20 along the line 22 and leached with sulphuric acid of from 1 to 50% concentration. Fairly concentrated sulphuric acid solution is preferred for reasons that will be described hereafter. The sulphuric acid leach solution is maintained at slightly elevated temperatures, e.g., 60° C., and dissolves some or all of the copper values in the concentrate, depending upon the form of the copper sulphides in the original ore, as described previously. As mentioned, all of the ferrous iron is also dissolved in this leaching operation. Some of the complex lead-acidic radical and sulphide compounds are converted to the but slightly acid-soluble sulphates; the zinc sulphides and other metal sulphides remain substantially unchanged.

The acid leach solution, designated by the number 1, thus contains both copper sulphate and ferrous sulphate and is sent to a recovery zone 24 along the line 26 for the recovery of the copper. There may also be a small amount of zinc, as zinc sulphate, in the leach solution. The zinc that dissolves does not occur originally in the sulphide form, but apparently is present as a silicate, an oxide, or a sulphate in the original concentrate. The leach solution No. 1 will thus usually contain a substantial amount of cupric copper sulphate, some iron as ferrous sulphate, and perhaps a small amount of zinc sulphate.

Under the conditions employed in the leaching step, no ferric iron is dissolved in leach solution No. 1. The absence of the ferric iron and the presence of the ferrous iron is highly advantageous in removing the copper from the leach solution, either by electrodeposition or by replacing it with a more electro-positive metal such as zinc. Thus, in electrodepositing copper, the presence of ferric iron in the electrolytic solution would invariably oxidize the cathodes generally used. On the other hand, because of the presence of ferrous iron in my solution, the ferrous iron reduces the oxygen produced during electrolysis and prevents an oxygen build-up (with consequent requirements of over-voltage) at the anode.

If any ferric iron should be present in removing cupric copper by means of an oxidation-reduction reaction with zinc metal, the zinc metal would react with the ferric iron to reduce it to the ferrous iron, while being itself oxidized, i.e., an oxidation-reduction reaction in addition to the zinc-copper reaction would result which, of course, is an inefficient use of the zinc. On the other hand, if only ferrous iron is present, as is the case in my solution, there is, and can be, no reaction between the zinc metal and ferrous iron.

In the oxidation-reduction reaction with zinc, the leach solution No. 1 is preferably neutralized so that the consumption of zinc is minimized. The neutralization takes place for example, by gasifying the sulphuric acid, which then passes along the line 28, to be reused as the leaching agent for the just-described iron and copper-leaching step. In order to facilitate the removal of sulphuric acid from leach solution No. 1, a fairly high acid concentration is initially employed, of the order of 15-50%, although acid concentrations as low as 1% have been used in some instances where the danger of readily dissolving impurities was great.

I have shown the zinc-copper oxidation-reduction method on the flow sheet, the zinc metal entering the copper recovery zone 24 along the line 30 and the precipitated copper being removed along the line 32. It is

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possible that traces of base metals such as cadmium may also be present in the leach solution No. 1, in which case such base metals would also be precipitated. However, such base metals are usually not found in the leach solution and the copper precipitate is generally extremely pure.

After removal of the copper from the neutral leach solution No. 1, the solution, now containing ferrous and zinc sulphate salts, is sent along the line 34 to an iron removal zone A, indicated by numeral 36, wherein the ferrous iron is oxidized by passing an oxygen containing gas, such as air, through the solution, whereupon approximately half the iron precipitates as ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) which leaves the recovery zone A along the line 38. It should be emphasized that the solution need not be neutral for this precipitation to take place. The neutral solution is advantageous only in copper precipitation by zinc, for reasons described.

The remaining ferric iron passes to iron recovery zone B (designated by the numeral 40) along the line 42, where it is precipitated, by the addition of zinc oxide, as hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Also, traces of any other base metals that may be present are thereby precipitated, with the exception of possible traces of magnesium, manganese and sodium. The zinc oxide employed in precipitating the ferric iron is obtained by later steps in the process, as will be described, either during the formation of the zinc metal or directly from the calcines formed in the second roasting step.

The final solution remaining comprises essentially zinc sulphate only, and passes from zone 40 along the line 44 to a zinc recovery zone to be described.

The concentrate not dissolved by the first leaching solution is sent to a second and higher-temperature roasting zone 50 along the line 52, and roasted at a temperature above 540° C., preferably within the range of 600 to 800° C. A minimum temperature of 540° C. is required, since, while the minimum decomposition temperature of the lead sulphide is 450° C., the minimum decomposition temperature of the zinc sulphide is 540° C. In this high-temperature roasting step, the zinc sulphides are converted to the oxides (and some to sulphates), the remainder of the copper is converted to copper oxide (and some to sulphate), the remainder of the complex sulfides are decomposed and oxidized, and traces of cadmium, antimony, bismuth, arsenic sulphides and the like are similarly converted. The lead sulphide present is converted to both the oxide and the sulphate. Silver sulphide (Ag_2S) is readily decomposed and reduced to the elemental form. It should be noted that since all ferrite forming components have been removed by the first leach, the high-temperature roast can be conducted without fear of loss of any zinc, copper, lead, or iron as insoluble ferrites.

Sulphur dioxide is also produced during the second roasting operation, passing from the zone 50 via line 54 to an acid plant for use in making sulphuric acid. The sulphuric acid is then used in the leaching operations at 20 or in the second leaching zone 56 now to be described.

The concentrate from the second roasting zone 50 is sent along the line 58 to the second acid leaching zone 56 where a sulphuric acid solution of fairly high concentration, e.g., between 15-50%, leaches substantially all of the zinc and copper values remaining in the concentrate. Traces of ferric iron values may go into the leach solution at this point. The leaching operation may be conducted in a single or multiple number of stages, as the particular ore concentrate may require.

Inasmuch as the concentrate after the second roasting contains all the zinc as zinc oxide, an alternative procedure sometimes followed is to take the requisite portion of the concentrate directly to the iron recovery zone B at 40 for the removal of iron and metal impurities by substitution of the iron and base metals for the zinc in zinc oxide. Whether this mode of purification of the first leach solu-

tion and recovery of the metal values therefrom is chosen, or whether zinc oxide, produced from the oxidation of the zinc pigs during production of zinc in later stages of my process, is used, is an economic question. Each has been found advantageous with different concentrates.

In following this alternate process and employing the calcines from the second roasting step at 50, a portion thereof is sent along the dotted line 53 to the iron recovery zone B at 40. The zinc-iron exchange takes place in zone B at 40 and the resulting zinc sulphate solution leaves along line 44.

The leach solution No. 2 is separated from the solid concentrates and leaves the zone 56 along the line 69, the leach solution No. 2 containing all of the remaining zinc and copper values and all the cadmium, bismuth, antimony, and arsenic (present in trace amounts). The copper, cadmium, bismuth, antimony and arsenic values are removed from the leach solution No. 2 by any appropriate means, such as by oxidation-reduction reaction with zinc dust entering a copper recovery zone 62 along the line 63. The copper recovered is sent, along with the traces of other elements aforementioned, to refining operations via line 64.

The remaining solution is comprised substantially of zinc sulphate from two sources, zinc sulphate produced by the second leaching step in zone 56 and the zinc sulphate produced by oxidation of added zinc metal in the copper recovery zone B at 62. The solution is sent along the line 66 directly to a zinc recovery zone 68 or bypassed to iron recovery zones A and B at 36 and 40, respectively, if the presence of iron and other impurities so requires. That is to say, the zinc sulphate solution may contain traces of ferrous (and ferric) iron which can be removed by oxidation of the ferrous to the ferric form in iron recovery zone A at 36, and by neutralizing with zinc oxide in the iron recovery zone B at 40, to thereby precipitate all the iron as ferric sulphate and hydrated ferric oxide (and to precipitate other impurities, if present), as described previously. Thus, if the concentration of ferrous and ferric iron or other impurities is sufficiently high to possibly interfere with subsequent zinc recovery (a maximum of about 0.007%), the zinc sulphate solution is sent to the aforementioned iron recovery zones A and B along the dotted line 70.

The zinc sulphate solution, leaving iron recovery zone B (40) along line 44 and/or leaving copper recovery zone B (62), then enters the main zinc sulphate line 66a to be sent to zinc recovery zone 68. The zinc is recovered by any of a variety of methods, for example, by electro-deposition. The spent electrolyte, containing some zinc sulphate and sulphuric acid, is then recycled along line 72 to the second leaching zone 56 for use in the leaching operations therein, as previously described.

The presence of magnesium and sodium is usually so small as not to interfere with the electrodeposition. If, after some time, however, substantial build-up of these elements does occur they can be removed prior to deposition of the zinc by any of a number of standard methods. The presence of manganese in the electrolyte is preferable inasmuch as it will act as a "built-in" depolarizing agent during zinc electrodeposition.

It will be noted that according to the foregoing, the copper is recovered in one or both of two process steps; that is, after the first and second leaching steps in zones 26 and 56. The amount of copper that goes into solution as a result of the first leaching step depends upon the form in which the copper is originally present in the ore, as explained previously. In some cases it has been found that practically all the copper is extracted after the first leaching operation. In other cases, the percentage of total copper extraction in the first leaching step is of the order of 10%. In any event, if one were to follow orthodox practices and conduct a single, high-temperature roast, the average recovery of copper is found to be in the neighborhood of 40-50%, whereas by fol-

lowing the two-stage roasting and leaching operation just described, recovery of copper is almost always 99+%. The high recoveries are thought to be due entirely to the prevention of the formation of copper ferrites which are acid-insoluble compounds and the chief source of loss in orthodox leaching and smelting operations.

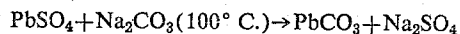
Similarly, with respect to zinc, by following the orthodox one-stage roasting operation at high temperatures, the average recovery of zinc, regardless of whether it is smelted from a selected concentrate or whether it is leached, is in the neighborhood of 60-80%. The loss is due primarily to the formation of ferrites or other undesirable compounds formed during the roasting operation. Our combined low-temperature roasting and high-temperature roasting step, which eliminates the undesirable formation of zinc ferrites, substantially increases the percentage of recovery of zinc so that it is substantially a complete recovery.

The zinc recovered in zinc recovery zone 68 is sent along line 74 where it is melted into pigs for shipment. A portion of the zinc is ground into dust to be sent, via line 76, to the copper recovery zones A and B at 24 and 62, respectively, for the oxidation-reduction reaction therein.

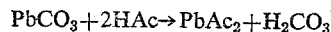
In melting the zinc to pig, there will be some oxidation of the zinc to zinc oxide (ZnO). The zinc oxide thus produced is sent from line 74 to iron recovery zone B at 40, via line 78, for the precipitation of impurities and iron as hydrated iron oxide, as previously explained.

The leached concentrates containing all of the gold, silver, lead and the majority of the iron values leave the leaching zone No. 2 along the line 80, and enter the lead conversion zone 82. The lead values are substantially entirely present in the form of lead sulphate because of the prior sulphuric acid leaching steps in leaching zones No. 1 and No. 2, respectively. In order to leach the lead values from the solids and still regenerate the leaching agent, the lead is first converted to the carbonate form in the conversion zone 82 and thereafter leached out as lead acetate with acetic acid. The lead acetate is then converted to sulphate by means of sulphuric acid whereby the lead sulphate is recovered as a precipitate and the acetic acid is regenerated for use in leaching the lead sulphate from the solid concentrates.

To this end, a hot near boiling sodium carbonate solution enters zone 82 along line 84 at a concentration of 10 to 40% and converts the lead sulphate in the solids to insoluble lead carbonate. A sodium sulphate solution thus leaves the zone 82 via line 83, according to the equation:



The lead-containing solids are then sent from the conversion zone 82 along the line 86 to a third leaching zone at 88 wherein the solids are leached with an acetic acid solution entering the zone 88 along line 89. The lead carbonate is thus decomposed and soluble lead acetate solution is formed according to the equation:



The lead then leaves the leaching zone No. 3 along the line 92 to a lead recovery zone 94. Sulphuric acid is then added to the solution of lead acetate in zone 94 whereupon the lead precipitates as lead sulphate, leaving the recovery zone along the line 96.

The acetic acid solution is regenerated (according to the equation $\text{PbAc}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{HAc} + \text{PbSO}_4$) leaving the recovery zone 94 along the line 100 to be recirculated to the leaching zone 88. Fresh acetic acid solution is added to the recirculating acetic acid line 89-90 along the line 102.

It should be noted that lead may be recovered from the system in other forms than the sulphate, inasmuch as the addition of any mineral acid which is more highly ionized than lead acetate will precipitate the lead as the lead combined with acidic radical of the mineral acid

employed. It should also be noted that lead can be recovered as a sponge metal from the lead recovery zone by electrolysis, if it is more desirable to sell the lead in this form.

The solids, after undergoing the acetic acid leaching treatment in leaching zone No. 3 at 88 are sent along the line 104 to a leaching zone No. 4 at 106 for the purpose of leaching out the silver and gold values from the remaining insolubles in the solids (such as ferric oxide, and silica) by standard means. For example, sodium cyanide enters the leaching zone 106 along the line 103 leaching out the silver and gold values as silver cyanide and gold cyanide, respectively. The soluble cyanide values leave the leaching zone No. 4 along the line 110 to be sent to a gold and silver recovery zone 112. It is to be emphasized that the gold and silver entering the leaching zone No. 4 is pure gold and silver metal, respectively, which readily is converted to the cyanide complex form. Thus, a short leaching time only is required. The gold and silver values are selectively converted to their reduced elemental form by reduction with zinc metal or by other standard methods.

A majority of the original iron in the concentrate, now in the form of ferric oxide, as well as other insolubles such as silica, are sent along the line 114 to appropriate reduction processes where the iron is recovered in zone C at 116. For example, the iron oxide may be reduced in a hydrogen atmosphere or by carbon monoxide gas in a blast furnace. The concentration of the iron oxide in the solids leaving the leaching zone No. 4 at 106 is usually of the order of 90-95%.

Examples which are typical of the process above described are set forth in detail below.

EXAMPLE I

Ground ore from the mine is sent to an oil flotation concentrating zone wherein the values are collectively concentrated. The assay of the flotation concentrate is as follows:

Element	Percentage and/or Weight
Silver.....	5.5 oz./ton.
Gold.....	0.1 oz./ton.
Lead.....	3.4% or 68 lbs.
Zinc.....	48.5% or 970 lbs.
Copper.....	0.38% or 7.6 lbs.
Iron.....	9.4% or 188 lbs.
Cadmium.....	0.03% or 4.6 lbs.
Antimony.....	0.07% or 14.0 lbs.
Aluminum, Magnesium, Vanadium.....	Traces.
Manganese, Bismuth, Arsenic.....	Traces.

From the above assay, it will be seen that the concentrate is high in zinc and iron.

One ton of the concentrate is sent to the low-temperature roasting zone 16 along the line 15 and roasted at 375° C. for approximately one hour. The roasted solids are then sent to the leaching zone No. 1 at 20 where they are leached with 2000 lbs. of 15% sulphuric acid solution at 60° C. for one-quarter of an hour. An assay of the leach solution No. 1 shows the following values present in the solution:

Values:	Weight, pounds
Iron (iron present as ferrous sulphate)	92.0
Copper	7.0
Zinc	52.0

The leach solution No. 1 is sent to the copper recovery zone A at 24 wherein, upon the addition of 75 lbs. of zinc dust, copper metal is quantitatively precipitated. The leach solution containing zinc and iron values is then sent to the iron recovery zone A along the line 34. Upon passing oxygen in an amount approximately equal to the stoichiometric amount necessary to convert the iron to the oxidized ferric form, approximately 50% of the iron in the solution is precipitated in the ferric sulphate form. The remaining leach solution is sent to iron

recovery zone B at 40 via the line 42 wherein the remaining iron is precipitated in the oxidized form of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ by reaction with 60 pounds of zinc oxide. The total iron precipitate weighed 92.0 pounds, taken as iron.

The solution remaining consists substantially entirely of zinc sulphate solution which is then sent to the zinc recovery zone 68 via line 44.

Returning now to the leached solids leaving the leaching zone No. 1 via line 52, they enter the high-temperature roasting zone 50 where the temperature is maintained at approximately 650° C. The solids are roasted for one hour, and then enter the leaching zone No. 2 where they are leached with 900 pounds of a 15% sulphuric acid solution for 15 minutes. The acid is maintained at a temperature of 60° C.

The resulting leach solution comprises a majority of the zinc values as well as all of the remaining copper, cadmium and iron values. The leach solution No. 2 is sent via line 60 to the copper recovery zone B at 62 wherein the copper and cadmium as well as traces of bismuth, antimony and arsenic are precipitated by replacement with zinc dust entering the recovery zone B along the line 63, this zinc dust being produced at the zinc recovery zone 68. The precipitated copper is then separated from the leach solution along with traces of cadmium, bismuth, etc., for later refinement, if necessary.

The remaining leach solution No. 2 is sent to the zinc recovery zone 68 via the line 66 along with the essentially chemically pure zinc sulphate solution from the iron recovery zone B which enters the line 66 from the line 44. Any trace amounts of ferric iron that are not precipitated by the copper recovery step at 62 do not interfere with zinc recovery by electrolysis in the zinc recovery zone 68. The electrodeposited zinc is taken to a zinc melting furnace along the line 74 and thereafter portions of the metallic zinc obtained are ground into dust and sent to copper recovery zones A and B along the line 76, as needed. Then the skimmings from the zinc melt (which are zinc oxide) are sent to the iron recovery zone B along the line 78, also as needed.

The amount of zinc obtained in the zinc recovery zone 68 was 962 pounds plus the amount employed in the iron and copper recovery steps. Also, the total copper and cadmium recovered in recovery zone B is 7.4 pounds copper and 4 pounds cadmium. It will thus be seen that over 99% of the zinc and copper present in the concentrates are recovered by the two-step roasting and leaching operation described. The cadmium recovery is 87%.

The leach solids residue from leaching zone 56 is then sent via line 80 to the lead conversion zone 82 where it is treated with 350 pounds of a 15% solution of sodium carbonate at 100° C. for 10 minutes. The residue is then filtered and washed and then treated with 150 pounds of a 10% acetic acid solution in leaching zone No. 3 at 88 to thereby leach the lead as soluble acetate from the residues. The lead acetate solution leaves the leaching zone No. 3 along the line 92 to be sent to a lead recovery zone 94 where it is recovered as lead sulphate by the addition of sulphuric acid. The amount of the lead recovered is equivalent to 68 pounds and is substantially a 100% recovery of the original lead as shown by the assay.

The remaining solids leave the leaching zone No. 3 along the line 104 and have been concentrated to 216.8 pounds as they enter the leaching zone No. 4 at 106. The solids are here treated with sufficient sodium cyanide solution to leach out the silver and gold values which leave the leaching zone No. 4 at 106, in the cyanide complex form, along the line 110 to be sent to the silver and gold recovery zone 112. The amount of silver and gold recovered in ounces is, respectively, 5.44 and 0.099 which, it will be noted, is in both cases over a 99% recovery of the assayed silver and gold.

The remaining residue is sent to a blast furnace, designated generally by iron recovery zone 116 wherein 96

pounds of pig iron is recovered. It will be seen that the total of the iron recovered from zones A and B and the final recovery zone C is 188 pounds which is equal to substantially 100% of the total assayed iron values in the concentrate. The final residue leaving zone 116 showed trace amounts of copper, a small amount of zinc (approximately $\frac{1}{2}$ of 1% of the total assayed amount) and showed no signs of lead.

EXAMPLE II

A high grade zinc-copper ore of complex sulphides assayed as follows, after the collective concentration thereof:

Values	Weight or Percentage
Zinc.....	526 lbs. or 26.3%.
Copper.....	234 lbs. or 11.7%.
Iron.....	320 lbs. or 16%.
Silver.....	126 oz. per ton.
Gold.....	1.6 oz. per ton.
Antimony, Bismuth, Arsenic.....	Traces.
Cadmium.....	

One ton of the finely divided concentrate was roasted at 375° C. for one hour and then leached with a 15% sulphuric acid solution at 60° C. for 15 minutes in leaching zone No. 1. The leach solution was then transferred to the copper recovery zone A where 193.0 pounds of copper was precipitated with 210 pounds of zinc obtained from previous processing. Iron in the amount of 166 pounds was recovered in the iron recovery zones A and B as ferric sulphate and hydrated ferric oxide, respectively, in a manner identical with that described in Example I. The chemically pure zinc sulphate solution, leaving the iron recovery zone B along the line 44, analyzed 72.4 pounds zinc per ton of concentrate.

The remaining solids were then roasted in a high-temperature roasting zone 50 at a temperature of 650° C. for 15 minutes and after the acid leaching step, the resulting leach solution was then sent to copper recovery zone B where 80 pounds of copper was recovered by replacement with zinc dust as described with reference to Example I. The remaining solution which comprises traces of ferric iron and which is substantially entirely composed of zinc sulphate passed into the zinc recovery zone 68 along with the essentially chemically pure zinc sulphate solution entering line 66 along the line 44. The total zinc recovered by electrolysis in the zinc recovery zone 68 was 522.4 pounds per ton of original concentrate plus, of course, the 210 pounds which was initially present for the precipitation of iron and copper.

Upon study of the figures, it will be seen that the total recovery of zinc amounts to 99+% of the total assayed zinc value in the original concentrate, and further, that over 99% of the copper was recovered in zones A and B as metallic copper. Traces of cadmium, bismuth and the like were precipitated in recovery zones A and B.

The remaining solids were then sent through the lead conversion cycle and then to the leaching zone No. 4 for the recovery of silver and gold values, as described with reference to Example I. The silver and gold recovered was in the amount of substantially 100% in both cases. No lead was recovered.

The amount of iron recovered in the remaining residue by appropriate reduction means in zone C was 153.4 pounds. Since 166 pounds was recovered as a result of the zone A and B steps described above, the total iron recovery was 319.4 pounds or 99+% of the total amount recoverable.

It is thus seen that substantially complete recoveries of all the values, namely: zinc, copper, iron, silver and gold, were made by the process of my invention. By way of comparison, one ton of the same bulk concentrate as set forth herein in Example II was roasted

at 650° C. without employing the first 375° C. roasting. The roasted product was then leached with 15% solution of sulphuric acid under the same conditions of time and temperature. The assay of the resulting solution was as follows:

Values:	Weights, lbs.
Zinc	370
Copper	119
Iron	2.6

That is to say, 0.8% of the total amount of iron was recovered, 70+% of the zinc was recovered, and 50+% only of the total amount of copper in the ore was recovered. The advantages of my process over the standard processes can thus be readily seen.

While I have shown and described a preferred embodiment of the process of my invention, it will readily be understood by those skilled in the art that changes and modifications may be made that lie within the scope of the invention. Hence, I do not wish to be limited by the specific examples and embodiments shown and described herein, but only by the appended claims.

I claim:

1. A process for the recovery of metal values from complex ores, which includes the steps of: roasting said ore at a temperature sufficiently low to prevent any substantial formation of acid insoluble compounds of said metal values, but sufficiently high to convert those metal values, which would have formed said acid insoluble compounds, to acid-soluble compounds; removing said acid-soluble compounds from said metal values remaining in said ore; and roasting said remaining ore residue containing said metal values at a temperature sufficiently high to convert said metal values to acid-soluble compounds.

2. The process of claim 1 wherein said acid insoluble compounds are principally composed of ferrites.

3. A process for recovering zinc, copper, iron, lead, gold and silver metal values from complex ores, which includes the steps of: roasting said ore at a temperature below which ferrites of any of said metal values are formed but above that temperature at which iron sulphides are decomposed; leaching said ore to dissolve thereby at least some of the copper and ferrous iron metal values in said ore; roasting said leached ore at a temperature higher than said first roasting temperature; and leaching said ore to dissolve thereby a substantial portion of the remaining metal values in said ore.

4. The process of claim 3 wherein the metal values recovered in the second leach include zinc and copper.

5. The process of claim 3 wherein the ore remaining after the second leaching is selectively treated for the recovery of lead, iron, silver and gold values.

6. The process of claim 3 wherein the ore is first roasted at a temperature below 400° C., and wherein the leached ore is roasted a second time at a temperature of above 540° C.

7. The process of claim 3 wherein the metal values in said ore are first collectively concentrated prior to said first roasting step.

8. A process for recovering metal values from complex ores, said metal values being selected from the group consisting of lead, zinc, copper, iron, silver and gold, which includes the steps of: roasting said ore at a temperature sufficiently high to decompose and convert some of said complex ores to an acid-soluble form, but below that temperature at which any substantial ferritic formation of any of said metal values occurs; leaching said ore with an acid to recover some of said metal values, including at least some of said copper values in said ore and to recover substantially all of said ferrous iron values remaining in said ore after said roasting; separating said acid leach solution from said ore, and selectively recovering said copper and iron values therefrom; roasting said remaining ore at elevated temperatures sufficiently high to decompose and convert the zinc

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and remaining copper values to acid-soluble compounds; leaching said roasted ore with acid to thereby dissolve substantially all the zinc and copper values remaining in said ore; and separating said leach solution from said ore and selectively recovering said zinc and copper values from said leach solution.

9. The process of claim 8 wherein the residue remaining after said second acid-leaching step is treated with an alkali metal carbonate solution to thereby convert the lead in said ore to an insoluble lead carbonate, said lead carbonate after separation from solution, being treated with an organic acid to thereby dissolve said lead values, thereafter separating said dissolved lead values from said ore, and treating said dissolved lead values with an acid to precipitate said lead values from said solution and regenerate the organic acid.

10. The process of claim 9 wherein the residue after said organic leach is selectively treated for the recovery of gold, silver and iron values.

11. A process for the recovery of metal from complex ores having lead, zinc, copper, iron, silver and gold values, as well as smaller amounts of metal impurities, which includes the steps of: selectively concentrating said metal values from said ore; roasting said ore at a temperature of between 340° to 400° C. whereby to decompose at least some of said complex ores and to render them acid-soluble, and to further oxidize a substantial amount of ferrous iron values present in said ore to the ferric form; leaching said roasted ore with acid to dissolve soluble copper, zinc and ferrous iron values in said ore in this first leach solution; separating said first leach solution from said first roasted concentrate; selectively precipitating copper, zinc and iron values from said first leach solution; roasting the concentrate remaining after said first acid leach at a temperature between 600 and 800° C. whereby to decompose the remainder of said complex ores and convert said remaining zinc values to the oxide and sulphate form and the remainder of said copper values to said oxide and sulphate form; acid leaching said roasted concentrate to dissolve substantially all of said zinc values and substantially all the remaining copper values in said second leach solution; separating said second leach solution from said roasted concentrate; and selectively precipitating said copper, zinc and iron values from said second leach solution.

12. The process of claim 11 wherein copper is precipitated from both first and second leach solutions by

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replacement with zinc metal, and said ferrous iron in said first leach solution is oxidized to the ferric form and precipitated partially as ferric sulphate and partially as hydrated ferric oxide.

13. The process of claim 11 wherein any base metal impurities in said first and second acid leach solution are recovered prior to the zinc precipitation by replacement with zinc metal, and any iron impurities in said first and second acid leach solution are precipitated prior to said zinc precipitation as ferric sulphate and ferric oxide.

14. The process of claim 13 wherein the zinc recovered in the metal form is partially oxidized, a portion of said zinc and at least a portion of said zinc oxides being employed in the recovery of copper and iron, respectively.

15. The process of claim 13 wherein the concentrate remaining after the second acid leaching step is heated and treated with a sodium carbonate solution to thereby convert the lead in said concentrate to lead carbonate, the resulting lead carbonate is then treated with acetic acid to leach the lead values from the concentrate as lead acetate, the lead acetate solution is then separated from said concentrate, and re-precipitated by treatment of said lead acetate with a mineral acid whereby said acetic acid is regenerated for reuse in the leaching of lead carbonates from said concentrate.

16. The process of claim 15 wherein the concentrates remaining after the acetic acid leach are treated with cyanide solution to leach the gold and silver values from said concentrate, and thereafter treating said remaining concentrate for iron by reduction of the ferric oxide therein.

17. The process of claim 1 wherein the ore is first roasted at a temperature below 400° C. and wherein the remaining ore residue is roasted a second time at a temperature of above 540° C.

18. The process of claim 1 wherein the ore is first roasted at a temperature between 340 and 400° C., and wherein the remaining ore residue is roasted a second time at a temperature above 540° C. but below 800° C.

References Cited in the file of this patent

UNITED STATES PATENTS

1,378,822	Lloyd	May 17, 1921
2,187,750	Marvin	Jan. 23, 1940
2,328,089	Mulligan	Aug. 31, 1943