United States Patent

Renken et al.

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[54] PROCESS FOR ELECTROWINNING ZINC FROM SULFIDE CONCENTRATES

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[52] **U.S. Cl.**.....**204/114,** 23/114

[51] **Int. Cl.**.....**C22d 1/22,** C01b 17/06

[58] **Field of Search**.....204/119, 114, 108; 75/117, 75/120; 23/125, 135, 114

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[57] **ABSTRACT**

This disclosure is directed to leaching zinc sulfide concentrates to facilitate the production of zinc and sulphur. solution. To provide for increased recovery the copper sulfate leach

The zinc sulfide is leached with a copper sulfate solution, preferably under oxidizing conditions, to produce a copper sulfide and a zinc sulfate solution. The elemental sulphur can be obtained from the copper sulfide by a subsequent oxidizing leach and the zinc metal can be obtained by electrolyzing the zinc sulfate leach may be accomplished in a staging operation to establish an excess of zinc sulfide concentrate in the initial leach step.

8 Claims, 5 Drawing Figures

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SHEET 1 OF 4

Fig. 1.

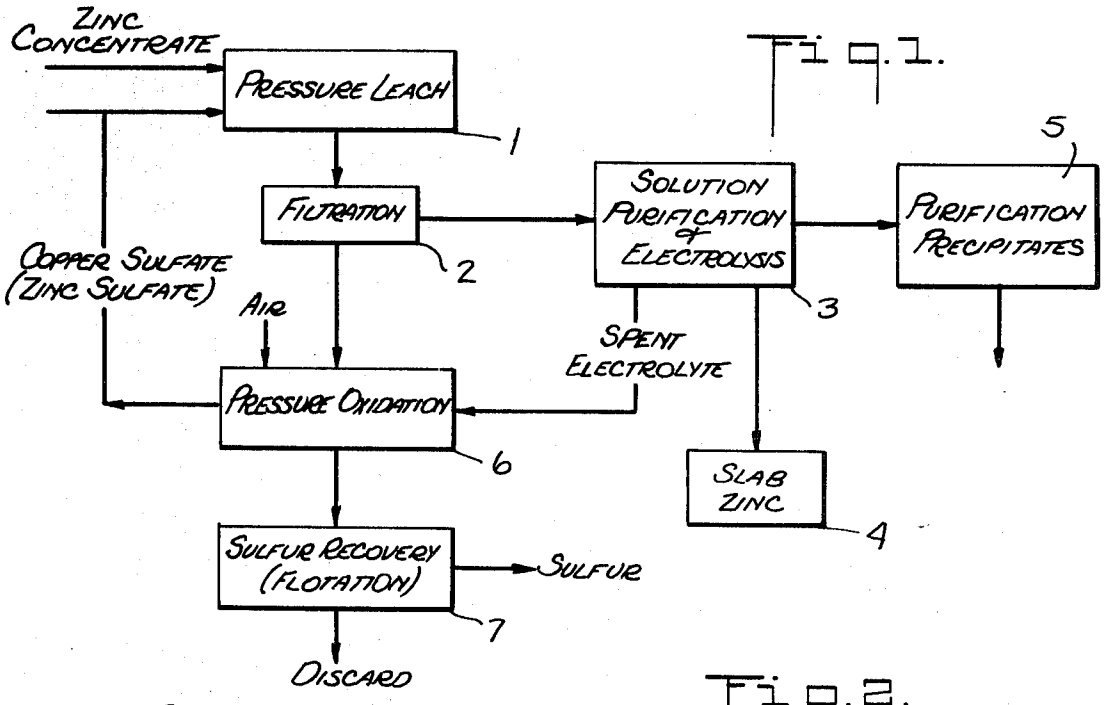
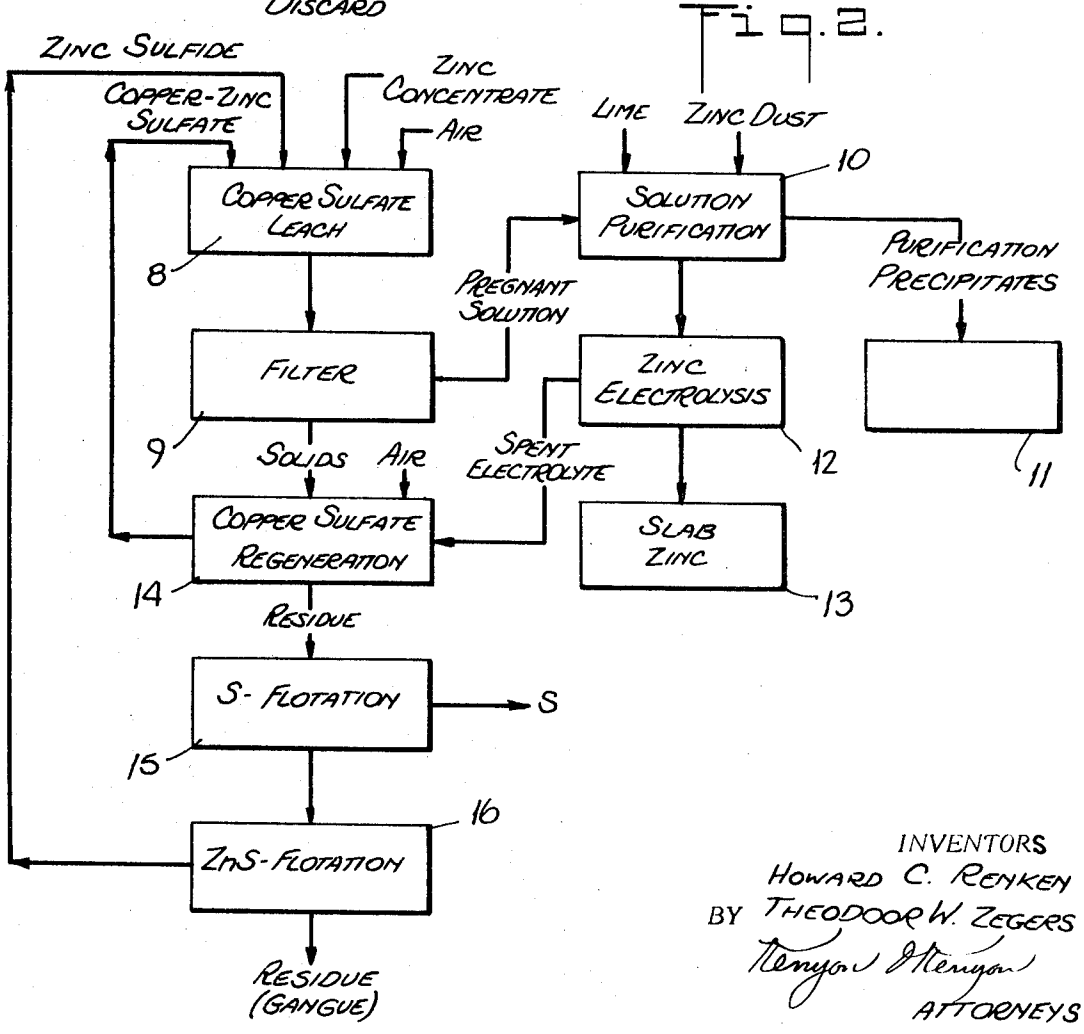
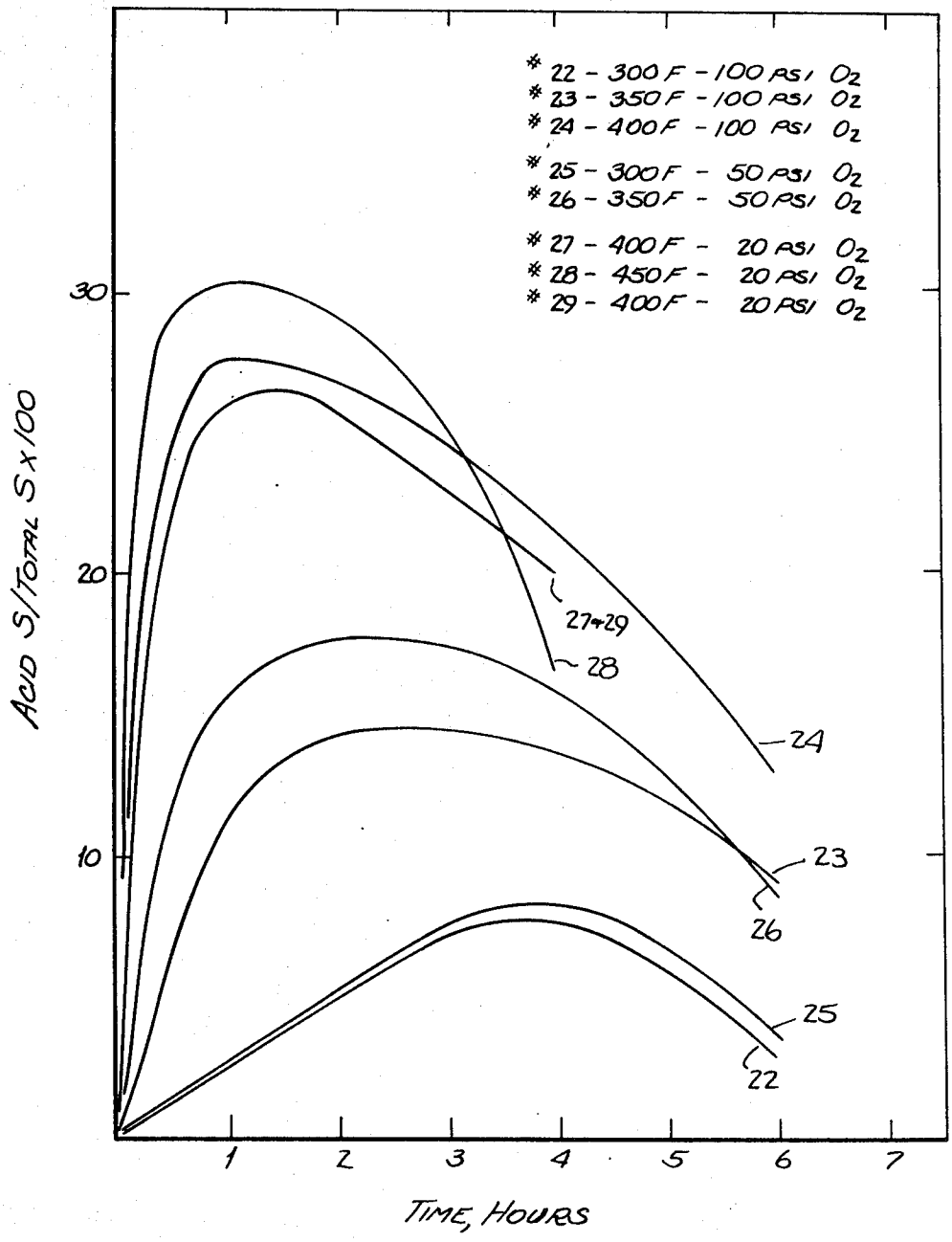


Fig. 2.



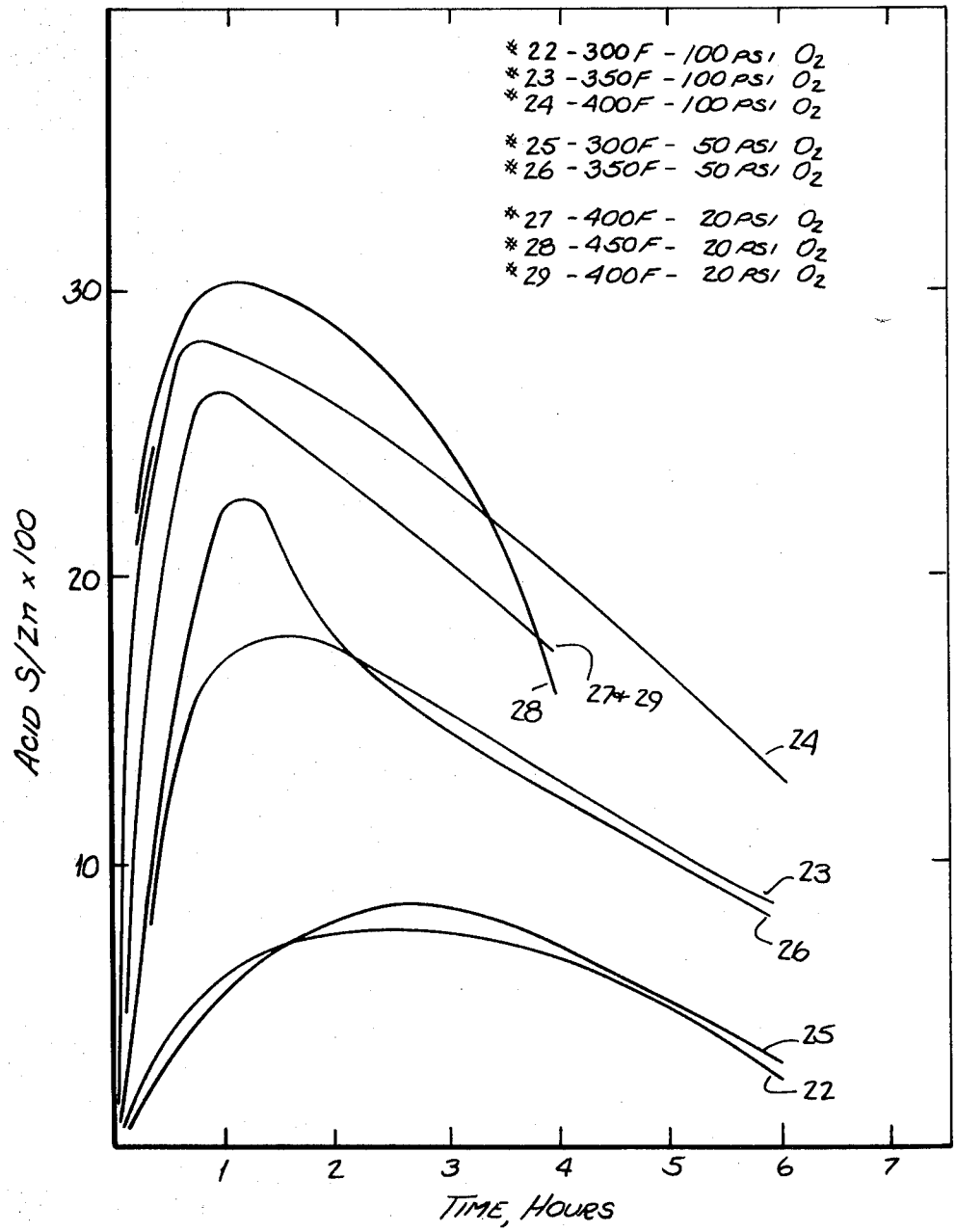
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Fig. 3.



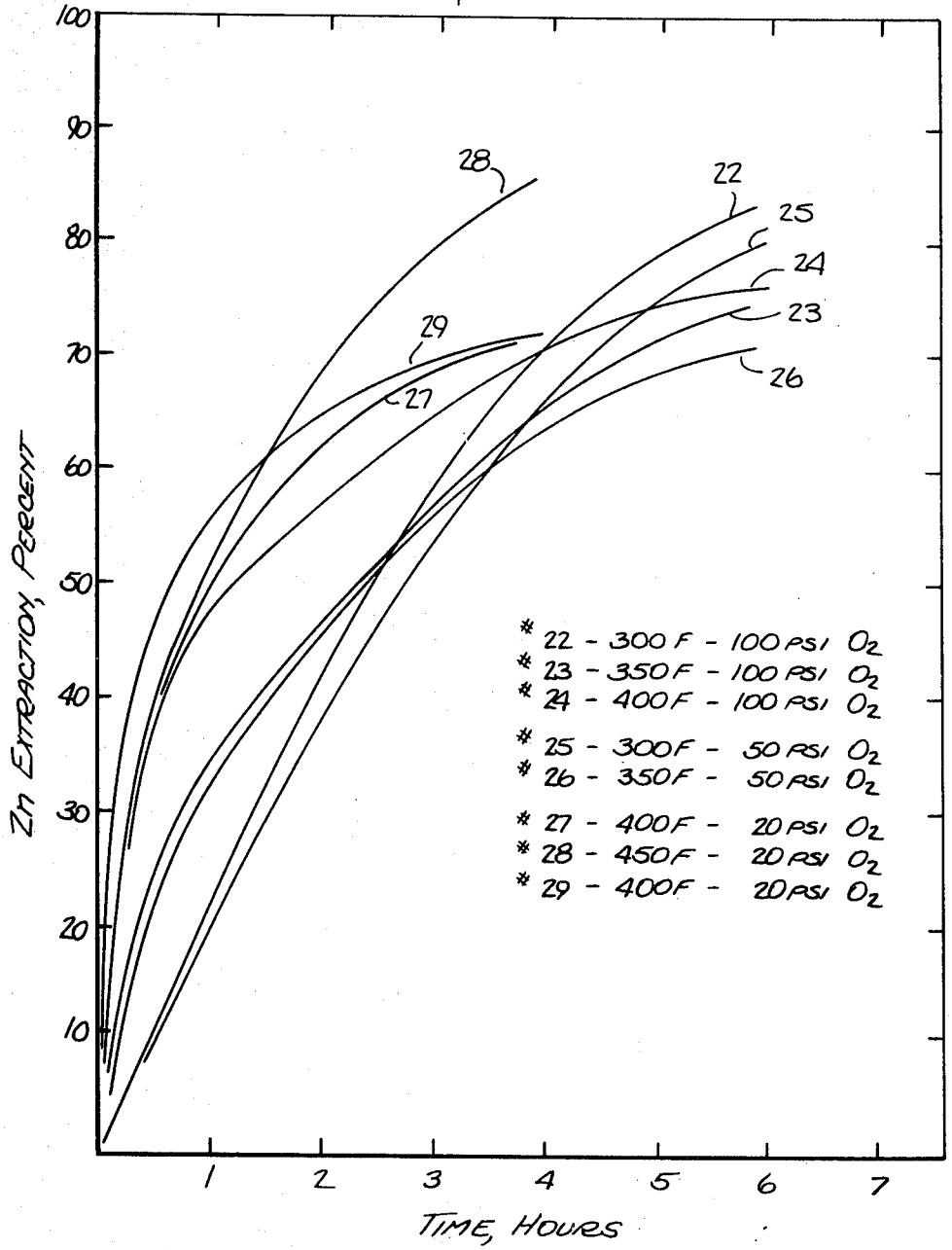
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Fig. 4.



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Fig. 5.



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PROCESS FOR ELECTROWINNING ZINC FROM SULFIDE CONCENTRATES

BACKGROUND

The production of zinc metal from zinc sulfide concentrates by the conventional electrolytic zinc process involves the following major steps:

1. Roasting of the zinc sulfide concentrates with air to zinc oxide and a sulphur dioxide-containing gas.
2. Conversion of the sulphur dioxide in the gas to sulphuric acid.
3. Dissolution of the zinc oxide in dilute sulphuric acid to form zinc sulfate.
4. Purification of the zinc sulfate solution.
5. Electrolysis of the zinc sulfate solution to produce zinc metal with the regeneration of sulphuric acid.

Modifications of this process have been sought to provide elemental sulphur while maintaining a high yield of zinc metal. Many theoretical chemical equations can be drawn to illustrate methods by which zinc metal and elemental sulphur could be extracted from zinc sulfide. Foremost among these are the uses of sulphuric acid, under oxidizing and non-oxidizing conditions, to leach zinc sulfide concentrates. However these proposals have not proven to be entirely satisfactory, due either to low leaching rates, the requirements of complex process equipment or unattractive cost factors.

It is therefore an object of this invention to provide an improved method of leaching zinc sulfide ores to recover values therefrom.

It is another object of the present invention to provide an improved method for the recovery of elemental sulphur and zinc metal from zinc sulfide concentrates, particularly by a modification of the electrolytic zinc process.

Other objects and advantages of the invention are set forth in conjunction with the following detailed description.

THE INVENTION

This invention is directed to the use of copper sulfate as a leaching agent for zinc sulfide concentrates, preferably under oxidizing conditions, to produce elemental sulphur and zinc metal.

The method of this invention includes first leaching the zinc concentrate under pressure by an exchange reaction with copper sulfate solution to give a zinc sulfate solution for electrolysis in accordance with conventional methods and a copper sulfide precipitate. Recovery of elemental sulphur and regeneration of the copper sulfate solution is accomplished by a second pressure leach reaction of the copper sulfide precipitate with spent electrolyte under oxidizing conditions. In this process, the copper is precipitated as cuprous sulfide with the concurrent production of sulfuric acid. To alleviate the difficulties in purification procedures caused by the sulfuric acid, the copper sulfate leach may alternatively be carried out under oxidizing conditions. Furthermore, by staging the operation to establish an excess of zinc concentrate in the initial copper sulfate leach, the amount of acid production and soluble sulfate formation can be minimized, with consequent higher recovery of elemental sulphur at high zinc extraction.

The invention is described in greater detail in conjunction with the following figures and working examples in which:

FIG. 1 is a process flow chart of the non-oxidizing copper sulfate leach of zinc sulfide to produce elemental sulphur and zinc metal.

FIG. 2 is a process flow chart of the oxidizing copper sulfate leach of zinc sulfide to produce elemental sulphur and zinc metal.

FIG. 3 is a graph of the production of acid sulphur (based on total sulphur) as a function of time in the process of FIG. 2.

FIG. 4 is a graph of the acid sulphur to zinc ratio as a function of time in the process of FIG. 2.

FIG. 5 is a graph of the calculated zinc extractions as a function of time in the process of FIG. 2.

In the process of FIG. 1 a zinc concentrate and copper sulfate solution are fed into a pressure leaching vessel 1. The zinc concentrate comprises predominantly zinc sulfide with minor amounts of other naturally occurring constituents, such as iron sulfides. The copper sulfate solution is largely regenerated in this process as referred to in greater detail below.

The mole ratio of copper to zinc feed to vessel 1 is from about 1:1 to 2:1, greater amounts of copper may also be used. The preferred ratio of copper to zinc is about 1.5:1.

The temperature in the vessel is from about to 300° to 550°F., preferably 400° to 450°F. The vessel itself is a corrosion resistant vessel, having external temperature control means and an internal stirrer (neither shown). The reaction is carried out continuously with a normal residence time of from about 1 to 7 hours.

The reaction product, which includes a copper sulfide and zinc sulfate solution is withdrawn from the vessel 1 and passed through filtration means 2. The filtration means is a conventional unit for the continuous separation of a liquid-solid slurry. The impure zinc sulfate solution is sent to a conventional electrolytic zinc process plant starting with the purification procedure. The electrolytic zinc process is well known and described in numerous texts, for example, "Zinc - The Science and Technology of the Metal, Its Alloys and Compounds", C. H. Mathewson, ed., pp. 174–225 (1959) and by Allen C. Jephson et al. in Journal of Metals (18, 947–956 (Aug., 1966)). In unit 3 the solution is purified, clarified, and electrolyzed to produce cathode zinc. The cathode zinc is smelted and cast into slabs which are stored as slab zinc in ware house 4 for shipment. Precipitates are kept separated in storage means 5. The spent electrolyte or acid from the electrolysis is sent to the pressure oxidation unit 6. Air, and the precipitate from filtration means 2, which is largely a copper sulfide, are concurrently fed to the pressure oxidation unit. This unit may be similar in structure to vessel 1. The reaction products from the means 6 are sulphur and a mixture of sulfates, predominantly copper sulfate with some zinc sulfate formed from zinc sulfide. The sulfates are recycled to the pressure leaching vessel 1. The sulphur is purified and recovered in a conventional flotation means 7.

In this process copper sulfate solution was found to be an effective agent for leaching zinc sulfide concentrate. Experiments set forth below established that a temperature of 400°F gave satisfactory zinc leaching rates. At this temperature, zinc extractions of about 80 percent after 4 hours were obtained when using 1.5 moles of copper in the leach liquor for every mole of zinc in the concentrate. At 450°F, an extraction of 85 percent was obtained under the same conditions. The presence of zinc sulfate in the leach solution did not affect the reaction rate.

It was found that copper precipitates principally as cuprous sulfide (Cu_2S), and not as cupric sulfide (CuS). Thermodynamic calculations also predict that cuprous sulfide is the stable form. The precipitation of Cu_2S is accompanied by the formation of appreciable amounts of sulfuric acid, which, however, is detrimental to maximum sulphur recovery. The following process minimizes this problem of acid formation.

FIG. 2 illustrates a preferred embodiment in which air or oxygen is fed to the pressure leach vessel 8 in addition to the zinc concentrate and copper sulfate. The oxygen partial pressure may be from about 5 to 150 psig, preferably from 10 to 50 psig. The reaction mixture is filtered in means 9 and the solution therefrom is purified in means 10 with lime and zinc dust in accordance with conventional procedures. The purification precipitates are stored in 11. The purified solution is electrolyzed in means 12, from which zinc metal is sent to storage 13. The spent electrolyte, air, or oxygen, and the solids from the filtration means 9, are reacted in vessel 14. The pressure oxidation in 14 yields the regenerated sulfate solutions which are recycled into the pressure leach vessel 8. The residue from the pressure oxidation includes sulphur which is purified in flotation unit 15 and zinc sulfide which is separated

in flotation unit **16**. The zinc sulfide is returned to the pressure leach vessel **8**.

The above processes are illustrated further by the following examples.

EXPERIMENTAL PROCEDURE - NON-OXIDIZING CONDITIONS

The conditions under which copper sulfate solutions can be used effectively for the leaching of zinc sulfide concentrate are shown in the following experiments.

These experiments were conducted in a Pyrex vessel contained within a 5-gallon autoclave and equipped with electrical resistance heating and a cooling coil for automatic temperature control. A glass or tantalum stirrer was used, the latter being more suitable for higher pulp densities.

The zinc concentrate used in the experiments was analyzed as follows:

Zn	54.3%
Cu	0.73%
Fe	8.2%
S	32.1%

The copper in the concentrate was present as chalcopyrite ($CuFeS_2$). The major part of the iron was found in a solid solution with zinc sulfide.

The main variables in these experiments were temperature, copper content of leach solutions, and the presence of zinc in the leach liquor.

EXAMPLES 1–6

The effect of temperature on the reaction of zinc sulfide with copper sulfate is shown in Examples 1–6. In all runs, 50 g of zinc concentrate was leached with 500 ml aqueous copper sulfate solution of indicated strength at various temperatures. The results of these experiments are listed in Table I.

TABLE I

Ex. No.	Time, hr.	Temp., °F.	Mol ratio of Cu to Zn in charge	Zn dissolved, percent	Cu precipitated, percent	Mol ratio, Cu precipitated:Zn dissolved
1	1	200	1.35	(a)	2.5	
2	4	200	1.00	(a)	2.5	
3	2	200	0.50	(a)	6.9	
4	1	300	1.51	26.2	29.2	1.68
5	5	300	1.10	42.6	64.0	1.64
6	1	400	1.25	63.2	93.5	1.84

[a] Zinc contents of solutions were not determined because almost no copper had precipitated.

The results indicate that a minimum temperature of 300°F is required and that 400°F is preferable to achieve acceptable zinc extractions in a reasonable time. The upper temperature limits are in part dictated by the equipment and economies. A suitable temperature range is from about 300°F to about 550°F.

The results indicate that more copper is consumed than necessary for the stoichiometric formation of CuS. For the formation of Cu_2S, the molar ratio of Cu precipitated to Zn dissolved is 1.6. The iron incorporated in the ZnS lattice will react similar to zinc. Some of the iron in the concentrate is combined with copper in chalcopyrite, $CuFeS_2$. This mineral does not react with copper sulfate, and polished sections of residue do not show a sign of attack. Since the concentrate contains 0.73 percent Cu, the amount of iron combined with it in $CuFeS_2$ is 0.64 percent. The balance of the iron, 7.56 percent of the concentrate, is then incorporated in the sphalerite lattice. For every mole of zinc we therefore have 7.56/54.3 · 65.4/55.85 = 0.163 moles of iron, reacting similarly. Every mole of zinc requires then 1.163 × 1.6=1.861 moles of copper. The copper precipitate of the leach conducted at 400°F (Table I, No. **6**) should therefore not contain CuS. The same conclusion was arrived at from thermodynamic considerations. Examination of polished sections of residues from other leaches carried out at 400°F confirmed the absence of CuS.

EXAMPLES 7–15

In a series of leaches at 400°F, the effects of time and initial copper to zinc ratio are shown. Again 50 g of zinc concentrate was leached with 500 ml copper sulfate solution in most experiments; exceptions are clearly identified in Table II which indicates the results.

TABLE II

Ex. No.	Time, hr.	Mol ratio of Cu to Zn in charge	Zn dissolved, percent	Cu precipitated, percent	Mol ratio of Cu precipitated to Zn dissolved
6–7	1	1.25	63.2	95.5	1.84
8	2	1.51	73.1	88.8	1.85
9	3	1.51	77.5	96.1	1.86
10	4	1.51	79.3	99.2	1.87
11	4	1.25	77.8	100.0	1.60
12	4	1.38	75.6	100.0	1.83
13	4	2.0	81.7	76.0	1.87
14[a]	4	1.25	71.5	100.0	1.74
15[b]	4	2.0	82.3	76.0	1.85

[a] 5.3 grams H_2SO_4 added. [b] 155 grams Zn-concentrate used.

Generally copper to zinc ratios of about 1.85 were obtained, indicating precipitation of Cu_2S. Exceptions are No. 11 and No. 14. In these examples the solution assays were confirmed by zinc assays of the residues. In both cases copper was completely precipitated. It is possible that under these conditions small quantities of CuS have been formed.

Comparison of Nos. 13 and 15 shows no effect of increased pulp density. This was to be expected because the concentration of copper ions per unit surface area was not changed in these experiments by increasing the pulp density.

EXAMPLES 16–19

Actual process liquors contain zinc sulfate carried over from spent electrolyte through the pressure oxidation (see FIG. 1). Some experiments were conducted which illustrated that this initial zinc content of the leach solution does not have any effect on the extraction. In addition, a pulp density was chosen to produce pregnant solutions suitable for normal zinc electrolysis practice. Previous examples had illustrated that a change in pulp density does not affect the rate of extraction.

In the earlier experiments at 400°F, a molar ratio of copper in solution to zinc in concentrate of 1.51 was used most frequently. For reason of comparison, the same ratio was used in these experiments, while zinc sulfate was added to the leach solutions.

The data pertaining to these experiments are listed in Table III.

These experiments show that the presence of zinc in the leach solution has no noticeable effect on the extraction. An extraction of 79.4 percent was obtained in experiment No. 16 which compares with 79.3 percent for run No. 10 in Table II, where no zinc was present in the initial leach solution.

TABLE III

Run No	16	17	18	19
Solid charge	100 g. Zn conc.	100 g. Zn conc.	100 g. Zn conc.	Residue from No. 18.
Leach solution	Synthetic [a]	Synthetic [a]	Pregnant liquor [b] from No. 17	Synthetic. [a]
Time, hr.	4	4	1	4.
Temperature, F	400	450	400	400.
Zn extraction, percent	79.4	85.0	5.5	78.5.
Fe extraction, percent	Not analyzed		52.9	63.5.
Cu in pregnant liquor, g.p.l.	14.8	7.87	Nil	6.68.
Molar ratio Cu precipitated to Zn dissolved	1.75	1.73	1.26	1.82.

[a] 500 ml. liquor containing 163 g.p.l. Cu and 57 g.p.l. Zn.
[b] 497 ml. liquor containing 7.87 g.p.l. Cu and 149.0 g.p.l. Zn.

One experiment (No. 17) was conducted at 450°F. An extraction of 85.0 percent was obtained compared to 79.4 percent under the same conditions at 400°F.

To obtain good zinc extractions at a reasonable rate, an excess of copper in the leach solution is desirable. In experiments No. 17, No. 18 and No. 19, it was shown that excess copper could be recovered in a leach in two stages. The excess copper in leach solution No. 17 was fully utilized in a 1-hour leach with fresh zinc concentrate. As pointed out below, CuS is likely to be formed under these conditions. This is confirmed by the copper to zinc ratio obtained in experiment No. 18. If then all the copper from the pregnant solution of run No. 17 is precipitated as CuS, an equal amount of copper will be required in run No. 19 to convert CuS, without dissolving any zinc. This accounts for the higher copper to zinc ratio obtained in run No. 19.

In the use of copper sulfate solutions for the leaching of zinc sulfide concentrate, the following reaction may occur to produce cupric sulfide.

$$Cu^{++} + ZnS \rightarrow CuS\downarrow + Zn^{++} \quad 1.$$

Alternatively the precipitation of cuprous sulfide can take place according to:

$$8Cu^{++} + 5ZnS + 4H_2O \rightarrow 4Cu_2S\downarrow + 5Zn^{++} + SO_4 = + 8H^+ \quad 2.$$

Measurements of the pH of leach liquors showed values generally below 0.7 and pH values of 0.2 were common. This indicated that the reaction (2) takes place to a considerable extent. Under these conditions the following reaction becomes important.

$$SO_4 = + H^+ \rightarrow HSO_4^- . \quad 3.$$

Calculations show that at pH<1, HSO_4^- dominates strongly over $SO_4 +$.

The second reaction then should actually be written:

$$8Cu^{++} + 5ZnS + 4H_2O + 3SO_4 = \rightarrow 4Cu_2S + 5Zn^{++} + 4HSO_4^- + 4H^+ . \quad 2'.$$

The relative importance of reactions (1) and (2′) is shown by the following reaction:

$$8CuS + 3Zn^{++} + 4H_2O + 3SO_4 = \rightleftarrows 4Cu_2S + 4HSO_4^- + 4H^+ + 3ZnS \quad 4.$$

$\Delta F°_{400°F} = -13{,}090$ cal/mole formula, and

$$\frac{(HSO_4^-)^4(H^+)^4}{(Zn^{++})^3(SO_4^-)^3} = 9.63 \times 10^5$$

These values show that at pH below about 0.5, CuS is stable relative to Cu_2S provided ZnS is present. During the copper sulfate leach, Cu_2S will first be precipitated on the ZnS particles. By the time the acidity of the solution is such that CuS could be formed, all ZnS particles will be covered with Cu_2S. This inhibits the formation of CuS according to equation (1).

Therefore, when the leaching operation is carried out in two stages, where in the second stage fresh zinc concentrate is contacted with pregnant liquor containing excess copper sulfate, the CuS would be formed.

EXAMPLE 20

The cuprous sulfide formed in the pressure leach can be leached with acid under oxygen pressure to yield elemental sulphur. In Canadian Pat. No. 712,989 granted to Sherritt Gordon Mines Limited, and incorporated herein by reference, a process is described based on the reaction:

$$Cu_2S + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O + S \quad 5.$$

Although this equation adequately described the overall reaction, calculations of the thermodynamics of the system indicate that CuS has to be formed as an intermediate product.

In Example 20 a 100 g sample of copper sulfide precipitate (residue run No. 16, Table III) was leached with simulated spent electrolyte under 250 psig air at 225°F for 2 hours. A residue of 74.1 g was obtained containing a trace of elemental sulphur. A polished section of the residue revealed that the original cuprous sulfide was almost completely converted to cupric sulfide. In this stage of the oxidation process no elemental sulphur can be formed.

In a continuation of this experiment, 42.8 g of the first-treated residue was mixed with 52.2 g fresh chalcocite (Cu_2S) and leached under the same conditions. A residue of 62.0 g was obtained with 4.83 percent elemental sulphur.

This experiment shows that the oxidation of cuprous sulfide takes place in two steps. In the first step, cuprous sulfide decomposes into cupric sulfide and copper ions. The formation of elemental sulphur from cupric sulfide takes place only after virtually complete conversion of Cu_2S.

As noted in Canadian Pat. No. 712,989 about 1 mole of sulphuric acid may be used for each mole of copper. The oxygen pressure is from about 5 to about 100 psig, and the temperature from about 175°F to 225°F. The Cu_2S is selectively oxidized at a rapid rate until about 95 percent of the copper is extracted and the sulphur bound to it is converted to elemental sulphur. Present results indicate that about 80 percent of the sulphur from decomposed cupric sulfide reports as elemental sulphur.

The copper sulfate formed in this leaching step is recycled to react with further zinc sulfide. The zinc sulfate which is formed is similarly recycled and as noted above has a negligible effect in the first leach step in 1, from which it passes to the electrolysis unit.

The results obtained in Examples 1–19 by leaching zinc concentrate with copper sulfate solutions were generally much better than the results obtained by leaching with sulfuric acid. Extractions of about 80 percent were obtained after 4 hours at 400°F with a copper sulfate deficiency. A slight excess of copper resulted in about 82 percent extraction. An extraction of 85 percent was achieved in a 4-hour leach at 450°F in spite of the copper deficiency. Thus extractions of about 80 percent are readily obtained under proper conditions. Above this point, the rate of extraction decreases because of the smaller surface area available for reaction.

Several alternatives are available to enhance the dissolution of zinc. One is to physically separate and regrind the coarse fraction prior to leaching. Alternatively, the unreacted zinc sulfide particles may be left behind in the residue and recovered during subsequent treatment of the residue. In the copper sulfate regenerating step (pressure oxidation, FIG. 1), the copper sulfide layer will be removed from the zinc sulfide particles. By selectively removing the unreacted zinc sulfide from the final residue by flotation, the zinc sulfide can be recycled, to result in high zinc recoveries. An additional advantage of this method is a beneficial effect on the sulphur recovery. The presence of zinc sulfide in the leach residue would result in milder oxidizing conditions towards the end of the copper sulfate regenerating step. This inhibits the formation of sulfuric acid and this improves the yield of elemental sulphur. Thus the presence of unleached zinc sulfide in the leach residue does not constitute a drawback for the overall process. This alternative is depicted in FIG. 2, but of course could also be employed in the method of FIG. 1.

A disadvantageous factor in the process of FIG. 1 is inherent formation of sulfuric acid which was noted to occur during the precipitation of cuprous sulfide. Because conventional procedures for purification of the pregnant solution prior to electrolysis require essentially neutral conditions, the use of a neutralizing agent might be required. A practical solution is a change in the leaching procedure to ensure production of CuS rather than Cu_2S, as illustrated in FIG. 2. The parameters for this process are illustrated in the following sequence of examples.

Zinc concentrate was leached with copper sulfate solutions at temperatures ranging from 300° to 450°F. under oxygen pressures from 20 to 100 psig. Copper precipitated initially as cuprous sulfide and leach solutions contained considerable quantities of acid. Immediately after precipitation of cuprous sulfide, an oxidation reaction converted cuprous sulfide to cupric sulfide under consumption of acid. This second reaction was strongly promoted by high oxygen pressures while the first reaction was promoted by high temperatures. Leach solutions obtained at 400°F. and 20 psig oxygen contained about

20 percent of the sulphur in solution as acid after 4 hours. Solutions from experiments at 300° F. and 100 psig oxygen were essentially free of acid at any time.

With time cupric sulfide dissolved, especially under high oxygen pressures. Because of this reaction, from 33 to 65 percent of the sulphur in the zinc concentrate was solubilized. The results indicate the advantages of a staging operation to combine high zinc extraction with low sulphur dissolution and an essentially acid free solution. Thus with a low zinc extraction, obtained by using an excess of zinc concentrate, the resulting leach solution is well suited for solution purification prior to zinc electrolysis. Elemental sulphur is produced from cupric sulfide in the residue, iron is rejected and excess zinc concentrate is recycled. This process provides for higher zinc recoveries than possible in the conventional roasting-electrolysis process and is suitable for treating middlings and other copper-zinc sulfide products.

EXPERIMENTAL PROCEDURE

OXIDIZING PROCEDURES

The zinc concentrate used in the following examples was analyzed with the following results: Zn – 51.2 percent; Cu – 0.96 percent; Fe – 8.3 percent; and S – 32.0 percent.

The experiments were performed in an Autoclave Engineers 5-gallon autoclave that was modified by placing a tantalum reaction vessel within a steel sleeve holder. The space between the steel sleeve holder and the autoclave wall was filled with water. A cooling coil was immersed in the water. This arrangement made it possible to cool the reaction mixture rapidly after termination of an experiment without exposing to coil to the corrosive leach liquors. The autoclave was heated to the desired reaction temperature by electric resistance heating; constant temperature was maintained by automatic control. During the experiments the slurry was vigorously agitated by a tantalum stirrer. Pressurized air was introduced into the solution through stainless steel tubing with its opening approximately 2 inches above the stirrer blades. Pressure was maintained at the desired level by a pressure regulator on the air cylinder. To avoid oxygen depletion during the reaction, gas was constantly removed from the autoclave at a rate of approximately 1.25 liters per minute (atmospheric pressure and room temperature). In each experiment the solid charge consisted of 200 grams of zinc concentrate which would require about 15 liters of oxygen to react completely according to Reaction (1). Consequently sufficient oxygen for complete reaction was provided every hour.

Slurry samples were taken at regular intervals. For this purpose a valve in the air supply line was closed momentarily and a second valve between the first one and the autoclave was opened to the atmosphere. The pressure in the autoclave forced a slurry sample up through the air inlet tube into a graduated glass cylinder. In most experiments two samples of 100 ml volume each were removed during a run.

EXAMPLES 21–26

A series of six leaching experiments was performed in which the temperature was either 300°F, 350°F, or 400°F, and the partial pressure of oxygen above the solution was 50 psig or 100 psig as indicated below. In all experiments, 200 grams of zinc concentrate was leached with one liter of solution containing 95.5 grams copper as cupric sulfate. The amount of copper present in the leach solutions was 105 percent of the amount required to dissolve all of the zinc and the iron associated with it in the zinc lattice as calculated from the reaction:

$$5ZnS + 4Cu^{++} + 2O_2 \rightarrow 5Zn^{++} + 4CuS + SO_4^{--} \quad 6.$$

and the analogous reaction for dissolution of iron.

The first experiment was terminated after 3 hours. The five other experiments each lasted 6 hours and slurries were sampled after 1 hour and after 3 hours.

Solution samples were analyzed for Zn, Cu, Fe, and S.

After the experiments were terminated, the slurries were filtered, the residues washed and dried and the filtrates combined with washings made up to 2 liters. Solutions and residues were both analyzed for Zn, Cu, Fe, and S. The results of these experiments are presented in Table IV.

TABLE IV

200 grams of concentrate, 1 liter solution, 6 hours except No. 1

Experiment No.	21	22	23	24	25	26
Temperature, F.	300	300	350	400	300	350
Oxygen partial pressure, p.s.i.g.	100	100	100	100	50	50
Solution after 1 hr., g.p.l.:						
Zn	N.S.	18.3	27.1	39.5	16.2	27.6
Cu	N.S.	63.7	41.7	14.0	57.5	35.7
Fe	N.S.	2.07	1.74	3.26	2.24	2.38
S	N.S.	42.8	40.7	40.3	39.8	39.7
Solution after 3 hr. g.p.l.:						
Zn	[a] 25.3	45.6	42.8	46.4	52.1	45.5
Cu	[a] 32.0	53.0	32.8	20.8	41.6	28.5
Fe	[a] 2.49	1.55	1.55	1.74	1.91	2.52
S	[a] 31.9	54.3	45.4	45.5	52.4	45.9
Solution (a) after 6 hr., g.p.l.:						
Zn		40.7	35.0	41.4	39.7	33.8
Cu		29.6	20.1	27.7	17.5	17.8
Fe		2.96	2.24	1.58	3.15	3.88
S		38.4	32.2	40.9	32.2	30.8
Final residue weight, g.	156.0	98.7	132.7	109.3	137.8	150.0
Residue analysis, percent:						
Zn	33.8	17.2	19.1	18.8	15.3	20.3
Cu	21.0	29.0	36.0	36.8	39.3	37.7
Fe	7.69	11.0	9.29	12.6	7.52	7.69
S	30.1	25.9	27.1	24.1	29.0	28.4
Zinc extraction, percent	49.5	83.8	75.1	76.5	80.3	71.1

(a) Based on 2 liters solution. N.S.=no sample.

Observation of solution samples and residue weights indicated that the best elimination of copper had been achieved within the first 3 hours of Run No. 24, at 400°F, and that some benefit could be expected from lower oxygen pressures. Accordingly further experiments were conducted at relatively high temperatures and low partial pressures of oxygen. The leaching time was reduced to 4 hours and the solution was sampled after 1 and after 2 hours. The results are discussed in further detail below.

EXAMPLES 27–30

Three experiments were performed at 400°F and 20 psig oxygen, and one at 450°F, and 20 psig oxygen. In all experiments 200 grams of zinc concentrate was used. Initial solution volume was one liter in three experiments, and 400 ml in the other run.

Results of these experiments are shown in Table V. Zinc extractions for all experiments were based on the distribution of zinc between solutions and final residue.

TABLE V

200 grams concentrate, 20 p.s.i.g. oxygen, 4 hours, 1 liter solution except as noted

Experiment No.	27	28	29	30 [a]
Temperature, F.	400	450	400	400
First sample [b] solution, g.p.l.:				
Zn	25.2	40.7	41.4	N.S.
Cu	5.98	10.8	11.7	N.S.
Fe	4.40	3.54	6.86	N.S.
S	25.8	40.8	45.5	N.S.
Second sample [c] solution, g.p.l.:				
Zn	42.5	38.2	45.6	N.S.
Cu	3.70	11.0	4.03	N.S.
Fe	6.61	2.90	7.74	N.S.
S	38.1	37.8	42.3	N.S.
Final solution (2 liters), g.p.l.:				
Zn	35.5	40.9	32.3	40.7
Cu	6.75	22.5	9.58	20.2
Fe	3.95	1.58	2.49	6.94
S	30.3	39.3	28.5	38.6
Final residue weight, g.	166.4	106.2	163.2	124.0
Residue analysis, percent:				
Zn	17.6	13.2	17.2	18.6
Cu	48.5	45.9	46.4	47.4
Fe	4.48	12.3	6.36	3.37
S	26.4	21.6	26.2	27.6
Zinc extraction, percent [d]	72.4	86.5	71.6	77.9

[a] 400 ml. solution.
[b] After 1 hour for Runs 7 and 8; after ½ hour for Run No. 9.
[c] After 2 hours for Run No. 7; after 1½ hours for Run No. 9.
[d] Based on distribution of zinc between solids and solutions.
N.S.=no sample.

Most leach solutions contained acid, evidence of formation of cuprous sulfide. This was also confirmed by sulphur deficiencies in the residues if all the copper was assumed to be present as cupric sulfide. The amount of sulphur as acid increased with increasing temperature, and ranged from about 3 percent at 300°F to about 20 percent of the total amount of sulphur in solution at 400°F.

The most predominant reactions taking place during leaching of zinc concentrate under conditions employed in this investigation were:

$$5ZnS + 8Cu^{++} + 4H_2O \rightarrow 5Zn^{++} + 4Cu_2S\downarrow + 8H^+ + SO_4 = \quad 2.$$

$$4Cu_2S + 8H^+ + 2O_2 \rightarrow 4CuS\downarrow + 4Cu^{++} + 4H_2O \quad 7.$$

$$5ZnS + 4Cu^{++} + 2O_2 \rightarrow 5Zn^{++} \rightarrow 4CuS\downarrow + SO_4 = \quad 8.$$

$$CuS + 2O_2 \rightarrow Cu^{++} + SO_4 =. \quad 9.$$

In addition iron sulfide leached entirely analogous to Reaction (4).

$$5FeS + 8Cu^{++} + 4H_2O \rightarrow 5Fe^{++} + 4Cu_2S\downarrow + 8H^+ + SO_4 =.$$

10.

Part of the dissolved iron subsequently precipitated according to one or more of the following reactions:

$$4Fe^{++} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3\downarrow + 8H^+ \quad 11.$$

$$4Fe^+A? + O_2 + 4SO_4 = + 2H_2O \rightarrow 4Fe(OH)SO_4\downarrow \quad 12.$$

$$4Fe^+A? + 4H^+ + O_2 + 6SO_4 = \rightarrow 2Fe_2(SO_4)_3 + 2H_2O. \quad 13.$$

In view of the small quantities involved any acid formation due to precipitation of iron would be negligible. The presence of acid in the leach solutions is thus attributed to a predominance of the acid forming Reaction (2) over the acid consuming Reaction (7).

The amount of sulphur found in final leach solutions indicated that Reaction (9), dissolution of cupric sulfide, took place. If Reaction (2), and (7), only take place, only 16 to 20 percent of the sulphur in zinc concentrate should have been dissolved during leaching. However, 33 to 65 percent was actually dissolved.

Table VI shows the dissolution of sulphur from zinc concentrate for the various experiments. Also shown are the percentages of sulphur converted to acid.

TABLE IV

Expt. No.	Temp., F.	Oxygen pressure, p.s.i.	Zinc extraction, percent	Theoretical [a] S dissolution, percent of S in concentrate	Actual S dissolution, percent of S in concentrate	S conversion to acid, percent of total S in solution
22	300	100	83.8	19.3	60.9	2.6
23	350	100	75.1	17.3	43.8	9.2
24	400	100	76.5	17.6	62.6	13.1
25	300	50	80.3	18.5	40.4	3.6
26	350	50	71.1	16.4	35.3	8.8
27	400	20	72.4	16.6	33.0	20.2
28	450	20	86.5	19.9	64.6	16.7
29	400	20	71.6	16.5	33.1	19.9
30 [b]	400	20	77.9	17.9	47.5	6.5

[a] Assuming no redissolution of CuS.
[b] 200 grams zinc concentrate in 400 ml. solution; all others 200 grams zinc concentrate in one liter solution.

It can be seen that up to 400°F, dissolution of sulphur was largely controlled by oxygen pressure. Best sulphur retentions were obtained at 400°F and 20 psig oxygen pressure. The experiments at higher oxygen pressures indicate a minimum sulphur extraction at 350°F. Thus sulphur extraction would have been lower at 350°F. and 20 psig than at 400°F and 20 psig oxygen. Zinc extraction, however, was relatively low in both experiments at 350°F, and quite large quantities of acid were formed. In FIG. 3, acid formation is shown as a function of time for all experiments where samples were taken. In all cases the amount of acid formed was at a maximum at a time prior to termination of the experiment. This indicates that Cu_2S was the primary copper precipitate and that CuS was formed by subsequent oxidation. FIG. 4 shows the ratio of acid sulphur versus zinc as a function of time. The general similarity of the corresponding curves in FIG. 3 and 4, indicates that the decline in acid content of the solutions was caused by the acid consuming Reaction (7) and not by an increase in total sulphur content according to Reaction (9). The data presented in Table VI show, however, that Reaction (9) did occur. Reaction (9) can only take place after CuS has been formed by Reactions (2) and (7). Hence, the increase of sulphur in leach solutions was initially determined by the stoichiometry of Reaction (2). Because iron reacted proportionally to zinc, the increase in sulphur under these conditions was directly proportional to the amount of zinc dissolved. In all experiments the amount of copper in solution had decreased sharply by the time the first sample was taken. Thus Reaction (9) did not occur to any measurable extent in the first hour. On this basis minimum values for the solution volumes at the time of first sampling were calculated. Similarly maximum values were calculated assuming Reaction (9) did proceed at a constant rate throughout the entire run. The zinc extraction curves are shown in FIG. 5. It appeared that Reaction (9) could indeed be neglected for the first hour of each experiment. Approximate zinc extractions at subsequent sampling times, were calculated by assuming Reaction (9) to proceed at a constant rate.

It has been shown that by proper choice of leaching conditions, cupric sulfide can be obtained as the condensed reaction product without formation of appreciable quantities of acid. To achieve adequate zinc extractions however it was necessary to prolong the reaction time which caused redissolution of cupric sulfide. This is equivalent to loss of sulphur from the concentrate. It was observed that redissolution of cupric sulfide only occurred after a considerable portion of zinc had been dissolved. Thus by providing sufficient zinc sulfide area, i.e., by using sufficient excess zinc concentrate, the tendency of redissolution of cupric sulfide would be minimized. The molar ratio of Zn to Cu should be greater than 1:1 and preferably from 1.2:1 to 1.5:1 and up to 2:1.

Alternatively when lower ratios of Zn to Cu are used, as from 1:1 to 1:2, the reaction should be carried to about 40 to 80 percent conversion, preferably from 50 to 60 percent conversion, based upon the extraction of Zn from the ZnS. The pregnant solution of such a leaching operation is essentially free of copper and acid, and suitable for solution purification prior to zinc electrolysis. The leach residue, containing cupric sulfide, oxidized iron and excess concentrate can be leached with return acid under conditions conducive to the formation of elemental sulphur. The resulting solution is suitable for leaching additional zinc concentrate. The solids can be separated by physical methods e.g., flotation, into three fractions; elemental sulphur, zinc concentrate, and iron reject. Zinc concentrate is of course returned to the copper sulfate leach. This shows the importance of excess of zinc concentrate in the initial stage to avoid dissolution of cupric sulfide. The use of excess concentrate in the first stage of the process is therefore considered a preferred method of operation.

This process, outlined in FIG. 2, provides higher zinc extractions than possible with the conventional roasting-electrolysis process, because the roasting step with its inherent formation of insoluble zinc ferrites is eliminated. The process can also be integrated with a conventional installation for treatment of middling fractions from the flotation circuit. Another application is the treatment of bulk flotation concentrates or treatment of concentrates from ores that cannot be effectively separated by selective flotation.

This invention has been described in terms of specific embodiments set forth in detail. Alternative embodiments will be apparent to those skilled in the art in view of this disclosure, and accordingly such modifications are to be contemplated within the spirit of the invention as disclosed and claimed herein.

We claim:

1. The process which comprises mixing zinc sulfide ore and a copper sulfate solution at an elevated temperature and pressure to form a copper sulfide and a zinc sulfate solution, separating said copper sulfide from said zinc sulfate solution, purifying said zinc sulfate solution, electrolyzing said zinc sulfate solution to form metallic zinc and sulfuric acid, mixing said copper sulfide with oxygen and said sulfuric acid at elevated temperatures and pressures to form copper sulfate solution and sulphur, separating said copper sulfate solution therefrom and mixing therewith fresh zinc sulfide ore to repeat said process.

2. The process of claim 1 wherein the mole ratio of zinc to copper is from 2:1 to 1:2.

3. The process of claim 1 wherein the mole ratio of zinc to copper is 1:1 to 1:2 and the conversion of zinc sulfide to zinc sulfate is from 40 to 80 percent.

4. The process which comprises mixing zinc sulfide ore and copper sulfate solution and an oxygen containing gas in a first pressure leaching vessel, discharging the reaction mixture to a filtering means, withdrawing the pregnant solution from the filtering means and treating said pregnant solution in a purification and electrolysis means to produce zinc metal and a spent sulfuric acid electrolyte, charging said sulfuric acid, air and the solids from said filtering means to a second pressure leaching vessel, regenerating copper sulfate solution in said second leaching vessel, recycling said copper sulfate solution to said first pressure leaching vessel, discharging the residue from said second leaching vessel to a sulphur flotation means, withdrawing sulphur from said flotation means, withdrawing unreacted zinc sulfide from said flotation means and recycling said zinc sulfide to said first pressure leaching vessel.

5. The process of claim 1 in which the amount of oxygen in said first leaching vessel is about 20 to 100 psig.

6. The process of claim 1 wherein the ratio of zinc sulfide to copper sulfate in said first pressure leaching vessel is in excess of the molar quantities needed for reaction.

7. The process of claim 1 wherein the ratio of Zn to Cu in said first pressure leaching vessel is 1:1 to 1:2 and the conversion of zinc sulfide to zinc sulfate therein is from 40 to 80 percent.

8. The process of claim 7 wherein the charge to said second leaching vessel is unreacted zinc sulfide, a copper sulfide, and about 1 mole of sulfuric acid per mole of copper.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,655,538 Dated April 11, 1972

Inventor(s) Howard C. Renken and Theodoor W. Zegers

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Abstract, line 2, delete "solution." ;

In the Abstract, line 3, delete the entire line ;

In the Abstract, line 9, after "sulfate" insert -- solution. To provide for increased recovery the copper sulfate -- ;

Col. 6, line 50, change "this" to -- thus -- ;

Col. 7, line 33, after "ing" change "to" to -- the -- ;

Col. 9, line 13, after "8." insert -- (2+7) -- ;

Col. 9, line 22, change "$4Fe^{+}A?$" to -- $4Fe^{++}$ -- ;

Col. 9, line 23, change "$4Fe^{+}A?$" to -- $4Fe^{++}$ -- ;

Signed and sealed this 25th day of July 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents