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Sulfuric Acid Extraction Technique for Recovering Zinc and Sulfur From Sphalerite

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A goal of the Bureau of Mines is to maximize the recovery of minerals and metals while minimizing pollution. To reach this goal the Bureau is conducting research to achieve major improvements in metals and minerals processing. The Bureau has investigated a laboratory-scale, ambient pressure technique which yields zinc sulfate and elemental sulfur from sphalerite (ZnS) concentrates by reaction with 80 to 85 pct sulfuric acid at 175° to 200° C. The objective was to help develop an economical hydrometallurgical method of producing zinc from sulfide concentrates that would eliminate the need for sulfur dioxide air pollution controls. More than 98 pct of the zinc was recovered as zinc sulfate after 3 hr at 175° C. Neutral zinc sulfate required for electrolysis was separated from the sulfuric acid solution by crystallization as $ZnSO_4 \cdot 7H_2O$ at 10° C. Up to 80 pct of the water in the recycled electrolysis solution was removed by the crystallization process; evaporation was used to further concentrate the sulfuric acid for reuse in leaching sphalerite. Advantages of the proposed method over conventional roasting and leaching are: virtual elimination of sulfur dioxide, production of a solid sulfur byproduct, and high zinc recoveries by elimination of zinc ferrite losses.

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Sulfuric Acid Extraction Technique for Recovering Zinc and Sulfur From Sphalerite

By H. H. Dewing and A. A. Cochran

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SULFURIC ACID EXTRACTION TECHNIQUE FOR RECOVERING ZINC AND SULFUR FROM SPHALERITE

by

H. H. Dewing[1] and A. A. Cochran[2]

ABSTRACT

The Bureau of Mines conducted a laboratory-scale investigation of a technique that produces zinc sulfate and elemental sulfur from sphalerite concentrates by reaction with sulfuric acid at 175° to 200° C and ambient pressure. The objective of the investigation was to develop a hydrometallurgical method of producing zinc from sulfide concentrates that does not generate sulfur dioxide pollutants. Reaction with 80- to 85-pct sulfuric acid produced 4 moles of sulfur for every 3 moles of sphalerite reacted, with minimal production of sulfur gases under optimum conditions. More than 98 pct of the zinc was recovered as zinc sulfate after 3 hours at 175° C. The reaction mixture was leached with simulated spent zinc electrolyte containing 13-pct sulfuric acid to recover zinc sulfate from the insoluble, high-sulfur residue. Neutral zinc sulfate, which is required for electrolysis, was separated from the sulfuric acid solution by crystallization as $ZnSO_4 \cdot 7H_2O$ at -10° C. Up to 80 pct of the water in the recycled electrolysis solution was removed by the crystallization process; evaporation was used to further concentrate the sulfuric acid for reuse in leaching sphalerite. Advantages of the proposed method over conventional roasting and leaching include virtual elimination of sulfur dioxide, production of a solid sulfur byproduct, and higher zinc recoveries due to elimination of zinc ferrite losses.

INTRODUCTION

This investigation was conducted by the Bureau of Mines in support of its overall goals of helping to maintain an adequate supply of minerals and metals for future national needs with minimum waste and environmental degradation. The objective of the investigation was to develop a hydrometallurgical method of producing zinc from ZnS (sphalerite) concentrates without the attendant formation of SO_2 (sulfur dioxide), which requires the use of air pollution controls. Experimental conditions were sought to produce elemental sulfur at atmospheric pressure concurrent with a high recovery of zinc.

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[1] Research chemist.

[2] Supervisory research chemist.

Both authors are with the Rolla Metallurgy Research Center, Bureau of Mines, Rolla, Mo.

Currently, zinc is commercially produced by roasting ZnS concentrates in air to produce ZnO and SO_2. ZnO in the calcine is leached with recycled electrolyte containing dilute H_2SO_4 (sulfuric acid). Various purification processes are used to recover cadmium and silver and to remove deleterious impurities before zinc is electrowon. The SO_2 produced by roasting is converted to H_2SO_4. Supplies of H_2SO_4 have increased in recent years as a result of antipollution regulations that require control of SO_2 emissions from industrial sources. Sulfuric acid may not be marketable in the geographical area where it is produced, and transportation costs diminish its value as a byproduct. If the sulfur could be recovered in elemental form, its market potential would be increased.

Over 60 pct of domestic primary demand for zinc is met by imports; the U.S. share of world zinc production has declined from 27 pct in 1960 to 9 pct in 1974 (2).[3] One way to help reverse this trend is to provide better technology for zinc production, especially technology that does not require costly pollution controls.

Direct leaching of metal sulfide concentrates with H_2SO_4 has been investigated. McKay and Halpern (7) studied the oxidation of pyrite with oxygen in acid solutions and observed a two-stage reaction; in the first stage, H_2S (hydrogen sulfide) and elemental sulfur were formed, and, in the second, SO_2 and H_2SO_4. Other investigators (3) determined the effect of many variables on the reaction and its products. Bjorling (1) reported on similar experiments with synthetic ZnS and H_2SO_4; elemental sulfur was produced, but the reaction rate was very slow. Using natural ZnS, Forward (4-6) was able to extract 95 pct of contained zinc in 4 hours at 115° C with an oxygen pressure of 20 lb/sq in. Sulfur formed solid pellets and occluded some of the $ZnSO_4$. Stanczyk and Rampacek (9), in similar experiments, formed H_2SO_4 at 200° C. Other researchers (8) have determined the reaction kinetics of ZnS dissolution in dilute H_2SO_4, which produces H_2S.

EXPERIMENTAL PROCEDURES

The feed for the tests was a typical Missouri ZnS concentrate. Chemical analysis and particle-size analysis of the head sample are given in tables 1 and 2, respectively. Calcium and magnesium occur in the concentrate, largely as carbonates. Concentrates containing such appreciable quantities of carbonates are usually preleached with dilute H_2SO_4 to remove Mg and CO_3 before roasting; however, the concentrate used in the present investigation was not preleached.

A 1,000-ml batch reactor was used to react 200-gram samples of the ZnS concentrate with 250 ml of H_2SO_4 solution. The reactor was sealed from the atmosphere, and gases evolved by the reaction were collected and measured over water, with minimum contact area between gases and water. Analysis of the water revealed that the amount of dissolved gases was negligible. Samples of the evolved gases were removed with a small gas syringe through a septum in

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

the reactor. The gas composition was determined by gas chromatography, using a Porapak Q column[4] at 25° C to separate air, CO_2, H_2S, and SO_2.

TABLE 1. - Chemical analysis of ZnS concentrate[1]

Element	Pct	Element	Pct
Zinc............	54.0	Manganese.......	0.27
Sulfur..........	31.2	Cadmium.........	.23
Iron............	5.92	Aluminum........	.15
Calcium.........	1.41	Cobalt..........	.02
Magnesium.......	.72	Nickel..........	.01
Lead............	.45	Chromium........	<.01
Copper..........	.27	Arsenic.........	<.01

[1] Balance is principally oxygen.

TABLE 2. - Particle-size analysis of ZnS concentrate

Particle size, mesh	Wt-pct
Plus 100....................................	0.4
Minus 100 plus 200..........................	23.0
Minus 200 plus 270..........................	20.4
Minus 270 plus 325..........................	16.4
Minus 325 plus 400..........................	7.6
Minus 400...................................	32.2
Total................................	100.0

The ZnS samples were heated in the reactor at 130° C for 30 min to remove all moisture prior to testing. After adding the acid, the mixture was stirred and the temperature was gradually increased to the desired level. After reaction, the mixture was cooled, then filtered or centrifuged to recover moderately concentrated H_2SO_4. The solids then were leached with hot, dilute H_2SO_4 (simulated depleted electrolyte) or water to dissolve the $ZnSO_4$. Filtration or centrifugation produced a residue consisting of elemental sulfur, insoluble portions of the concentrate, and unreacted ZnS. The filtrate was cooled, and $ZnSO_4 \cdot 7H_2O$ was crystallized out and filtered.

In other tests, reaction rates were determined by reacting 200 grams of ZnS with 250 ml of 83-pct H_2SO_4 at approximately constant temperature. Small samples of the reaction mixture were removed at intervals and quenched in water. The insoluble residue was filtered, dried, weighed, and analyzed for zinc.

Isothermal tests were made in a 1,000-ml flask maintained at constant temperature by an oil bath. Five-gram samples of ZnS were added through an air lock to the sealed flask, which contained 50 ml of H_2SO_4 solution and air. Gases in the flask were sampled and analyzed by chromatography, and the volume of sulfur gases under standard conditions was calculated.

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[4] Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

RESULTS AND DISCUSSION

Isothermal Tests

The desired reaction was to combine ZnS and H_2SO_4 to produce $ZnSO_4$, S, and H_2O. Isothermal tests were conducted at several temperatures and acid concentrations to determine the changes in the relative amounts of H_2S and SO_2 evolved during the reaction. An excess of acid was used, which kept the acid concentration almost constant during the reaction. Figures 1 and 2 show the quantities of gases evolved at various acid concentrations and at two temperatures. In all tests, some H_2S formed initially and then reacted with the mixture to form sulfur. Sulfur dioxide evolved as the reaction progressed. The reaction is sensitive to changes in H_2SO_4 concentration; 75-pct H_2SO_4 produced large amounts of H_2S (fig. 2), and 87.5-pct acid yielded SO_2 primarily (fig. 1). In these tests using an excess of acid, the optimum acid concentration to minimize sulfur gas evolution was about 80 pct.

The evolution of H_2S and SO_2 was attributed to the following generalized reactions:

$$ZnS + H_2SO_4 \rightarrow ZnSO_4 + H_2S \quad (1)$$

and

$$ZnS + 4H_2SO_4 \rightarrow ZnSO_4 + 4SO_2 + 4H_2O. \quad (2)$$

Figures 3 and 4 show the quantities of gases evolved at different temperatures and two acid concentrations. Increased temperatures resulted in increased amounts of SO_2. In most tests, the amount of SO_2 produced leveled off after a time; thereafter, little or none was produced. This suggests that the SO_2 and the reaction mixture were nearly in equilibrium. Figures 1

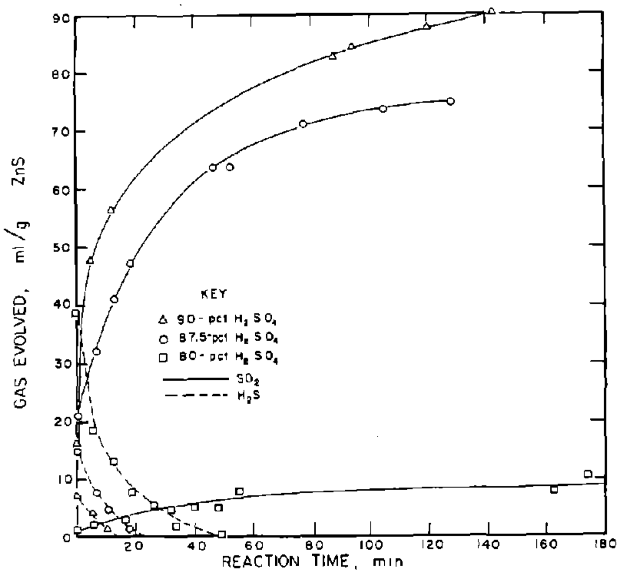

FIGURE 1. - Effect of H_2SO_4 concentration on sulfur gas production at 180° C.

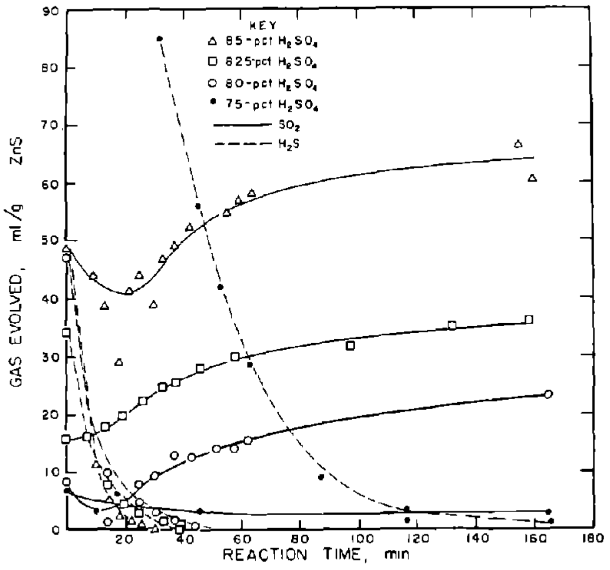

FIGURE 2. - Effect of H_2SO_4 concentration on sulfur gas production at 185° C.

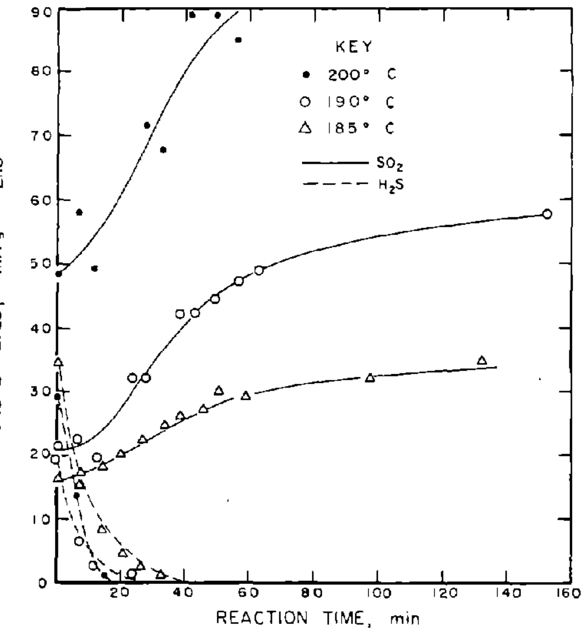

FIGURE 3. - Effect of reaction temperature on sulfur gas production (82.5-pct H_2SO_4).

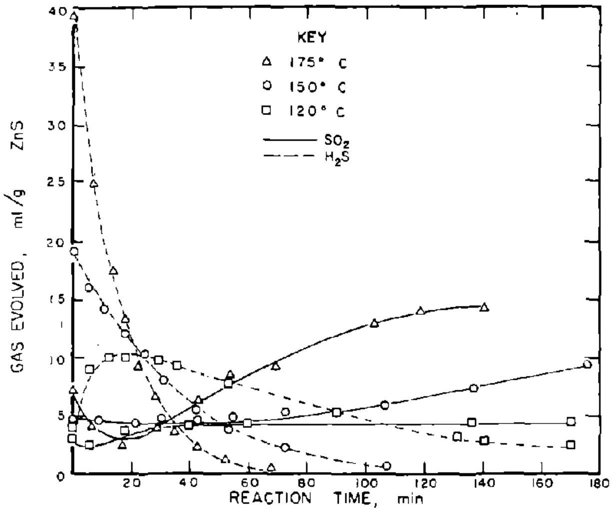

FIGURE 4. - Effect of reaction temperature on sulfur gas production (80-pct H_2SO_4).

through 4 show that acid concentration is a more critical factor than temperature in determining whether H_2S or SO_2 is primarily produced.

Hydrogen sulfide was found to disappear from the system by a first-order reaction at 120° to 185° C. An Arrhenius activation energy of +13 kcal/mole for the reaction was determined from a plot (fig. 5) of the logarithms of the temperature-dependent rate constant as a function of reciprocal temperature (1/T). The rate of disappearance of H_2S from the system is given by

$$-\frac{d[H_2S]}{dt} = 1.55 \times 10^5 \exp(-13.0/RT)P_{H_2S}, \qquad (3)$$

where T is the temperature, R is the gas constant, and P_{H_2S} is the pressure of H_2S.

The activation energy of +13 kcal/mole for the disappearance of H_2S indicates that the reaction was not diffusion controlled. (Diffusion controlled reactions have activation energies on the order of 1 kcal/mole.) The H_2S probably reacted with SO_2 in the vapor phase.

The ZnS concentrate contained some calcium and magnesium carbonates, which, when contacted with acid, release CO_2. The large initial evolution of H_2S is probably because the CO_2 sweeps the H_2S out of the reaction mixture.

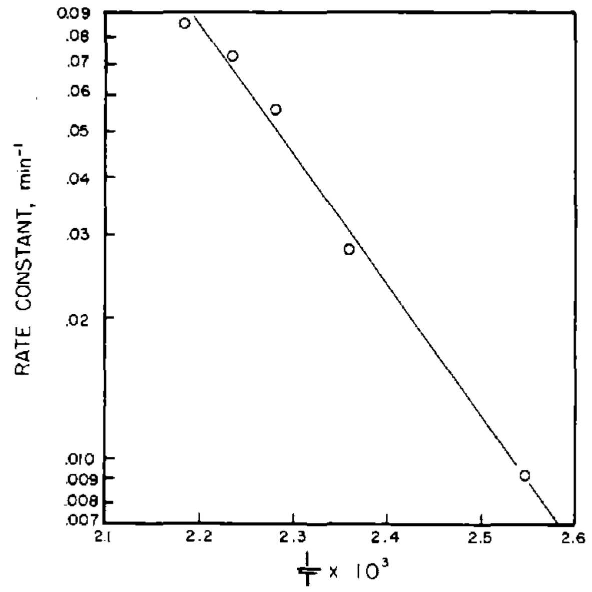

FIGURE 5. - Arrhenius determination of rate of reaction of H_2S.

Table 3 shows the results of tests in which H_2S was bubbled through H_2SO_4 solutions from two different depths. The acid temperature was 180° C, and the H_2S flow rate was 100 ml/min. The percentage of H_2S that reacted to form elemental sulfur increased as the depth traversed increased, and as the acid concentration increased. If the ZnS were introduced at the bottom of the reaction vessel, the amount of H_2S produced would be less as the depth of acid was increased.

TABLE 3. - Reaction of H_2S with H_2SO_4

H_2SO_4 concentration, pct	Pct H_2S reacted by sparging	
	3-inch depth	6-inch depth
77.5..........	40	60
82.5..........	55	76
85.0..........	69	85

Reaction Stoichiometry

Table 4 gives the results of batch tests in which far less excess acid was used and conditions were near optimum for the formation of elemental sulfur. Initial acid concentrations ranged from 83 to 85 pct, and only small amounts of sulfur gases were produced. The average yield of sulfur was 1.33 moles per mole of ZnS reacted. Stoichiometry of the reaction is given by

$$3ZnS + 4H_2SO_4 \rightarrow 4S^\circ + 3ZnSO_4 + 4H_2O. \qquad (4)$$

TABLE 4. - Batch tests of $ZnS-H_2SO_4$ reaction

Test	H_2SO_4 concentration, wt-pct	Av temp, ° C	Time, hr	Zinc recovery, pct	Molar ratio of S° produced to ZnS reacted	Sulfur gases, pct of S in ZnS
1........	85	174	2.5	97.5	1.30	0.5
2........	83	176	1.5	94.4	1.32	<.3
3........	84	161	3.5	93.1	1.32	<.3
4........	84	174	3.0	98.4	1.30	.5
5........	84	176	1.0	92.0	1.43	<.3
6........	85	176	2.5	94.5	1.40	<.3
7........	85	182	4.0	98.3	1.37	<.3
8........	85	185	6.0	99.8	1.21	([1])

[1] Not determined.

The effect of reaction temperature on stoichiometry was negligible. Higher temperatures accelerated the reaction and the consequent rate of heat evolution from the moderately exothermic reaction. With long reaction times, as in tests 7 and 8 (table 4), zinc recoveries approached 100 pct. High temperature and long reaction time (test 8) resulted in decreased sulfur recovery; this was attributed to the oxidation of elemental sulfur by H_2SO_4, as follows:

$$S^\circ + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O. \tag{5}$$

The formation of SO_2 by reaction of ZnS and H_2SO_4 cannot be supported because of the near absence of unreacted ZnS after the first 2 hours of reaction.

Rate of Reaction

A series of leaching tests were conducted in which the reaction time and the temperature were varied. The concentration of unreacted ZnS was calculated from the weight and analysis of the leach residue using an empirically derived equation, and the logarithms of these values were plotted as a function of time (fig. 6). The approximate linearity of the plots indicates that the reactions were approximately first order, depending on ZnS concentration. The rate constants were determined from the slopes. The extrapolated lines do not go through one point because different times were required to stabilize the temperatures at the desired values. The finely ground ZnS reacting with an excess of acid solution is a pseudohomogeneous mixture. The integrated rate equation for a first-order reaction is

$$[ZnS] = [ZnS]_{t=0} \exp(-k_T t), \tag{6}$$

where k_T is the temperature-dependent rate constant and [ZnS] is the concentration of unreacted ZnS at time t.

The following Arrhenius equation was used to determine the effect of temperature on the reaction rate constant:

$$k_T = A_0 \exp(-E^\circ/RT), \tag{7}$$

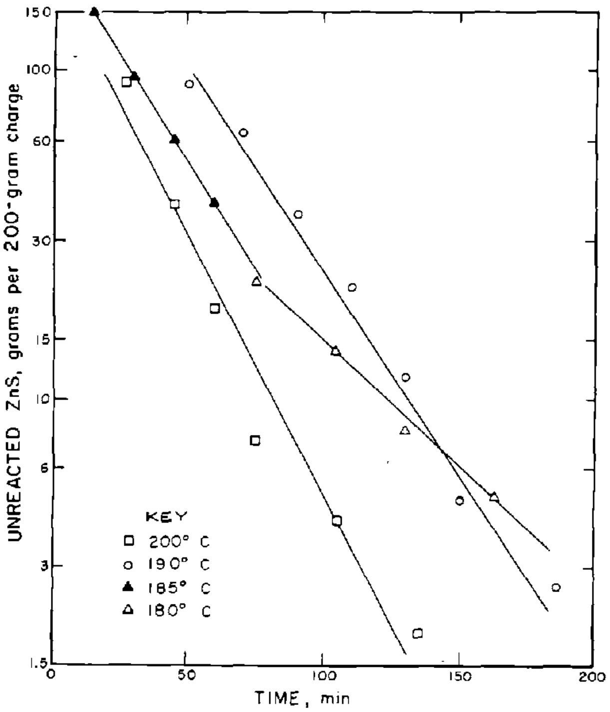

FIGURE 6. - Effect of temperature on the rate of reaction of ZnS with 85-pct H_2SO_4.

where A_0 is the frequency factor and E° is the Arrhenius activation energy of the reaction. The values were calculated to be 4.2×10^6 min^{-1} for the frequency factor and 17.4 kcal/mole for the activation energy. The reaction time needed to obtain 98.0 pct conversion of ZnS at 200° C was calculated to be 1.3 hours; at 180° C, 3.2 hours would be needed. These calculated values compare satisfactorily with experimental zinc recoveries given in table 4.

Separation of Reaction Products

The reacted mixture contained $ZnSO_4$, H_2SO_4, S, and unreacted solids. In one approach, the insoluble residue was removed by leaching the soluble components with water and filtering. The filtrate contained the H_2SO_4 and $ZnSO_4$. The acid must be separated from the $ZnSO_4$ in order to use the electrolytic zinc process, which requires a neutral zinc sulfate solution for purification.[5]

The flowsheet in figure 7 illustrates the laboratory method designed to minimize losses of zinc and dilution of the acid streams, and to produce neutral zinc sulfate for electrolysis. To recover moderately concentrated acid in the initial separation, the reacted $ZnSO_4$-H_2SO_4 mixture was filtered or centrifuged, and then washed by mixed washes (mixed with the solids) or elution washes. Various combinations of these operations were tested; the results are given in table 5. The last process in table 5 was chosen for most of the laboratory work.

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[5] Distillation of the water and H_2SO_4 from the $ZnSO_4$ was studied, but energy requirements were prohibitive. In tests using submerged hot airflows and vacuums to lower the boiling point of H_2SO_4, it was not possible to completely distill the acid from the $ZnSO_4$; up to 8 pct of the acid was decomposed to SO_2. This approach was abandoned.

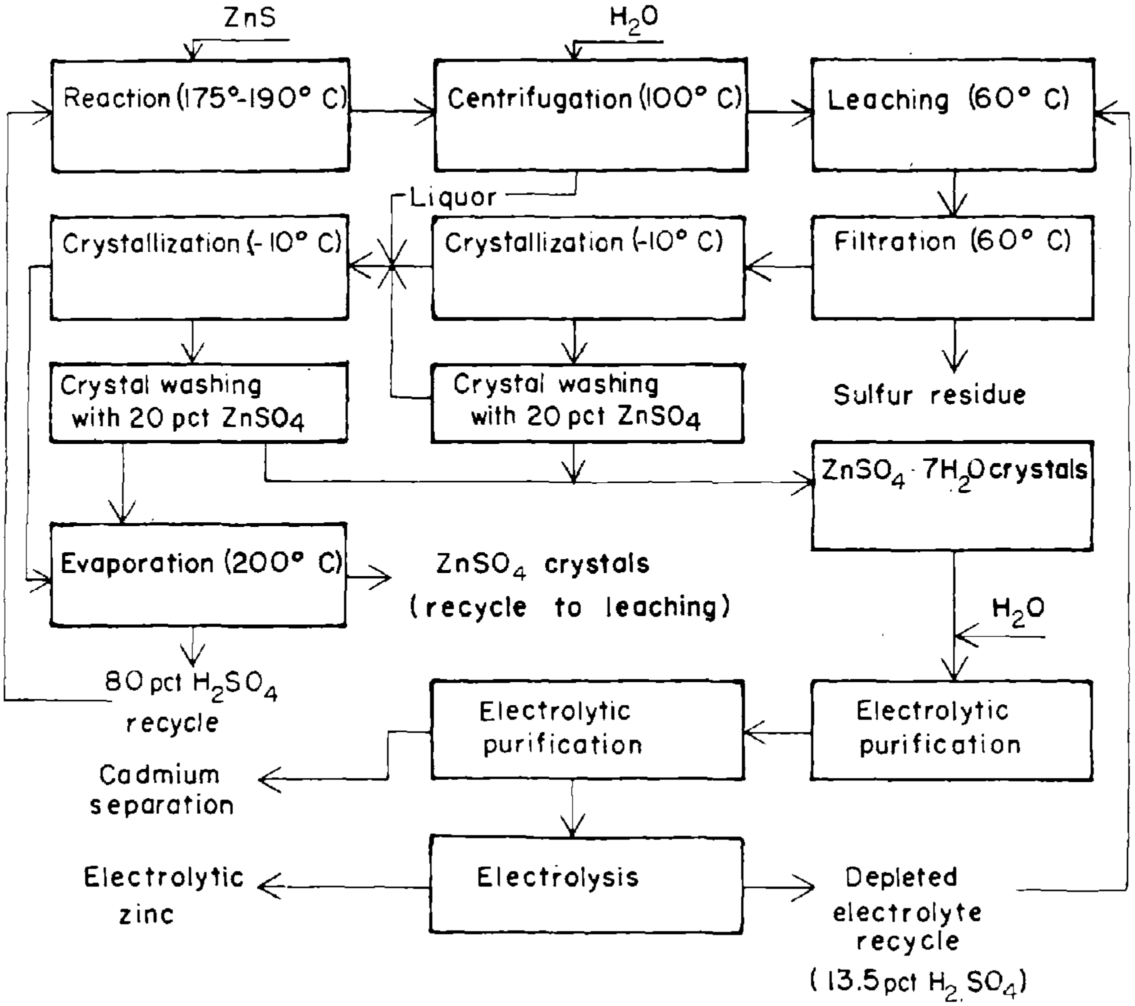

FIGURE 7. - Laboratory method flowsheet.

TABLE 5. - Separation of H_2SO_4 from reaction products of 100-g charges of ZnS

Process	H_2SO_4 recovered, pct	$ZnSO_4$ dissolved, pct
Vacuum filtration, then 3 50-ml elution washes, all at 25° C....................	90	50
Vacuum filtration, then 3 100-ml mixed washes, all at 25° C....................	90	58
Centrifugation at 25° C, then 3 60-ml mixed washes at 0° C....................	90	18
Centrifugation at 100° C, then 3 70-ml mixed washes at -10° C..................	95	17
Centrifugation at 100° C, then 2 70-ml mixed washes at -10° C..................	70	5
Centrifugation at 100° C, then 2 70-ml mixed washes at 25° C..................	90	10

Simulated spent zinc electrolyte solution was used to leach the solids from the centrifugation step. Filtration was then used to separate the sulfur and unreacted solids from the $ZnSO_4$-H_2SO_4 solution. An analysis of a typical leach residue is given in table 6. The filtrate was cooled to crystallize $ZnSO_4 \cdot 7H_2O$. Yields were dependent on the final temperature of the solution, and as much as 80 pct of the $ZnSO_4$ was crystallized at -10° C. The concentration of H_2SO_4 in the crystal liquor increased as $ZnSO_4 \cdot 7H_2O$ crystallized because of the water of hydration in the crystals. Leach solutions with an initial H_2SO_4 content of 22 pct contained 40-pct H_2SO_4 after crystallization of $ZnSO_4 \cdot 7H_2O$; this concentration results in a significant reduction in the cost of recycling the acid back to the leaching step.

TABLE 6. - Analysis of typical residue obtained by water-leaching reaction products

Component	Pct	Component	Pct
Total sulfur.....	79.5	Zinc.............	1.7
Elemental sulfur.	71.8	Copper...........	.53
Iron.............	3.6	Cadmium..........	.24
Calcium..........	2.8	Nickel...........	.07
Lead.............	2.7	Cobalt...........	.05

The solubility of $ZnSO_4$ in H_2SO_4 solution decreases as temperature decreases and as acid concentration increases. The crystal form of $ZnSO_4$ in equilibrium with $ZnSO_4$ solution is $ZnSO_4 \cdot 7H_2O$ up to 38° C and $ZnSO_4 \cdot 6H_2O$ from 38° to 60° C. Above 60° C, zinc sulfate crystals are less hydrated. Increasing the H_2SO_4 concentration decreases the dehydration temperature and the solubility of $ZnSO_4$. The triple point of equilibrium between $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$ occurs at 18° C and 25 pct H_2SO_4; the solution contains 21.3 pct $ZnSO_4$.

The product consisted of dense, granular crystals of $ZnSO_4 \cdot 7H_2O$ that readily settled from the mother liquor. However, a considerable amount of acid remained on the crystals after filtration. Elution washing in a column 2 cm ID by 50 cm long with a 20-pct $ZnSO_4$ solution at 0° C removed the adhering acid. Table 7 gives the results of elution-washing tests; 99.5 pct of the acid was removed by washing with a quantity of neutral $ZnSO_4$ solution equivalent to about 10 pct of that produced by the process. The $ZnSO_4$ crystals were dissolved in water, and the solution was purified and electrolyzed. The acid filtrate from the crystallizers was concentrated by evaporation and recycled. A material balance obtained from a series of 12 tests is given in table 8.

TABLE 7. - Crystal washing in elution column at 0° C

Fraction	$ZnSO_4$ solution, ml	Zinc added, g	Zinc eluted, g	Pct of total zinc	H_2SO_4 eluted, g	Pct of total H_2SO_4
Mother liquor from crystallization.........	130	0	11.34	29.4	37.92	91.33
1st wash fraction........	26	2.08	4.08	10.6	3.38	8.14
2d wash fraction.........	7	.56	1.36	3.5	.10	.24
3d wash fraction.........	9	.72	1.83	4.7	.06	.14
$ZnSO_4$ crystals...........	NAp	NAp	20.00	51.8	.06	.14
Total...............	172	3.36	38.61	100.0	41.52	100.00

NAp Not applicable.

TABLE 8. - Laboratory method material balance

Process material	Volume, ml	Zn in $ZnSO_4$, g	H_2SO_4, g	H_2O, g	Zn in ZnS, g	S°, g
Reactor:						
200-g ZnS concentrate.........	NAp	NAp	NAp	NAp	108	NAp
83-pct H_2SO_4.................	300	NAp	438	60	NAp	NAp
SO_2 offgas....................	1,000	NAp	NAp	NAp	NAp	NAp
CO_2 offgas....................	6,000	NAp	NAp	NAp	NAp	NAp
Centrifuge:						
Wash water added..............	150	NAp	NAp	150	NAp	NAp
H_2SO_4 solution removed........	80± 8	.4	100	126	NAp	NAp
Leaching and filtration:						
Leaching solution added.......	550	NAp	88	500	NAp	NAp
Filtration wash added.........	30	NAp	NAp	30	NAp	NAp
Filtration filtrate...........	700±25	NAp	NAp	NAp	NAp	NAp
Sulfur residue (90 g).........	NAp	NAp	NAp	NAp	3.5	64.4
1. Crystallization and wash:						
Acid-free $ZnSO_4 \cdot 7H_2O$ crystals...............	NAp	74.5±3	NAp	NAp	NAp	NAp
Crystal liquor..........	475±25	NAp	NAp	NAp	NAp	NAp
Crystal wash solution...	70	5.5	NAp	70	NAp	NAp
2. Crystallization and wash:						
Acid-free $ZnSO_4 \cdot 7H_2O$ crystals...............	NAp	17.1±7	NAp	NAp	NAp	NAp
Crystal liquor..........	560±30	NAp	NAp	NAp	NAp	NAp
Crystal wash solution...	30	2.5	NAp	30	NAp	NAp
Evaporation:						
$ZnSO_4$ crystals...............	NAp	16.7±4.3	36	9	NAp	NAp
80-pct H_2SO_4.................	140	.2	208	52	NAp	NAp

NAp Not applicable.

Purification and Electrolysis of $ZnSO_4$ Solution

The $ZnSO_4$ from the crystallization step was dissolved in water to form a near-saturated solution of about 200 g/l for electrolysis. Iron was removed by precipitation as $Fe(OH)_3$ (ferric hydroxide) from a neutral solution after oxidation with $KMnO_4$ (potassium permanganate). The permanganate also caused the manganese in solution to precipitate as MnO_2 (manganese dioxide). The iron precipitation is also effective in removing traces of antimony, which is detrimental to the electrolysis of zinc.

Up to 2 g/l of $CuSO_4$ (copper sulfate) and 20 mg/l of As_2O_3 (arsenic trioxide) were added to the solution after it was heated to 90° C. High-purity zinc dust then was added at intervals for 1 hour to cement out Cu, Co, As, and Ni. Cobalt and nickel contents each were reduced from about 400 ppm to less than 1 ppm by this treatment. Excessive amounts of manganese in solution interfered with complete cementation of cobalt. In some cases, the iron precipitation and the addition of zinc dust had to be repeated to obtain solutions sufficiently pure for electrolysis. Excessive amounts of cobalt and nickel in solution cause deposits of zinc to redissolve after several hours of electrolysis.

The purified solutions were electrolyzed in test cells using aluminum cathodes and platinum anodes, with a current density of 5 to 10 A/dm^2. Dense, coherent zinc deposits were obtained in 24-hour tests. The current efficiencies were over 90 pct, and no dissolution of the deposits was observed.

In continuous operation, minor impurities often build up to high levels. Intermediate products were analyzed to determine the distribution of impurities from the ZnS concentrate (table 9). Most of the Cu, Pb, and Ca, and about one-half of the Fe, remained in the sulfur residue. Cadmium, which is often a byproduct of zinc processing, is not lost and could be recovered by commonly employed purification processes. Iron, cobalt, and nickel also are removed by standard purification procedures. Magnesium would build up in process streams and would have to be removed by preleaching with dilute acid.

TABLE 9. - Distribution of impurities in experimental process materials, pct

Process material	Cu	Ni	Co	Cd	Pb	Fe	Mg	Ca
Sulfur residue........	97.8	79.2	50.0	8.0	99.7	55.4	2.3	98.0
Centrifugation solution.............	.3	1.8	2.0	23.2	.1	.1	6.0	.5
$ZnSO_4 \cdot 7H_2O$ crystals...	.5	10.0	24.5	26.8	.1	18.8	39.5	.5
Crystal liquor........	1.4	9.0	23.5	42.0	.1	25.7	52.2	1.0
Composite........	100	100	100	100	100	100	100	100

SUMMARY

Sphalerite concentrates were reacted at ambient pressure with sulfuric acid to produce $ZnSO_4$ and S. Sulfur was produced in the ratio of 4 moles for 3 moles of ZnS reacted under optimum conditions. Sulfur dioxide gas was produced when the acid concentration was excessive, and H_2S was produced when the acid was dilute. When 80- to 85-pct H_2SO_4 was used, small, varying amounts of SO_2 and H_2S were produced during the reaction; the quantity varied with temperature. The reaction rate of finely ground ZnS concentrate is temperature-dependent, and the reaction has an activation energy of 17.4 kcal/mole. More than 98 pct of the zinc was recovered as soluble $ZnSO_4$ by reaction at 175° C for 3 hours.

The soluble reaction products were separated from sulfur and other insoluble residue by leaching with recycled electrolysis solutions containing 12 to 15 pct H_2SO_4. Zinc sulfate was separated from the H_2SO_4 by crystallization at -10° C as $ZnSO_4 \cdot 7H_2O$, which removes water from the leach solution and concentrates the H_2SO_4 up to 40 pct. The H_2SO_4 then can be concentrated to 80 pct by evaporation and recycled to react with fresh ZnS concentrate. Neutral $ZnSO_4 \cdot 7H_2O$ was obtained by elution washing of the crystals with saturated $ZnSO_4$ solution.

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