

RI 8949

RI

8949

PLEASE DO NOT REMOVE FROM LIBRARY

Bureau of Mines Report of Investigations/1985

Chlorine-Oxygen Leaching of a Low-Grade Zinc Sulfide Flotation Concentrate

By G. A. Smyres and T. G. Carnahan



UNITED STATES DEPARTMENT OF THE INTERIOR



Report of Investigations 8949

Chlorine-Oxygen Leaching of a Low-Grade Zinc Sulfide Flotation Concentrate

By G. A. Smyres and T. G. Carnahan



UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
Robert C. Horton, Director

Library of Congress Cataloging in Publication Data:

Smyres, G. A. (Gary A.)

Chlorine-oxygen leaching of a low-grade zinc sulfide flotation concentrate.

(Report of investigations ; 8949)

Bibliography: p. 9-10.

Supt. of Docs. no.: I 28.23:8949.

1. Zinc--Metallurgy. 2. Zinc sulphide. 3. Leaching. 4. Flotation.
5. Chlorine. 6. Oxygen. I. Carnahan, T. G. (Thomas G.). II. Title. III.
Series: Report of investigations (United States. Bureau of Mines); 8949.

TN23.U43 [TN796] 622s [669'.52] 84-600390

CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Chemistry of chlorine-oxygen leaching.....	2
Materials and equipment.....	4
Experimental procedure.....	4
Results and discussion.....	6
Chlorine requirements.....	6
Effects of pressure, temperature, and percent solids.....	6
Effect of temperature on oxygen suppression of H ₂ S.....	7
Sulfate control.....	8
Liquid-solid separation.....	8
Zinc solution purification.....	8
Summary and conclusions.....	9
References.....	9

ILLUSTRATIONS

1. Conceptual flowsheet for chlorine-oxygen leaching of low-grade zinc concentrate.....	3
2. 500-mL reactor.....	5
3. 1-gal reactor.....	5
4. Effect of reactor operating pressure on zinc and copper extraction.....	6
5. Effect of temperature on zinc and copper extraction.....	6
6. Effect of pulp solids on zinc and copper extraction.....	7
7. Effect of temperature and reactor operating pressure on suppression of H ₂ S formation using oxygen.....	8

TABLES

1. Composition of concentrate.....	4
2. Effect of chlorine concentration on extraction of metals from zinc concentrate.....	6
3. Oxygen consumption as a function of temperature.....	7
4. Flocculation test results.....	8

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	L	liter
c/min	cycle per minute	lb	pound
cm	centimeter	mg	milligram
ft	foot	mL	milliliter
ft ²	square foot	min	minute
ft/min	foot per minute	mm	millimeter
g	gram	pct	percent
gal	gallon	ppm	parts per million
g/L	gram per liter	psig	pound per square inch, gauge
h	hour	s	second
in	inch	W	watt
kg	kilogram	V	volt

CHLORINE-OXYGEN LEACHING OF A LOW-GRADE ZINC SULFIDE FLOTATION CONCENTRATE

By G. A. Smyres¹ and T. G. Carnahan²

ABSTRACT

The Bureau of Mines conducted laboratory studies to determine the feasibility of chlorine-oxygen leaching for treating low-grade zinc sulfide flotation concentrates. Recovery of zinc sulfides by flotation from complex fine-grained sulfide ores is substantially higher in low-grade bulk sulfide concentrates than in the high-grade cleaned concentrates required for smelter feed. However, there is no commercial process in the United States for the treatment of low-grade bulk zinc sulfide concentrates.

Leaching experiments using reactors of 500-mL and 1-gal capacity were conducted on a bulk concentrate containing 19.3 pct Zn, 35.6 pct Fe, and 39.4 pct S. The effects of pressure, temperature, and percent solids on extraction were investigated. The chlorine-oxygen leaching procedure showed promise for treating the concentrates. Zinc extractions of 95 pct or more were obtained by leaching at 50 pct solids in the temperature range of 100° to 120° C. Zinc extractions by leaching with chlorine followed by oxygen at reactor pressures of 50 to 100 psig were independent of pressure.

¹Metallurgist.

²Supervisory metallurgist.

Reno Research Center, Bureau of Mines, Reno, NV.

INTRODUCTION

Hydrometallurgical processes have assumed new significance for treating sulfide concentrates, particularly in view of the stringent environmental constraints being placed on smelting and refining operations and the need to treat progressively lower grade and more complex ores (1-10).³

In a conventional roast-leach-electrowin zinc plant, excessive iron in the concentrate is a problem because insoluble iron-zinc ferrites are formed during roasting. To minimize this difficulty, most domestic zinc plants will not accept a concentrate containing more than 7 pct Fe or less than 50 pct Zn. This usually precludes the use of zinc sulfide concentrates when fine grinding will not liberate the sphalerite or when the sphalerite mineral contains excessive iron.

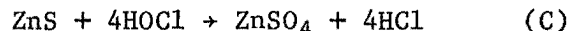
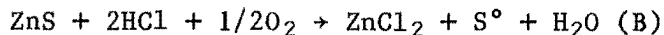
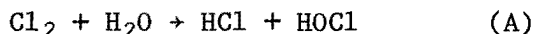
When a clean zinc concentrate suitable for roast-leach-electrowinning is produced from a complex fine-grained sulfide ore, there is generally a loss of zinc to the tailings. Such was the case when the commercial bulk zinc concentrate used in this investigation was cleaned to produce a concentrate acceptable to domestic zinc producers. The commercial bulk concentrate contained 75 pct of the zinc from the ore but was low in grade and high in iron; however, when cleaned and made suitable for use by zinc producers, the overall zinc recovery was 35 to 45 pct (11). Hence, by producing a bulk concentrate, zinc flotation recovery is improved; but zinc extraction from the bulk concentrate requires a nonconventional

process. The Bureau's chlorine-oxygen leaching technique (12-15) shows promise for treating complex low-grade sulfide concentrates and has the potential for producing high-purity zinc without the constraints of the maximum iron and minimum zinc concentration limits imposed by current commercial processing.

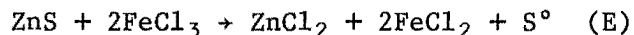
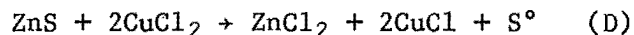
A conceptual flowsheet for treating low-grade zinc concentrate using the Bureau's chlorine-oxygen leaching technique is shown in figure 1. The concentrate is slurried and reacted with chlorine and then oxygen to leach zinc and other base metals while iron is rejected to the residue. The pregnant solution is recovered by filtering the pulp, and the filter cake is washed with water to remove soluble zinc. Lime and H₂S are added to the wash water to precipitate base metals, which are returned to the reactor. The pregnant solution is purified by zinc-dust cementation (15), which produces a precipitate of cadmium, lead, silver, and copper metals. The purified ZnCl₂ solution is then evaporated to produce ZnCl₂ crystals. After drying, the ZnCl₂ is fed to a molten-salt bath and electrolyzed at 535° C to produce molten zinc metal and chlorine (16-17). The chlorine is recycled to the reactor to leach fresh concentrate. To determine the feasibility of using this technique for testing low-grade zinc concentrates, experiments were conducted to investigate key parameters involved with the leaching, liquid-solid separation, and solution-purification steps of the flowsheet.

CHEMISTRY OF CHLORINE-OXYGEN LEACHING

Reactions A through C are pertinent in the leaching of sphalerite.



Secondary leaching reactions that probably occur include the following:



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

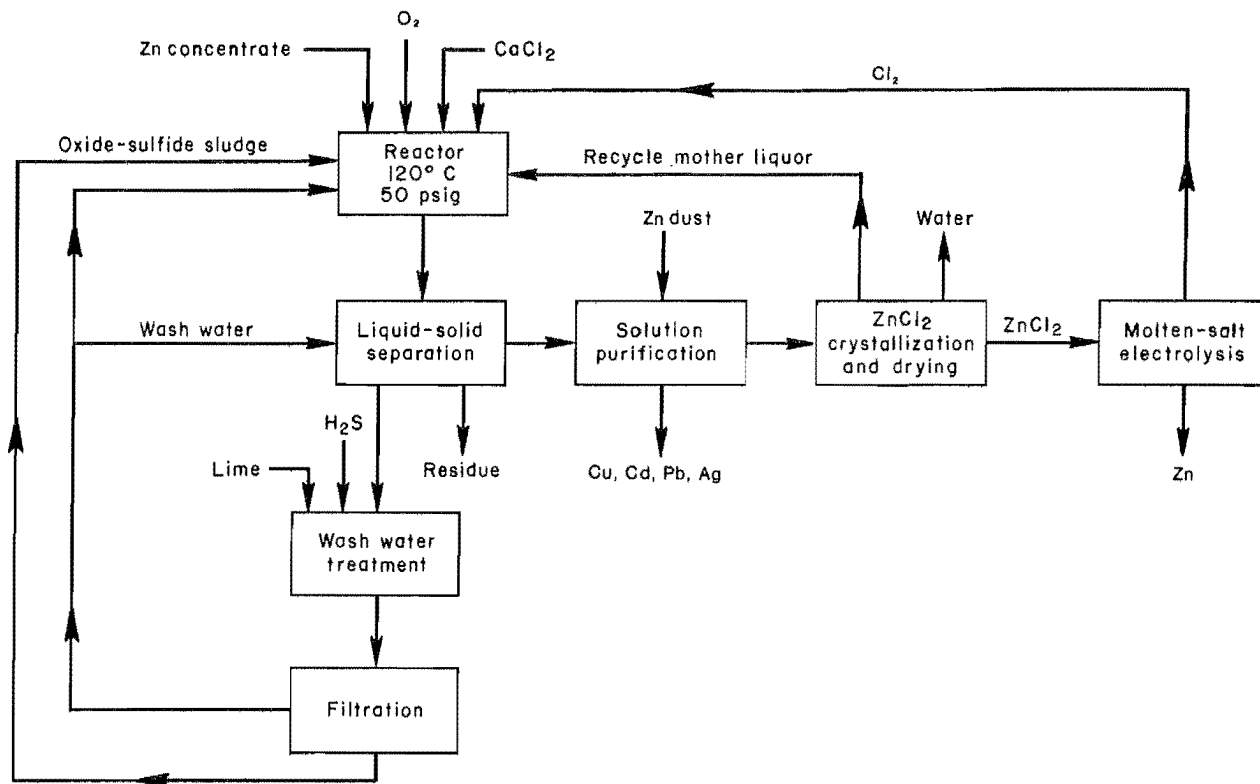
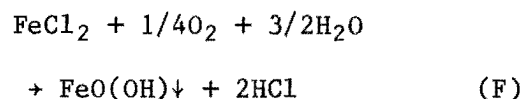


FIGURE 1. - Conceptual flowsheet for chlorine-oxygen leaching of low-grade zinc concentrate.

CuCl_2 and FeCl_3 are formed by aqueous oxidation of copper- and iron-bearing sulfide minerals in the feed.

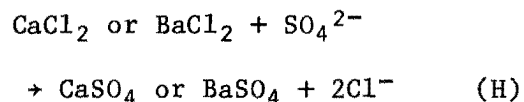
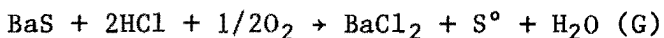
Although chlorine-oxygen leaching of sphalerite can occur without copper being present, the leaching rate is faster with copper (1). Studies to systematically evaluate the effects of copper in chlorine-oxygen leaching were not conducted. In the case of the low-grade sphalerite concentrate investigated, there was sufficient copper impurity to accelerate the leaching.

Under ideal conditions, chlorine-oxygen leaching solubilizes all of the valuable base metals, and the iron remains in the leach residue. Chloride control is required to ensure that there is enough chloride to satisfy the counter-ion needs of the zinc, copper, cadmium, and lead to ensure that no chloride remains for the iron, which is precipitated from solution as goethite, as shown in the next column.



When the final pH after reaction is almost 1.7, the solution is iron-free.

Sulfate ions should be removed from solution to minimize valuable metal losses by precipitation of a basic sulfate mineral such as beaverite, $[\text{PbCu}_3\text{Fe}_2(\text{OH})_6(\text{SO}_4)_4]$. This can be accomplished by adding BaS , CaCl_2 , or BaCl_2 to the reactor to form insoluble sulfates as shown in reactions G and H.



If a chloride salt is added, the chloride makes up for losses to the leach residue.

MATERIALS AND EQUIPMENT

The analysis of the commercial bulk zinc concentrate used is given in table 1. Electron microprobe examination of the concentrate indicated that the major minerals were sphalerite, pyrite, and chalcopyrite.

TABLE 1. -Composition of concentrate, percent

(Commercial low-grade bulk ZnS flotation concentrate)

Zn.....	19.3	Insol.....	1.6
Cu.....	.66	Mg.....	.061
Fe.....	35.6	Ni.....	<.002
Ag.....	.0014	Pb.....	.10
Al.....	.52	S ²⁻	38.8
Ca.....	.036	Si.....	.19
Cd.....	.036	SO ₄ ²⁻	1.8
Co.....	.057		

Leaching experiments were conducted in reactors of 500-mL and 1-gal (3,800-mL) capacity. The 500-mL reactor was a modified Parr⁴ hydrogenation bottle capable of operating at pressures up to 60 psig and was provided with a thermocouple insert and a chlorine and oxygen delivery system. A gauge guard was used to protect the pressure gauge from the chlorine. Although the reactions were exothermic, a heating mantle (100 W, 115 V) with a temperature controller was required to maintain the temperature in the bottle because heat loss from this small-scale reactor was large. Agitation

of pulp during leaching was provided by shaking the bottle at a rate of 225 c/min.

The rate of oxygen flow into the 500-mL reactor was measured by a Hastings oxygen flowmeter-totalizer. Timers were used for shutting off the heater and shaking mechanism. A Fluke 2200B datalogger was used to record time, gas flow, and temperature data at equal time intervals. Figure 2 shows the 500-mL reactor, the control section, and oxygen mass flowmeter. Chlorine was added from a lecture bottle through a 1/4-in-OD Teflon fluorocarbon polymer tube to the reactor.

The 1-gal reactor was a Pfaudler glass-lined steel reactor with a steel jacket (fig. 3). It had a titanium shaft and a 5-in-diam four-bladed titanium turbine-type impeller. The reactor jacket was designed to allow either steam heating or water cooling. Chlorine and oxygen additions to the reactor were determined by gas-bottle weight loss, which was measured with a top-loading 10-kg balance. An air heat gun was used to warm the chlorine bottle during chlorine additions. Temperature and pressure were measured by thermocouple and gauge, respectively.

Filtration experiments were conducted with a standard EIMCO 0.1-ft² filter disk. The polypropylene filter cloth used on the filter disk was constructed of 0.01-in-diam thread with a rectangular weave of 100 threads per linear inch by 50 threads per linear inch.

EXPERIMENTAL PROCEDURE

The amount of chlorine required for leaching was determined in the 500-mL reactor. One hundred grams of concentrate was slurried with water in the reactor, and chlorine at room temperature was added to the reactor. The amount of chlorine added was determined by weighing the bottle before and after the chlorine addition. All of the chlorine was added

before the oxygen bottle was connected to the reactor. Oxygen was admitted to the slurry as the reactor was heated to the operating temperature. The temperature and pressure were maintained until the flowmeter indicated there was no further oxygen consumption. The slurry was cooled to room temperature and vacuum filtered through Whatman No. 5 filter paper in a 15-cm-diam Buchner funnel. From 350 to 500 mL of water was used to wash the filter cake.

⁴Reference to specific products does not imply endorsement by the Bureau of Mines.

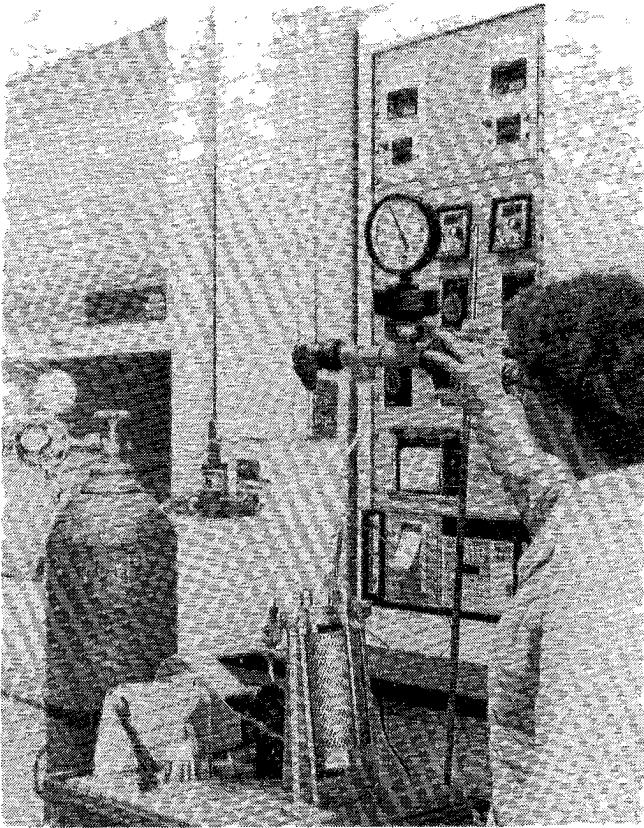


FIGURE 2. - 500-mL reactor.

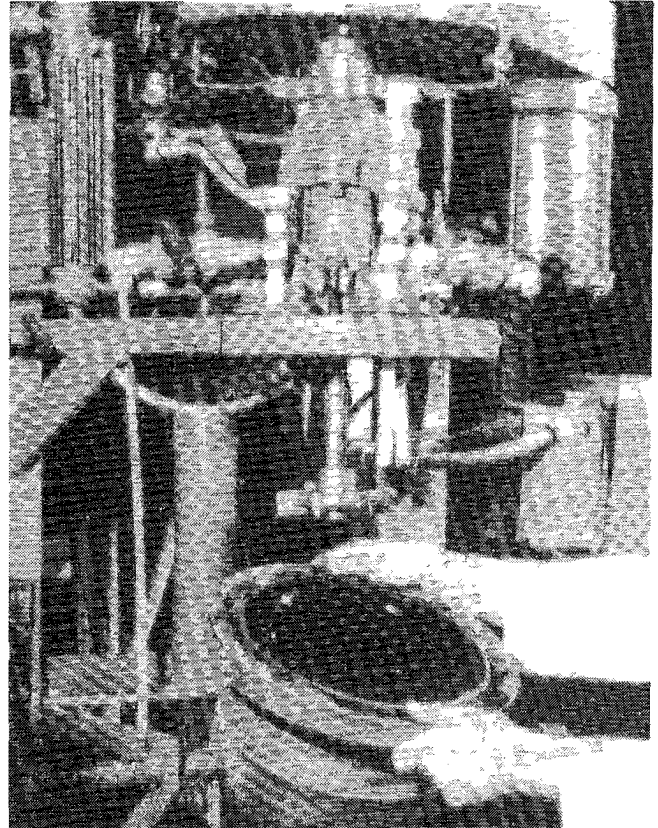


FIGURE 3. - 1-gal reactor.

The effects of pressure, pulp solids, and temperature on leaching were determined in the 1-gal reactor. The weights of concentrate used to make up pulp solids of 30, 50, 60, and 70 pct were 1,286, 2,600, 3,150, and 4,200 g, respectively. Water additions were 3,000, 2,600, 2,100, and 1,800 g, respectively. After chlorine addition, the reactor was pressurized to 30 to 100 psig with oxygen, and the slurry was mixed with an impeller operating at a tip speed of 1,300 ft/min. The temperature was increased to the desired operating level. A leaching time of 7-1/2 h was used to allow the experiments to be completed during normal working hours.

Filtration rates were determined with a standard 0.1-ft² leaf filter. The filter disk, with the filter cloth facing down, was placed in a stirred slurry. The filter disk was removed from the slurry after 30 s and held for 90 s with the filter cake facing upward to simulate cake drying.

The filtrate was mixed at 75° C for 30 min with twice the theoretical amount of zinc necessary to cement the copper, lead, cadmium, nickel, and cobalt and was then filtered. After cooling to about 30° C, additional zinc dust--about one-fourth the amount of dust used in the first cementation--was mixed with the solution for another 30 min and filtered. The second (30° C) cementation step was necessary because metals were redissolved when the cementation product was left in contact with the hot ZnCl₂ solution. The metals redissolved so fast at elevated temperatures that it was not practical to separate the cementation product soon enough to prevent the metals from redissolving.

Metal analyses of leaching solutions and residues were made by atomic absorption spectroscopy. Sulfur analyses were performed using wet-chemical methods. Silver in the concentrate was analyzed by fire assay.

RESULTS AND DISCUSSION

CHLORINE REQUIREMENTS

A series of experiments was conducted in the 500-mL bottle reactor at 50 pct solids, 110° C, and 50 psig to determine the chlorine-to-concentrate weight ratio that would give high zinc extractions while minimizing iron extractions. The experimental results are summarized in table 2. A chlorine-to-concentrate ratio of 0.184 was sufficient for high zinc extractions and minimized iron in solution. Zinc extraction variation was due to analytical errors in assessments of the high-zinc content solutions. Achieving the lowest iron concentration consistent with high zinc extraction was important because this minimized iron impurity in the $ZnCl_2$ later produced by evaporative crystallization of the pregnant solution. All subsequent experiments to determine interactions between pressure, temperature, and percent solids were conducted with a chlorine-to-concentrate ratio of 0.184.

TABLE 2. - Effect of chlorine concentration on extraction of metals from zinc concentrate

Cl ₂ -to-concentrate weight ratio	Metal dissolved, pct			Fe in filtrate, g/L
	Zn	Cu	Fe	
0.184	98	61	0.0	0.0017
.192	92	75	.5	.33
.200	97	80	.7	.69
.206	97	85	1.3	1.4
.208	100	100	8.7	13.0

EFFECTS OF PRESSURE, TEMPERATURE, AND PERCENT SOLIDS

The effect of oxygen pressure on extractions of zinc and copper was determined at reactor pressures from 50 to 100 psig, at 50 pct solids and 100° C. The 1-gal reactor was used in this experiment and in all subsequent experiments. Figure 4 shows that the zinc and copper extractions were independent of oxygen pressure.

The effect of temperature on the metal extractions was determined using

temperatures from 80° to 140° C, at 50 pct solids, with the reactor pressurized to 100 psig with oxygen. The results are shown in figure 5. Zinc and copper extractions increased with increasing temperature up to 120° C. The decrease in metal extractions at higher temperatures was attributed to the formation of a molten-sulfur coating on unreacted sulfides. At 140° C, the residue from leaching showed two distinct fractions. A sulfur-coated residue, which was a black mass, contained, in percent, 2.8 Zn, 0.55 Cu, and 26.4 S°. The rest of the residue contained, in percent, 0.40

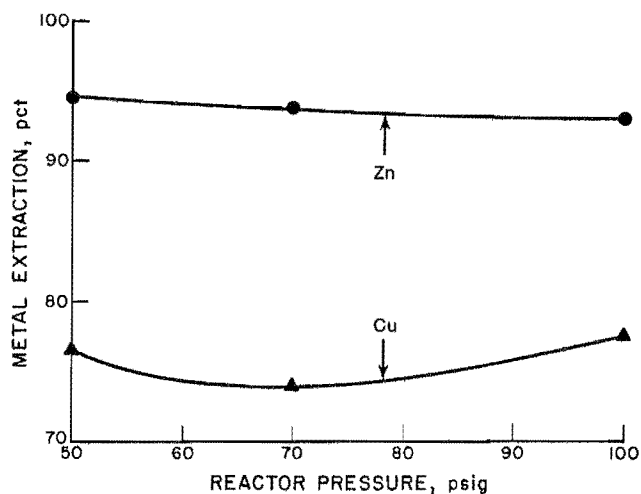


FIGURE 4. - Effect of reactor operating pressure on zinc and copper extraction.

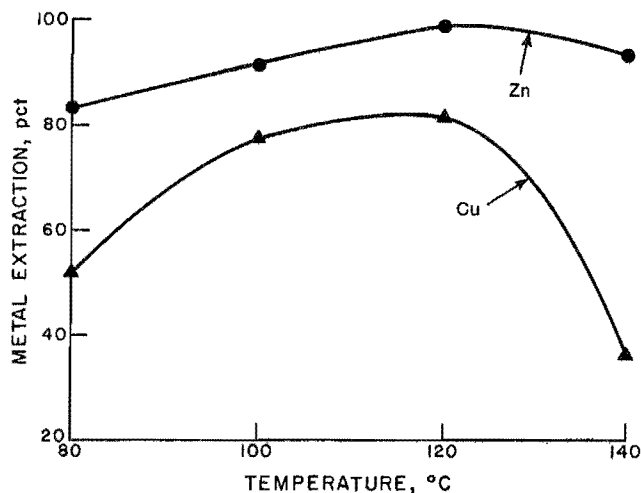


FIGURE 5. - Effect of temperature on zinc and copper extraction.

Zn, 0.06 Cu, and 1.0 S°. Lower metal extractions at 80° and 100° C indicated the need for a longer reaction time (more than 7-1/2 h).

The effect of pulp solids on leaching was determined at 100° C and reactor pressures from 50 to 70 psig. At less than 60 pct solids, the leached solids settled normally and a layer of pregnant solution above the pulp was obtained. The pulp approached the consistency of whipped cream at 60 pct solids and of mashed potatoes at 70 pct solids. At these higher pulp solids levels, aeration was hindered and gave less formation of sulfate. When less sulfate is formed, the amount of chlorine has to be increased to obtain good metal extractions because sulfate substitutes for chloride ions. With insufficient chlorine, as was the case at 60 and 70 pct solids, extractions were less than those at solids levels below 60 pct (fig. 6). Copper extraction was affected to a greater extent than zinc because CuCl_2 will leach metal sulfides while being oxidized to insoluble atacamite $[\text{Cu}_2(\text{OH})_3\text{Cl}]$ as the pH increases.

Oxygen consumption as a function of temperature for 30 and 50 pct solids at 70 psig is shown in table 3. Oxygen consumption increased with increasing temperature, indicating that more sulfur was oxidized to sulfate when the temperature increased. However, at 50 pct solids and

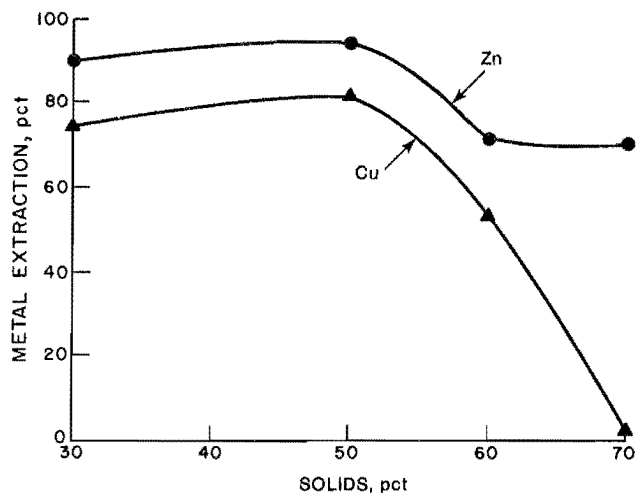


FIGURE 6. - Effect of pulp solids on zinc and copper extraction.

120° C, the consumption of oxygen decreased. This decrease was probably the net result of hindered aeration, less oxygen partial pressure, and possibly less sulfur surface area because of molten sulfur particle agglomeration.

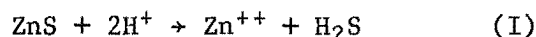
TABLE 3. - Oxygen consumption as a function of temperature

(O_2 -to-concentrate ratio at 70 psig)

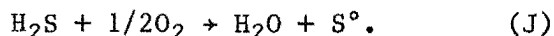
Temp, °C	Pulp solids	
	30 pct	50 pct
80.....	0.13	0.12
100.....	.13	.14
120.....	.19	.09

EFFECT OF TEMPERATURE ON OXYGEN SUPPRESSION OF H_2S

Formation of H_2S in the absence of oxygen is inevitable because the primary reaction between ZnS and acid proceeds as follows:



The formation of H_2S can cause a sudden surge in the reactor pressure that can burst the rupture disk. The presence of sufficient oxygen causes H_2S to oxidize into elemental sulfur and water according to the reaction,



Experiments were conducted to determine the effects of temperature and operating pressure on H_2S formation. The results presented in figure 7 were determined by careful observation when rapid buildup of pressure due to H_2S began. The data were obtained by leaching the zinc concentrate at 50 pct solids and varying the temperature and reactor pressure. The reactor pressure was regulated by the addition of oxygen. H_2S formation was detected under the conditions represented in the shaded region of the figure. The data show, for example, that leaching at 110° C (at 50 pct solids) required a minimum reactor oxygen pressure of 45 psig to suppress the H_2S formation and that higher temperatures required higher pressures.

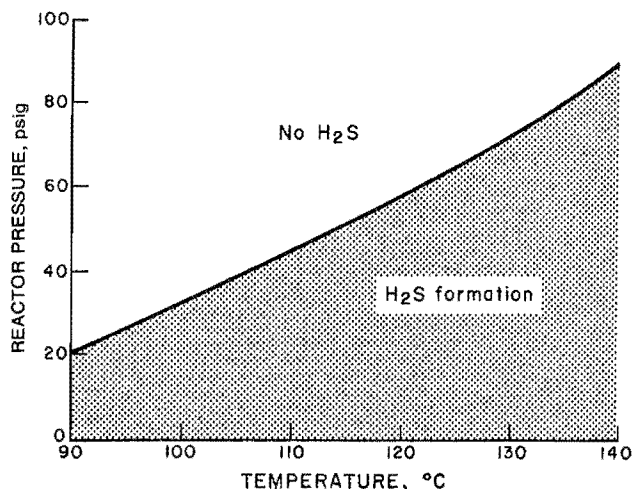


FIGURE 7. - Effect of temperature and reactor operating pressure on suppression of H_2S formation using oxygen.

Based on H_2S formation information, leaching conditions were controlled by using sufficient oxygen pressure to suppress H_2S and favor the formation of elemental sulfur.

SULFATE CONTROL

Chlorine-oxygen leaching converts part of the sulfide content of the concentrate into sulfate (reaction C). The sulfide that was converted amounted to 8 to 11 pct of the total sulfur content in the feed. Sulfate concentrations were about 50 g/L SO_4^{2-} after leaching. Control of sulfate is required to prevent sulfate contamination of the $ZnCl_2$ crystals produced in the process. To remove sulfate ions from the pregnant solution during leaching, chlorine-oxygen leaching tests using $CaCl_2$ and BaS were conducted. When $CaCl_2$ was used, sulfate in the filtrate was decreased to 1.1 g/L. With BaS , the sulfate content of the filtrate was 0.04 g/L.

LIQUID-SOLID SEPARATION

The slurry from chlorine-oxygen leaching was slimy and would not settle or filter easily. To determine how the material would behave in actual process equipment, a series of flocculation tests

was conducted with slurry at a 40 pct solids. The results are summarized in table 4. Addition of a nonionic polymer flocculant increased the settling rate from 0.2 to 9.9 in. in 30 min when the quantity of flocculant was increased from 0 to 1.0 lb/ton of solids. The pulp obtained from the addition of 0.6 lb of flocculant per ton of solids was used to determine the filtration rate. The results obtained with the standard 0.1-ft² leaf-filter apparatus were 21 lb of filtrate and 23 lb of filter cake per square foot per hour. The moisture content of the filter cake was 24 pct.

TABLE 4. - Flocculation test results

Flocculant, ¹ lb/ton solids	Settling rate in 30 min, in
0.0.....	0.2
.4.....	6.0
.6.....	7.8
1.0.....	9.9

¹Separan MGL flocculant (Dow Chemical Co.).

ZINC SOLUTION PURIFICATION

Purification of the $ZnCl_2$ solution was accomplished by zinc cementation (15). The solution for purification contained, in grams per liter, 97 Zn, 4.5 Fe, 2.0 Cu, 0.15 Cd, 0.011 Ni, 0.022 Pb, and 0.041 Co. After addition of 6.0 g/L Zn, the metal impurity concentrations were much lower, except for iron. The lower concentrations were, in grams per liter, < 0.001 Cu, < 0.001 Cd, < 0.002 Ni, < 0.003 Pb, and 0.0049 Co; however, the iron concentration remained at 4.5 g/L Fe. As these data indicate, zinc will not cement iron. Thus, it is important that chlorine-oxygen leaching be conducted under conditions that will yield a minimal amount of iron in solution. When leaching conditions are ideal, high zinc extraction can be achieved while producing a solution that contains less than 1 mg/L Fe (13).

SUMMARY AND CONCLUSIONS

Chlorine-oxygen leaching extracted more than of 95 pct of the zinc contained in a concentrate that was not suitable as feed for a conventional roast-leach-electrowin plant because of its low zinc and high iron content. The recommended leaching conditions, based on the experimental data are (1) 50 pct solids, (2) 100° to 120° C, and (3) pressurize with oxygen to 50-70 psig. In an actual process, CaCl₂

or BaS would be added to eliminate sulfate from solution, part of the zinc filtrate would be recycled to the leaching reactor to maintain an adequate ZnCl₂ feed concentration for crystallization, and the precipitated copper and zinc compounds separated from the wash water would be recycled to the leaching reactor to achieve good zinc and copper extractions.

REFERENCES

1. Demarthe, J. M., L. Gandon, and A. Georgeaux. Method of Selectively Bringing Into Solution the Non-Ferrous Metals Contained in Sulphurized Ores and Concentrates. U.S. Pat. 4,230,487, Oct. 28, 1980.
2. Dutrizac, J. E., and R. J. C. MacDonald. The Dissolution of Sphalerite in Ferric Chloride Solutions. *Met. Trans. B*, v. 9B, 1978, pp. 543-551.
3. Smyres, G. A., P. R. Haskett, B. J. Scheiner, and R. E. Lindstrom. Decomposition of Sulfide Ores. U.S. Pat. 3,981,962, Sept. 21, 1976.
4. Garcia, D. J., and A. M. Palacios. Hydrometallurgical Process for Treating Complex Minerals. Spanish Pat. 475,187, May 16, 1979.
5. Kawulka, P., W. J. Haffenden, and V. N. Mackiw. Recovery of Zinc From Zinc Sulphides by Direct Pressure Leaching. U.S. Pat. 3,867,268, Feb. 18, 1975.
6. Mackiu, V. N., and H. Veltman. Recovery of Zinc and Lead From Complex Low-Grade Sulfide Concentrates by Acid Pressure Leaching. *CIM Bull.*, v. 60, No. 657, 1967, pp. 80-85.
7. Parker, E. G. Oxidative Pressure Leaching of Zinc Concentrates. *CIM Bull.*, v. 74, No. 829, 1981, pp. 145-150.
8. Sohn, H. Y. Developments in Physical Chemistry and Basic Principles of Extractive and Process Metallurgy in 1982. *J. Met.*, v. 35, No. 4, 1983, pp. 36-41.
9. Scott, T. R. Continuous, Co-Current, Pressure Leaching of Zinc-Lead Concentrates Under Acid Conditions. Ch. in *International Symposium (2d) on Hydrometallurgy*, ed. by D. J. I. Evans and R. S. Shoemaker (AIME Annu. Meeting, Chicago, IL, Feb. 25-Mar. 1, 1973). AIME, 1973, pp. 718-750.
10. Warren, G. W. Review Developments in Hydrometallurgy-1982. *J. Met.*, v. 35, No. 4, 1983, pp. 42-47.
11. Goodwin, C. M. (Cities Service Co.). Private communication, 1978; available upon request from T. G. Carnahan, BuMines, Reno, NV.
12. Scheiner, B. J., G. A. Smyres, and R. E. Lindstrom. Lead-Zinc Extraction From Flotation Concentrates by Chlorine-Oxygen Leaching. Pres. at Soc. Min. Eng. AIME Fall Meeting, Salt Lake City, UT, Sept. 10-12, 1975, Soc. Min. Eng. AIME Preprint 75-B-314, 10 pp.
13. Scheiner, B. J., D. C. Thompson, G. A. Smyres, and R. E. Lindstrom. Chlorine-Oxygen Leaching of Complex Sulfide Concentrates. Pres. at 106th AIME Annual Meeting, Atlanta, GA, Mar. 6-10, 1977. *Metall. Soc. AIME Preprint A-77-86*, 10 pp.

14. Sawyer, Jr., D. L., G. A. Smyres, J. J. Sjoberg, and T. G. Carnahan. $\text{Cl}_2\text{-O}_2$ Leaching of Massive Sulfide Samples From the Southern Juan De Fuca Ridge, North Pacific Ocean. BuMines TPR 122, 1983, 8 pp.

15. Atkinson, G. B., J. E. Murphy, and J. A. Eisele. Purification of $\text{Cl}_2\text{-O}_2$ Leach Liquors by Zinc Cementation. BuMines RI 8707, 1982, 9 pp.

16. Shanks, D. E., F. P. Haver, C. H. Elges, and M. M. Wong. Electrowinning Zinc From Zinc Chloride-Alkali Metal Chloride Electrolytes. BuMines RI 8343, 1979, 17 pp.

17. Hill, S. D., D. L. Pool, and G. A. Smyres. Electrowinning Zinc From Zinc Chloride in Monopolar and Bipolar Fused Salt Cells. BuMines RI 8524, 1981, 24 pp.