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MICROBIOLOGICAL LEACHING OF A BULK ZINC-LEAD CONCENTRATE

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by

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Paper Presented at the CIM
Conference of Metallurgists

Quebec City

August 26-29, 1973

ABSTRACT

Microbiological leaching of a bulk zinc-lead flotation concentrate has been investigated. Batch leaching tests on bench scale and in a tank (22 l slurry volume) reproduce zinc extractions of 85->99% at leach rates of up to 1.3 g/l/hr. Dissolved zinc concentrations of up to 96 g/l were obtained. The extraction of cadmium and copper, and the extent of sulphatization of lead during leaching were also investigated. The iron content (primarily Fe^{3+}) of leach solutions was in the range of 2-5 g/l. Preliminary estimates of operating costs are presented and alternative methods of treatment of lead residue are discussed.

INTRODUCTION

The McArthur River zinc-lead deposit is located 380 miles north-west of Mount Isa in northern Australia and contains approximately 200 x 10^6 tons of ore. The material is a Precambrian sedimentary deposit in which the mineral grains are small and frequently intergrown. Even with very fine grinding, it has not been possible to produce separate lead- and zinc concentrates at an acceptable recovery. The best mineral dressing technique developed so far produces a bulk zinc-lead concentrate containing approximately 25% zinc and 10% lead. Several alternate procedures including the Imperial Smelting process, acid-pressure leaching (1) and microbiological leaching have been investigated to assess their suitability for treatment of McArthur River material.

Microbiological leaching is a process utilizing the bacterium *Thiobacillus ferrooxidans* to convert metal sulphides to soluble sulphates. *T. ferrooxidans* is an autotrophic organism (i.e. it forms its cell mass by fixing carbon dioxide) which functions best in an acidic environment (pH ∿2) and can develop a tolerance for high metal concentration in solution. For leaching of zinc sulphides, the main reaction which occurs is:

$$ZnS + 2O_2 \xrightarrow[\text{nutrients}]{\text{T. ferrooxidans}} ZnSO_4.aq$$

In microbiological leaching tests, an aqueous slurry of concentrate (5-30% pulp density) is inoculated with an active culture of T. ferrooxidans. Small quantities of nutrients (soluble ammonium and phosphate salts) are added, and the mixture is supplied with air slightly enriched in CO_2. Initially the pH of the slurry is adjusted to 2.5-3.0, but during leaching the pH may decrease to 2.0-1.5 due to oxidation and hydrolysis of iron sulphides.

The purpose of this paper is to present the results of batch microbiological leaching tests on McArthur River ores and concentrate, and to discuss the general feasibility of the process for recovery of zinc.

METHODS AND MATERIALS

Analyses of ore- and concentrate samples used in this study are presented in Table 1. After thorough mixing, portions of the samples were wet ground for 1 hour at 40% solids in a laboratory ball mill, and air dried. Leaching tests were done on samples in both the "as received" and "ground" conditions. Screen size analyses of materials tested are presented in Table 2.

Initial leaching experiments were done according to a previously developed method (2) in which 8 g portions of test material were placed in 70 ml of a nutrient medium contained in baffle bottomed 250 fl Erlenmeyer flasks. The pH of the slurry was adjusted to 2.5 with sulphuric acid, a 5 ml inoculum of zinc acclimatized T. ferrooxidans was added, and samples were leached at 35 C on a gyratory shaker (3). In all experiments, a CO_2 enriched (0.2%) air atmosphere was used (4).

During leaching, aliquots of solution were removed for analysis at appropriate intervals. A constant volume of slurry was maintained by addition of distilled water. On completion of leaching, liquid and solid phases were analysed and a material balance was made with corrections for material removed in sample aliquots and added in the inoculum.

Larger scale batch leaching experiments on concentrate were done in a 30" high by 12" diameter baffled stainless steel tank agitated by a centrally mounted turbine. The usual experiment involved 22 l of a 10 weight % slurry.

LEACHING OF ORE SAMPLES

Results of leaching tests on ore samples (Table 3) indicated high extraction (>80%) of zinc from all inoculated samples. Results of parallel experiments without bacteria are presented for comparison. The zinc extractions obtained during leaching of as-received and ground material were similar, but the rate of extraction was substantially better for ground ore. Typical leaching curves (dissolved zinc vs time) are shown in Figure 1. These curves show a long initial "lag" time when little microbiological leaching occurs. This result is characteristic of initial tests on new material and reflects the time required for the bacteria to adapt to a new substrate.

LEACHING OF CONCENTRATE SAMPLES

Results of initial leaching tests on concentrate #1 showed that high zinc extractions were also obtainable with this material. The experimental results (Table 4) showed that zinc extractions close to 100% were obtainable at a pulp density of 10 wt %. At this pulp density the maximum zinc concentration in solution was 28.3 g/l. Results of leaching tests at higher pulp densities (Table 4) showed a decrease in percentage extraction of zinc. At the time of the study this effect was considered to be due to inhibition of bacterial action due to the high level of dissolved zinc. More recent work (4, 5) has indicated that the amount of nutrients (soluble nitrogen and phosphorus) available was not adequate to maintain bacterial growth at the higher levels of substrate used. Thus addition of larger amounts of ammonium and/or phosphate would be required to maintain high leach rates and obtain good extractions at pulp densities above approximately 20%.

The best results obtained in the small scale experiments, was a dissolved zinc level of 84 g/l with 94% extraction. Leaching rates in these experiments were limited by the rate of oxygen transfer into solution.

When concentrate #2 was leached in the stirred tank, a leach rate of 1300 mg/l/hr was obtained and the zinc concentration reached 96 g/l equivalent to a 92.8% extraction (Table 5). Torma et al (4), using a different concentrate, have produced zinc concentrations as high as 119 g/l.

LEACHING OF CADMIUM AND COPPER

Leaching of cadmium paralleled that of zinc (Table 5). In the tank leach tests on concentrate #2 the cadmium extraction was 91.1% compared with 92.8% extraction of zinc. Copper extraction was found to be partially dependant on the fineness of grinding before leaching. In the tank leach test on concentrate #2, copper extraction was 83.5%. Also, much of the copper extraction occured during the later stages of the batch test. It was not determined whether this was due to an initially slow leaching of copper or whether the original copper minerals were attacked and copper was reprecipitated on surfaces of other sulphide minerals. In small scale leach tests on concentrate #1 "as received" (i.e. -325 mesh), copper extractions were in the range of 53-56%, while on reground samples (100% -400 mesh) copper extraction was increased to the range of 66-73%.

SOLUTION PURIFICATION AND ELECTROLYTIC RECOVERY OF ZINC

After leaching and liquid-solid separation by settling, leach solutions had a pH of 1.5-2.0 and contained - in addition to zinc - 2-5 g/l of iron as ferric sulphate, minor amounts of copper, cadmium, arsenic and other trace metals. A further component of the solution is the biomass generated in leaching. If this biological material is not removed during solution purification, then a fibrous floc is formed in the liquor during electrolysis. This material does not appear to have any effect on the surface of the cathode deposit but is adherent and would affect the purity of remelted cathodes. Results of more recent work (6) have shown that most of the biological material can be removed from solution by a preliminary neutralization to pH 2.0-2.2 with fine calcium carbonate and filtration. The fine $CaSO_4.2H_2O$ formed in neutralization acts as a filter aid so that the bacteria and any fine solids carried over from thickening are effectively removed. In the second stage of neutralization, solution pH is raised to 3.5 with calcium carbonate, effectively removing iron from the solution as a hydrous oxide precipitate. Other trace impurities such as arsenic, antimony and germanium which have detrimental effects on current efficiency in electrolysis are removed by precipitation with the hydrous iron oxide. The leach solutions produced in this study also require treatment with zinc dust to remove copper cadmium, nickel, and cobalt in pregnant solutions before electrolysis.

Results of only one experiment on electrowinning of zinc from biological leach solutions are available (4). Good cathodes were obtained, but current efficiency was approximately

78%, compared to more normal values of greater than 90%. However, no attempt was made to improve current efficiencies by modifying the purification process.

RECYCLE OF SPENT ELECTROLYTE

Recycling of spent electrolyte to leaching will be necessary since in normal electrolytic practice zinc levels in electrolyte are not reduced below 50 g/l. However, for biological leaching, only a small fraction (less than 10%) of the free acid formed in electrolysis is required to neutralize basic material (carbonates, oxides etc.) in the concentrate and to maintain a suitable starting pH for leaching. Neutralization of spent electrolytes with calcium carbonate has been found to be a suitable method of treatment. It has been found necessary to filter all the recycled solutions through a layer of the neutralization product ($CaSO_4.2H_2O$). If recycled solution is not treated in this way, then bacterial leaching is inhibited by some component of the recycled solution.

BUILD-UP OF IMPURITIES IN RECYCLED SOLUTION

The only cation which is likely to accumulate in recycled solution is magnesium. Solution levels of monovalent cations (sodium, potassium, ammonium) are maintained at low levels by precipitation of basic iron sulphates (Jarosites) during leaching. Other metallic impurities are controlled by the pregnant solution purification.

SULPHATION OF LEAD

Lead minerals in the concentrate samples received were highly oxidized (>80% of the lead was acetate soluble in concentrate #2 as received). In general, >90% of lead in the leach residues was in the sulphate form. Leaching tests have also been done on a lead-zinc concentrate from a Canadian source in which initially only 8% of the lead was acetate soluble. The lead in the leach residue from these tests was 84% acetate soluble, indicating a high conversion of lead from the sulphide to sulphate form.

TREATMENT OF LEACH RESIDUE

The residue from microbiological leaching of McArthur River concentrate contains approximately 20% lead plus minor amounts of silver. The lead is mainly (>90%) in the sulphate form, but attempts to concentrate this lead sulphate by flotation have been unsuccessful (7). Leaching with ammonia-ammonium sulphate solutions has produced satisfactory lead recoveries from acid pressure leach residues (8) but did not effectively recover silver.

Silver has been recovered from microbiological leach residues by leaching with concentrated calcium chloride brine (6). Tests were not done on the residues produced in this study, but it is considered probable that lead (9) as well as silver could be recovered from this material by brine leaching.

CONTINUOUS PROCESSING

All leaching tests in this study were done on a batch basis, but a recent study (5) has shown that continuous leaching of zinc sulphide concentrates is feasible. In that study, zinc concentrate and nutrient medium were fed continuously to an aerated leaching vessel, and residue was continuously withdrawn. Leach rates up to 1.3 g/l/hr were maintained for periods of several weeks. At the maximum leach rates, heat generated by leaching was greater than that required to maintain the temperature of the 12 litre reactor at 35 C and external cooling was required. A schematic flowsheet showing the unit operations required for continuous leaching and recovery of zinc is shown in Figure 2. The process is similar to the one proposed for microbiologically leaching chalcopyrite (10).

COMPARISON OF MICROBIOLOGICAL- AND ACID PRESSURE LEACHING

A recent article by Scott (1) describes pilot plant studies on acid pressure leaching of bulk lead-zinc concentrate from the same source as the material used in this study. It is not possible to compare performance of the systems in detail since our work was on a smaller scale and in batch. However, the salient features of the two processes are summarized in Table 6.

COST OF MICROBIOLOGICAL LEACHING

Estimates of the capital cost for a microbiological leaching plant are not available.

The operating costs for microbiological leaching are primarily power for oxygen transfer to the slurry and calcium carbonate for elimination of excess sulphuric acid. On the basis of experimental results a range of operating costs for the leaching stage has been calculated. These costs are presented in Table 7. Reagent and power costs for acid pressure leaching (1) are presented for comparison. An oxygen transfer efficiency of 3 lb/hp hr would be characteristic of a comparatively fast leaching system, while an efficiency of 5 lb/hp hr represents an "oxygen limiting" system with slower leaching and longer residence times.

CONCLUSIONS

This investigation has shown that zinc recoveries of >90% can be obtained by microbiological leaching of a bulk zinc-lead concentrate. Zinc solutions suitable for electrolytic recovery can be produced, and spent electrolyte can be recycled to leaching after neutralization with calcium carbonate and filtration. Cadmium and copper are solubilized with zinc and can be separately recovered. Projected operating costs for microbiological leaching of zinc concentrates are comparable to estimated costs for an acid pressure leaching system.

ACKNOWLEDGEMENT

This study was sponsored by Mimets Development Pty Ltd. Their permission to publish the results of the investigation is acknowledged.

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Table 1

ANALYSES OF ORE AND CONCENTRATE SAMPLES

Sample		Analysis, %				
		Zinc	Lead	Cadmium	Copper	Iron
Ore	Composite "H"	10.4	3.1	---	---	---
	Composite "A"	9.2	4.1	---	0.18	---
	Grab	13.3	7.8	---	---	---
	Concentrate 1	25.35	8.36	0.06	0.44	12.4
	Concentrate 2	25.2	10.2	0.07	0.58	12.8

Table 2

SCREEN SIZE ANALYSES OF ORES AND CONCENTRATES

		WEIGHT % IN SIZE RANGE			
		+100m	−100 +325m	−325 +400m	−400m
Ore samples (average values)	As received	82	12	2	4
	Reground	−	−	−	>99
Concentrate 1	As received	−	1	4.5	94.5
	Reground	−	−	−	100
Concentrate 2	Reground	−	−	−	100

Table 3

MICROBIOLOGICAL EXTRACTION OF McARTHUR RIVER ORE SAMPLES

Sample	Condition	Bacteria Present	Zn leach rate (mg/l/hr)	% Zn Extracted	% Cu Extracted
Composite H	As received	Yes	25	82.6	
		No	2	27.9	
	Ground	Yes	105	90.1	
		No	<1	12.4	
Grab	As received	Yes	12	86.7	
		No	3	41.8	
	Ground	Yes	135	98.5	
		No	<1	3.8	
Composite A	As received	Yes	25	88.3	44.5
		No	<1	16.5	0.4
	Ground	Yes	90	92.7	45.2
		No	<1	11.5	0.6

Table 4

ZINC EXTRACTION FROM REGROUND CONCENTRATE No. 1

g OF CONCENTRATE PER 75 ml	MAXIMUM Zn CONCENTRATION	% Zn EXTRACTION
8	28.3	100
10	37.0	100
+10*	68.0	94
+15*	76.0	85
15	55.0	100
+10*	84.0	94
20	69.0	99
25	79.0	89

*** Added later without any acid addition**

Table 5

RESULTS OF TANK LEACHING TEST : CONCENTRATE No. 2

METAL	SOLUTION CONCENTRATION, g/l	% EXTRACTION
Zinc	96	92.8
Cadmium	0.26	91
Copper	2.1	83.5
Iron	5.2	9.5
Magnesium	0.6	---

Table 6

OPERATIONS OF MICROBIOLOGICAL- AND ACID PRESSURE LEACHING

OPERATION	ACID/PRESSURE LEACHING	MICROBIOLOGICAL LEACHING
Regrinding	nil (feed at -325m)	feed at -400 mesh
Oxidant	oxygen, 75 psig	air, 10-12 psig
O_2 required lb/T Zn	~ 840	~ 3000
Residence time	2.5 hr	40-60 hr
Reactors	pressure autoclaves	open tanks
Major power requirements	oxygen plant autoclave agitation	low pressure blowers tank agitators
Heat requirement	small	nil (cooling may be necessary)
Sulphuric acid requirement	0.2 - 0.4 T / T Zn	nil
Other reagents	$CaCO_3$	CO_2 $CaCO_3$ (~ 2T / T Zn) NH_3 (3 lb / T Zn) H_3PO_4 (~5 lb / T Zn)
Zn extraction	>90%	>90%
Pregnant solution	120 g/l Zn	up to 120 g/l Zn

Table 7

REAGENT AND POWER COSTS FOR ZINC LEACHING

ACID PRESSURE LEACHING (1)	
Acid	
Limestone	
Flocculant	
Oxygen	
TOTAL	0.82¢/lb Zn

MICROBIOLOGICAL LEACHING	Oxygen transfer efficiency	
	3 lb/hp hr	5 lb/hp hr
Electric power (0.5¢/KWH)	0.87¢/lb Zn	0.52¢/lb Zn
Limestone ($2/T	0.20 "	0.20 "
	1.07	0.72

Figure 1
MICROBIOLOGICAL LEACHING OF SAMPLE G

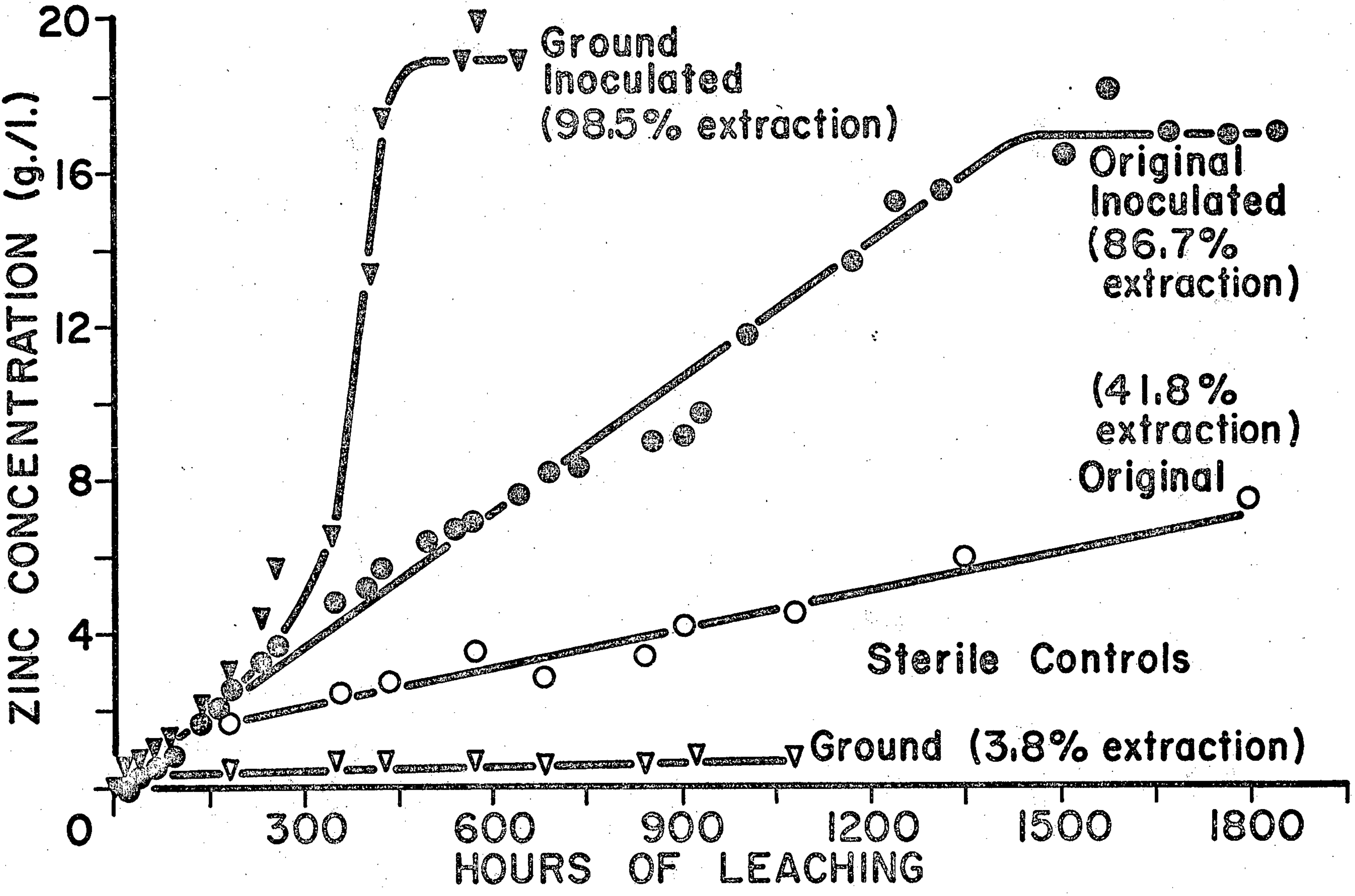

Figure 2

SCHEMATIC DIAGRAM OF MICROBIOLOGICAL LEACHING PROCESS FOR BULK ZINC-LEAD CONCENTRATE