THE INTEGRATION OF ZINC BIOLEACHING WITH SOLVENT EXTRACTION FOR THE PRODUCTION OF ZINC METAL FROM ZINC CONCENTRATES

M.L. Steemson, F.S. Wong, and B. Goebel

MIM Holdings Ltd. Hydrometallurgy Research Laboratories, 22 Corunna St., Albion, Brisbane 4010, Australia

ABSTRACT

A novel process has been developed for zinc metal production from zinc concentrates by integrating zinc bioleaching with zinc solvent extraction and electrowinning. The zinc bioleaching stage was developed from small scale continuous trials through to the construction and operation of a 1300L scale pilot plant. Using both a commercial zinc concentrate, and a mixed lead / zinc concentrate as feedstocks, zinc extractions of 95-99% were obtained, depending on the process conditions. The integration of zinc bioleaching with solvent extraction and electrowinning has significant advantages including a simplified flowsheet resulting in low capital costs, high zinc recoveries and the supply of the key reagent requirements (such as sulphuric acid and CO_2) for the bioleach.

A fully integrated zinc pilot plant based on the integrated process was operated over a 12 month period, treating both the zinc concentrate and mixed lead / zinc concentrate feeds. Overall zinc recoveries of 96% (for the zinc concentrate) and 93-96% (mixed lead / zinc concentrate) were obtained, with routine production of SHG zinc cathode.

1 INTRODUCTION

The bioleaching of zinc concentrates using mesophilic aerobic autotrophs has previously been extensively studied in batch shakeflask[4] and agitated tests[5], and to a more limited extent, in small scale continuous trials[1,2]. The potential benefits of commercial zinc bioleaching are significant, in that low grade, or difficult to treat zinc concentrates using conventional technology can be handled in a bioleach based system. A major hurdle has been the integration of the product liquor produced from bioleaching with a zinc electrowinning unit.

The current paper focuses on the development of the bioleach circuit, and its integration with solvent extraction and electrowinning. This integration has substantial benefits, such as satisfying the acid demand during bioleaching and producing a readily accessible source of carbon dioxide, but imposes process constraints on the bioleach stage. Results are presented for two zinc concentrate sources, a high grade commercial concentrate, and a bulk lead / zinc concentrate.

2 BIOLEACH CIRCUIT DEVELOPMENT

2.1 General

The zinc bioleaching circuit was developed in two stages. Initially, process development trials were undertaken on a fully continuous mini-pilot unit over a period of 12-18 months. This unit investigated the effect of key process variables, such as temperature, configuration, residence time, feed types and simulated recycling issues for the overall process. Additionally, liquors produced from the mini-pilot were used to develop the metal recovery circuit, and various automatic control strategies were developed.

The results of the mini-pilot trials were applied to the design and operation of a fully automated 1300 L scale zinc bioleach pilot plant, which was operated with two feedstocks over a period of 12 months, including commissioning.

The following discussion related to some of the key bioleaching results obtained from the mini-pilot and pilot plants, and scale-up results observed.

2.2 Mini-Pilot Campaigns

Materials and Equipment

A schematic of the mini-pilot plant bioreactor system is shown in Figure 1. The unit consisted of 4L temperature controlled, aerated, agitated bioreactors, with a modular framework to enable various configurations to be tested. Feed slurry to the unit was via an agitated 20L feed vessel, which was fitted with a splitter box and air activated pneumatic doser to enable accurate feed dosing. The pH in each bioreactor was monitored via Leeds and Northrop pH/Eh controllers, with pH being controlled by sulphuric acid addition (either as fresh dilute acid or zinc solvent extraction raffinate). The target pH was 1.6-1.7.

The unit was monitored continuously on a 24 hour basis using a PC based process controller, which monitored key functions such as the feed slurry flowrate, air flowrate and pH. Alarm functions were incorporated to notify operators of any operational problems.

In a typical trial, the bioreactors were operated on batch mode with the specific zinc concentrate feed until logarithmic growth was well established. The bacterial culture employed was a bacterial leach culture from Mt. Isa which had been adapted to increasingly high zinc tolerances. The culture was determined using both classical enrichment and isolation procedures and modern molecular approaches to comprise a mixed bacterial population of Thiobacillus Ferrooxidans, Leptospirillum Ferrooxidans, Thiobacillus Thiooxidans, Sulfobacillus strains, Thiobacillus Caldus, Acidiphilium Cryptum, Acidiphilum Organovorum and other mixed heterotrophic organisms. Nutrients were varied across the trials to optimise the requirement, but were typically 1.5 gpl $(NH_4)_2SO_4$ and 0.4 gpl mono-ammonium phosphate ($NH_4H_2PO_4$). All zinc concentrates employed were obtained direct from stockpiles, with no washing of flotation reagents employed.

When bacterial growth was initiated, continuous feed to the mini-pilot was commenced, and sequentially ramped up to the desired residence time over a period of several days. When the desired residence time was attained, the chemical and biological response of the system was monitored for several overall residence times (typically 10 or more to account for process upsets). Sufficient time was allowed at each residence time tested to ensure that steady state behaviour was obtained.

Mini-Pilot Results

Mini-pilot trial results are presented for two zinc concentrate feeds, a commercial zinc concentrate, and a mixed lead / zinc concentrate. Assays and sizing data for these feeds are shown in Table 1.

Selected results of the mini-pilot plant using the two feedstocks are shown in Tables 2 and 3. The results indicate that bioleaching of the zinc concentrates was an efficient and effective technique for solubilising the zinc. A residence time of 3 days was suitable for extracting 94% of the zinc in the zinc concentrate, and 96.5% of the zinc in the finer lead / zinc concentrate feed. The final zinc tenor in both cases was 25-30 gpl Zn.

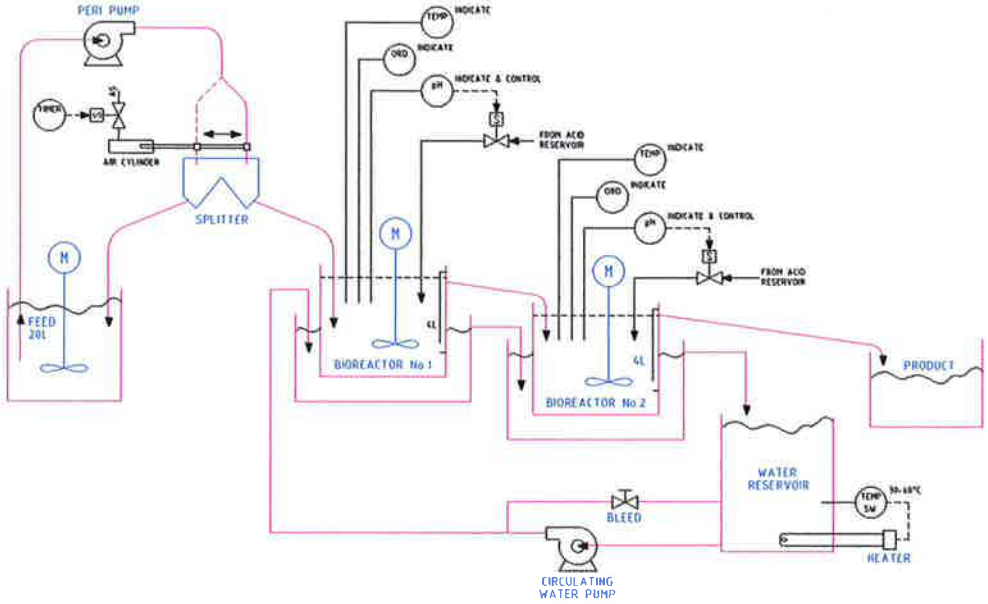

FIGURE 1 Schematic of Mini-Pilot Plant Bioreactor System

TABLE 1 Feed Characterisation Data for Zinc Concentrates used in Continuous Bioleaching Trials

Elemental Assay	Zinc Concentrate	Lead / Zinc Concentrate
Zinc	48.6 %	43.8 %
Lead	2.7 %	11.3 %
Iron	8.6 %	6.1 %
Copper	0.12 %	0.80 %
Cadmium	0.14 %	0.09 %
Silica	2.7 %	3.9 %
MgO	0.34 %	0.25 %
Sulphur	32.6 %	31.0 %
P80 Particle Size	35 µm	10 µm

The data further indicates that the bulk of the zinc is being extracted in the first vessel of the reactor, with the final vessel acting as a polishing agent. The specific zinc extraction rates in the first reactor were typically 12-13 g/L-day for the zinc concentrate, and 23 g/L-day for the lead / zinc concentrate. Experimentally, it was observed that the specific zinc extraction rate was proportional to the iron oxidation rate in the first reactor, indicating that bacterial ferrous oxidation was the rate determining mechanism.

2.3 Pilot Plant Trials

Materials and Equipment

The mini-pilot scale information was as the basis for the design of a 1300L scale bioleaching pilot plant, as part of an integrated zinc refinery based on bioleaching. Based on the mini-pilot configuration runs, a 4 vessel design was adopted with the first two units operating in parallel. This configuration was advantageous in that maximum bacterial numbers growth was promoted in the first reactors, with the final unit acting as a scavenger.

TABLE 2 Summary of Zinc Concentrate Mini-Pilot Results
(1 x 4L, 2 x 2L Configuration, 40 °C, 6-8% Solids Feed
0.1 vvm air with 2% CO_2 as aeration)

OPERATING TIME (days)	OVERALL RESIDENCE TIME (days)	METAL EXTNS (%)		Specific Zinc Extn. (g/L-day)			Acid Cons. (kg/t)	Bacterial Numbers ($*10^{-7}$) / cc		
		Zinc	Iron	Vessel 1	Vessel 2	Vessel 3		Vess. 1	Vess. 2	Vess. 3
27	3.7	93.8	75.6	12.1	2.9	0	41	590	755	1154
27	3.2	93.8	69.8	13.9	5.1	0	34	3176	3062	1352
8	2.6	88.7	68.2	12.4	8.0	0.3	101	662	704	1352

TABLE 3 Summary of Lead / Zinc Concentrate Mini-Pilot Results
(2 x 4L Configuration, 40 °C, 6-8% Solids Feed
0.1 vvm air with 2% CO_2 as aeration)

OPERATING TIME (days)	OVERALL RESIDENCE TIME (days)	METAL EXTNS (%)		Specific Zinc Extn. (g/L-day)		Zinc Mass Balance (%)	Acid Cons. (kg/t)
		Zinc	Iron	Vessel 1	Vessel 2		
22	4	97.4	76.5	16.2	.76	94	13
26	3	96.6	78.9	22.5	3.2	96	43
49	2.2	94.5	76.2	24.4	3.8	92	50
10	1.5	93.9	80.2	27.6	3.3	108	88
4	1	90.8	73	28.7	6.4	103	84

The pilot bioleach units were 330 L temperature controlled, agitated, aerated reactors. Agitation for each unit was via Lightnin A315 hydrofoil impellors. Temperature control of each bioreactor to 40-45 °C was via thermistor controlled valves activating either warm or cold water which was circulated through the vessel jackets. As per the mini-pilot units, each bioreactor was fitted with an individual Leeds and Northrop pH/Eh controller activating acid addition via dosage pumps. However, the acid demand was largely met in all feed types tested by the sulphuric acid contained in recycled zinc raffinate which was used for feed slurrying. Thus, automatic acid addition via the pH controllers (again using zinc raffinate) was only used for fine tuning.

In order to boost the zinc extractions beyond the results obtained in mini-pilot runs, a significant part of the thickened product residue was recycled for further zinc extraction. Using zinc concentrate feed, 80-90% of the residue could be recycled, without an adverse effect on solid density levels. Using the lead / zinc concentrate, with higher solids densities in the bioreactors, only 50-70% of the residue could be recycled.

As per the mini-pilot plant, the pilot bioreactor unit was continuously monitored over a 24 hour basis using a PC based process controller, which monitored key functions including the feed slurry flowrate, feed slurry levels, air flowrate, agitator failure and pH. Alarm functions were incorporated to notify operators of any operational problems.

The operation and start-up of the pilot plant was similar to the mini-pilot trials. Indeed, bacterial culture from the mini-pilot plant was used as inoculum for the pilot plant. Similar nutrient addition levels were employed as to the mini-pilot.

Pilot Plant Results

The final average results for pilot plant runs utilising the zinc concentrate and lead / zinc concentrate depicted in Table 1 are shown in Table 4. For zinc concentrate feed, incorporating residue recycle, a final zinc extraction of 96-98.7% was obtained, depending on the residence time and target zinc tenor. This was slightly higher than the 94% recovery found in small scale continuous trials, and reflects the benefits of residue recycle. The specific zinc extraction in the first bioreactor tanks was 12-14.5 g/L-day, which was similar to small scale results. Iron extraction had improved from 70-75% to 90-95%, again reflecting the improved performance of the system using residue recycle.

An interesting feature of the results with zinc concentrate feed, was the ability of the system to achieve high zinc extractions at high zinc tenors of up to 60 gpl. Over 96% zinc recovery was obtained at a 45 gpl Zn product liquor (at 3 days overall residence time) and at over 60 gpl Zn (with 4.2 days overall residence time). Clearly, the bacteria had adapted to high zinc tolerances over time (initially 40 gpl Zn was the limited zinc tolerance).

Using the mixed lead / zinc concentrate feed, specific zinc extractions of 18 g/L-day were found in the first bioreactors, which are slightly worse than the 23 g/l-day found in small scale trials. At 4.5 days residence time, and a 45 gpl Zn target product liquor, the final zinc extraction was 98.7%, which was slightly better than comparable small scale continuous results, and reflects the benefits of residue recycle. By 'pushing' the system to 3days residence time, with a 60 gpl Zn product liquor, 95% of the zinc was still extracted, alongside of 48% of the iron. These results clearly indicate the oxidative the continuous zinc bioleaching system.

TABLE 4 Summary of Pilot Plant Bioleach Trial Results
(40-45 °C, 6-8% Solids Feed, 0.1 vvm air with 1.5% CO_2 as aeration)

FEED	TRIAL No.	OP. TIME (days)	CONDITIONS				METAL EXTNS (%)		Specific Zinc Extn. (g/L-day)				Mass Balance (%)		Residue Grade (%)	
			Solids (%)	Target Zn (gpl)	RT (days)	Recycle (%)	Zinc	Iron	Vess. 1	Vess. 2	Vess. 3	Vess. 4	Zinc	Lead	Lead	Zinc
Zinc Conc.	2	30	6	30	3	90	98.7	95.4	9.9	10.2	2.7	2.2	92	96	15.4	14
	3	17	6.7	30	3	90	98.7	95.3	10.9	9.4	3.5	4.4	91	89	16.9	13
	4	17	9	45	4.2	90	98.6	95.4	10.4	10.2	6.4	4.0	95	94	18	13.3
	5	15	9	45	3-4	85-90	97.8	91.9	11.3	13.3	8.4	5.9	106	99	17	14.7
	6	28	9	45	3	80-85	96.2	91.3	12.4	13.4	10.1	6.0	103	90	18.5	18.5
	7	6	12.4	>60	4.2	80	96.4		14.4	14.6	9.1	4.5	115	101	18.5	17.9
Pb/Zn Conc.	A	10	10	45	4.5	70	98.7	82.8					96	61[2]	30.7	6.5
	B2	22	12.2	60	3	70	94.9	48.1	18.1[1]	17.6	11.7	8	101	111	33	9

1 Results for entire B Run.
2 Insufficient time for steady state to be attained.

Aside from the chemical performance, it is interesting to examine the residues produced from the continuous bioleach trials. Under the conditions of operation employed in the trials, no elemental sulphur was found, indicating that complete oxidation of sulphides to sulphate had occurred. Furthermore, XRD and chemical analysis of lead / zinc concentrate residue indicated that no plumbojarosite had formed, with the lead being present as anglesite ($PbSO_4$). Only in situations where jarosite was present in the feed, was substantial quantities of jarosite present in the product residue.

A further interesting observation was the bacterial population within the system. Typical bacterial total counts were 3-15 x 10^9 / cc, with MPN (most probable number) counts of 10^6-10^8 / cc. The highest dilutions in the MPN tests were examined microscopically, and found to be of spiral morphology, which is indicative of Leptospirillum Ferrooxidans.

3 INTEGRATION OF BIOLEACHING WITH SOLVENT EXTRACTION AND ELECTROWINNING

3.1 Process Description

A key issue in the bacterial leaching of base metals is the integration of the bioleaching stage into a complete robust process. To date, although extensive batch and some continuous zinc bioleaching studies have been undertaken, the integration of zinc bioleaching to produce zinc metal has received little attention.

The objective of the current zinc program was to develop a novel zinc refining system based on zinc bioleaching . Figure 2 presents a flowsheet of the developed process. The following are the key processing stages:

- Bioleaching of the zinc concentrate to achieve high zinc recoveries (95-98%). Acid and CO_2, which are important reagents in zinc bioleaching are provided by further processing stages. With lead / zinc concentrate feed, a saleable lead / silver product is produced.
- Precipitation of the ferric and ferrous iron in solution in an iron precipitation stage using alkaline neutralisation.
- Solvent extraction (SX) of the iron free zinc containing solution in a 1-2 stage solvent extraction train. If necessary, raffinate recycle can be employed to reduce the zinc tenor of the SX feed liquor.
- Electrowinning of loaded zinc electrolyte produced from zinc solvent extraction to produce zinc metal, and spent zinc electrolyte, for recycle to the SX strip stages.
- Neutralisation of excess acid in the system, using a suitable alkali (such as commercial grade limestone).
- Recycle of the zinc raffinate to the bioleaching stage to provide the acid requirement for bioleaching.
- Bleeding of part of the zinc raffinate for copper, cadmium, magnesium and other impurity control.

For a more detailed discussion of the developed process, please refer to Steemson et al[3].

The process flowsheet discussed above has several significant advantages:

- Capital items are minimised when compared to a conventional zinc refinery. With the choice of an appropriate zinc extractant, there is no requirement for zinc purification stages.
- The process is ideally suited for non-standard zinc 'concentrates' (e.g. high lead or halogen materials) that would be difficult to treat by conventional processing.

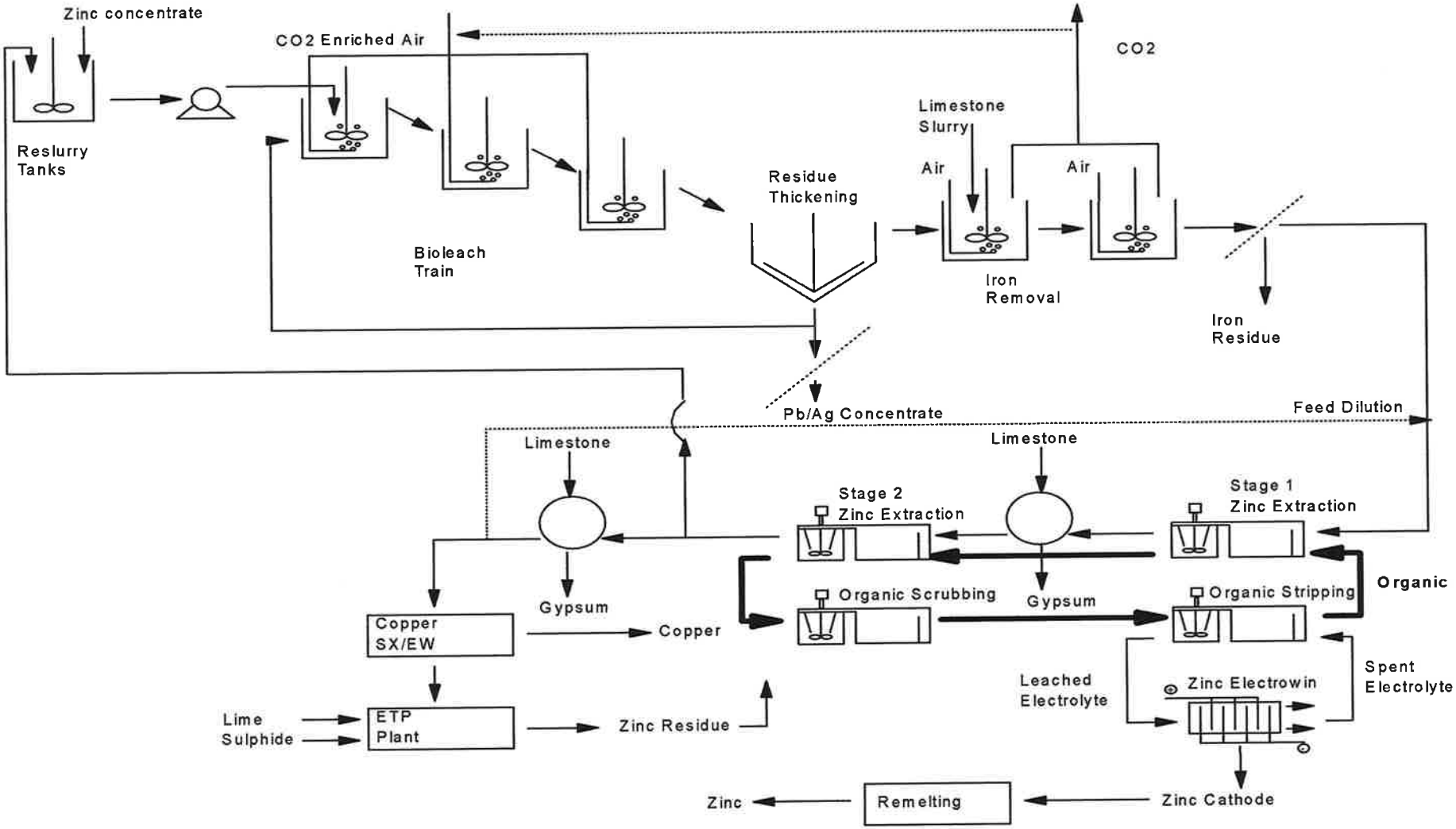

FIGURE 2 Schematic of Integrated Bioleaching / Solvent Extraction / Electrowinning Process for Zinc Production from Zinc Concentrates

- The zinc tenor from bioleaching and that required can be matched. This is a major problem in that the zinc bioleach stage zinc tenor should be maximised to reduce capital requirements, but the solvent extraction stage has a limited tolerance to zinc. Using D_2EHPA (di-ethyl hexyl phosphoric acid) as the zinc extractant, it was found that a 20-25 gpl Zn tenor could be readily treated by SX in a two-stage process, while still producing zinc raffinate of sufficient acidity to neutralise any acid consumers in the feed concentrate.
- Minimal heating or cooling is required in the system if the zinc bioleach is operated at 40-45 °C.
- By appropriate solvent extraction design, impurities (such as cobalt, copper and nickel) present in conventional zinc tankhouses can be substantially eliminated.
- The only reagent requirements are alkali for acid neutralisation (generally cheap commercial grade limestone), commercial grade fertiliser for bioleach nutrients, flocculants, and standard electrowinning additives.
- Gypsum is produced as a sulphur containing byproduct, which can be saleable to plasterboard manufacturers.

The major current disadvantage of the integrated process is the production of a bulky iron residue, which must be disposed of. The volume of this material can be reduced by operating the iron removal stage as a goethite reactor, but this entails heating and cooling of liquors.

3.2 Typical Integrated System Results

A integrated zinc bioleach / solvent extraction / electrowinning pilot plant, incorporating the 1300 L scale bioleach discussed in Section 2.2 was operated over a period of 12 months, with routine production of SHG Grade zinc metal. The typical production throughput was 20 kgs of zinc cathode per day (140 kgs over a standard 7 day plating cycle). The following is a typical description of the system results, when treating the zinc and lead / zinc concentrates discussed in Section 2.0.

1. *Bioleach Train*: Discussed in Section 2.0.

2. *Iron Neutralisation*: The iron content of the zinc bioleach solution was typically 3-4 gpl Fe, of which 90% was Fe^{3+}. At 40 °C, it was found that, using 25% w/w limestone as the neutralisation agent, the total iron level could be readily reduced to <10 ppm in 6 hours of neutralisation at pH 4.0. Zinc losses to the cake where a potential problem, but, by reslurrying and refiltering the cake, total zinc losses were reduced to <0.5%.

3. *Zinc Solvent Extraction*: The zinc solvent extraction circuit operated with 2 extraction stages using commercial limestone to neutralise acid from he first stage prior to introduction to the second stage. The organic used was 25% v/v D_2EHPA in Shellsol 2046 as the diluent. The organic to aqueous ratio was 3:1. After scrubbing with diluted electrolyte, the organic was stripped of zinc using Spent Electrolyte (60-70 gpl Zn, 180 gpl H_2SO_4) to produce a Loaded Electrolyte containing 80-100 gpl Zn. The pilot unit was fully automatic, and could be operated in on/off mode via a group start/stop facility.

   The SX unit was capable of producing a 4-6 gpl Zn raffinate (containing 19 gpl H_2SO_4) from a 28-30 gpl Zn feed. The average zinc removal in each extraction stage was 12.3 gpl (Stage 1) and 11.5 gpl (Stage 2). No cadmium, copper, cobalt or nickel deportment to the Loaded Electrolyte was noted.

   The gypsum produced from interstage neutralisation assayed at 0.3-0.4% Zn, which reduced to 0.05% Zn upon reslurrying and refiltration. Discussions with plasterboard manufacturers indicated that the rewashed material was suitable for plasterboard manufacture.

4. *Zinc Electrowinning*: Zinc electrowinning tests were conducted at 35 °C in a pilot electrowinning cell with 4 aluminium cathodes, each of area 0.48 m^2, and 5 silver lead anodes. The cell ΔZn was 5 gpl. The cathodic current density was 425 A/m^2, with a cathode to anode distance of 50 mm (centre to centre). Additives employed in the electrowin included strontium carbonate for lead control, and glue to improve plating morphology.

   The zinc specification from the pilot tankhouse generally met SHG specifications. Copper was the only marginal element, but problems with copper were largely due to busbar corrosion. As busbar corrosion problems were alleviated, copper levels in the zinc cathode reduced. The average current efficiency was 88-90%, which would improve in commercial cells, owing to improved stability of operation.

4 CONCLUSIONS

An integrated process has been developed which couples zinc bioleaching with solvent extraction and electrowinning (SX/EW) to produce zinc metal from zinc concentrate feeds. To demonstrate the process, a fully integrated pilot plant was constructed and operated over a 12 month period. Using a commercial zinc concentrate, overall zinc recoveries of 96% were obtained (98-99% during bioleaching). Using a lead / zinc concentrate feed, an overall zinc recovery of 93-96% (95-99% during bioleaching) was obtained . The advantages of coupling bioleaching with an SX/EW stage are significant, and include capital cost reductions over conventional zinc refineries, the capacity to treat 'difficult' zinc concentrates (such as those containing high lead or halogen contents), and the supply of key reagents to the bioleach.

The 1300L continuous bioleach stage in the pilot plant was scaled up from 8L small scale mini-pilot trials. In general, both the metallurgical and biological response of the pilot plant was similar to the mini-pilot studies.

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