

IMPROVING ZINC RECOVERY AT PERILYA BROKEN HILL CONCENTRATOR BY CHANGING THE GRINDING CHEMISTRY

CHRISTOPHER GREET & MICHAEL MYLLYNEN
Magotteaux, Australia

DAVID MACKAY
Perilya Broken Hill Mine, Australia

ABSTRACT

An extensive body of work examining the electrochemical interactions between grinding media and sulphide minerals exists in academia however, the question on industries lips is: "Does this have relevance to an operating concentrator?"

This paper provides an account of the metallurgical test work completed at Perilya's Broken Hill mine in far west New South Wales, Australia. The work completed extended over a number of years, and included laboratory studies using the Magotteaux Mill[®], which eventually lead to a full plant trial.

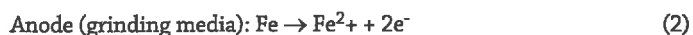
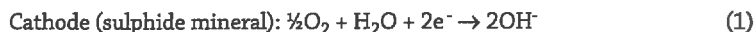
Broadly, the laboratory results indicated that a 21 percent chrome alloy would produce the optimum pulp chemical conditions for the best zinc metallurgy. The pulp chemical changes predicted by the laboratory work were achieved in the plant. Further, when the plant converted to 21 percent chrome grinding media in October 2007, the change in media type resulted in statistically significant improvements in the zinc concentrate grade (0.6 ± 0.3 percent), and zinc recovery (1.8 ± 1.3 percent). The improvement in zinc concentrate grade can be attributed to better selectivity for sphalerite against iron sulphides (pyrrhotite).

The work demonstrates that using a robust laboratory schedule such as the Magotteaux Mill[®] can effectively predict plant performance.

INTRODUCTION

The key to a successful separation in mineral processing is the preparation of particles with adequate liberation under the correct pulp chemical conditions.

While the importance of liberation on flotation separations is generally understood and well documented in the literature [12, 17, 18, 30], the importance of pulp chemistry is more nebulous, particularly with regard to the impact of grinding environment. Extensive work examining the electrochemical interactions between grinding media and sulphide minerals has been completed [1, 5, 8, 13, 14, 16, 21, 25, 28, 29, 31]. Broadly, these studies indicate that most sulphide minerals are more noble than the grinding media used during comminution. Therefore, the sulphide minerals are cathodic with respect to the forged steel grinding media, and the following reactions apply:



Unfortunately, in a real ore system the galvanic cells are considerably more complex because the sulphide mineral can act as either an anode or cathode depending on its contact with other sulphide minerals, media and reagents [5]. Sufficit to say a galvanic couple between the grinding media and the sulphide mineral(s) exists, which increases the corrosion rate of the forged steel media. The corrosion products of the grinding media, iron oxy-hydroxide species, invariably precipitate on to the surfaces of the sulphide minerals thereby affecting their floatability [19].

One method of preventing the contamination of the sulphide surfaces and improve metallurgical performance is to substitute inert grinding media into the system. As ceramic grinding media is unsuitable in many applications and stainless steel grinding media cost prohibitive, high chrome white iron is a viable alternative to forged steel media. High chrome grinding media is generally superior to forged steel media in terms of abrasive and corrosive wear. Of particular importance to the flotation process is high chrome media's better corrosion resistance, where the surface of the ball oxidises rapidly to form a passive chromium oxide surface layer which acts as a barrier to further electron transfer, significantly reducing the corrosion process.

While much of the above discussion is academic, the question on industry's lips is: *Does this have relevance to an operating concentrator?*

METHODOLOGY

In the past, many laboratory studies have not used plant-operating conditions during testing. This has led to a suspicion of laboratory results. To avoid this complication a new tool, the Magotteaux Mill®, has been developed [15].

The Magotteaux Mill® (Figure 1) allows the researcher to generate a product in the laboratory that has nominally the same physical properties (particle size distribution) and pulp chemical properties (pH, Eh, dissolved oxygen, temperature, oxygen demand and EDTA extractable iron) as an equivalent sample taken from the plant. This is achieved by grinding an appropriate sample to achieve the particle size distribution of the flotation feed, and manipulating the pulp chemistry, by purging the system with an inert gas, so that it matches the plant mill discharge.

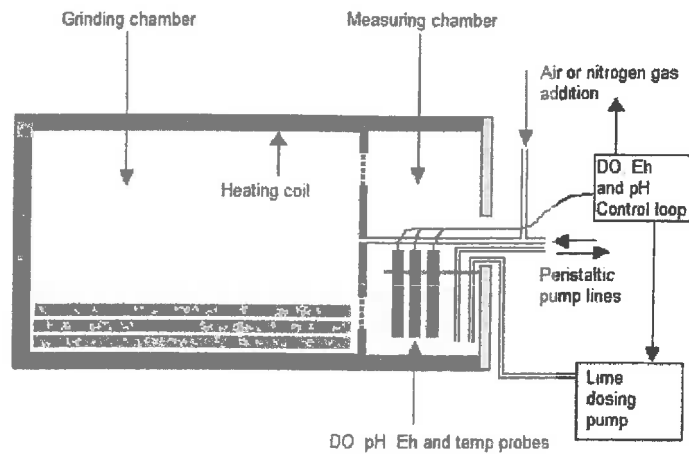


Figure 1: Schematic representation of the Magotteaux Mill®.

The experimental strategy adopted to achieve the desired outcomes is completed in three phases:

Phase 1 - Plant data collection: The collection of plant data is vital to the success of the test program, for this data forms the basis of the calibration process by defining the target parameters. This initial step involves:

- The completion of a pulp chemical and EDTA extractable metal ion survey of the grinding and adjoining flotation circuit;
- Determination of the oxygen demand at strategic points within the circuit;
- The completion of a metallurgical survey; and
- The collection of a bulk sample of the grinding circuit feed for further testing.

It is important to note that the metallurgical survey must include both a down-the-bank survey of the flotation stage immediately following grinding, and a block survey of the plant to determine overall metallurgical performance.

Phase 2 - Magotteaux Mill® calibration: The data collected in Phase 1 essentially describes the circuit under consideration, and provides targets for the Magotteaux Mill® calibration. The calibration process uses the same grinding media as the operating plant. The objective of the calibration process is to produce a laboratory mill discharge which has the same particle size distribution as the conditioned flotation feed, and the pulp chemistry of the plant grinding mill discharge. To achieve this match involves careful manipulation of the Eh, pH, dissolved oxygen and grinding time, such that all the measured parameters line up when grinding the bulk sample collected during the metallurgical survey. This task is not trivial.

Once the Magotteaux Mill® is calibrated, oxygen demand and flotation tests are completed on the ground ore.

Phase 3 - Media testing: With the Magotteaux Mill® calibrated, alternative grinding media are substituted into the mill for testing. The procedure determined during the calibration process for the current grinding media is then applied while grinding the bulk sample employing the alternative grinding media. In this way, it is possible to measure changes in pulp chemistry and flotation response. The changes observed are attributed to the variations in grinding media composition, as the only intentional parameter being changed in the test is the grinding media.

APPLICATION TO PERILYA BROKEN HILL

Broken Hill

The Broken Hill silver-lead-zinc ores are probably the most famous in Australia, and have particular significance in mineral processing as it is these sulphide ores which provided the impetus (in the early part of last century) to develop an industrial flotation practice [2]. The process eventually superseded most other separation techniques because of its efficiency, both metallurgical and economic.

Mineralogy

The Broken Hill ore bodies are coarse grained, massive sulphide deposits [22], containing galena, marmatite (high iron sphalerite), chalcopyrite, pyrrhotite and arsenopyrite. The principal non-sulphide gangue minerals are quartz, feldspar, rhodonite, fluorite, calcite, and garnet.

Process Flow Sheet

Perilya's Broken Hill concentrator (known as NBHC in earlier times) is described elsewhere [27]. All three parallel lines are *identical*, with the following configuration. Ore from the fine ore bin feeds a rod mill. The rod mill discharge flows in to a sump where it combines with the primary ball mill discharge, and is pumped to the primary cyclone bank. The primary cyclone underflow feeds the primary ball mill, and the overflow gravity feeds to the lead primary rougher flotation cells. The lead primary rougher tailing discharges into a sump and combines with the secondary ball mill discharge. This slurry is pumped to the secondary cyclone pack. The secondary cyclone underflow reports to the secondary ball mill feed, while the secondary cyclone overflow (from the three lines) feeds lead secondary rougher/scavenger flotation. The lead rougher/scavenger concentrate is cleaned in two stages to produce the final lead concentrate. The lead scavenger tailing is conditioned with copper sulphate and collector before zinc rougher/scavenger flotation. The zinc rougher/scavenger concentrate is cleaned in three stages to produce the final zinc concentrate.

Metallurgical Performance

The coarse grain size of the valuable minerals has significant ramifications on the metallurgical performance of these ores. In the first instance, liberation of valuables from each other and non-sulphide gangue is readily achieved, at comparatively coarse particle sizes. Therefore, selectivity of valuable minerals against gangue minerals is good, and as a consequence concentrate grades are high [4, 27]. The coarse particle size distribution also enables high recoveries of valuables to concentrates to be achieved relatively easily, as is evident in Table 1.

Table 1: Typical metallurgical results for the year ending June 1990 [27]

Product	Grade			Recovery, %		
	Pb, %	Ag, ppm	Zn, %	Pb	Ag	Zn
Plant feed	5.20	50	10.10	100.0	100.0	100.0
Lead final concentrate	71.30	618	4.10	92.0	83.2	2.7
Zinc final concentrate	1.00	20	51.50	3.4	7.4	92.5
Final tailing	0.32	6	0.65	4.6	9.4	4.8

However, as the ore reserves at Broken Hill decline the feed grades have deteriorated, and this has had a deleterious effect on both the concentrate grades and metal recoveries. Thus, one of the challenges at Broken Hill in recent times has been to make incremental improvements to the separation efficiency of the flotation process.

LABORATORY STUDIES

An extensive body of laboratory test work has been completed on the Broken Hill ores examining the impact of grinding chemistry on lead and zinc flotation response [6, 7, 9, 10, 11, 26]. Each of these studies has indicated that converting from forged steel grinding media to a high chrome alloy has altered the pulp chemistry of the system and had a positive impact on zinc metallurgy.

Pulp Chemistry

Employing the methodology described above, pulp chemical surveys were completed through the grinding and flotation circuits. Table 2 contains the target parameters for calibrating the Magotteaux Mill® on the bulk sample of rod mill feed [11], and shows the plant targets collected from the Broken Hill concentrator, and the actual Magotteaux Mill® discharge particle size distribution and pulp chemical data, for tests completed employing forged steel grinding media.

Table 2: The plant targets and actual Magotteaux Mill® discharge with forged steel grinding media

Parameter	Process stream	Plant targets	Magotteaux Mill® discharge	Match
P ₈₀ , µm	Cyclone overflow	203 ± 4	202	Yes
% passing 106 µm	Cyclone overflow	54 ± 5	47	No
pH	Mill discharge	8.84 ± 0.5	8.39	Yes
Eh, mV (SHE)	Mill discharge	54 ± 50	17	Yes
DO, ppm	Mill discharge	0.80 ± 0.5	0.53	Yes
EDTA iron, %	Lead rougher feed	2.15 ± 0.5	1.73	Yes

The changes in the pulp chemistry of the laboratory mill discharge for each alloy are listed in Table 3. The data in Table 3 show that the pH was increased subtly to more alkaline pH values when grinding with high chrome grinding media. It is likely that this increase in pH was due to galena oxidation [3]. It is apparent that changing from forged steel to a high chrome alloy resulted in a shift in the Eh of the mill discharge to more oxidising pulp potentials (*i.e.* an average increase of 150 mV). The dissolved oxygen content of the mill discharge pulp was approximately the same for all media types. However, the EDTA extractable iron values determined for the high chrome alloys were reduced to one third of that reported for forged steel. These data suggest that grinding with high chrome would shift the grinding chemistry to more oxidising conditions, and the level of grinding media corrosion products present in the system would be lower (*i.e.*, a reduction in the percentage EDTA extractable iron). These changes in the grinding chemistry should have a positive impact on sphalerite flotation.

Table 3: Pulp chemistry data for Magotteaux Mill® discharge for rod mill feed sample with different grinding media

Media	Parameters				
	P ₈₀ , µm	pH	Eh, mV (SHE)	DO, ppm	EDTA Fe, %
Forged	202	8.39	17	0.53	1.73
15% Cr	204	8.56	156	0.57	0.54
21% Cr	202	8.51	181	0.84	0.52
30% Cr	199	8.61	183	0.75	0.51

Zinc Flotation

In Figure 2 it is apparent that all three high chrome alloys produce a superior zinc grade/recovery curve when compared with forged steel. For example, at 40 percent zinc concentrate grade, the zinc recovery with respect to zinc circuit feed, was increased from 93.2 percent for the forged steel to 94.5 percent for the 21 percent chrome alloy, an increase of

1.3 percent (Table 4). The 21 percent chrome alloy also produced the highest zinc concentrate grade. That is, at 94 percent zinc recovery, the zinc concentrate grade was nominally six percent higher after grinding with 21 percent chrome rather than forged steel. This increase in concentrate grade can be attributed mainly to improvements in selectivity for sphalerite against iron sulphides (pyrrhotite).

Table 4: Zinc recoveries and diluent grades, at 40 percent zinc grade

Test	Zn recovery, %	Grade, %				
		Ag, ppm	Cu	Pb	IS	NSG
Forged	93.16	34	0.13	1.54	3.24	24.85
15% Cr	93.77	40	0.14	1.50	4.14	23.96
21% Cr	94.48	44	0.15	1.67	4.14	23.74
30% Cr	93.64	40	0.15	1.41	4.55	23.63

Table 4 shows the zinc recoveries and diluent grades, at 40 percent zinc grade, relative to zinc circuit feed for the zinc rougher stage of sequential lead/zinc rougher flotation tests completed on rod mill feed samples, ground with forged, 15, 21 and 30 percent chrome grinding media.

The flotation kinetics data (Table 5) show that the sphalerite flotation rate constant and maximum zinc recovery was increased when high chrome media were employed. The gangue mineral flotation rate constants have all increased slightly when grinding with high chrome. However, it is likely that the selectivity remains nominally the same as the gangue mineral maximum recoveries remained substantially the same.

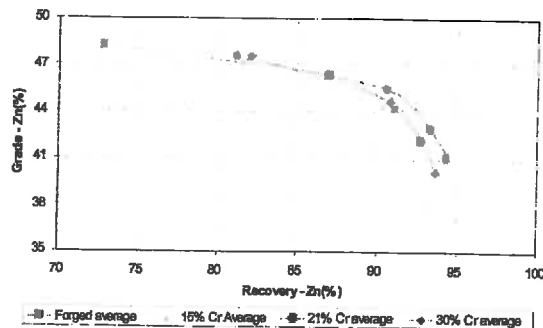


Figure 2: Zinc grade/recovery curves relative to zinc circuit feed for rougher stage.

Figure 2 shows the zinc grade/recovery curves relative to zinc circuit feed for the zinc rougher stage of sequential lead/zinc rougher flotation tests completed on rod mill feed samples ground with forged, 15, 21 and 30 percent chrome grinding media.

Table 5: Flotation rate constant and maximum recovery data for zinc rougher stage

Test	Kinetic data									
	Zn		Pb		Ag		IS		NSG	
	k, min ⁻¹	R _{max} , %	k, min ⁻¹	R _{max} , %	k, min ⁻¹	R _{max} , %	k, min ⁻¹	R _{max} , %	k, min ⁻¹	R _{max} , %
Forged	3.26	90.34	0.98	19.50	1.31	33.11	1.24	8.73	0.60	2.47
15% Cr	4.28	92.24	1.13	25.88	1.71	35.88	1.65	9.36	0.77	2.86
21% Cr	4.16	92.75	1.15	29.52	1.69	41.74	1.63	5.35	0.71	2.88
30% Cr	4.37	92.40	1.12	30.53	1.88	43.76	1.46	11.09	0.64	2.92

Table 5 shows the flotation rate constant and maximum recovery data for the zinc rougher stage of sequential lead/zinc rougher flotation tests, with respect to zinc circuit feed, completed on rod mill feed samples, ground with forged, 15, 21 and 30 percent chrome grinding media.

PLANT TRIAL

Based on the results obtained in the laboratory, an industrial test was conducted in 2006 with the forged steel media charge in Line 2 primary ball mill dumped and replaced with 21 percent chrome grinding media. The pulp chemistry and metallurgical performance of the Line 2 grinding and primary lead rougher flotation were compared to that measured for Line 3 (operated with forged steel). The positive results [20] obtained from this industrial test prompted Perilya Broken Hill to dump and recharge all eight ball mills with 21 percent chrome media in October 2007.

Plant Pulp Chemistry

The laboratory test work suggested that one could expect a shift to more oxidising pulp potentials in the ball mill discharge of nominally 160 mV, when changing from forged steel to 21 percent chrome grinding media. Pulp chemical surveys of Line 3 (forged steel) and Line 2 (21 percent chrome) clearly show that Line 2 primary ball mill discharge is more oxidising than Line 3, and the average difference in the Eh between the two lines was about 175 mV (Figure 3). The more oxidising pulp potentials in the primary ball mill discharge of Line 2 do carry through to the primary cyclone overflow and into the secondary overflow.

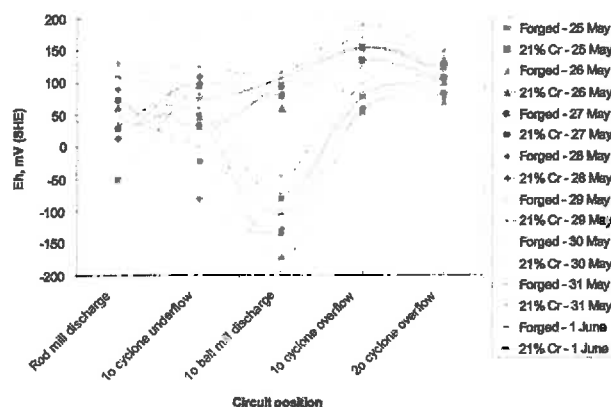


Figure 3: The Eh profile through the primary grinding and lead rougher circuit.

The dissolved oxygen profile follows a similar trend to the Eh, with higher levels of dissolved oxygen in the 21 percent chrome circuit. The elevated levels of dissolved oxygen in the pulp are carried through to the secondary cyclone overflow.

The EDTA extractable iron profile (Figure 4) provides an excellent indication of the differences in the corrosion resistance of the two grinding media types. It is apparent that the circuit employing forged grinding media produced higher concentrations of EDTA extractable iron than Line 2 with 21 percent chrome. For example, Line 3 primary cyclone overflow recorded an average of 1.1 percent EDTA extractable iron compared with 0.6 percent for Line 2. This suggested that the addition of high chrome grinding media to the primary ball mill in Line 2 effectively reduced media corrosion to about half of that noted for forged steel.

Similar pulp chemical differences to those observed in the laboratory were noted in the plant. That is, the laboratory test work suggested that a change to 21 percent chrome grinding media would result in a shift in Eh to more oxidising pulp potential of nominally 160 mV, the dissolved oxygen content would increase marginally and the EDTA extractable iron would be reduced to approximately one third of that noted for forged steel in the conditions flotation feed. The difference between Line 2 and Line 3 ball mill discharges in terms of Eh was 175 mV, while the dissolved oxygen content of the pulp was increased from 0.5 ppm for forged steel to an average of 2.0 ppm for the 21 percent chrome alloy. The EDTA extractable iron was reduced to about half. These data suggest that the Magotteaux Mill® test was able to predict with reasonable reliability what would happen to the pulp chemistry as the media was changed from forged steel to 21 percent chrome in the plant.

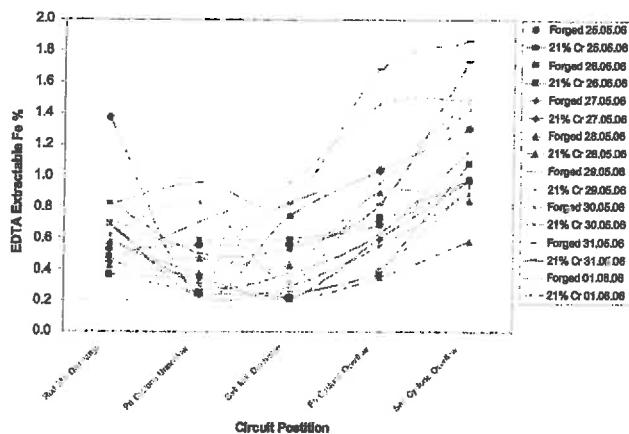


Figure 4: The EDTA extractable iron profile through the primary grinding and lead rougher circuit.

Plant Metallurgical Performance

In the laboratory these differences in pulp chemistry resulted in significant improvement zinc metallurgy. Perilya Broken Hill provided Magotteaux with the shift data for the 17 months from December 2006 through to May 2008 for analysis. The data was cleansed to remove start-up shifts and shifts with lower than normal throughput. The shift data was then grouped into two separate periods:

- **Period 1:** 14 December 2006 to 24 August 2007 (100 percent forged steel grinding media); and
- **Period 2:** 4 October 2007 to 2 May 2008 (100 percent 21 percent chrome grinding media).

Zinc Feed Grade

The mean zinc feed grade for each period was on average approximately 5.5 percent, with the t-test indicating that there was no statistical difference in the zinc feed grade between periods. Therefore, based on zinc feed grade, a valid comparison of the metallurgical performance of the two periods can be made.

Zinc Losses in the Lead Circuit

The zinc losses to the lead concentrate for Period 1 and Period 2 have been compared. The student t-test data indicated that the zinc losses to the lead concentrate were statistically the same for both periods, at 3.3 percent. That is, substituting 21 percent chrome grinding media for forged steel had no effect on zinc recovery to the lead concentrate.

Zinc Concentrate Grade

A comparison of the zinc concentrate grade versus zinc feed grade for Period 1 and Period 2 can be found in Figure 5. An examination of Figure 5 reveals that zinc concentrate grade was higher during Period 2 for all feed grades, when compared with Period 1. The difference in the average zinc concentrate grades was determined (using the student t-test) to be a statistically significant at 0.6 ± 0.3 percent, with greater than 99 percent confidence.

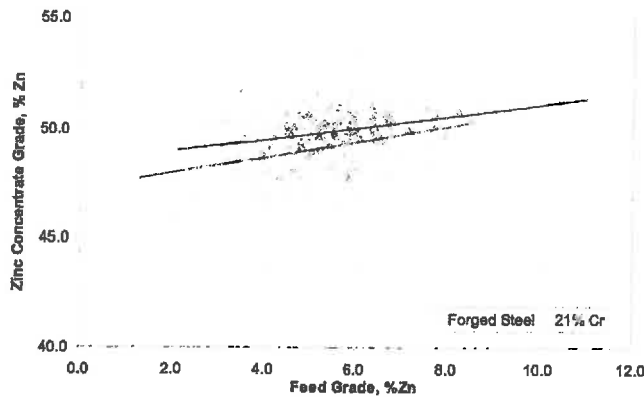


Figure 5: Zinc concentrate grade versus zinc feed grade for periods 1 and 2.

The improvement in zinc concentrate grade can be attributed to better selectivity for sphalerite against iron sulphides (pyrrhotite). The *t*-test data clearly showing that the recovery of iron sulphides into the zinc concentrate was reduced by 3.2 ± 1.2 percent, with greater than 99 percent confidence, once the circuit had been converted to 21 percent chrome grinding media.

The data indicated that the selectivity for sphalerite against non-sulphide gangue was the same for both periods.

Zinc Recovery

The zinc recovery versus zinc feed grade data are presented in Figure 6 for Periods 1 and 2. Figure 6 reveals that zinc recovery for 21 percent chrome was higher than forged steel grinding media for all zinc feed grades up to 8 percent. The student *t*-test data suggested that the zinc recovery was improved by an average of 1.8 ± 1.3 percent, with greater than 99 percent confidence.

Recovery-by-Size Data

The zinc recovery-by-size data for the three periods can be found in Figure 7. These curves constructed from the monthly composite data for each period. The zinc recovery-by-size curves display the same general trend for each media type. That is, the best zinc recoveries for all three alloys occurs for the intermediate size fractions (-100/+10 microns). The zinc recoveries deteriorate for the fine (-10 micron) and coarse (+100 micron) size fractions.

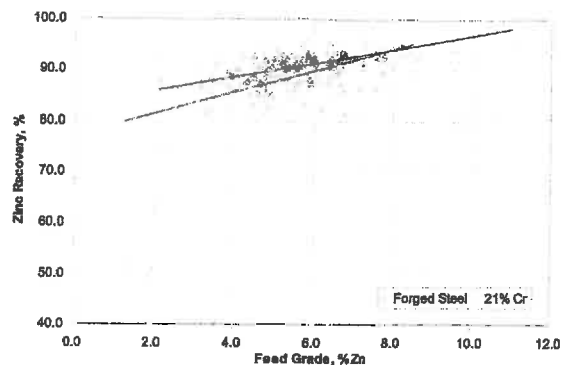


Figure 6: Zinc recovery versus zinc feed grade for periods 1 and 2.

However, it is apparent that converting the plant from forged steel grinding media to high chrome grinding media had a positive impact on the zinc recovery across all size fractions. Potentially, the biggest improvement in zinc recovery has occurred in the very fine (-5 micron) size fractions, where the zinc recovery of these sphalerite particles has increased from 78 percent for forged steel to 90 percent for the 21 percent chrome alloy. The improvement in recovery across the +5 micron size fractions was of the order of 3 percent.

The zinc distribution by size in the zinc scavenger tailing for the three periods appears in Figure 8. Again, these data show the same general trend, with the greatest loss of sphalerite from the plant occurring in the fine (-5 micron) and coarse (+100 micron) size fractions. Greater than 80 percent of the sphalerite leaving the circuit is accounted for in these two size fractions, for both grinding media types. By far the greatest single loss of zinc from the circuit occurs in the finest size fraction, with this data suggesting that the -5 micron sphalerite accounts for between 28 and 44 percent of the zinc in the final tailing, depending on grinding media type. Forged steel grinding media resulted in the biggest loss of fine sphalerite from the circuit. Further, as the chrome content of the grinding media increased the loss of fine sphalerite from the circuit decreased.

Finally, an examination of the iron sulphide recovery-by-size data (Figure 9) clearly demonstrates that the application of high chrome grinding media during primary grinding resulted in a decrease in the iron sulphide particles across all size fractions. The non-sulphide gangue recovery-by-size data showed no significant difference between grinding media types.

CONCLUSIONS

The paper provides an account of the metallurgical test work completed at Perilya's Broken Hill mine in far west New South Wales, in Australia. The work completed extended over a number of years, and included laboratory studies using the Magotteaux Mill®, which eventually lead to a full plant trial.

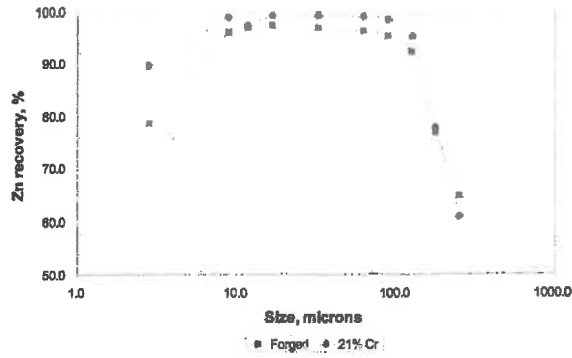


Figure 7: Zinc recovery-by-size to the zinc concentrate for periods 1 and 2.

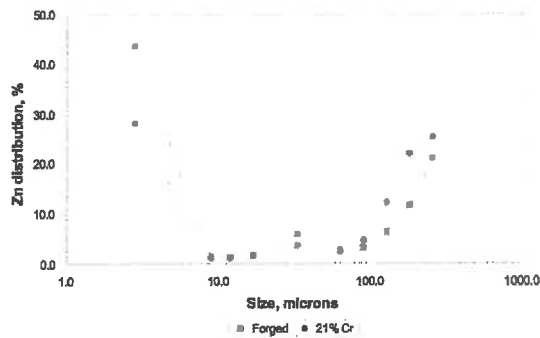


Figure 8: Zinc distribution-by-size in the zinc scavenger tailing for periods 1 and 2.

Broadly, the laboratory results indicated that a 21 percent chrome alloy would produce the optimum pulp chemical conditions for the best zinc metallurgy. The change from forged steel to 21 percent chrome grinding media produced:

- A shift in the ball mill discharge Eh of 160 mV, to more oxidising pulp potentials
- A subtle increase in the dissolved oxygen content of the pulp; and
- A reduction in the percentage of EDTA extractable iron by two thirds.

These pulp chemical changes suggest that a change in grinding media was effective in altering the grinding chemistry. Further, the laboratory study showed that the change to a more inert grinding media would have a positive impact on zinc flotation performance, with the potential to improve both zinc concentrate grades and recoveries.

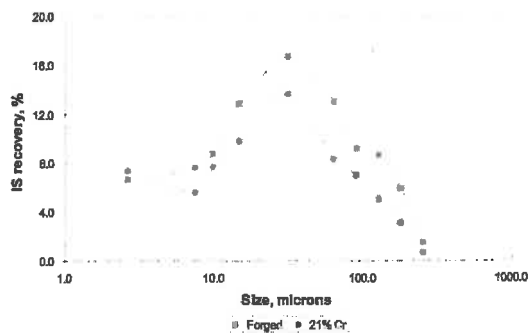


Figure 9: Iron sulphide recovery-by-size to zinc concentrate for periods 1 and 2.

In October 2007 the concentrator was converted from forged steel to 21 percent chrome grinding media. Prior to dumping all eight mills and loading them with a graded charge of 21 percent chrome balls, the pulp chemistry of the system was measured, and the shift data for nine months were collected. Following the conversion further pulp chemistry and metallurgical data were collected.

Analysis of the pulp chemical data shows that the conversion from forged steel to 21 percent chrome grinding media resulted in:

- A shift in the ball mill discharge Eh of 175 mV, to more oxidising pulp potentials
- An increase in the dissolved oxygen content of the pulp; and
- A reduction in the percentage of EDTA extractable iron by a half.

The change in media type resulted in statistically significant improvements in the zinc concentrate grade (0.6 ± 0.3 percent), and zinc recovery (1.8 ± 1.3 percent). The improvement in zinc concentrate grade can be attributed to better selectivity for sphalerite against iron sulphides (pyrrhotite).

The Perilya concentrator has continued to use high chrome grinding media to this day. The work demonstrates that using a robust laboratory schedule such as the Magotteaux Mill® can be used effectively to predict plant performance.

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