



# The significance of grinding environment on the flotation of UG2 ores

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## Synopsis

A large body of work exists discussing the impact of grinding media on mineral flotation. Generally, the work indicates that a change to a less electrochemically active grinding environment has positive benefits on downstream processing. There is a fear, however, that these benefits may not be realized when treating low sulphide containing ores, typified by UG2 style deposits.

A series of experiments was developed to test the flotation response of UG2 ores using the Magotteaux Mill® to determine if measurable differences in the pulp chemistry could be discerned using a range of grinding media types. Further, the flotation responses of the contained sulphides (chalcopyrite, pentlandite and pyrrhotite) were determined.

The data collected provided strong evidence that the grinding environment can significantly influence the pulp chemistry and flotation characteristics of all sulphide minerals, even when the ore contains less than 0.5 per cent total sulphide. The results show that the change to an inert media type produced a substantial improvement in the flotation rate of all sulphide minerals, as well as the PGMs.

## 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 (Johnson, 1987; Jackson, *et al.*, 1989; Young, *et al.*, 1997; Greet and Freeman, 2000), the importance of pulp chemistry is more nebulous, particularly the impact of grinding environment. Extensive work examining the electrochemical interactions between grinding media and sulphide minerals has been completed (for example, Iwasaki *et al.*, 1983; Natarajan and Iwasaki, 1984; Yelloji Rao and Natarajan, 1989(a); Yelloji Rao and Natarajan, 1989(b)). Broadly, these studies indicate that most sulphide minerals are more noble than the grinding media used during comminution, therefore a galvanic couple between the media and the sulphide mineral(s) exists, which increases the corrosion rate of the grinding

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 (Johnson, 2002).

Cullinan *et al.* (1999) completed laboratory experiments examining the effect of different ferrous based grinding media on galena flotation performance in the lead circuit of the Mount Isa Mines lead/zinc concentrator. On a size-by-size basis, their work indicated that grinding with high chrome grinding media increased the maximum galena recovery of the -3 micron fraction from 63 per cent (for forged steel grinding media) to 79 per cent (Figure 1). This improvement could not be attributed to entrainment, since slightly higher water recovery values were obtained when grinding with forged steel grinding media.

Improvements in selectivity for galena against sphalerite and iron sulphides were also observed when high chrome grinding media was employed.

Pulp chemical measurements recorded during these tests indicated that grinding with forged steel resulted in significantly more reducing conditions than those observed when high chrome grinding media was used (Table I). The other feature of the pulp chemistry was the elevated levels of oxidized iron species (as measured using an EDTA extraction technique (Rumball and Richmond, 1996; Cullinan *et al.*, 1999; Greet and Smart, 2002)) recorded for the forged steel case, which were 1.56 times greater than the values reported for the high chrome alloy. The elevated levels of EDTA extractable iron for the forged steel grinding media were the result of increased corrosion between this media type and the sulphide minerals in the ore. It was postulated that the

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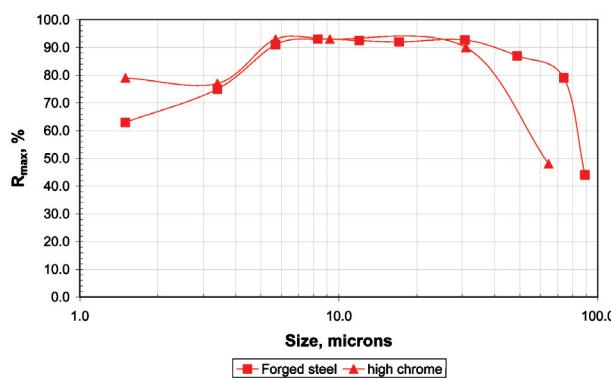


Figure 1—Maximum galena recovery versus particle size for Mount Isa lead/zinc ore ground with different grinding media types (Cullinan et al., 1999)

improvement in fine (~3 micron) galena flotation response when the ore was ground with high chrome grinding media was due to lower levels of oxidized iron species within that system.

Cullinan (1999) completed more fundamental work examining the effect of the grinding environment on galena flotation. In these tests, 100 grams of Rapid Bay galena was ground in different mills: mild steel mill using forged steel balls; a stainless steel mill using high chrome balls; and a ceramic mill using ceramic balls. The resultant recovery versus time curves are provided in Figure 2, and illustrate that the galena recovery increased markedly as the media type changed from forged to high chrome, to ceramic. The pulp chemistry measurements taken for these experiments are listed in Table II. Whereas the variations in pH and Eh were comparatively minor, the amount of EDTA extractable iron decreased dramatically as the grinding media type was changed to more inert materials. This corresponded to an increase in the galena flotation response, again suggesting that the corrosion products on the grinding media impact on flotation response.

Samples of galena were collected after grinding in the three different milling environments, and their surfaces examined using X-ray photoelectron spectroscopy (XPS). The atomic concentrations of oxygen, lead, iron and sulphur for galena particles ground using the three different grinding media are listed in Table III. There is a marked difference in the surface concentration of iron. That is, it decreased from 16.6 per cent for the forged steel case to below the detection limit for ceramic grinding media. The XPS spectral data

(Cullinan, 1999) suggested that the iron present on the surface occurred as oxy-hydroxide species (i.e.  $\text{Fe(OH)}_3$ ,  $\text{FeOOH}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Fe}_3\text{O}_4$ ). When the sample was ion etched, to determine the thickness of these oxidized iron surface layers, there was no appreciable alteration in the  $\text{Fe}2\text{p}$  spectra or the atomic concentration, which suggested that these layers were relatively thick. The surface concentration of these species decreased as the grinding media became less reactive, and resulted in increasing exposure of the lead

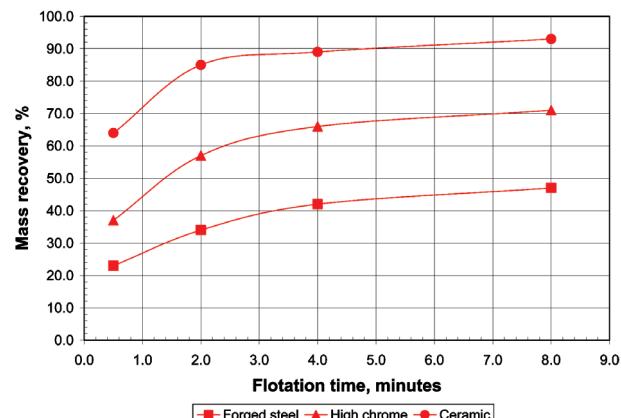


Figure 2—Mass recovery versus flotation time curves for rougher flotation tests completed on 100 grams of Rapid Bay galena ground to a  $P_{50}$  of 9 microns using forged steel, high chrome, and ceramic media. The tests were completed in demineralized water (pH 7), and employed 1 000 grams per tonne of sodium ethyl xanthate collector

Table II

## Pulp chemical measurements for Rapid Bay galena ground with different grinding media types (Cullinan, 1999)

Media type	pH	Eh, mV (SHE)	Per cent EDTA extractable Fe
Forged steel	5.5	300	1.24
High chrome	5.5	300	0.16
Ceramic	5.0	370	0.02

Table III

## Composition, determined via XPS, of the unetched surfaces of Rapid Bay galena ground with forged steel, high chrome and ceramic grinding media (Cullinan, 1999).

Media type	Atomic composition, %			
	O	Pb	Fe	S
Forged steel	53.1	15.6	16.6	14.7
High chrome	50.0	20.6	10.2	19.2
Ceramic	33.6	32.0	<0.1	34.4

(Note: The data was normalized to remove the percentage of surface carbon.)

Table I

## Pulp chemical measurements for Mount Isa lead/zinc ore ground with different grinding media types (Cullinan et al., 1999)

Media type	pH	Eh, mV (SHE)	Per cent EDTA extractable ...		
			Pb	Zn	Fe
Forged steel	7.8	72	1.7	0.053	1.11
High chrome	8.2	275	3.1	0.071	0.71

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sulphide surface. These findings were consistent with the EDTA extraction data provided in Table II.

These results suggest that the iron debris from forged steel grinding media can have a significant deleterious effect on the flotation performance of fine (-3 micron) galena. Other work (Matthews, 2002) confirms this, and clearly shows that ferric hydroxide has a depressing effect on galena flotation. By changing the media type to an inert material (i.e. ceramic grinding media) the galena flotation response can be markedly improved. It is postulated that similar effects would be noted for other sulphide minerals.

Cullinan's work (1999) and the efforts of Peng (2003) provide strong evidence that the iron contamination on the surfaces of minerals ground with forged steel emanate from the grinding media. Further, the corrosion products from the galvanic couple between the forged steel grinding media and the sulphide minerals within the ore drive the pulp chemistry of the system. Therefore, changing the grinding media to a less reactive material should have positive implications for pulp chemistry and flotation behaviour. That is, conditioning the particle surfaces during grinding, by using the most appropriate grinding media may have significant positive ramifications on downstream processing.

## 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 (Greet, *et al.*, 2004).

The Magotteaux Mill® (Figure 3) allows the researcher to generate a product in the laboratory that has nominally the same physical properties (particle size distribution) and pulp chemical properties (Eh, pH, dissolved oxygen, 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 gas, so that it matches the grinding mill discharge.

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 programme, 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 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
- The collection of conditioned flotation feed for laboratory testing
- 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 that 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 dissolved oxygen, Eh 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. These data are compared with the results of tests conducted on the conditioned flotation feed. If they are the same, a match is achieved.

### 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.

When the flotation results of tests completed on the bulk sample prepared in the Magotteaux Mill® using the current grinding media are correlated with the metallurgical survey of the plant, it is possible to determine the scale-up between the laboratory and the plant. Knowing this relationship (scale-up), and the laboratory flotation response of the bulk sample when ground with high chrome grinding media, a prediction of the plant performance can be made if the alternative grinding media were to be used. Thus, this approach provides a robust laboratory methodology that firstly provides a link between the laboratory and the plant using the existing grinding media and secondly investigates changes to the pulp chemistry and metallurgical outcome when high chrome

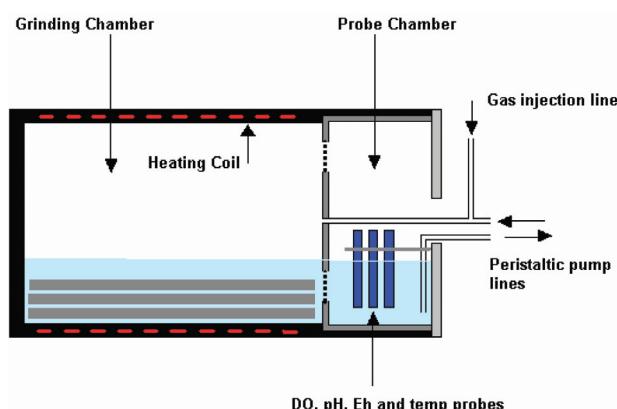


Figure 3—Schematic representation of the Magotteaux Mill®

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grinding media is substituted into the grinding circuit. Further, it provides a means of estimating plant performance should the best high chrome grinding media be installed in the plant.

If used correctly, this strategy will provide an excellent screening procedure that will yield valuable information about the 'best' grinding media for the operation. This should focus pilot-plant and plant trials on only the most promising of grinding media types.

## Results

### Head grade and mineralogy

Once the ore had been crushed to 100 per cent passing 1.7 mm and thoroughly mixed representative samples of the ore were split out and submitted for assay. From the elemental assays the total sulphide and non-sulphide gangue component was determined. Table IV lists the head assay.

A representative sample of the -600/+106 micron size fraction was prepared for mineralogical analysis by QEMSCAN at Intellection. The QEMSCAN analysis provided quantitative information about the mineral species present. Table V lists the modal analysis and the liberation characteristics of the sample. It is immediately apparent that this ore has very low levels of sulphide (0.06 per cent total sulphide). The dominate species present is chromite, with very little quartz. The sulphides are less than 30 per cent liberated, and have strong associations with one another. The sulphides appear to be locked with other non-sulphide gangue, and do not have a strong connection with the chromite. The chromite is mostly liberated (greater than 85 per cent), and is mostly associated with the other non-sulphide gangue.

### Pulp chemistry

The Magotteaux Mill® was calibrated so that the particle size

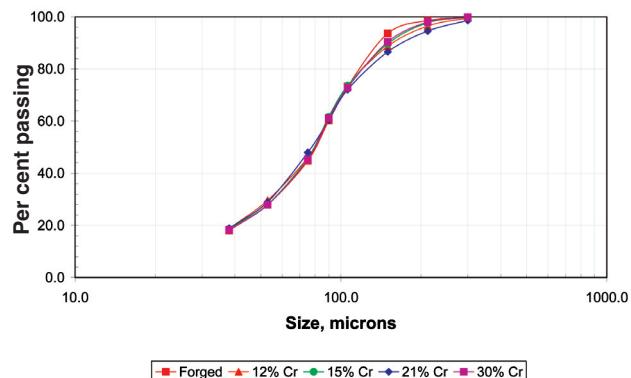


Figure 4—Particle size distribution data a UG2 ore ground with forged steel, 12, 15, 21 and 30 per cent chrome grinding media

Table VI

### Magotteaux Mill® discharge pulp chemistry for tests completed a UG2 ore prepared using forged, 12, 15, 21, and 30 per cent chrome grinding media

Media	Pulp chemistry			
	pH	Eh, mV (SHE)	DO, ppm	EDTA Fe, %
Forged steel	9.16	-211	0.16	0.290
12% Cr	9.36	11	0.20	0.034
15% Cr	9.06	16	0.07	0.021
21% Cr	9.47	86	0.04	0.020
30% Cr	9.42	52	0.02	0.014

distribution (Figure 4) was approximately the same for each of the grinding media (forged steel, 12, 15, 21, and 30 per cent chrome). An examination of Figure 4 suggests that the particle size distributions were nominally the same, therefore any changes observed in the flotation tests are not due to variations in the feed size.

With careful manipulation of the grinding parameters in the Magotteaux Mill® with the 12 per cent chrome alloy the pulp chemical parameters targeted (natural pH; Eh 60 mV (SHE); and 0.5 ppm of dissolved oxygen) were obtained. Once this recipe was known it was applied to the other grinding media to be tested. The resultant pulp chemical readings recorded for the Magotteaux Mill® discharge for each media type are provided in Table VI.

These data indicate that changing the grinding media

Table IV

### The head assay of the UG2 ore

Assay						
PGM4E, g/t	Cu, %	Ni, %	Fe, %	S, %	Sulphide, %	NSG, %
4.15	0.025	0.108	14.15	0.118	0.357	99.64

Table V

### The modal and liberation data for the UG2 ore

Mineral	Modal, %	Liberation data						
		Liberated	Locked with ...					
			Pe	Ch	Po	Cr	Q	NSG
Pentlandite (Pe)	0.03	23	-	8	20	8	0	41
Chalcopyrite (Ch)	0.01	29	11	-	10	4	0	46
Pyrhotite (Po)	0.02	18	23	8	-	3	0	48
Chromite (Cr)	67.95	85	0	0	0	-	0	15
Quartz (Q)	0.04	28	0	0	0	0	-	72
Other non-sulphide gangue	31.95							

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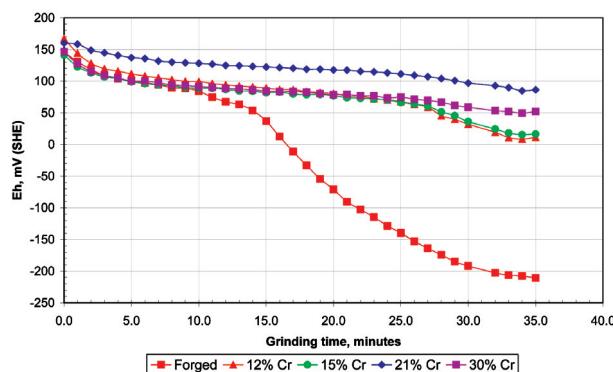


Figure 5—The Eh profile during grinding for each grinding media type for tests completed on a UG2 ore

from forged steel to high chrome produced an increase in the Eh to more oxidizing pulp potentials of greater than 200 mV. However, changing from 12 per cent chrome grinding media to 30 per cent resulted in a smaller shift Eh, to slightly more oxidizing values. The Eh profiles recorded during grinding are displayed in Figure 5. Both the pH and the dissolved oxygen values were increased with a change from forged steel to high chrome grinding media. There were only marginal differences in pH and dissolved oxygen values between the high chrome alloys.

The EDTA extractable iron data for the tests completed with forged, 12, 15, 21, and 30 per cent chrome grinding media are listed in Table VI. These data suggest that there was a marked decrease in EDTA extractable iron as the chrome content of the grinding media increased. This indicated that the corrosion of the grinding media decreased with chrome content, and essentially means that for the high chrome alloys there is less iron hydroxide species derived from the grinding media. This suggests that the system is cleaner, which should result in an improvement in the flotation response.

### Flotation response

The flotation tests were completed in triplicate, and Figure 6 contains the average PGM+Au grade/recovery curves for laboratory rougher flotation tests completed using forged, 12, 15, 21, and 30 per cent chrome grinding media. The PGM+Au recovery and diluent grades, at 200 ppm PGM+Au concentrate grade are listed in Table VII. Conversely, the PGM+Au concentrate grade and diluent recoveries, at 75 per cent PGM+Au recovery are provided in Table VIII. The flotation kinetic data are available in Table IX.

It is apparent from Figure 6 that with the exception of the 12 per cent chrome alloy the high chrome grinding media produced superior PGM+Au grade/recovery curves to that generated when the ore was ground with forged steel. However, it must be pointed out that all the high chrome alloys produced superior PGM+Au kinetics when compared with forged steel. At 200 ppm PGM+Au concentrate grade, the PGM+Au recovery for the forged steel case was nominally 7.4 per cent lower than that achieved with the 15 per cent chrome grinding media (Figure 6 and Table VII). Conversely,

Table VII

**PGM+Au recovery and diluent grades, at 200 ppm PGM+Au concentrate grade for laboratory rougher flotation tests completed on a UG2 ore ground with forged, 12, 15, 21, and 30 per cent chrome grinding media**

Test	PGM+Au recovery, %	Diluent grades, %		
		Cu	Ni	NSG
Forged	63.99	0.35	0.95	96.03
12% Cr	61.97	0.49	1.09	94.30
15% Cr	71.40	0.44	0.98	95.39
21% Cr	67.96	0.56	0.93	95.02
30% Cr	66.59	0.46	0.99	95.21

Table VIII

**PGM+Au grade and diluent recoveries, at 75 per cent PGM+Au recovery for laboratory rougher flotation tests completed on a UG2 ground with forged, 12, 15, 21, and 30 per cent chrome grinding media**

Test	PGM+Au grade, ppm	Diluent recovery, %		
		Cu	Ni	NSG
Forged	131.1	29.48	15.03	2.35
12% Cr	110.2	29.41	16.05	2.75
15% Cr	168.3	27.22	13.77	1.87
21% Cr	130.1	32.47	15.46	2.28
30% Cr	133.0	27.90	14.71	2.45

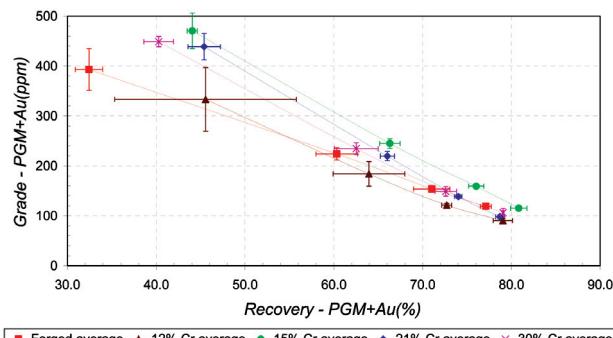


Figure 6—PGM+Au grade/recovery curves for laboratory rougher flotation tests completed on UG2 ore ground with forged, 12, 15, 21, and 30 per cent chrome grinding media

at 75 per cent PGM+Au recovery, the PGM+Au concentrate grade for the forged steel grinding media was nominally 30 ppm lower than that achieved by the 15 per cent chrome alloys (Figure 6 and Table VIII). The improvement in PGM+Au concentrate grade observed with 15 per cent chrome grinding media can be attributed to improved selectivity for PGM+Au against non-sulphide gangue (Table VIII).

However, when the kinetics for copper and nickel data

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**Table IX**

**Kinetic data for laboratory rougher flotation tests completed on a UG2 ore ground with forged, 12, 15, 21, and 30 per cent chrome grinding media**

Media	Kinetic data							
	PGM+Au		Cu		Ni		NSG	
	$k, \text{min}^{-1}$	$R_{\text{max}}, \%$						
Forged	1.01	73.45	0.46	30.61	0.65	15.10	0.23	2.77
12% Cr	1.83	72.96	1.93	28.35	1.61	15.50	0.21	3.72
15% Cr	1.59	75.98	1.70	28.04	1.30	14.40	0.20	3.18
21% Cr	1.79	73.98	2.28	31.98	1.64	15.33	0.19	3.47
30% Cr	1.40	73.59	1.58	27.15	1.11	14.62	0.18	3.57

are examined it is apparent that a shift from forged steel to high chrome grinding media resulted in substantial increases in the recovery of both metals (Table IX). Of the high chrome alloys tested it was the 15 per cent chrome grinding media that produced the best copper and nickel metallurgy.

These data suggest that the 15 or 21 per cent chrome alloy produces the best metallurgy for these ore. However, further laboratory testing is required to confirm this.

## Link between pulp chemistry and flotation response

The improvement in metallurgical performance can be linked to changes in the pulp chemistry of the system, as the grinding media was changed from forged steel to high chrome. That is, in changing from forged steel to high chrome grinding media the following general trends were observed, namely:

- The Eh shifted to more oxidizing pulp potentials
- The dissolved oxygen content of the pulp increased (subtly)
- The levels of EDTA extractable iron decreased.

These trends are shown in Figure 7.

It is no coincidence that both the Eh and dissolved oxygen are related to the levels of EDTA extractable iron present in the pulp, and that variations in these parameters have an impact on flotation response. The EDTA extractable

iron data provides a reasonable indication of the magnitude of grinding media corrosion. In the case of forged steel the corrosion rates are high, which manifest themselves as high EDTA extractable iron readings. High corrosion results in lower dissolved oxygen content in the pulp, and low Eh values (Figure 7). By changing from forged steel to high chrome grinding media, the corrosion mechanisms at play change dramatically, such that the media corrosion resistance increase at the chrome content increases. Therefore, as the corrosion component of media wear decreases the levels of EDTA extractable iron decrease. This in turn causes the dissolved oxygen to increase and the Eh of the pulp to shift to more oxidizing values. Thus, by changing to a more inert grinding media the system becomes cleaner (i.e. a reduction in the levels of iron oxy-hydroxy species), which should result in an improvement in metallurgical response.

These changes in pulp chemistry appeared to have a positive impact on the metallurgical response. That is, the best PGM+Au, copper and nickel recoveries coincided with the lower EDTA extractable iron values (Figure 8), which corresponded to the higher dissolved oxygen content and more oxidizing pulp potentials (Figure 7).

The implication is that the type of grinding media employed does influence the pulp chemistry, and does affect metallurgical performance (in this case flotation rate

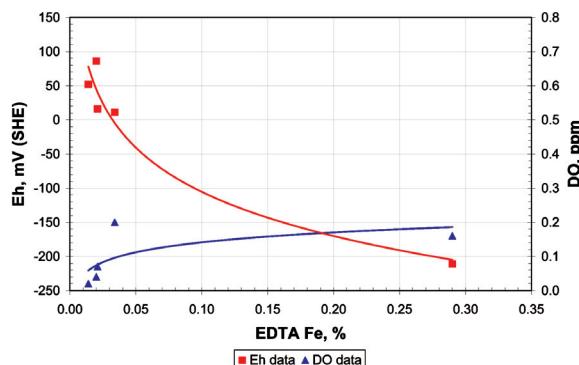


Figure 7—The EDTA extractable iron versus Eh and dissolved oxygen content relationship for a UG2 ore ground with forged, 12, 15, 21, and 30 per cent chrome grinding media

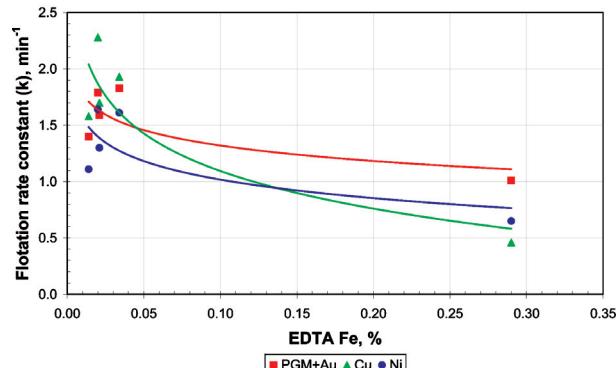


Figure 8—The EDTA extractable iron versus flotation rate constant for PGM+Au, copper and nickel for a UG2 ore ground with forged, 12, 15, 21, and 30 per cent chrome grinding media

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constant). Therefore, by changing to a more inert grinding media it may be possible to place the pulp chemistry of the system in a more favourable regime, and improve the metallurgical response of the flotation circuit.

These data suggest that it may be possible to alter the chemistry of a UG2 ore system, and improve the metallurgy. Further investigations are in hand examining these effects at pilot-plant and plant scale. The observations made to date are positive and align themselves well with the laboratory studies. That is, while this study was completed in Adelaide tap water, the pilot-plant and plant data collected to date suggest that a change in grinding environment at this scale does produce similar variations in the pulp chemistry.

One final point to note is that the mineralogy of the system will dominate the pulp chemistry, and must be taken into account when making the grinding media alloy selection. Alloy selection is not a one-size-fits-all proposition. In some instances employing the most inert grinding media can result in a grinding environment that is overly oxidizing, and this may result in oxidation and depression of the sulphide minerals to be recovered. The work presented above is a clear example of this. Shifting from a 12 to a 15 per cent chrome alloy saw a significant improvement in the metallurgical response of the platinum bearing minerals (sulphides); however, grinding with alloys with greater than 15 per cent chrome resulted in a deterioration in the grade/recovery curve. When the pulp chemistry for is examined the higher alloys do tend to have higher Eh values than the 12 and 15 per cent chrome grinding media. A comment worthy of note is that this phenomenon has been observed in other sulphide mineral systems.

## Conclusions

In all instances, changing from forged steel to high chrome grinding media had an impact on the pulp chemistry by:

- Shifting the Eh to more oxidizing potentials
- Increasing the level of oxygen in the pulp
- Reducing the amount of EDTA extractable iron in the pulp.

The change to high chrome grinding media had a positive impact on PGM+Au, copper and nickel metallurgical performance. In particular, the flotation rates of the PGM+Au, copper and nickel were markedly increased. The 15 per cent chrome alloy was judged to be the best alloy for this mineral system in the laboratory. It is recommended that further work be conducted to confirm this observation using conditions that are closer to the site (for example process water).

Employing a more inert media type will probably have a deleterious effect on flotation as the chemistry of the system may become too oxidizing and depress the platinum-bearing sulphide minerals.

## Further work

Work is currently underway examining the impact of grinding environment on UG2 ores at both pilot-plant and plant scale.

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