Development of a viable process for the recovery of zinc from oxide ores

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Synopsis

The Skorpion Zinc Project demonstrated the viability of the production of zinc from non-sulphide (commonly called 'zinc-oxide') ores, using the leach/solvent extraction/electrowinning process route. The success of Skorpion raised the profile of a number of other zinc oxide deposits, considered to be similar. However, a study of three such deposits demonstrates that the application of whole-ore-leaching may be limited and that the concentration of zinc, or at least the separation from acid-consuming gangue minerals, prior to leaching is essential to the successful recovery of zinc from these deposits. The recovery of zinc is dependent on an understanding of the geology of the deposit, the mineralogical association of zinc minerals with gangue minerals (Boni, 2005) and limitations of mining practice.

Flowsheet development and the associated metallurgical test work to derive an economically viable treatment route from two of these deposits are discussed. Key parameters affecting zinc recovery by gravity separation and flotation are presented, demonstrating that even minor differences in mineralogy have a profound impact on zinc recovery and reagent consumption. The study also deals with the determination of appropriate design parameters through metallurgical mapping of the dense media separation process.

Introduction

The whole-ore-leaching concept applied at Skorpion Zinc in Namibia relies on the economical leaching of zinc minerals with sulphuric acid solutions under atmospheric conditions. Economic viability is premised on the selective mining of the zinc oxide ore from a limestone pit shell.

Subsequent to the successful commissioning of Skorpion Zinc in 2003, a number of deposits, historically considered to be similar to Skorpion, have been investigated in greater detail and exploration activities stepped up. Green Team International (Pty) Ltd (GTI) has been involved in the development of two such projects for Metalline Mining and Zincore Metals Inc., respectively. In both cases, it was found that whole-ore-leaching is unlikely to be economically viable due to the presence of sulphuric acid consuming gangue minerals, which in contrast to Skorpion, are present throughout the deposits.

Metalline's Sierra Mojada (SM) Project is located in the state of Coahuila, Mexico and was discovered in 1879 as a silver deposit. Later, silver-copper deposits in the area gained importance, and finally lead was also discovered as a lead-carbonate (cerussite) manto. Oxide zinc was discovered in the 1920s. Without exception, exploitation of these deposits has always been through selective mining with shipping of high grade zinc ore directly to customers, such as smelters and fertilizer producers.

The Accha-Yanque property covers over 30 000 hectares and consists of 41 concessions over a 30 kilometre distance in Southern Peru. Accha is 70 km from the Andean town of Cuzco at the north end of the property with Yanque at the south. A number of zinc prospects, with limited exploration, occur between these two deposits. Zincore Metals are currently prioritizing the development of Accha and Yanque, for which a greater body of knowledge exists.

Metallurgical design and test work carried out to date was aimed at developing viable flowsheets for the treatment of run of mine (ROM) ore from these deposits, using proven technology. Test work comprised both mineralogy and bench-scale metallurgical test work. Although considerable work has been done on the SM and Accha deposits, test work on Yanque commenced recently and is not dealt with here.

Mineralogy

Both qualitative and quantitative mineralogical work was carried out on mineralized samples from the SM and Accha deposits. The main mineralogical associations are shown in Table I, based on semi-quantitative X-ray diffraction (XRD) work.

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Table I

Comparison of the mineralogy of SM and Accha ores from semi-quantitative XRD work

Mineral	Chemical formula	SG	Occurrence (%)	
			SM	Accha
Dolomite	$CaMg(CO_3)_2$	2.84	20–100	<5
Calcite	$CaCO_3$	2.71	5–20	10–100
Goethite	$FeO(OH)$	3.80	5–20	5–40
Smectite	$(Na)_{0.6}Ca_{0.3}K_{0.1}Al_6Si_6O_{20}(OH)_4.2(H_2O)$	2.35	-	-
Kaolinite	$Al_2Si_2O_5(OH)_4$	2.60	-	0–5
K-feldspar	$KAlSi_3O_8$	2.44	-	0–7
Illite	$K_{0.6}(H_3O)_{0.4}Al_{1.3}Mg_{0.3}Fe^{2+}_{0.1}Si_{3.5}O_{10}(OH_2)\cdot H_2O$	2.75	-	0–20
Quartz	SiO_2	2.62	<5	0–50
Cerussite	$PbCO_3$	6.58	<5	0–35
Hemimorphite	$Zn_4(Si_2O_7)(OH)_2$	3.45	5–20	0–80
Minrecordite	$CaZn(CO_3)_2$	3.45	<5–20	-
Hematite	Fe_2O_3	5.30	<5	-
Willemite	$Zn_2(SiO_4)$	4.05	<5	-
Smithsonite	$ZnCO_3$	4.45	<5	0–90
Sauconite	$(Na.K.Ca/_2)_{0.35}(Zn,Mg,Fe,Al)_3(Si,Al)_4O_{10}(OH)_2.4(H_2O)$	2.45	-	0–50

SM contains appreciable quantities of both calcite and dolomite, while dolomite is virtually absent from Accha. The abundance of acid-consuming gangue minerals in the mineralized samples indicates that atmospheric leaching of ROM ore will not be economically viable for any of these deposits and it will not be possible to selectively mine zinc oxide ore with low acid consumption.

Other similarities between the deposits include the presence of goethite as the dominant iron-rich gangue mineral. Zinc occurs mainly as hemimorphite and smithsonite although some sauconite (Zn smectite) and minrecordite have also been observed. However, a striking difference between the deposits is the abundance of clay minerals in Accha, while the FeOx manto (main economic target) at SM is virtually devoid of clay minerals. Sauconite does, however, occur in the Smithsonite manto, which is not at an advanced stage of investigation. In the case of Accha, mineralogical characterization suggests that some zinc mineralization occurs as zinc clay (e.g. zinc smectite = sauconite). Accha contains significant levels of cerussite, introducing lead as a potential by-product. Although not a primary objective of the test work, some work has therefore been conducted on the recovery of lead. SM does feature some lead occurrences, but the relative amounts of galena and cerussite are unknown and lead is not a priority at this stage.

Initially, metallurgical test work focused on the separation of the acid-consuming gangue minerals from the ROM to produce leach feed material, which could be processed economically in an on-site refinery. Later, the concentration of zinc from other gangue minerals was also evaluated, which offers the potential to produce a concentrate, which may be transported economically to a remote refinery. Flexibility in refinery location introduces potential advantages for fiscal regime, infrastructure and power costs.

Gravity separation

The difference in specific gravity (SG) among the various zinc and acid-consuming gangue minerals makes gravity separation an attractive option due to the relatively low capital and operating costs of most gravity separation techniques.

Dense media separation (DMS) was evaluated at bench scale through heavy liquid separation (HLS) test work. Samples comprised whole-dril-core sections, from dedicated metallurgical test work drilling. The core sections were shipped to Mintek in South Africa where composites were prepared in collaboration with project geologists and mineralogists.

Samples were prepared for HLS test work through screening at 6 mm, followed by cone crushing of the oversize material. The screening and crushing steps were repeated to achieve 100% passing 6 mm. The sample was finally screened at 1.18 mm with the oversize material being used for HLS test work and the undersize retained for evaluation of other gravity separation and concentration techniques.

HLS tests were done, using a mixture of Tetra Bromo Ethane (TBE) and acetone to produce densities less than 2.96 g/cm^3, and TBE mixed with ferrosilicon to produce densities greater than 2.96 g/cm^3.

The recovery vs. density relationships for key elements obtained from HLS tests with the SM metallurgical composite sample are shown in Figure 1. The figure also shows the SG values of the various mineral species identified through XRD work. It is possible to achieve 88% zinc recovery and approximately 95% Ca elimination when feeding 7.6% Zn and cutting at a density of 3.0 g/cm^3.

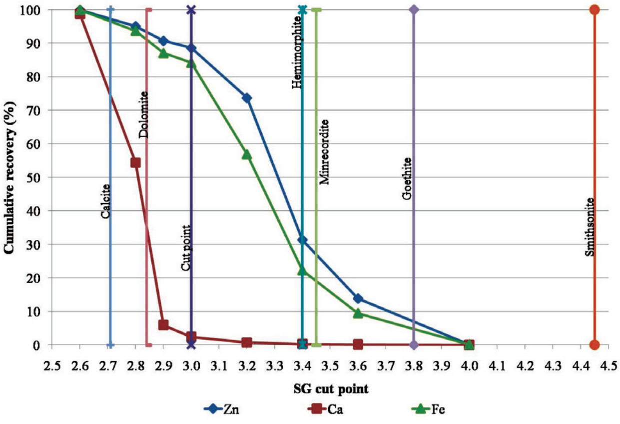

Figure 1—HLS test results for SM metallurgical composite sample

The corresponding curve for the Accha metallurgical composite is shown in Figure 2. The most efficient density cut point for the separation of zinc from calcium is 2.7 g/cm^3. Furthermore, the zinc curve shows an inflection point at a density of 2.4 g/cm^3. The inflection point at a lower density strongly suggests the presence of lower density zinc minerals, such as sauconite, a zinc clay mineral. The inflection point is present in the aluminium graph as well, which is a component of sauconite.

The HLS test results indicate relatively high efficiency of calcium elimination (reduction of acid consuming gangue) for both SM and Accha. The results suggest that a single DMS step should be included for both SM and Accha prior to leaching.

A major limitation in the application of DMS is the treatment of fine material as hydrodynamic effects have an impact on gravimetric separation at finer particle sizes (England, *et al.*, 2002). It is therefore uncommon to find DMS plants operating with feed material less than 1 mm. Comminution test work and simulation work on SM confirm that as much as 30% of the ROM reports to the -1 mm fraction during crushing to a top size of 6 mm. For Accha, the quantity of -1 mm material produced during crushing to a top size of 6 mm was found to be 42%.

Due to the particle size limitation of DMS, a range of alternative gravity separation techniques was evaluated to deal with the -1 mm fraction. These included, shaking table, spiral and Knelson concentrator test work, none of which achieved significant calcium elimination. The inability to treat -1 mm material would have a major impact on project viability. Furthermore, the abundance of high density iron oxide gangue minerals, such as goethite and hematite, also limits the zinc concentrate grade achievable by gravity separation to 19.1% zinc in the case of SM and 14.8% zinc in the case of Accha. The ability to produce a concentrate, which may be transported to a remote refinery, reduces the significance of resource size, infrastructure and proximity to cheap utilities on overall project economics. It was clear that alternatives needed to be investigated to firstly treat the -1 mm material but also to increase the oxide concentrate grade.

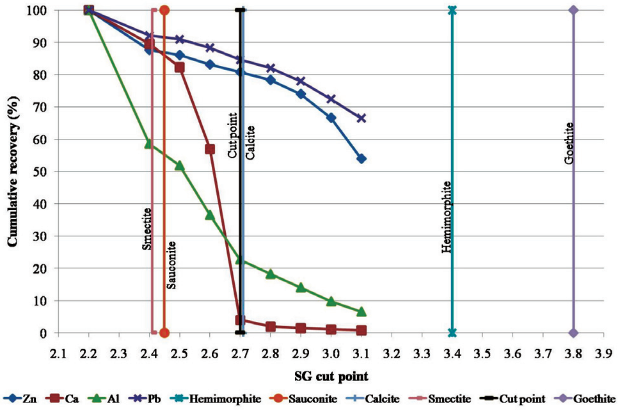

Figure 2—HLS test results for Accha metallurgical composite sample

Flotation

In order to achieve zinc concentration at relatively fine particle sizes and selectively recover zinc minerals from iron minerals, flotation with primary amines was evaluated. This technology is well known and has been commercially applied at a number of industrial-scale plants (Caproni, *et al.*, 1979). Although some of the commercial plants are no longer operational, a sufficient body of knowledge exists on the mechanism of flotation. Firstly, the flotation feed material is deslimed as amines collect on the large specific surface area of fine particles, thereby increasing overall reagent consumption and also limiting amine adsorption onto zinc oxide particles. Desliming is done in a cyclone with a cut point of around 20 μm. Secondly, sodium hexa μeta phosphate (Calgon) may be added to reduce the impact of the remaining slimes. Other oxides, normally floated by primary amines, are then depressed by adding sodium silicate, which is known to be a particularly effective depressant for the flotation of zinc and lead from clay (sodium and silicon), iron oxides and calcite (Marabini, *et al.*, 1994). Sodium sulphide is then added as an activator, directly followed by the addition of the primary amine collector. The action of the sodium sulphide is twofold. Firstly, it acts as a pH modifier, with flotation recovery increasing with increase in pH, and secondly as an activator, enhancing the adsorption of free amine on the surface of the zinc oxide particles (Rey, *et al.*, 1954).

Milling to a top size of 212 μm to prepare plant feed suitable for flotation generates in the range of 30 to 40% slimes (-20 μm) material. Although the fundamental principles of flotation of slimes and coarse material are similar, the procedures are different and will therefore be dealt with separately.

Coarse flotation

The available literature and previous experience of Mintek were used to compile the basic flotation procedure, which comprised adding a depressant (Calgon) with conditioning for one minute, followed by sodium silicate for another minute. The pH is then increased to 11.5 using sodium sulphide after which the collector is added with a total conditioning time of two minutes, followed by flotation for eight minutes. The collector used was a blend of primary amine (Armac C), pine oil and kerosene at a ratio of 15/1.5/1. The reagent addition to achieve acceptable zinc recovery (greater than 80%) and selectivity (at least 90% Ca rejection) is dependent on the mineralogy of the various deposits. In general, it was found that an increase in clay content resulted in higher overall reagent consumption. A summary of the typical rougher reagent dosages used on the different ore types is presented in Table II.

Table II

Typical rougher reagent dosage

	SM g/t	Accha g/t
Calgon	150	500
Sodium silicate	500	800
Sodium sulphide	3000	4500
Collector	300	1000

Table III shows the recovery of zinc from the SM metallurgical composite through primary amine flotation, utilizing the procedure described above.

Subsequent to the successful primary amine flotation of zinc from the SM metallurgical composite, it was considered likely that the same procedure will be successful to recover zinc from Accha. However, two key differences were anticipated to have at least some impact on the viability of primary amine flotation, namely the presence of clay minerals and cerussite.

At the commencement of test work on Accha only preliminary sample material was available as the drilling programme had only just commenced. Early test work was therefore done on a preliminary composite sample and later verified with the Accha metallurgical composite. Initial tests with the preliminary sample were carried out with the same reagent additions as used for SM, and generally poor recoveries were achieved. Figure 3 shows that acceptable Zn recovery could be achieved only when milling to a top size of 106 μm. The dramatic impact of milling to a coarser top size on zinc recovery indicated that liberation alone was unlikely to be responsible for the poor zinc recovery at the coarser grind. Instead, it was suspected that milling to a finer top size liberated more clay material, which reports to the slimes fraction, which is removed prior to flotation. This is also supported by Figure 4, which shows the relationship between zinc recovery and aluminium content in the flotation feed.

Upon receipt of the representative Accha metallurgical composite sample it was decided to further explore the impact of clay minerals on zinc recovery by primary amine flotation. Furthermore, it was decided to evaluate both bulk lead/zinc flotation as well as sequential lead/zinc flotation to produce separate concentrates for downstream refining.

The possibility of recovering lead as a by-product by floating the lead with Potassium Amyl Xanthate (PAX) prior to zinc flotation was pursued. A summary of the results is presented in Table IV.

It was found that lead recoveries around 70% were achievable but only at relatively high collector dosages (300 g/t PAX). However, zinc recovery in the second stage was low (33%) even at an amine addition of 1 000 g/t. With the acceptable lead recovery in the first stage it was considered likely that the poor zinc recovery in the second stage was due to the presence of slimes. A test was therefore carried out, under similar conditions but with a desliming step between the lead and zinc flotation stages. This test yielded acceptable zinc and lead recoveries, as shown in Table IV. The sequential flotation option is considered to be technically feasible but more work is required to optimize reagent addition.

Table III

Primary amine flotation of zinc from the SM metallurgical composite sample

Zn feed grade	8.2%
Cumulative Zn recovery	84.0%
Zn conc. grade	38.8%
Ca feed grade	21.2%
Cumulative Ca recovery	2.3%
Ca conc. grade	2.8%
Fe feed grade	6.4%
Cumulative Fe recovery	24.1%
Fe conc. grade	8.7%

The impact of clay minerals, observed during sequential lead/zinc flotation resulted in the selection of a relatively high amine dosage for the bulk lead/zinc flotation tests. The bulk flotation procedure used may be summarized as follows:

Table IV

Summary of sequential lead/zinc flotation

		300 g/t PAX, 1 000 g/t collector (amine/pine oil/kerosene)	
		No desliming	Desliming between stages
	Zn feed grade (%)	7.9	8.7
	Ca feed grade (%)	24.2	22.2
	Pb feed grade (%)	3.6	2.8
Pb stages	Cumulative Zn recovery (%)	0.6	1.5
	Zn conc. grade (%)	1.2	2.6
	Cumulative Ca recovery (%)	0.03	0.9
	Ca conc. grade (%)	0.2	3.8
	Cumulative Pb recovery (%)	70.3	68.2
	Pb conc. grade (%)	69.1	37.7
Zn stages	Cumulative Zn recovery (%)	32.6	84.7
	Zn conc. grade (%)	28.5	21.1
	Cumulative Ca recovery (%)	1.0	11.3
	Ca conc. grade (%)	2.7	7.2
	Cumulative Pb recovery (%)	5.1	12.5
	Pb conc. grade (%)	2.1	1.0

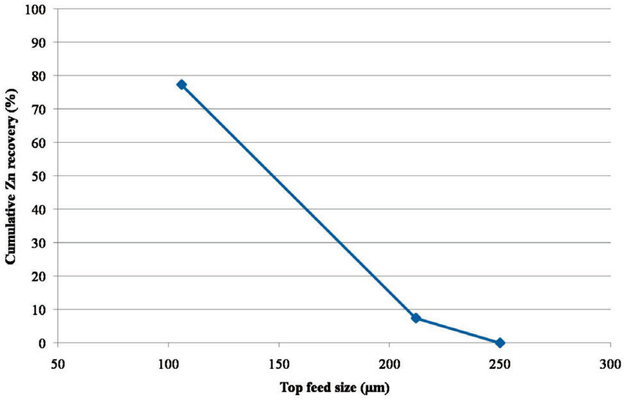

Figure 3—Impact of grind size on flotation recovery from early Accha composite sample

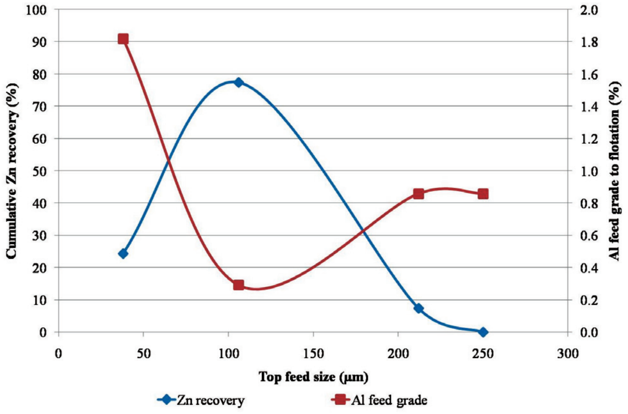

Figure 4—Zinc recovery by primary amine flotation vs. aluminium content in flotation feed

- ➤ 500 g/t calgon for 1 minute
- ➤ 800 g/t sodium sulphide for 1 minute
- ➤ 4 500 g/t sodium sulphide for 45 seconds
- ➤ 1 000 g/t collector for 2 minutes
- ➤ Float for 8 minutes
- ➤ 2 000 g/t sodium sulphide for 30 seconds
- ➤ 300 g/t collector for 2 minutes
- ➤ Float for 8 minutes.

The results are presented in Table V and indicate relatively high zinc and lead recoveries.

A simulated atmospheric sulphuric acid leach test was carried out on the concentrate produced through the above procedure, which yielded a leach residue containing 23.3% lead. A lead flotation test was done on the leach residue under the following conditions:

- ➤ 800 g/t sodium silicate for 2 minutes
- ➤ Increasing the pH to 10 by adding sodium sulphide (40 kg/t)
- ➤ 300 g/t PAX for 2 minutes
- ➤ Float for 6 minutes
- ➤ Increase pH to 10 by adding sodium sulphide (3 kg/t)
- ➤ 300 g/t PAX for 2 minutes
- ➤ Float for 6 minutes.

It must be noted that the high sodium sulphide dosage may be reduced by increasing the pH with alternative reagents like soda ash due to the low initial pH of 6 (as a result of being an acid leach product). The results obtained are shown in Table VI.

Slimes flotation

Zinc oxide flotation from slimes is not well known. However, zinc oxide flotation without desliming is successfully applied at industrial scale (Pereira, *et al.*, 2005). Furthermore, flotation of platinum group metals (PGM) in South Africa is carried out at relatively fine particle size distribution (d80 of around 75 μm). The principles of flotation from fine material were therefore applied to the flotation of zinc from slimes generated during the milling of the SM metallurgical composite sample.

Although industrial-scale desliming would be carried out at 10-20 μm, this cut point is considered impractical for bench scale test work and it was therefore decided to deslime at -38 μm. Initial tests with a single rougher stage were unsuccessful, even at high reagent dosage, and it was found that multiple scavenger steps were required to achieve acceptable recoveries. Furthermore, a cleaner and re-cleaner step were required to produce acceptable zinc concentrate grades. The basic flotation procedure is schematically shown in Figure 5 and features multiple scavenger and cleaner stages.

The flotation conditions, required to achieve reasonable mass pulls for SM and Accha flotation respectively, are summarized in Table VII. In the case of Accha, it was found that higher collector dosages were required to obtain reasonable mass pull, most likely due to the higher clay content.

Slimes flotation results achieved with the metallurgical composite sample from SM are presented in Table VIII. The flotation procedure was found to be successful and although reagent consumption is higher than that of coarse flotation, the step was found to be economically viable for SM and essential to achieving a reasonable overall zinc recovery.

Table V

Lead/zinc bulk flotation results

Zn feed grade	8.2%
Ca feed grade	24.1%
Pb feed grade	3.1%
Cumulative Zn recovery	79.4%
Cumulative Ca recovery	2.2%
Cumulative Pb recovery	73.4%
Zn conc. grade	26.4%
Ca conc. grade	2.1%
Pb conc. grade	9.3%

Table VI

Lead flotation on leach residue results

Zn feed grade	1.6%
Ca feed grade	7.1%
Pb feed grade	23.3%
Cumulative Zn recovery	38.0%
Cumulative Ca recovery	53.0%
Cumulative Pb recovery	94.1%
Zn conc. grade	1.4%
Ca conc. grade	8.3%
Pb conc. grade	48.3%

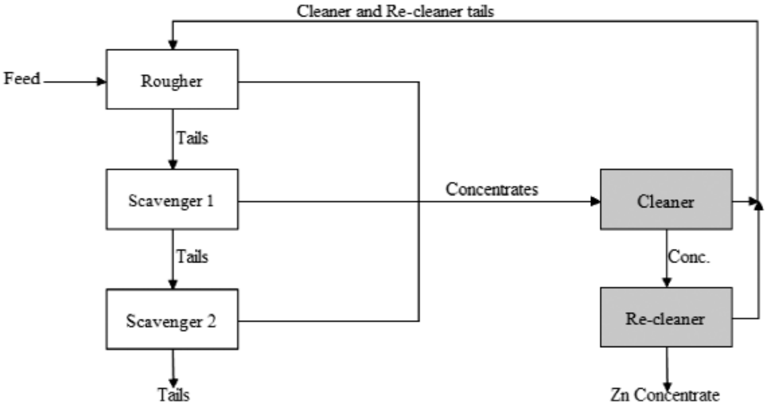

Figure 5—Slimes flotation procedure

Table VII

Slimes flotation conditions

		SM g/t	Acchag/t
Rougher	Calgon	2000	2000
	Sodium silicate	500	800
	Sodium sulphide	4500	5000
	Collector	500	1000
Scavenger 1	Sodium sulphide	4500	1500
	Collector	300	500
Scavenger 2	Sodium sulphide	4500	1500
	Collector	300	500

Table VIII

SM slimes flotation results

Zn feed grade	12.5%
Cumulative Zn recovery	79.0%
Zn conc. grade	33.1%
Ca feed grade	25.1%
Cumulative Ca recovery	5.1%
Ca conc. grade	6.9%
Fe feed grade	14.1%
Cumulative Fe recovery	47.6%
Fe conc. grade	6.8%

Slimes flotation results achieved with the Accha metallurgical composite sample are presented in Table IX. The slimes flotation step increases overall zinc and lead recovery. The collector consumption requires some optimization though, after which the economic viability of the step will be evaluated. The authors are currently carrying out further locked cycle test work to optimize collector addition and zinc concentrate grade.

Metallurgical mapping of HLS

Both SM and Accha display significant mineralogical variability, with ROM zinc grade ranging from 0 to 40%. In order to adequately address the impact of variability on the mine plan and the metallurgical design, it was decided to carry out metallurgical mapping. Although mapping was done for both DMS and flotation circuits, the results discussed below apply to the DMS circuit only.

It was decided to fit the following simple relationship to bench-scale test work results, from a number of samples, selected to characterize the variability of the deposits.

$$\text{Zinc recovery (\%)} = \frac{\text{Zinc feed grade} - C}{\text{Zinc feed grade}} \times 100 \qquad [1]$$

where, C equals a fixed quantity of non-liberated zinc, which will be lost to the floats fraction in DMS. The key assumption is therefore a fixed zinc loss, regardless of feed grade.

Figure 6 shows the results of metallurgical mapping with a range of samples from the SM deposit. Equation [1] was fitted to the experimental data, using a fixed zinc loss (C) of 2.08%. Although some scatter exists, the experimental data fits the theoretical Equation [1] reasonably well. It was therefore decided to utilize Equation [1] in the determination of the economic cut-off grade of each block in the resource model. This means that the cut-off grade will not necessarily be uniform throughout the deposit but will be dependent on mining cost, metallurgical treatment cost and anticipated zinc recovery.

Figure 7 shows the results of metallurgical mapping of HLS test results for the Accha metallurgical sample, and it is immediately apparent that the amount of scatter in the data is far more significant than for the SM metallurgical sample. The scatter was investigated further by revisiting the geological logs, compiled upon receipt of the metallurgical sample drill core. As shown in Figure 7 (circled data points), samples identified as containing significant amounts of clay appear to yield lower overall zinc recovery and also contribute to a fair amount of scatter. The best fit grade vs. recovery equation (Equation [1]) is also at a fixed loss (C) value of 2.83% for the entire sample set and at a value of 1.35% when excluding clay samples.

It must be noted that although the results indicate

Table IX

Accha slimes flotation results

Zn feed grade	6.4%
Cumulative Zn recovery	67.9%
Zn conc. Grade	12.3%
Ca feed grade	22.6%
Cumulative Ca recovery	39.5%
Ca conc. Grade	4.4%
Pb feed grade	2.4%
Cumulative Pb recovery	60.1%
Pb conc. Grade	1.62%

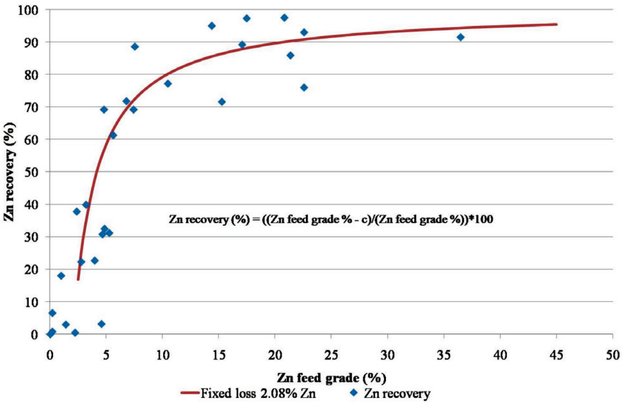

Figure 6—SM metallurgical mapping

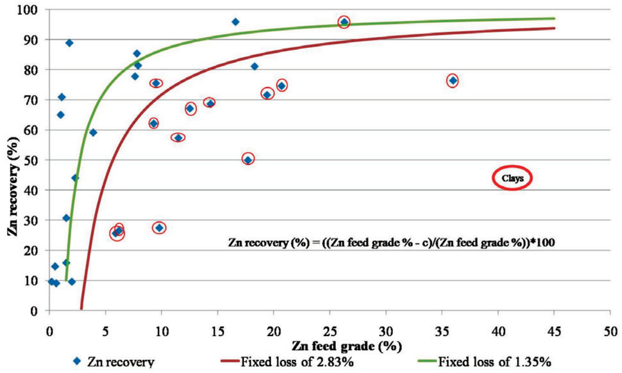

Figure 7—Accha metallurgical mapping

significant impact of clay, sample selection for metallurgical mapping was premised on maximizing variability, both for zinc grade and association with other minerals. Therefore, the impact of clay on the Accha metallurgical composite sample, which is considered more representative of the overall deposit, is much less than would be suggested by Figure 7.

Conclusions and further work

It is technically feasible to remove acid-consuming gangue minerals from the ROM zinc oxide ores by more than 90% and to produce a concentrate with a zinc grade in the order of 25 to 35%. This offers numerous advantages for refinery sizing and site selection as it may be economically viable to transport zinc concentrate at high Zn grades.

It was also found that a clear understanding of mineralogical association, particularly in the presence of clay minerals, is required to quantify overall zinc recovery.

Further work will focus on the confirmation of economic viability of a concentrator flow sheet, comprising a combination of DMS and primary amine flotation. The overall viability will, however, be affected by mining cost and as the mine designs for both projects are currently in progress, overall economic viability is the subject of current feasibility studies.

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