

CANATUAN CU/ZN FLOTATION METALLURGY - DEALING WITH ZINC PRE-ACTIVATION

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ABSTRACT

TVI Resource Development (Phils) Inc. Canatuan mine is a polymetallic ore deposit located in the Province of Zamboanga del Norte on the island of Mindanao in the Philippines. The deposit consisted of an oxidized capping of gossan overlying a Besshi type volcanogenic massive sulphide lens which is near surface and flat lying. Construction and development of a sulphide processing plant began in early 2007 and commissioned in November 2008. During the initial stages of sulphide operation, high copper (Cu)-low zinc (Zn) ore was fed to the plant. Marketable copper concentrate at 91-95% recovery was produced utilizing a high-pH bulk sulphide rougher flotation and 2 cleaning stages. Because of increased levels of Zn of the ore body, a Cu/Zn separation circuit was initiated in early 2010 following an intensive laboratory test work program. This Cu/Zn separation circuit was necessitated because of the copper ion pre-activation of the sphalerite that lead to the zinc being readily recovered to the copper rougher concentrate. In-situ activation of zinc (in the pit and stockpiles) was caused by the leaching of secondary copper minerals in the ore (particularly from the dominant copper species, chalcocite and covellite). This problem required the development of metallurgically complex and intensive reagent regime to effectively depress the activated sphalerite. As well, the immediate reactivation of zinc after it has been depressed, at the onset of Cu/Zn separation flotation, added additional metallurgical complexity to the process. Subsequent to the Cu/Zn separation circuit, an unconventional, yet proven effective, simultaneous cyanide detoxification-zinc flotation circuit was set-up to recover the zinc. Laboratory test work results realized Cu-Zn recovery differential from a Cu/Zn separation circuit of over 40-45%. This performance has been achieved in the plant, at 72% Cu overall recovery. With the gradual improvements on-going with zinc circuit capacity and effective zinc separation being achieved, zinc recovery has currently reached 40%.

KEYWORDS

Copper, zinc, sulphide, separation, activation, depression, flowsheet

INTRODUCTION

TVI Pacific Inc. is a publicly-traded resource company focused on the production, development, exploration and acquisition of resource projects in the Philippines. TVI currently produces copper and zinc concentrates from its Canatuan mine, is developing the Balabag gold property for anticipated production in the second half of 2012 and is initiating an aggressive exploration program at its high-impact Tamarok property. TVI also has oil interests in various stages of discovery, drilling and exploration in Alaska, Niger and off-shore Philippines.

An affiliate of TVI Pacific Inc, TVI Resource Development (Phils) is operating the Canatuan mine located in the Province of Zamboanga del Norte on the island of Mindanao in the Philippines. Its polymetallic ore deposit with copper, zinc, gold and silver as valuable metals consists of an oxidized capping of gossan overlying a Besshi type volcanogenic massive sulphide lens which is near surface and flat lying. Initially, gold and silver dore was produced from gossan ore through “hybrid” carbon-in-leach and Merrill Crowe circuits from 2001–2007. Increased cyanide consumption, when the underlying primary sulphide portion of the deposit was largely exposed, prompted the end of gossan operation.

The second phase of the mining operation required construction and development of a sulphide flotation processing plant. The project began in early 2007 and was commissioned in November 2008. The plant was initially designed to process high Cu-low Zn ores (with Cu to Zn ratio > 5:1) to produce marketable copper concentrate only. The concentrates produced at the Canatuan mine are shipped to a coastal warehouse facility at Santa Maria Port approximately 30 kilometers away. From this port, approximately 5,000 tonne loads of copper concentrate are shipped according to a 5-year off-take agreement with MRI Trading AG. Commercial copper production was declared on March 1, 2009, when copper concentrate inventory levels surpassed the 5,000 tonne shipping threshold.

Increased zinc levels in the ore body, as it was continuously being mined, prompted the construction of a Cu/Zn separation circuit as extension of the previous flotation circuit. The construction was completed in early 2010 following an intensive laboratory test work program. The Cu/Zn separation circuit was commissioned in November 2009 focusing on zinc depression, with the zinc initially rejected until maximum separation efficiency was realized. As of April 2011, the Canatuan mill has also commenced the production of a zinc concentrate.

GEOLOGY AND MINERALOGY

The Canatuan deposit is mainly comprised of an iron-oxide gossan underlain by massive sulphide. Volumetrically, more than half of the original massive sulphide has been oxidized to gossan. Both units are hosted by a felsic sequence that is generally 50m thick and altered to an assemblage of quartz, sericite, chlorite and pyrite. The transition between the gossan unit and the massive sulphide is evident at the zone of the water table. The gossan / sulphide relationship suggests that the deposit has been uplifted while the hanging wall of the felsic sequence has been eroded.

The in-situ gossan consists mainly of iron oxide-hydroxides with minor silicate gangue. Distinct gossan textures have been observed such as “massive gossan”, in which the box-work fabric is more or less preserved; “banded gossan” in which banding from oxidation of the different sulphide strata along with sericite and saprolite are preserved; and “rubbly gossan” which consists of blocks of either of the two types noted within an unconsolidated saprolitic matrix.

The oxidation of the sulphide minerals in the gossan unit has resulted to the depletion of elements such as S, Zn, Cu, Pb, Fe and conversion of massive sulphide into a porous limonitic box-work. During oxidation, the base-metal content was reduced by an order of magnitude. Zinc showed the strongest depletion, followed by copper and then lead. This also indicates the respective mobility of each metal. Meanwhile, the gold and silver content of the gossan were considerably higher than that of the massive

sulphide. The leaching of base-metals during oxidation had enhanced the concentration of the relatively less mobile gold and silver in the gossan.

Underlying the oxide unit is the sulphide body which occurs as either massive or banded sulphide. The semi-massive to massive sulphide is composed of >50% coarse-grained pyrite, <10% chalcopyrite and combined sphalerite, galena and tennantite. On the other hand, banded sulphides are composed of 10-50% pyrite with inter-layering of pyrite rich quartz-sericite schist with minor copper minerals. The chalcopyrite is incompletely replaced by bornite, which in turn is partly replaced by covellite. Chalcocite occurs as sooty coatings throughout the massive sulphides, mainly in the interval immediately underlying the current water table. This implies a more extensive nature of supergene process in the upper layers of the ore body. The copper and other base-metals that were leached during the formation of gossan are believed to have been precipitated and accumulated in the transition zone. Hence, there is a complex nature of sulphides in the supergene-enriched zones as well as in areas that are highly jointed and structurally exposed to water penetration.

MINING OPERATION

Canatuan sulphide open pit operation is designed such that the water from the pit (acid mine drainage) flows to the lowest elevation and is impounded at the tailings dam. This is unlike the typical open pit operations where a burrow will be dug out from the mountain and mechanical dewatering systems are applied. Canatuan operations cut the mountain along its contour thus making the water free to flow outside the pit without impounding it. The bench height utilized in pit is 3 meters based on the ore block model generated from Gemcom software with a bench slope of 60 degrees from horizontal.

Pit operations utilized the following activities: grade control drilling, blasting, loading, hauling and blending. In grade control drilling, a 6 by 6 meter grid pattern is being utilized in the pit with sampling activity for every meter depth. If indicated, hard rock materials are in need of blasting, then a 3 by 3 meter grid pattern is used. The depth of grade control drilling depends on the mine pit limit for the specific month. Loading of ore or waste is being done using CAT Backhoe Excavator 336D and 320D. Ore is being classified into 4 types: massive sulphide, banded sulphide, gossan and schist. Depending on the cut-off grade, these are then loaded into 10-wheeler dump trucks and hauled into the blending area. The materials below the cut-off grade are sent to the waste dump areas. After considering mill parameters, the ore materials are blended in the stockpile area using CAT Payloader 950H before dumping it into the crusher.

CHALLENGES ON METALLURGY

The nature of Canatuan sulphide deposit allowed the staged processing of the ore from high Cu-low Zn ores to low Cu-high Zn ores. Due to this mineralogical stratification, emphasis on the high Cu-low Zn ores was set for the initial 1-2 years of operation. This provided some time to gather enough plant data to study the metallurgical properties of Cu and Zn and assess the most applicable flowsheet for the subsequent processing of higher zinc ores.

High Cu ores were processed using a simple circuit consisting of a bulk sulphide rougher with 2 cleaning stages floating all valuable sulphides and rejecting gangue particularly pyrite, quartz, and clays. At an average feed grade of 1.5-2.0% Cu and Cu:Zn ratio of greater 5:1, the plant was commissioned at 1200 TPD which was gradually ramped up to 2500 TPD through plant performance optimizations and capacity upgrades. A high pH reagent regime with optimum setting of 11.5-12.0, using lime as pH regulator, was employed. Fortunately, a coarse grind of about 120 microns was determined to be sufficient enough to attain optimum recovery at an acceptable grade requiring no necessary regrinding in the cleaning stages. Isopropyl ethyl thionocarbamate (IPETC) collector was initially used and methyl isobutyl carbinol (MIBC) as frother, at 45 g/t and 30 g/t respectively.

During the initial stages of high-Cu circuit commissioning, Cu recovery was low at about 20-30%. The problem was later determined to be related to the frother, wherein MIBC, which worked well in the

lab, did not work well in the plant. MIBC was later replaced with Nasfroth HEL after plant trials of various frothers. This stabilized the production at 91-95% Cu recovery.

As one of the indications of the impending metallurgical challenges in handling succeeding higher zinc ores, plant data for the high Cu ores indicated that zinc was readily floatable at even faster kinetics and higher recovery than copper, without introduction of any zinc activation (refer to Table 1 for Cu and Zn recovery profile in the bulk roughers). However, the inherent low zinc content in the feed then, did not require zinc depression and a marketable Cu concentrate was still readily produced. Pyrite, moreover, was also activated but this was managed by employing longer lime conditioning, prompting the relocation of lime addition into the primary grinding circuit.

Table 1 - Typical bulk rougher Cu and Zn kinetics

Flotation time	Cu Rec, %	Zn Rec, %
5 min	86.70	93.74
10 min	91.71	95.04
15 min	92.07	95.16

A modal mineralogical study was conducted by Blue Coast Metallurgy Ltd of Canatuan flotation products (Martin 2010). General mineral composition of the ore is shown in Table 2. The copper mineral speciation is shown in Figure 1.

Table 2 - Modal composition of bulk

	Abundance
Pyrite	18.1
Chalcopyrite	0.7
Bornite	0.2
Chalcocite	1.3
Covellite	0.2
Ultrafine Cu inclus	0.1
Sphalerite	1.7
Quartz	49.6
Feldspar	1.6
Mica	10.1
Kaolinite	4.2
Chlorite	7.9
Fe & Ti Oxides	3.8
Other	0.4

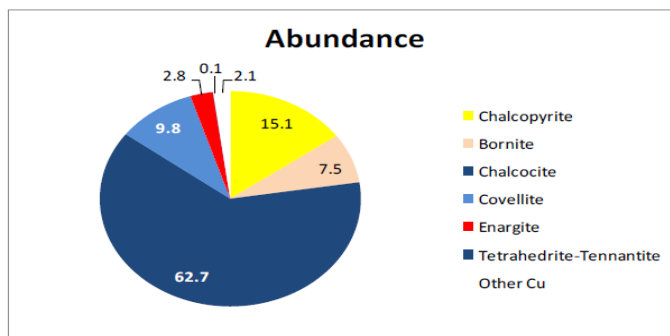


Figure 1 - Speciation of copper bearing minerals rougher feed

It is important to note the dominant presence of secondary copper minerals wherein 63% of the copper in the feed is chalcocite and a further 10% is represented by covellite. Secondary copper mineralization in the feed from these figures was, significantly, about 1.2% (Cu head assay). This content of copper, as soluble secondary sulphides, was far above the “danger limit” for Zn activation, seen elsewhere in the industry, as being critical at levels as low as 0.1% Cu.

At that point, it was important to note that the soluble copper (expressed as copper oxide) accounted for 20 to 30 percent of the total copper in the mill head. If the soluble copper was present as tarnishing on the surface of copper sulphides, then over 90% recovery of total copper in the plant would be impossible to attain but rather a considerable amount would be lost to the tailings. There should, therefore, be substantial concentration of soluble copper elsewhere and that is postulated to be at the surface of sphalerite. This meant that the sphalerite was in a state of what could be called “super activation”.

For the Canatuan ore, zinc activation is associated with the leaching of the dominant secondary copper species, chalcocite and covellite, in the ore, shedding a lot of copper sulphate solution throughout the deposit. This occurrence is further exacerbated by the highly fragmented nature of the ore (in parts, the rock is so fragmented that the ore is often only ripped and not necessarily blasted) allowing the copper containing solution to permeate readily throughout the rock. Suffice to say, the photo of the pit shown in Figure 2 depicts this metallurgical challenge.



Figure 2 - Canatuan sulphide ore showing sporadic precipitation of copper sulphate (CuSO_4) from in-situ leaching of secondary copper minerals

To prove that zinc was being recovered not by attachment to copper sulphides but by true flotation, the liberation of both copper and zinc were studied at the current milling grind size of 100-120 microns. Liberation of both copper and zinc sulphides was in excess of 75%. At copper recovery of over 94%, relatively little zinc would be expected to be carried to the copper concentrate if the mechanism was physical attachment only. This proved that bulk of the zinc sulphides was being recovered by true flotation.

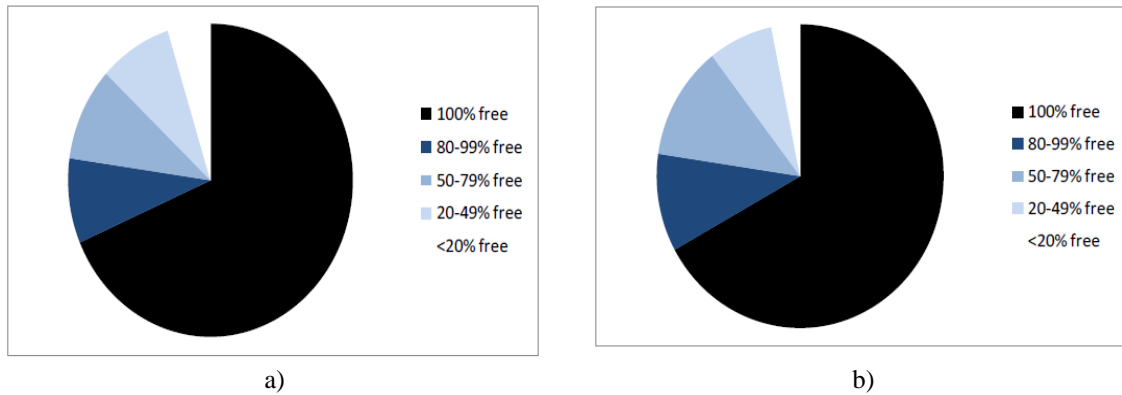


Figure 3 - Liberation of the copper sulphides (a) and sphalerite (b) in the rougher feed

In addition to impending Cu/Zn separation difficulty, the relatively high levels of arsenic (As) in the ore added complexity to the operation. The arsenic in the ore was identified from optical mineralogy carried out by Optimet and confirmed by electron microprobe analysis, to be present as the mineral tennantite. Although efforts to selectively depress arsenical copper mineral using various oxidants have been employed in bench scale tests, the problem is further complicated by the mineralogical texture of tennantite intimately associated with copper minerals. It was determined, through mineralogical analysis at the National Institute of Geological Sciences in University of the Philippines that the tennantite exists as fine veins (about 5-20 microns) disseminated within the host copper minerals making it metallurgically difficult to treat. Tedious ore blending strategies and selective mine planning of high arsenic areas were initially utilized to control arsenic. Moreover, Cu concentrate grade was closely managed to stay under the 0.5% As rejection limit.

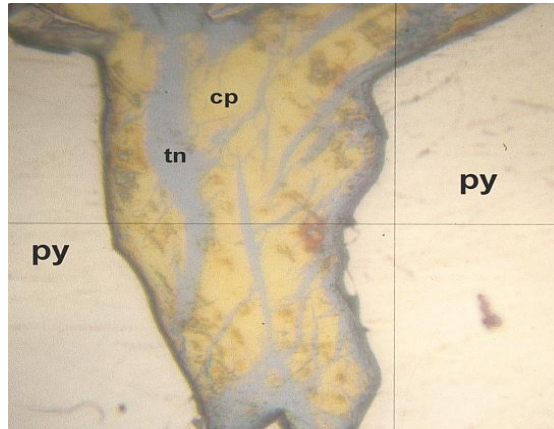


Figure 4 - Close up of chalcopyrite (cp) replaced by tennantite (tn). The chalcopyrite grain is 0.24 x 0.115 mm. The thickest tennantite veinlet is 0.02 mm wide. The thinner veinlet is 0.005 mm.

PROBLEM APPROACH

As a preliminary step in formulating a tactical approach for separating copper from zinc, the reaction chemistry and physical responses of various zinc deactivators and depressants were studied. The approach was centered on the understanding that, in order to effect separation, copper abstraction from the surface of activated sphalerite is critical.

A series of tests were set off to determine the degree of copper abstraction from the surface of sphalerite using sodium cyanide (NaCN), sulfuric acid (H_2SO_4), ammonium hydroxide (NH_4OH), ethylenediaminetetraacetic acid (EDTA) and sodium sulphide (Na_2S) using mill bulk concentrate at equal dosages of 500g/t. Results of the tests are summarized in Table 3. The figures are indicative enough to suggest a possibility of abstraction using any of the aforementioned reagents.

Reagent	Dosage (g/t)	Conditioning (min)	Copper abstracted (ppm)
NaCN	500	30	173
H_2SO_4	500	30	110
NH_4OH	500	30	98
EDTA	500	30	105
Na_2S	500	30	120

Having established this background information, a series of tests were outlined as an initial attempt for separating copper from zinc. Exploratory tests, involving regrinding of mill high copper ore final concentrate samples and subjecting them to zinc depression, were performed as outlined in Table 4. The use of H_2SO_4 was disregarded due to the inability to react with copper ions.

Table 4 - Cu/Zn separation initial reagent regimes tested

Code	Deactivator	Depressant
A	ZnSO ₄ (by ZnS/Zn ⁺² equilibrium shift)	None
B	ZnSO ₄	SMBS*
C	NaCN (by complex formation)	None
D	NaCN	SMBS
E	NH ₄ OH	None
F	NH ₄ OH	SMBS
G	EDTA (by complex formation)	None
H	EDTA	SMBS
I	NaCN/ZnSO ₄	None
J	NaCN/ZnSO ₄	SMBS
K	NaCN/ZnSO ₄	low pH
L	NaCN/ZnSO ₄	SMBS, low pH

* sodium metabisulphite

Three regrind sizes were utilised with ten reagent schemes at preset reference dosage levels. Results, however, failed to give any indicative lead with the schemes considered. For all the ten reagent schemes, no zinc depression was apparent and zinc recoveries were still higher than copper. This was true for all regrind sizes from P₈₀ of 39 microns down to approximately 6 microns indicating that particle size did not play an important role in zinc depression under the conditions of the tests (high pH, feed saturated with lime (CaO)/calcium ions and collector coated - the same conditions that would arise if the zinc circuit was to receive feed from bulk sulphide float of the present flotation operation). Some plant practices reported that zinc depression was very difficult in the presence of lime and Ca²⁺ ions while others indicated excellent depression at high pH with lime. This meant that the presence or absence of lime/Ca²⁺ ion and high or low pH zinc depression must be ore specific. Some other factors involving flotation chemistry which are specific to the present ore, seemed to be affecting zinc depression.

To investigate the extent of the difficulty in terms of ore characteristics, a high chalcopyrite ore with low secondary copper sulphides was sought in the pit and tested for Cu/Zn separation. Average assay of the bulk sample was 0.62% Cu-0.82% Zn. Several ideas were also incorporated in this set of tests. The bulk sulphide flotation portion was essentially the same as the high-Cu flotation operation except for the use of new collector – a 1:1 combination of dithiophosphate (DTP) and potassium amyl xanthate (PAX) instead of IPETC being used in the mill. The Cu-Zn separation portion was a basic separation scheme involving regrinding and differential flotation with the inclusion, however, of desorption and filtering stages. One step that was not used in previous tests was the desorption step to remove collector coatings and a significant amount of activating ions from the surface of zinc. These depressant schemes were all tested with soda ash (Na₂CO₃) and lime.

Depressant 1: Ferrous sulphate (FeSO₄) - Zinc hydroxide (Zn(OH)₂)

Depressant 2: NaCN - Zinc sulphate (ZnSO₄)

Depressant 3: Na₂S - ZnSO₄

Depressant 4: Na₂S - Sodium sulphite (Na₂SO₃) - SMBS (Na₂S₂O₅)

Depressant 5: Na₂S - Na₂SO₃ - Na₂S₂O₅ - Sodium thiosulphate (Na₂S₂O₃)

Depressant 6: Na₂S - Na₂SO₃ - Ammonium sulphate ((NH₄)₂SO₄) - (Na₂S₂O₃)

Out of these tests, depressant schemes 2 and 3 gave good indication of separation using either soda ash or lime as indicated in the summary of results in Table 5. Concentrate grades however, were generally low, as could be expected with the use of soda ash (soda ash was not a good depressant for pyrite which was the main diluent in the concentrate, aside from non-sulphide gangue). With a low grade ore and a single cleaning stage, little upgrading of concentrate was realised. These results tended to confirm that, aside from the specific type of depressant, the pulp environment, as represented by pH modifiers and pre-treatments in the desorption stage were all important in the Cu-Zn separation.

Table 5 - Summary of results using depressants 2 and 3

Depressant	Bulk Ro. Conc		Bulk Clnr Conc		Cu/Zn Sep Conc		Cu/Zn Sep Rec	
	%Cu	%Zn	%Cu	%Zn	%Cu	%Zn	%Cu	%Zn
Depressant 2 - soda ash	3.11	4.16	4.20	5.65	18.39	16.61	72.44	48.57
Depressant 3 - soda ash	2.17	3.09	3.22	4.59	3.54	2.22	98.27	43.26
Depressant 2 - lime	3.31	4.63	6.75	9.51	19.11	8.43	82.48	25.81
Depressant 3 - lime	3.95	4.95	7.83	9.81	9.43	8.61	97.03	70.72

At this stage, the results of the tests so far conducted, indicated good separation of copper and zinc could be achieved with sodium sulphide/zinc sulphate and sodium cyanide/zinc sulphate depressants with either soda ash or lime for this high chalcopryrite ore. However, when these schemes were tested using ores with high secondary copper mineralisation, results could not be duplicated confirming that the difficulty was mainly controlled by the ore type.

Having an initial reagent regime that worked effectively for high chalcopryrite ores, another test work program, to further enhance this flowsheet into a more robust and ore-versatile reagent scheme that could handle secondary ore deposits was instigated. These flowsheets were used as benchmarks for developing a reagent scheme with SMBS, NaCN, ZnSO₄ and Na₂S as core reagents. Developmental tests were conducted at the Canatuan on-site metallurgical laboratory and latter at SGS Minerals Services in Lakefield, Canada. These programs lead to the development of a flowsheet that could handle high secondary copper ores. Figure 5 shows the flowsheet from the successful locked cycle test.

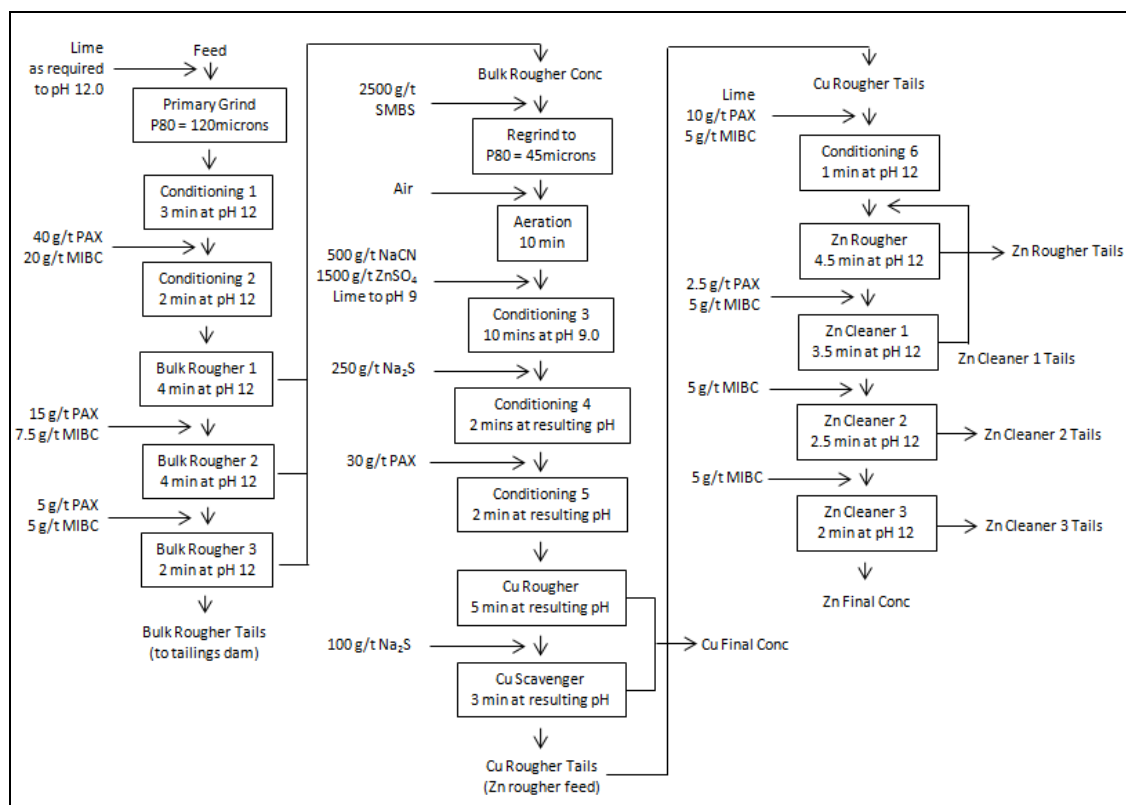


Figure 5 - Cyanide-based reagent scheme flowsheet

Results of the locked cycle test is shown in Table 6

Table 6 - Summary of results of locked cycle test using cyanide-based regime

Product	Weight	Assays		% Distribution	
	%	% Cu	% Zn	Cu	Zn
Cu Final Conc	3.66	23.6	13.4	81.4	41.3
Zn Final Conc	0.72	2.85	52.3	1.9	31.6
Zn Rougher Tail	10.7	0.2	1.01	2.0	9.1
Bulk Rougher Conc	16	5.76	7.1	86.9	96
Bulk Rougher Tail	84	0.17	0.06	13.1	4.0
Head	100	1.06	1.19	100	100

From the test work program conducted into developing this flowsheet, the following general observations were drawn:

1. The addition of SMBS in the regrind mill after bulk flotation was the initial important step for the reagent scheme to work. Removing or relocating SMBS from the regrind caused loss of separation.
2. Aeration after regrinding improved the Cu/Zn separation. Aeration supplied dissolved oxygen (DO) required for the complete conversion of SMBS to SO_2 . The addition of SMBS in the regrind and the subsequent aeration forms a collector desorption step - a decisive and critical requirement, prior to Zn depression. Complete collector desorption was apparent after subsequent aeration, as manifested by the complete disruption of froth during introduction of air. The resultant drop in pH also aided disruption of collector. On the other hand, too much air added, effected separation, as aeration drove the Eh too positive and required more reducing agent to drive the Eh back to a negative potential.
3. The sensitivity of the reagent regime to collector type was not pronounced.
4. There was an observed tendency of zinc to be reactivated after being deactivated and depressed, at the onset of flotation. This effect was proven to be caused by the increase in Eh as air was continuously introduced into the pulp through the progress of flotation.
5. The cyanide/zinc sulphate complex acts to depress zinc and moreover drove the pulp potential more negative. A 3:1 ZnSO_4 :NaCN ratio was considered optimum. The complex was also proven to precipitate some dissolved copper ions (which activate zinc).
6. There was a preferred range of Eh wherein Cu/Zn separation became more efficient.
7. The reagent scheme was temperature sensitive. (Ambient pulp temperatures in the Philippines are elevated and between 38°C to 45°C .) This is believed to be related to the higher volatilization rate of hydrogen cyanide gas (HCN) at elevated temperatures wherein at certain temperature limit, cyanide is lost to the air as HCN. Elevated temperature conditions also aids in the Cu/Zn separation by making the pulp less viscous as can be observed in the regrind mill discharge, where temperature becomes highly elevated.
8. Zinc oxide (ZnO) proved to be superior to ZnSO_4 in terms of kinetics, recovery and separation. The use of ZnO reduced sulphuric acid in the system (unlike ZnSO_4 which is a source of acid) minimizing the leaching process. Moreover, the reduction in acidity in turn required lower lime addition to get the system into the right pH. However, the cost-benefit of using ZnSO_4 in the Philippines superseded using ZnO.
9. The use of Na_2S as Eh modifier proved to be efficient in controlling zinc reactivation. Stage addition of Na_2S was employed to keep the zinc depressed throughout the duration of Cu/Zn separation flotation stage, by driving the pulp to negative potential. Moreover, Na_2S precipitated dissolved copper ions, preventing the reactivation of zinc.
10. Increased addition of Na_2S killed some copper flotation thought to be particularly chalcopryrite. It also slowed the kinetics of other copper sulphide mineral flotation.
11. Zinc was easily recovered in the zinc flotation even without the use of activator CuSO_4 . The inherent high Cu ion content in the feed to the zinc circuit negated the necessity of adding CuSO_4 .

MOVING TO CU/ZN PLANT COMMISSIONING

Commissioning 1 - Non-cyanide Based Reagent Regime

The Cu/Zn separation circuit was commissioned initially using a previously developed non-cyanide reagent scheme. This scheme was motivated by the drive to eliminate the use of cyanide because of its perceived negative environmental impact. Initial testing did not include a zinc circuit.

The flowsheet consisted of bulk sulphide rougher flotation wherein copper and zinc are floated. The bulk rougher concentrate proceeded to a regrind mill to attain a grind of P_{80} of 45 microns and wherein SMBS, $ZnSO_4$, and Na_2S were added. An aeration stage was then included followed by collector addition. Copper was floated in a series of banks and the copper rougher tails joined the bulk rougher discharge, as final tailings.

The initial stages of commissioning had presented some difficulties. The plant could not reproduce the favourable results obtained with this reagent scheme in the laboratory. The inconsistencies in results obtained and the pressure for production prompted the deferral of the plant test until a more robust and ore-flexible flowsheet could be developed. However, the possible use of this flowsheet may be revived once the level of secondary copper in the ore has gone down to a tolerable level.

Commissioning 2 - Cyanide-based Reagent Regime

A second wave of commissioning was initiated using the cyanide-based regime developed with minor modifications on the existing circuit including the construction of a cyanide detoxification plant. In the same way as the initial plant trial, Cu/Zn separation circuit was optimized initially, whilst rejecting the tails without floating the zinc. Initially, good indication of zinc depression was achieved though only modest and with some inconsistencies still apparent. The flowsheet utilised is shown in Figure 6.

Plant Controls Implemented

Due to the highly sensitive nature of the Cu/Zn separation process to ore changes, close control of the feed was implemented by initiating strict blending strategies accompanied by plant controls and monitoring in order to gradually stabilize the circuit. One of the key controls implemented in order to get the plant results closer to laboratory results, was the understanding of the relationship between mass flow and the right dosages of depressants. In this regard, laboratory bulk concentrate grade and % solids were closely duplicated in the plant to simulate the reagent chemistry in terms of depressant dosages per unit of mass and grade of material being treated. Due to the high sensitivity of the process, construction of a surge tank for the bulk rougher concentrate (Cu/Zn separation feed) stabilized the flow by absorbing circuit shocks caused by intermittent fluctuations in the feed and operational upsets.

Advanced laboratory ore testing of the scheduled feed was initiated in order to optimize the parameters for a certain ore blend, prior to feeding the plant. Plant streams monitoring by measurements of critical parameters including Eh, pH and DO were implemented on a regular basis for quick trouble shooting of plant deviation against laboratory results. All of these operational controls resulted in a better understanding of the reagents and parameters, their cause and effect and this in turn lead to a gradual optimization of the plant.

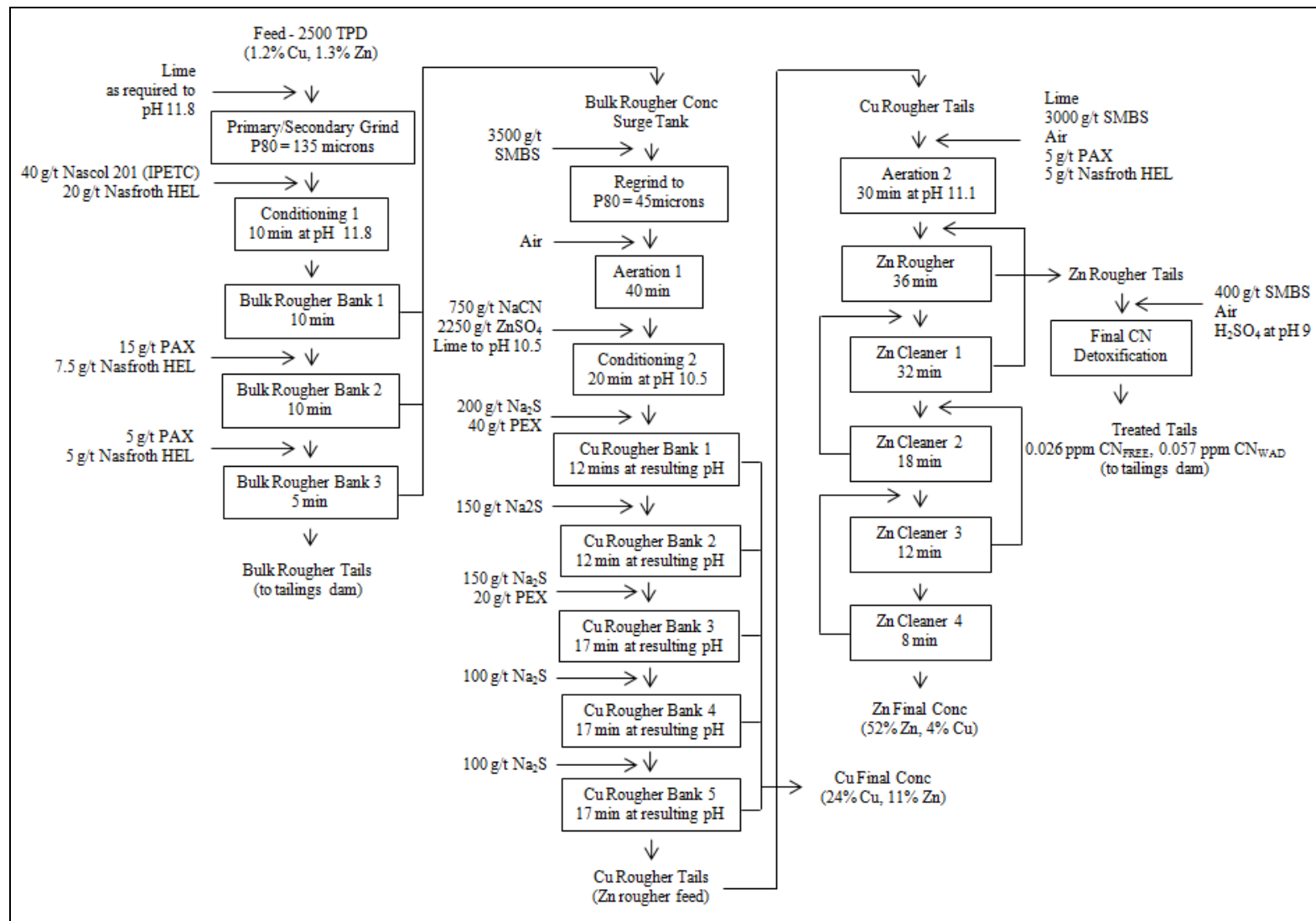


Figure 6 – Current Canatuan Cu/Zn plant flowsheet established

Plant Modifications

After duplicating laboratory results in the plant for the Cu/Zn separation circuit, the zinc flotation circuit was commissioned employing a rougher with 4 cleaning stages. As an initial strategy in producing acceptable zinc concentrate (>50% Zn, <5% Cu), the last bank of the Cu/Zn separation flotation was used to maximize removal of copper and produce better quality feed for the zinc circuit. In effect, this middling concentrate with about 15% Cu, 15% Zn was floated but rejected to tailings thereby losing some recovery. Initially, PAX and Nasfroth HEL frother at 5 g/t each were added for zinc flotation without any depressants. It is important to note that despite all the heavy depression used in Cu/Zn separation, zinc was able to float even without the use of any additional zinc activation. The use of CuSO_4 was disregarded because of the inherent high Cu ion content in the feed to the zinc circuit. Aeration was employed prior to the zinc rougher flotation in order to disrupt excess Na_2S which depressed zinc. The excess Na_2S , upon contact with air is converted to sulphydryl species such as thiosulphate (S_2O_3), sulphite (SO_3) and sulphate ions (SO_4) and losses efficiency as a zinc depressant.

It was decided to also utilize the zinc circuit as a cyanide detoxification stage (given aeration from the flotation cells). 3000 g/t of SMBS was added with air in the conditioner before the zinc rougher. As can be seen in Table 7, partial detoxification was effected in the zinc circuit. Interestingly, cyanide detoxification was effected at the optimum pH for zinc flotation in the region of 11.0 - 11.5 which is in contrast to established optimum pH for a conventional air/ SO_2 process. Another interesting discovery out of this test was the apparent depression of copper (chalcopyrite) that aided the production of on-spec zinc concentrate. In order to confirm the positive copper depression provided by SMBS, this reagent was removed from the circuit. Subsequently, there was an immediate increase of copper content in the zinc concentrate. The phenomenon was later found out to be related to the pulp Eh, wherein at a potential greater than +20 mV, chalcopyrite was depressed. SMBS is an effective oxidant and will drive the Eh to positive potential. This plant practice has proven that simultaneous zinc flotation and detoxification was possible for Canatuan ore.

Current Results

A summary of current plant results and parameters is shown in Table 7. At the current flowsheet and reagent dosages as earlier shown in diagram 2, a maximum Cu/Zn separation in the range of 40 – 45% has been achieved with 72% copper and 41% zinc separate overall recoveries.

Table 7 - Summary of plant data (March / July 2011)

Stream	%Cu	%Zn	Stream	Eh, mV	pH	DO, ppm
Feed Grade	1.23	1.28	Bulk Flotation	47.3	11.82	6.22
Bulk Rougher Conc	9.93	10.65	Regrind Discharge	47.59	6.53	1.41
Cu Conc	24.16	11.16	Aeration 1	138	6.07	3.83
Zn Conc	4.07	51.89	Conditioning 2	-205.9	10.85	0.5
Recovery	72.12	41.07	Cu Rougher	-59.07	11.46	2.05
			Aeration 2	17.24	11.11	3.09
Stream	CN _{FREE}	CN _{WAD}	Zn Rougher	27.67	11.09	4.66
Zn Circuit Feed	73.19	295.23	Zn Cleaner	90.28	11.14	6.02
Zn Circuit Discharge	1.124	16.07	Final Detox Discharge	208.25	9.58	6.68
Final Detox Discharge	0.026	0.057				

Overall Observations

1. pH during aeration played a critical role. A pH requirement below 7 was necessary to effect collector desorption. Above pH 7, desorption was ineffective as manifested by the voluminous froth formation affecting subsequent Cu/Zn separation.
2. Too much introduction of air during aeration affected the separation. Too much air drove the Eh to highly positive potential which required more NaCN and Na₂S as reducing agents to get the pulp potential back to target -200 mV before proceeding to Cu flotation. In contrast, too low air addition also effected separation due to incomplete conversion of SMBS into SO₂ when the DO level dropped as indicated by the unattained target pH during the desorption step and low DO.
3. Removal of the stage addition steps for Na₂S reactivated the zinc in the latter stages of Cu/Zn flotation. At the current addition of NaCN and Na₂S, complete precipitation of dissolved copper ions to copper sulphide was not realized as indicated by the high dissolved copper in the zinc circuit discharge. This proved that the cause of reactivation was more potential related and not reactivation by the presence of high dissolved copper in the system as initially thought. A typical dissolved copper ions profile in the Cu/Zn separation conditioners and flotation banks is shown in Table 8.

Table 8 - Dissolved copper (ppm) profile in Cu rougher circuit

Conditioning 2	Bank 1	Bank 2	Bank 3	Bank 4	Bank 5
243	196	184	142	128	92

4. Excessive addition of Na₂S killed some copper with chalcopyrite more prone to over dosage. Due to the addition of Na₂S, most of the copper lost to the zinc circuit was apparently chalcopyrite.
5. Zinc preferred to float at positive Eh greater than +20 mV. Below such potential, zinc was depressed.

FUTURE PLANT IMPROVEMENTS

1. A bulk cleaning stage could improve rejection of pyrite in the bulk rougher concentrate before proceeding to Cu/Zn separation treatment. This would reduce the consumption of depressants since pyrite competes for reagents and could have a detrimental effect on the separation chemistry. Overall increase in capacity and reduced material handling as well as ease of upgrading in the zinc circuit could also be benefits when bulk cleaning is employed.
2. Due to the foreseen increase in arsenic content in the deposit as seen in the mine plan, the need to depress arsenic has become inevitable in order to produce saleable copper concentrate. Due to the established close association of tennantite with chalcopyrite, the increase in levels of arsenic is parallel with increasing chalcopyrite content at the deeper portion of the deposit. Previous bench scale test on Canatuan ore conducted by Intermet had indicated the possibility to selectively depress arsenical copper in a potential controlled environment. Using potassium permanganate (KMnO₄) as an oxidant, tennantite was floated away from chalcopyrite at an optimum Eh of +200mV (versus a saturated KCl electrode). The use of reducing agents, particularly Na₂S, to selectively depress tennantite associated with chalcopyrite has also been proven to work in the Canatuan lab. Though copper mineral / arsenic separation has never been scaled up to an operating plant, the impending necessity to depress arsenic from the Canatuan concentrate requires making this work.
3. In anticipation of the decreased levels of secondary copper in the ore in the latter stages of mine life, bench scale testing is currently underway to develop a less complex reagent scheme that can handle chalcopyrite-sphalerite separation. Positive indication with over 60% Cu/Zn separation has been achieved using a flowsheet with permutations of the current plant scheme and that of the previous flow sheet developed for high chalcopyrite ores. The exclusion of cyanide in the reagent recipe eliminates the need for a detoxification process.

CONCLUSIONS

With the inherent nature of in-situ activation of Zn by Cu from leaching of secondary Cu minerals, Canatuan ore is considered metallurgically difficult to treat. This required a complex flowsheet with intensive reagent regime based on a SMBS-NaCN-ZnSO₄-Na₂S reagent core which exploited the varying preferences of Cu and Zn in relation to pulp potential. Sensitivity of the Cu/Zn separation chemistry also required close control of parameters and reagent dosages. However, given the nature of the ore, Cu/Zn separation was very successfully improved from a -5% recovery separation to a +45% separation.

The possibility to affect cyanide pre-detoxification simultaneous to zinc flotation has been proven to work effectively with Canatuan ore. The effective depression of misplaced Cu and depression of pyrite in the Zn flotation circuit has been proven to work successfully in an environment favourable to cyanide detoxification. The positive potential created by the addition of SMBS and additional oxidation with air during flotation worked well for both zinc flotation and cyanide detoxification. However, the high pH requirement of 11.0-11.5 for effective zinc flotation is in contrast to conventional air/SO₂ process optimum pH.

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