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## **A PULP-CHEMICAL STUDY OF SKARN ORE FEED BLENDS AT THE OK TEDI CONCENTRATOR, PAPUA NEW GUINEA**

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Parallel metallurgical and pulp chemical surveys have been performed at Ok Tedi Mining Ltd (Papua New Guinea) for skarn ore feed blends. Metallurgical results showed a variation in recovery at similar grade, suggesting uniform depression of activated minerals by a precipitate. Significant activation of pyrite was also indicated. This paper highlights results of pulp chemical surveys, which characterise the slurries in terms of oxygen demand (indicating sulfide reactivity) and pulp particle surface coatings. The surface analytical techniques of ethylene diamine tetra acetic acid (EDTA) extraction, X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS) analyses were used to confirm Cu activation of pyrite, and the depression of chalcopyrite by hydroxy precipitates of Ca, Fe, Al and Si.

### INTRODUCTION

The Ok Tedi copper-gold deposit is located at Mt. Fubilan in the Western Province of Papua New Guinea. The ore deposit is a porphyry-skarn intrusive system located within the raised sediments of the Hindenberg ranges in the Star Mountains of Papua New Guinea. Copper mineralisation resulted from the intrusion and alteration of monzonite and monzodiorite porphyry stocks. Subsequent leaching and redeposition of copper minerals resulted in a leached cap of significant gold overlaying a secondary enriched copper ore. Below this was the primary porphyry ore body. The current ore body consists of porphyry ores, which are effectively ringed by skarn ore bodies. The skarn ores exhibit high iron mineralisation, and higher copper and gold content than porphyry ores. The principal copper mineral is chalcopyrite, with minor bornite, chalcocite and covellite. Most gold occurs in association with

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copper, but is also intruded into pyrite systems. The copper-gold mineralisation typically consists of fine-medium-grained (< 100 µm) disseminated sulfides and gold. Table 1.1 shows the average ore processing characteristics at Ok Tedi, based on laboratory flotation tests (Lauder, 1997).

Table 1. Average ore processing characteristics from laboratory flotation database (Lauder, 1997). R.W.I. is the relative work index, and lime consumption was that required to achieve pH 11.5

Ore Type	R.W.I	Lime kg/t	Head Grade			Recovery (%)	
			% Cu	% ASCu	g/t Au	Cu	Au
Monzonite	11.7	1.60	0.96	0.07	0.60	87.6	75.2
Monzodiorite	11.5	2.01	0.57	0.05	0.56	80.2	70.6
Siltstone	14.1	1.94	0.66	0.07	0.53	75.6	61.9
Endoskarn	13.4	2.13	0.73	0.06	0.69	73.5	63.7
Magnetite skarn	10.8	1.86	2.45	0.18	2.72	72.9	64.3
Pyrite skarn	13.3	2.20	2.57	0.22	2.79	60.3	53.7
Calc-Silicate Skarn	13.3	2.40	1.72	0.20	1.97	67.2	61.2
Oxide Skarn	15.1	4.14	1.75	0.81	1.95	22.8	57.8

Ore for the remainder of mine life includes 60% porphyry sulfide-intrusive (0.6% Cu, 0.6g/t Au) and 35% sulfide skarn. The skarn ores represent 50% of copper and gold to mine life. The sulfide skarn includes 6% pyrite skarn, 17% magnetite skarn and 12% endoskarn. Oxide skarn ore is virtually depleted. However, oxide skarn was included in feed blends of reported surveys.

#### THE CONCENTRATOR

The Ok Tedi concentrator is located approximately one kilometre from the mine and consists of two parallel grinding and flotation circuits in mirror image. Modules 1 and 2 process ore at approximately 15 MTPA (2000 tph) per line. Both Modules consist of a SAG mill (13% ball charge of 120mm steel balls) followed by two parallel ball mills (32% load of 50mm steel balls) in closed circuit with ten D26B Krebs cyclones. Cyclone underflows are split to feed two flash flotation cells per ball mill. Flash flotation concentrates are fed to the final cleaner tank cells. Cyclone overflows become rougher feed at approximately 40% solids and P<sub>80</sub> 150-200 microns.

The flotation circuit for each module consists of rougher-scavenger, cleaner, recleaner, column and tank cell. The rougher-scavenger flotation bank consists of 30 Outokumpu OK-38 m<sup>3</sup> cells, in parallel lines of 15. The flash cell concentrates, rougher concentrates from cells 1 to 3, column and recleaner concentrates, are combined to feed the final cleaner tank cell. Concentrate from rougher-scavenger

cells 4 to 9 is fed to the column cell, and concentrate from cells 10 to 15 (scavengers) is fed to the low grade concentrate regrind circuit. The regrind mills use 25mm grinding balls, and have a nominal cyclone overflow  $P_{80}$  of 40 microns.

The nominal rougher feed grades are 0.8% copper and 0.8g/t gold. Cytec S-7249 collector (a mixture of di-isobutyl di-thio phosphate and di-isobutyl mono-thio phosphate) is added (relative to copper in plant feed) to SAG mills at 3-4kg/tonne of Cu and also stage added to scavenger cell 9 tail at 1kg/tonne. Slaked lime is added to SAG feed, and is controlled to a rougher feed pH of 11.5. Approximately 25g/t OTX140 frother (an alcohol - glycol blend) is added to SAG mill feed.

## EXPERIMENTAL

### STRATEGY

Metallurgical surveys of the Ok Tedi concentrator were performed in conjunction with plant pulp chemical surveys. The pulp chemical surveys included 'probe' surveys of plant streams, examining Eh, pH, dissolved oxygen (D.O.) and temperature. Ethylene diamine tetra acetic acid (EDTA) extraction surveys of plant streams were also performed along with pulp solution analysis. The Ian Wark Research Institute (IWRI) performed particle surface analysis of selected stream samples. Particle size distributions and mineral liberation were examined by the IWRI using optical microscopy, and by JK Tech (University of Queensland) using Mineral Liberation Analysis (MLA). For surveyed pulps the feed  $P_{80}$  was shown to vary from 90 to 250  $\mu\text{m}$ . However, copper minerals were liberated in all surveys.

### PULP CHEMICAL SURVEY METHODS EH, PH, D.O. & TEMPERATURE

The Eh is a measure of the mixed potential generated by electrochemical interactions within the mineral pulp. It therefore may indicate the dominant electrochemical process within the pulp. The relative rate of pulp oxidation is expressed by the rate of oxygen consumption (rate of decrease in dissolved oxygen D.O.). Eh also varies in accordance with pulp D.O. levels. Furthermore, the electrochemical oxidation of collectors during adsorption onto value minerals is dependent on D.O., as oxygen reduction occurs during the electrochemical reaction. The optimum Eh for dithiophosphate or xanthate adsorption onto chalcopyrite is approximately 0.2 V SHE (Grano et al., 1991). The pulp pH is a measure of the alkalinity of the solution. All probe measurements were for a period of 2 minutes, and commenced approximately 15 seconds after sampling. Pulp D.O. was measured as % saturation.

### EDTA EXTRACTION OF HYDROLYSED METAL IONS

EDTA (ethylene diamine tetra acetic acid) has been shown to solubilise oxidised metallic species, but not the metal sulfides (Rumball & Richmond, 1996).

Consequently, EDTA extraction followed by ICP analysis may give an indication of oxidation levels in a mineral pulp. The method includes extraction of a 0.01 dm<sup>3</sup> pulp sample, followed by conditioning with 0.09 dm<sup>3</sup>, 3% EDTA (di sodium salt) for five minutes (with nitrogen purging). The sample is then filtered through 0.45 µm milled pore. The filtrate is analysed by ICP, using EDTA standards. Species concentrations are expressed relative to the proportion of that element in the dry weight of the filter cake (Kant, Rao, & Finch, 1994).

#### XPS ANALYSIS

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Physical Electronics X-ray Photoelectron Spectrometer, model 5600. XPS is an analytical technique involving an incident x-ray beam applied to the surface of solid samples. The x-ray photons expel inner shell electrons from surface atoms of the sample. The result is a spectrum of the kinetic energy of emitted electrons (x-axis, expressed as electron binding energy 'B.E.', which is characteristic of an element in a particular oxidation state) and the intensity of the electron beam (which is indicative of surface concentration). Therefore, surface concentrations of, for example, Cu(II) compared to Cu(I) may be ascertained. The penetration of an x-ray photon is considerably greater than that of an ion beam (used in ToF-SIMS). Consequently, XPS measures the oxidation state of elements over a number of atomic layers (approximately 5 to 10). Furthermore, the incident x-ray beam is not highly focused, but irradiates a surface area of approximately 1 cm<sup>2</sup>. Therefore, XPS spectra provide an average measure of the atomic surface concentration and oxidation state of elements in atomic surface layers, with a small penetration of the bulk of the sample. XPS is the only technique, which gives the oxidation state of the elements in surface coatings on solids.

Sample preparation for analysis was according to the method of Smart (St.C. Smart, 1992) and included solution replacement at pulp pH (using NaOH), to remove some ultrafine particles.

#### ToF-SIMS ANALYSIS

Time of flight secondary ion mass spectrometry (ToF-SIMS) analyses were performed using a PHI TRIFT 2100 spectrometer equipped with gallium liquid metal ion gun (LMIG). This instrument allows spectroscopy for characterisation of chemical composition and imaging for mass spectra to be taken from the pre-selected areas (eg. particles). The system uses a pulsed primary ion beam to desorb and ionise species from a sample surface. Damage to the uppermost monolayer is minimised by applying extremely low primary ion fluxes. In order to maintain static conditions, typical analysis time ranged from 4 to 5 minutes with primary ion doses of around 3x10<sup>12</sup> ions per cm<sup>2</sup>.

Sample preparation for analysis was according to the method of Smart (St.C. Smart, 1992). As etching was not included in this work, particle surface coatings may

have been examined in the analyses. Each sample was deposited onto a piece of indium from a water suspension and whilst still wet, introduced into the spectrometer preparation chamber. Prior to analysis the samples were outgassed under vacuum for approximately 12 hours.

The current work required identifying and quantifying individual surface species such as sulfur, copper, collector etc. Because of the surface heterogeneity, the analytical results can differ significantly between particles. Therefore, a sufficiently large number of grains must be analysed to allow detection and exclusion of particles, which are unreasonably different from others in the set (outliers). It also should be noted that SIMS spectral intensities are different for different chemical species/fragments. Therefore, spectra for different chemical fragments may not be compared directly. However, normalised elemental intensities for the same fragment, may be compared between spectra for the same particle type (eg. collector on chalcopyrite in concentrate compared to collector on chalcopyrite in tailing). Because normalisation in ToF-SIMS is relative to the substrate, peak intensities may not be compared directly between different substrates (eg. chalcopyrite compared to pyrite). However, intensity ratios may be used (eg. Cu to S) for comparing proportions of chemical species on different substrates.

## RESULTS AND DISCUSSION

### METALLURGICAL SURVEYS

The concentrator metallurgical balance is a fundamental indicator of plant performance and is therefore the primary reference. If the metallurgical balance suggests inadequate performance of a flotation unit, then pulp chemical data may be used to assist the interpretation of this phenomenon, and to provide a basis for possible remedial action. Metallurgical balances for plant surveys at Ok Tedi on 19/1/00, 15/3/00, 16/3/00, 17/3/00 and 21/3/00 are reported for the rougher-scavenger sections. Copper grade-recovery curves are shown in Figure 1. Comparison is made with 11/12/98 and 30/11/99 surveys because of the improved metallurgical performance shown in those surveys. The 11/12/98 survey was for monzonite/sulfide skarn feed and showed excellent plant performance.

Other data for rougher feed pulps of surveys is shown in the Table of Appendix 1. Figure 2 shows copper selectivity against iron. Flotation recovery by entrainment is approximated in Figure 2 by the average recovery of silicates for the March surveys. It is apparent from Figure 2 that an iron mineral (pyrite) was strongly activated to flotation. The poor copper grades of the 19/1/00 and 15/3/00 surveys were due to increased pyrite flotation. From Appendix 1 (point 3) the Cu:S ratio for rougher feed pulps of surveys are shown. It is apparent that for the survey of 12/11/98, the Cu:S ratio was much higher (at 0.4) than for other surveys. The implication is that there was little pyrite in the feed of the 11/12/98 survey.

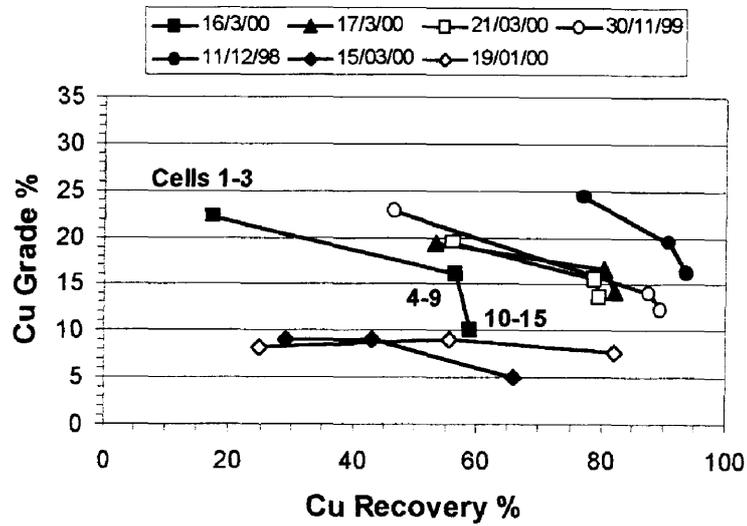


Fig. 1. Copper grade-recovery curves for rougher-scavenger surveys at Ok Tedi

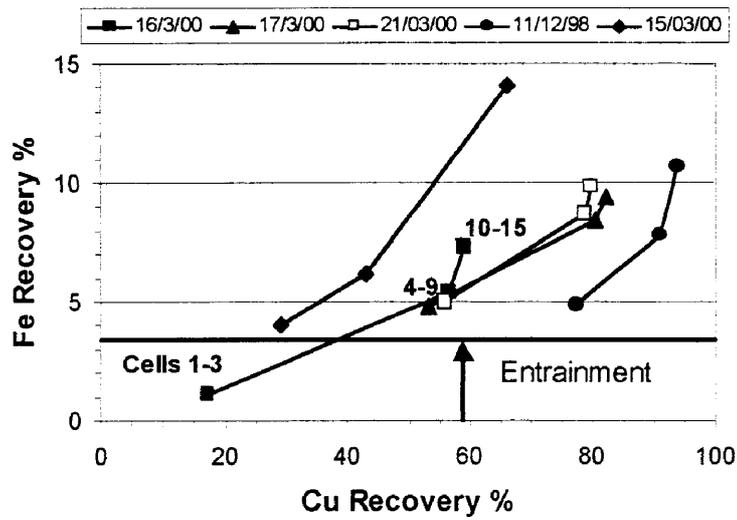


Fig.2. Cu-Fe selectivity curves for rougher-scavenger surveys at Ok Tedi

From Figure 1, it is apparent that the predominant metallurgical effect was a significant variation in chalcopyrite recovery at similar grade to other surveys. This suggests a general depression of all minerals in the Ok Tedi pulp.

From Figures 1 and 2 therefore, it is apparent that two pulp chemical phenomena are effecting a poor flotation performance of skarn blends.

These phenomena are :

1. The depression of chalcopyrite (and other mineral) flotation recovery, and
2. The inadvertent activation of pyrite.

Survey data indicates a correlation between feed tonnage rate (which correlates approximately with grind size) and recovery (see Appendix 1, points 3 and 4). This was despite optical microscopy and MLA analysis indicating liberation of chalcopyrite in all surveys. However, recovery by size analysis indicates significant losses of chalcopyrite in coarse fractions. The implication is that pulp depressant species were limiting the recovery of the more marginally floatable chalcopyrite particles in both the fine and coarse size fractions during the surveys.

#### PULP CHEMICAL SURVEYS

Two different pulp chemical surveys were performed in conjunction with each metallurgical survey. The first involved probe analysis of fresh plant pulp samples for readings of Eh, pH, dissolved oxygen (D.O.) and temperature. Figure 4 shows a selection of D.O. demand curves from the 22 plant streams analysed on survey days during January and March 2000. Some minor variability in results is indicated. However, the significant result is shown in a comparison of the two streams, which have been circled.

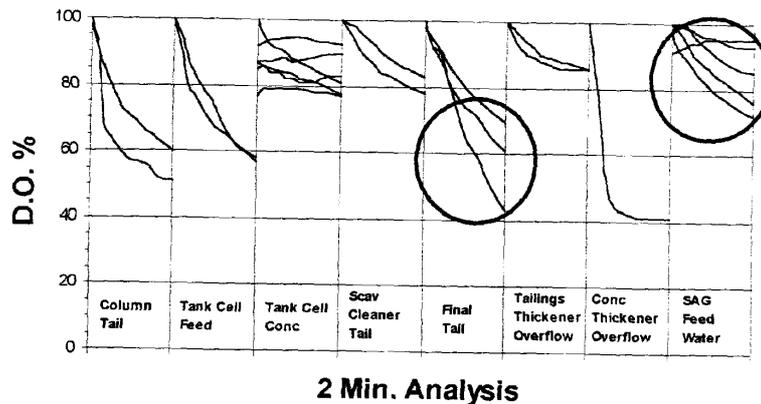


Fig. 3. Dissolved oxygen (D.O.) readings as % saturation taken over two minutes immediately after pulp sampling, during Ok Tedi surveys

Interpretation of the D.O. demand curves shown in Figure 3 is based on a comparison with the D.O. demand curves for water, such as that shown for SAG feed water in the figure. The D.O. demand for water generally shows a decrease in D.O. from saturation (100%) to approximately 80% of saturation over a two minute reading. With this as a 'baseline' curve indicating no significant D.O. demand, it is apparent from a comparison with the final tailing stream of the plant, that the final tailing stream consistently showed significant dissolved oxygen demand during

survey days. This suggests that the sulfide mineral particle surfaces (particularly pyrite) were not electrochemically passivated in the surveyed pulps.

The cessation of sulfide mineral particle oxidation may be caused by a build-up of an insulating surface layer of oxide, a phenomenon referred to as 'electrochemical passivation'. This is particularly important in relation to pyrite flotation. Passivated pyrite has a surface coverage of  $\text{Fe}(\text{OH})_3$ . This is strongly hydrophilic and may counteract any adsorbed hydrophobic species such as collector-activator complexes, limiting its flotation. The implication of the significant D.O. demand of the concentrator tailing streams is that pyrite was not passivated during the surveys, and was therefore more susceptible to activation and flotation.

#### EDTA EXTRACTION AND SOLUTION ANALYSIS

EDTA sampling involved taking a  $0.01 \text{ dm}^3$  syringe sample of pulp, which was conditioned in  $0.09 \text{ dm}^3$  excess EDTA solution. The remainder of the pulp sample was filtered for water analysis. Concentration in the solution phase is then analyzed by ICP. EDTA extractable cations are expressed as a percentage of the same element in the conditioned solids (eg. % EDTA Cu). Table 2 shows a comparison of average % EDTA Cu for rougher feed pulps of Mount Isa Mines Copper, Northparks Mines, and Ok Tedi. It is apparent from Table 2 that Ok Tedi surveyed pulps contained significantly higher concentrations of oxide copper. This suggests significant sulfide oxidation, and therefore, of acidity of the ore feed, along with potential for pyrite activation.

The difference between EDTA extractable cations, and cations in solution in the absence of EDTA, is a measure of the precipitation onto particle surfaces within the pulp. This precipitation may be a result of pulp oxidation and dissolution into the solution phase, followed by random precipitation onto particle surfaces. Alternatively, precipitation may be a result of surface oxidation of mineral particles and precipitation at the surface of those particles. This second type of precipitation is more mineral specific.

Table. 2. A comparison of rougher feed % EDTA Cu for three chalcopyrite concentrators

Concentrator	EDTA Cu, %
Mount Isa Mines	0.02
Northparks Mines	0.65
Ok Tedi Mining	4.50

Both cations and anions are included in the analysis of EDTA liquors. Anion concentrations may also increase in the solution phase when EDTA solubilizes the cation. This gives an indication of the type of precipitated salts that were present in the pulp. An example of the EDTA extractable cation data from surveys is shown for copper, in Figure 4. Sample points from pulp streams for Figure 4 are shown in Table 3.

Table 3. Sample points for Figure 4

Sample Number	Plant Stream	Sample Number	Plant Stream
1	SAG Discharge Screen U/S	12	Rou-Scav Cells 10-15 Concentrate
2	Ball Mill Discharge	13	Rou-Scav Cell 15 Tail
3	Primary Cyclone O/F	14	Final Tail
4	Flash Cell Concentrate	15	Scavenger-Cleaner Tail
5	Rougher Feed	16	Low Grade Regrind Discharge
6	Rougher Cell 1 Concentrate	17	Low Grade Regrind Cyclone O/F
7	Rougher Cell 1 Tail	18	Column Cell Tail
8	Rougher Cells 2-3 Concentrate	19	Tank Cell Feed
9	Rougher Cell 3 Tail	20	Tank Cell Concentrate
10	Rougher Cells 4-9 Concentrate	21	Tank Cell Tail
11	Rougher Cell 9 Tail		

Increased % EDTA Cu in tailings streams compared to preceding concentrate streams in Figure 4, suggests that  $\text{Cu}(\text{OH})_2$  is depressing chalcopyrite. This assumes that the majority of  $\text{Cu}(\text{OH})_2$  is associated with chalcopyrite surfaces (which was suggested by higher PPM values for concentrates of 19/1/00). This suggests that  $\text{Cu}(\text{OH})_2$  may be functioning as a flotation depressant in the pulp. However, the very high % EDTA Cu for tailings streams of the 23/3/00 survey (45% EDTA Cu) does not imply that 45% of the chalcopyrite particles in the tailing were oxide. Rather, the implication is that a significant quantity of the  $\text{Cu}(\text{OH})_2$  in this pulp was dispersed, being precipitated onto much more than just chalcopyrite surfaces. Significant surface exposure of  $\text{Cu}(\text{OH})_2$  was also indicated in the XPS analysis of rougher feed samples, shown below in Figure 6.

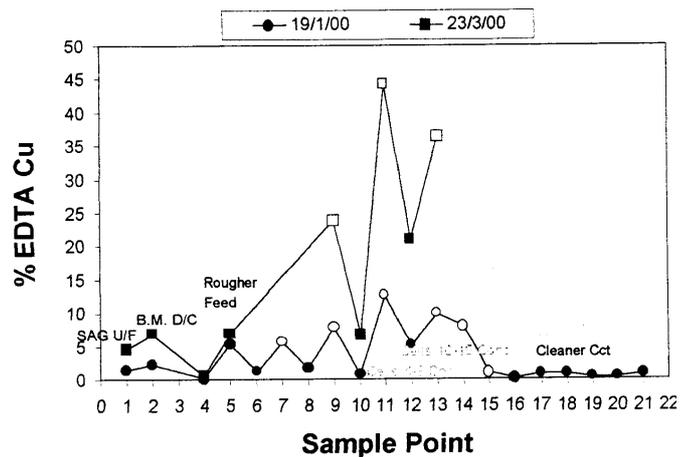


Fig. 4. Examples of EDTA extraction surveys, showing % EDTA Cu for plant streams. Tailings streams are shown in white

From EDTA and solution analysis, it was apparent that all  $\text{Cu}(\text{OH})_2$  was precipitated in the survey pulps. Approximately 80% of all EDTA extractable Ca was also precipitated. Sulphate levels in extracted solutions correlated approximately with Cu. However, for thermodynamic reasons, sulfate and calcium will have combined to form gypsum. However, there was approximately 10 times more EDTA extractable Ca in the pulps on average, compared to Cu,  $\text{SO}_4$  or Fe, which were the other predominant oxide precipitates. Furthermore, concentration values for Ca were double for tailings samples, compared to the preceding concentrates. EDTA analysis therefore indicated Ca as a significant depressant of chalcopyrite flotation in surveyed pulps. During the time of the plant surveys, lime consumption was not recorded at Ok Tedi. However, it is known that lime usage increases with acidity of the feed ore (cf. Table 1) and varies from 2 to 5kg/t of feed ore. It may be noted that the natural pH of some of the feeds surveyed was approximately pH 4. A correlation between oxide skarn percentage in the feed blends and Ca levels in the pulp was found for surveyed pulps (see Appendix 1). However, insufficient data was available to show a correlation between Ca precipitation and decreased chalcopyrite recovery.

#### XPS ANALYSIS

XPS analysis was performed on rougher feed samples from Ok Tedi surveys of 17/1/00 and 19/1/00, and are shown in Figure 5. In both instances the plant flotation performance was poor (cf. Figure 1). Daily blend data (Appendix 1) shows a contribution of oxide copper from oxide skarn and sulfide skarn (magnetite) on 17/1/00. On the 19/1/00, the blend included 84% sulfide skarn (Magnetite) and 16% Endoskarn. On the 19/1/00, the feed acid soluble copper (ASCu) was 0.34%, which was the second highest ASCu value for all surveys (only 15/3/00 was worse, with 0.41%). EDTA analysis was also performed for 19/1/00 and showed 5.2% EDTA extractable Cu at rougher feed, which was comparable to March surveys using different ore blends (3.9 to 6.8% EDTA Cu in March).

XPS analysis confirmed the considerable surface exposure of Cu(II), which represents  $\text{Cu}(\text{OH})_2$  precipitation within the pulp, compared with Cu(I) which is found in  $\text{CuFeS}_2$  and other copper sulfides. Figure 5 includes a spectrum for an MIM Cu chalcopyrite pulp (scavenger concentrate). This spectrum provides a comparison with an unoxidised chalcopyrite pulp, and highlights differences in the more oxidized Ok Tedi skarn ore feed. The spectra are charge corrected, based on charge shifting of  $\text{C}_{1s}$  peaks.

Figure 5 shows the spectral region for  $\text{Cu}_{2p}$  electron binding energies. The  $\text{Cu}_{2p}$  photoelectron spectrum includes two major peaks for the two spin states of the  $\text{Cu}_{2p}$  electrons. The major peak is for the  $\text{Cu}_{2p_{3/2}}$  electron and has a binding energy of 932.4 eV. The second peak is situated at a further 19.8 eV, for the  $\text{Cu}_{2p_{1/2}}$  electron. The Ok Tedi  $\text{Cu}_{2p}$  spectra show some differences to that of MIM Cu. As well as the two Cu peaks, a broad peak occurs between approximately 962 to 964 eV. This peak is an Auger peak for Ca, with a binding energy of 961.6 eV. This indicates the presence of

calcium precipitates from lime. In the Cu spectra, a broadening of the primary  $\text{Cu}_{2p}$  peak, and a broad multiple peak at slightly higher binding energy (known as 'satellites') are indicative of the presence of Cu(II). That is,  $\text{Cu}(\text{OH})_2$ , was present in significant quantities on the surfaces of particles in Ok Tedi rougher feed magnetite skarn pulp, relative to Cu(I). Cu(I) was present as a component of Cu sulfides and possibly as adsorbed Cu on pyrite surfaces if the adsorption process occurred during grinding. A deconvolution of the major peak and satellites was performed (not shown). This indicated that on 17/1/00 and 19/1/00, on average approximately half of the Cu exposure was  $\text{Cu}(\text{OH})_2$ . However, it should be noted that copper in the feed was only 2.6%, suggesting a relatively small proportion of the feed was  $\text{Cu}(\text{OH})_2$  precipitates. This was considerably less than the dispersion of other depressants such as Ca (cf. EDTA analysis).

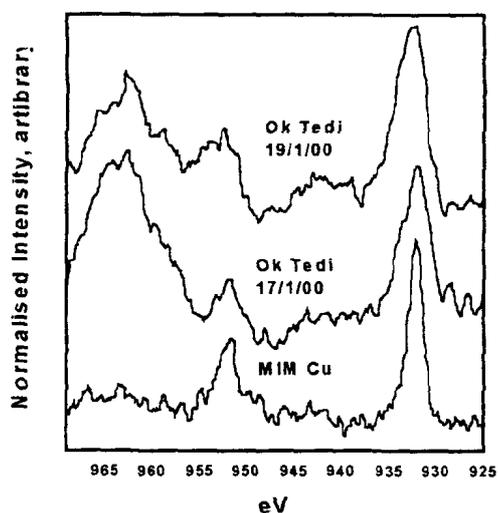


Fig. 5. XPS  $\text{Cu}_{2p}$  spectra for Ok Tedi rougher feed compared to MIM Cu

#### ToF-SIMS ANALYSIS

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analyses were performed on final concentrate (tank cell) and final tailing samples from the 16/3/00 survey. Included in Figures 6 to 9 is a statistical analysis of 58 Cu sulfide particles and 58 pyrite particles. 30 Cu sulfide and 24 pyrite were analysed in the final tailing, and 28 Cu sulfide and 34 pyrite in the final concentrate. The normalised intensities for each surface species of interest have been averaged over the total number of particles of that type in the stream. Standard deviations were also calculated along with 95% confidence intervals for the normalised intensities, using 't' tests.

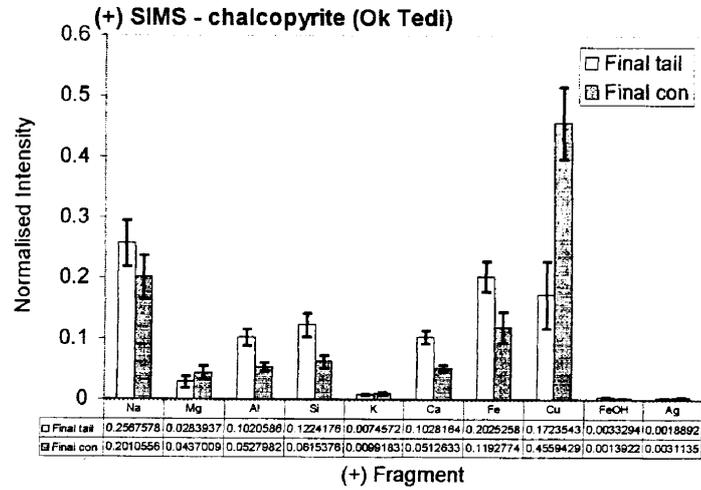


Fig. 6. (+) SIMS. Ok Tedi. Mass spectra for chalcopyrite in the final tail and final concentrate (confidence intervals calculated for P=95%)

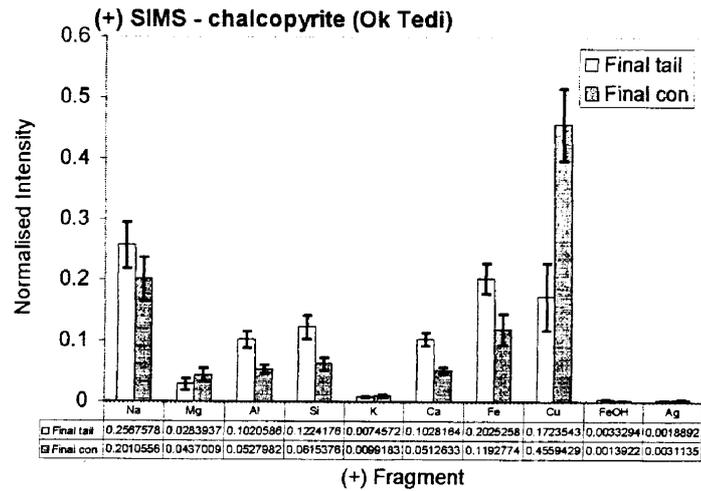


Fig. 7. (+) SIMS. Ok Tedi. Mass spectra for pyrite in the final tail and final concentrate (confidence intervals calculated for P=95%)

Statistically significant data are obtained from the averages of normalised intensities (shown in Figures 6 to 9), also from ratios of normalised intensities, and from a 'hydrophobicity index'. The hydrophobicity index has been a recent development at the IWRI and is proving a valuable tool in the interpretation of particle floatability (giving reason for particle location in a concentrate or tailing stream). The hydrophobicity index is a ratio of averaged normalised intensities for fragments representing hydrophobic surface species (CH and S, but not sulfate), and averaged normalised intensities for fragments representing hydrophilic surface

species (O and OH). The relative surface concentrations of these hydrophobic and hydrophilic indicators for the two samples analysed were calculated (each species is expressed as a proportion of total CH, S, O and OH). Expressed as ternary diagrams, the hydrophobicity index (not shown) clearly indicated that the balance between collector adsorption and oxidation products on particle surfaces was the primary determinant in particle floatability and hence recovery to concentrate. This confirmed the results of EDTA analysis, which indicated oxide precipitates were concentrated in tailing stream samples.

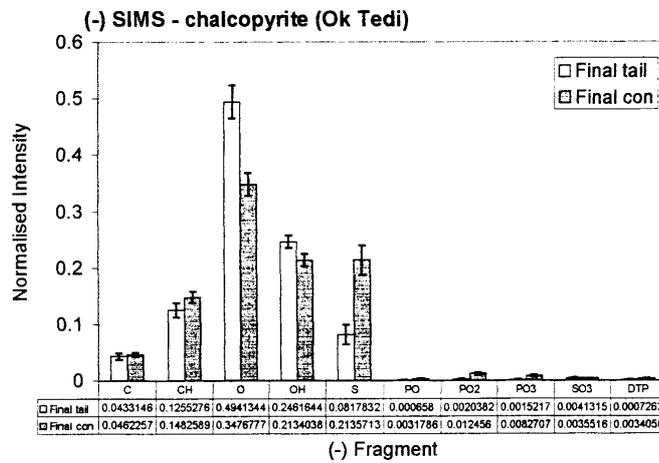


Fig. 8. (-) SIMS. Ok Tedi. Mass spectra for chalcopyrite in the final tail and final concentrate (confidence intervals calculated for P=95%)

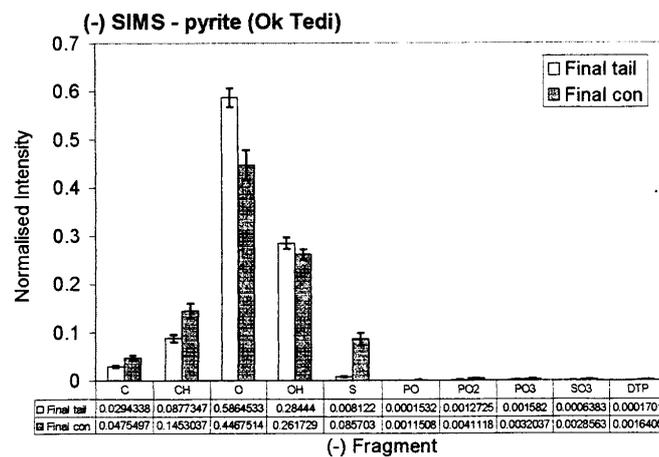


Fig. 9. (-) SIMS. Ok Tedi. Mass spectra for pyrite in the final tail and final concentrate (confidence intervals calculated for P=95%)

ToF-SIMS normalised intensities give no indication of surface concentration. Therefore, data interpretation is based on comparisons. From the analysis of chalcopyrite particles in Figure 6, Ca and Fe along with Al and Si were shown to be more prevalent on tailings chalcopyrite particle surfaces compared to concentrate particles. All of these species showed approximately double the intensity on the final tailing chalcopyrite compared to the final concentrate.

On pyrite particles however (Figure 7), the increased normalised intensity for depressant species on tailings particles was 1.4 times for Ca, 1.1 times for Fe and 1.6 times for Al and Si. These ratios for pyrite differed to chalcopyrite, and suggest that these surface adsorbed species affected the pyrite and chalcopyrite hydrophobic/hydrophilic balance to different extents. Because chalcopyrite interacts with collector more strongly than pyrite (and will have very hydrophobic surface regions), it is probable that a higher surface concentration of hydrophilic precipitates was required to depress chalcopyrite particles, compared to pyrite. The greater surface concentration of calcium on final tailings chalcopyrite (and pyrite) compared to concentrate, confirmed EDTA extraction analysis, which indicated similar trends.

Another phenomenon indicated in the analysis of pyrite particles (Figure 7), was that Cu species had adsorbed onto pyrite particle surfaces, resulting in pyrite activation. The normalised intensity for Cu on pyrite in the concentrate was 7.3 times greater than for Cu on pyrite in the tailing (Figure 7). From Figure 9, the intensity of the 'CH' fragment on pyrite (collector) was 1.6 times greater on the concentrate compared to the tailing. This compares to 2.0 times the intensity for phosphate, also a collector fragment. This suggests that some adsorbed Cu on pyrite (possibly as Cu(I) sulfide), interacted with dithio phosphate collector. Copper and collector adsorption were therefore the most significant contributing factors to the flotation behaviour of pyrite in surveyed skarn pulps at Ok Tedi.

Physisorbed Cu(II) as hydrophilic  $\text{Cu}(\text{OH})_2$  may also have been present on the pyrite surface. However, no indication of a general depression of flotation by  $\text{Cu}(\text{OH})_2$  was observable from ToF-SIMS analysis, due to the dominance of the activating effect of Cu in conjunction with dithio phosphate collector.

## SUMMARY AND CONCLUSIONS

A comparison of rougher-scavenger copper grade-recovery curves from metallurgical surveys of skarn feed blends at Ok Tedi, has indicated a variation in copper recovery with similar copper grade. This suggested a general depression of chalcopyrite and activated pyrite in the surveyed skarn pulps. Significant pyrite activation was shown. Feed tonnage (and by inference feed P80) was shown to correlate with decreased copper recovery. However, mineralogical analysis indicated adequate chalcopyrite liberation in all size fractions. Recovery by size analysis however, has indicated a depression of marginally floatable, liberated chalcopyrite in fine and coarse size fractions.

Pulp chemical surveys indicated dissolved oxygen (D.O.) demand was significant in concentrator pulps, and that pyrite surfaces were therefore not passivated as  $\text{Fe}(\text{OH})_3$ . This implied that Cu activation and collector adsorption would have been enhanced on pulp pyrite surfaces. EDTA extraction analysis suggested  $\text{Cu}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  were flotation depressants in surveyed pulps. XPS analysis confirmed the presence of  $\text{Cu}(\text{OH})_2$  precipitates in rougher feed pulps. ToF-SIMS analysis, unequivocally showed that the significant pyrite flotation in surveyed pulps was due to the activation of pyrite by copper and collector. The so-called 'hydrophobicity index' of ToF-SIMS analysis indicated that ratio of oxy-hydroxide precipitates to collector on particle surfaces, determined the division of chalcopyrite particles between concentrate and tailings. ToF-SIMS analysis identified Ca, Fe, Al and Si as depressants of both chalcopyrite and pyrite. ToF-SIMS was technically unable to identify  $\text{Cu}(\text{OH})_2$  on activated particles.

At present, insufficient data is available to indicate any clear correlation between the identified pulp chemical depressant species and decreased chalcopyrite recovery in Ok Tedi skarn blend pulps. It is apparent that finer grinding, along with limitation of the acidic components of the feed blend, may result in improved recovery of chalcopyrite for skarn ore feed blends at Ok Tedi.

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## APPENDIX 1

## Data from Metallurgical and Pulp-Chemical Surveys

Date	18/1/00		13/3/00		15/3/00		17/3/00		19/3/00		21/3/00		11/12/98		30/11/99			
	17/1/00	19/1/00	14/3/00	16/3/00	18/3/00	20/3/00	10/12/98	29/11/99										
1	Feed	Cu %	2.61	0.81	0.74	0.97			1.45	2.59	1.50							
		Au g/t		0.80	0.62	0.72			0.86	2.47	1.28							
		S %		3.88	3.68	3.47			15.70	6.41								
		Fe %		13.30	12.27	13.28			21.03	47.89								
		SiO <sub>2</sub> %		46.80	49.39	47.21			34.08									
2	Cu:S	Ratio		0.21	0.20	0.28			0.09	0.40								
3	Ro-Scav	Rec.	82	66	60	82			80	94	90							
4	Module Feed	tph	1102			2074	742			1698	917	1079						
5	Monzonite (MP)	%		18.20	37.10	29.90	58.20	29.30	12.30	44.50	50.20	55.40	37.80	35.80	23.40			
		Cu %		0.28	0.62	0.69	0.70	0.52	0.52	0.50	0.52	0.68	0.82	0.60	0.68			
	Acid Sol	Cu %		0.02	0.05	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.06	0.04	0.02			
	Monxodiorite (MD)	%		0.20	47.50	8.10	40.00	53.80	57.70	28.30	2.40		3.30	5.30				
		Cu %		0.50	0.50	0.47	0.38	0.38	0.38	0.38	0.38		0.53	0.57				
	Acid Sol	Cu %		0.03	0.03	0.03	0.03	0.03	0.03	0.03		0.02	0.02					
	Pyrite	Skn %												31.70	2.20			
		Cu %												2.00	0.76			
	Acid Sol	Cu %												0.24	0.08			
	Sulfide	Skn %	98.60	100	68.20	2.60	12.80	16.40	0.20	12.80	12.00	24.40	45.20	35.40	100	58.90	32.50	66.80
		Cu %				1.02	0.99	2.77	3.90	0.80	3.90	2.47	1.97	1.94	1.86	1.86	1.96	2.00
	Acid Sol	Cu %	0.18	0.17	0.15	0.06	0.11	0.25	0.34	0.10	0.34	0.24	0.14	0.16	0.16	0.16	0.18	0.21
	Endoskarn	%		31.80	64.60					1.50								
		Cu %			0.88					1.52								
	Acid Sol	Cu %		0.09	0.05					0.10								
	Siltstone (SLT)	%				32.30												
		Cu %				0.98												
	Acid Sol	Cu %				0.06												
	Oxide	Skn %	1.40		14.80	2.70	13.30	1.60	4.10	16.50	2.80	2.00	9.20					2.20
		Cu %			1.13	3.21	3.21	1.81	3.21	2.43	2.73	3.21	1.45					0.30
	Acid Sol	Cu %	2.13		2.13	2.13	2.13	2.13	1.54	2.13	2.13	0.89						0.02
6	Blend	ASCu %	0.21	0.17	0.13	0.35	0.10	0.35	0.06	0.12	0.32	0.14	0.12	0.15	0.16	0.12	0.15	0.15
	2 day average				0.15		0.23	0.21	0.09				0.13		0.14		0.15	
7	Plant daily	ASCu %			0.34		0.41	0.25	0.06				0.18		0.25		0.08	
	Plant daily	Cu %			2.24		1.05	1.08	0.63				1.05		2.80		1.08	
8	EDTA Ex. Ro-Feed																	
	PPM	Cu			478		468.9	119.2				235.5						
	PPM	Fe			645		244.9	1026			488							
	PPM	S			343		209.5	148.1			260.6							
	PPM	Ca			3060		7442	4472			9353							

Putubu K.J., Morey S.M., Grano R.S., *Ocena oddziaływań chemicznych w zawiesinie flotacyjnej skarnowych rud w zakładzie wzbogacania Ok Tedi, Papua Nowa Gwinea*, Fizykochemiczne Problemy Mineralurgii, 35, 2001, 125-140 (jęz. ang.)

Dokonano równoległej oceny metalurgicznej i chemicznej mieszanki rud typu skarnowego w Ok. Tedi Mining Ltd. (Papua Nowa Gwinea). Wyniki metalurgiczne wskazują na zmienność uzysków przy zbliżonych zawartościach metalu w koncentratkach, co wskazywałoby na jednakową depresję aktywowanych we flotacji minerałów. Przedmiotem artykułu jest ocena oddziaływań chemicznych w zawiesinie flotacyjnej w świetle zapotrzebowania na tlen decydujących o reaktywności minerałów siarczkowych. Badania powierzchniowe w oparciu o ekstrakcję przy użyciu kwasu wersenowego (EDTA), rentgenowskiej spektroskopii elektronowej oraz jonowej spektrometrii masowej (ToF-SIMS) potwierdziły aktywowanie pirytu miedzią oraz depresję chalkopirytu przez wytrącone wodorotlenki Ca, Fe, Al. i Si.