

The development of statistical ToF-SIMS applied to minerals recovery by froth flotation

Roger St. C. Smart,^{a,b,*}  Andrea R. Gerson,^b Mark C. Biesinger^c 
and Brian R. Hart^c

The role of surface chemistry in recovery of minerals is central to several processes such as froth flotation, leaching, and electrostatic separation. In separation of base metals (eg, Cu, Pb, Zn, and Ni) by froth flotation of their minerals, usually sulphides, the attachment of these mineral particles, after hydrophobic collector addition, to air bubbles is used in operation. The stability of this bubble/particle attachment in both pulp and froth phases is dependent on the hydrophobic/hydrophilic ratio of surface species on individual mineral particle surfaces. The surfaces of individual mineral particles are a complex, distinctly non-uniform array of hydrophobic collector molecules and hydrophilic species (eg, oxidation products, adsorbed ions, fine particles, and precipitates). Hence, this ratio varies widely between different particles of the same mineral. It has been shown to determine whether particles report, correctly or incorrectly, to concentrate or tail (residue). To improve poor flotation recovery or grade, the analysis needed is the variation of this ratio by particle and as a statistical distribution between different mineral phases across a flotation circuit (eg, feed, successive concentrates, and tails). This requires surface analysis of a large number of particles with high spatial resolution and chemical speciation. In this Surface Science Western special issue article, methods to achieve this, using time-of-flight secondary ion mass spectrometry and principal component analysis, developed between the Ian Wark Research Institute and Surface Science Western over 25 years are reviewed with applications to flotation. They are equally applicable to interferences in leaching, extraction, and electrostatic separation processes. Copyright © 2017 John Wiley & Sons, Ltd.

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The role of surface analysis in minerals processing

The chemistry of surface species on different mineral particles can define the efficiency of their separation in processing by froth flotation, leaching, chemical extraction, or electrostatic separation. This chemistry can be changed, advantageously or deleteriously, by many factors including chemical alteration of the surface layers of the minerals induced by reactions in air or pulp solution; galvanic interactions; attachment of colloidal precipitates, aggregates, and flocs arising from dissolution of minerals and grinding media; the adsorption of reagents to specific surface sites; and competitive adsorption between mineral reaction (particularly oxidation) products and flotation reagents (eg, conditioners and collectors), or leaching and extractant reagents.

In separation of base metals (eg, Cu, Pb, Zn, Ni, and Sn) by froth flotation of their value minerals, usually sulphides, the attachment of a hydrophobic collector-conditioned mineral particle to an air bubble and the stability of this bubble/particle attachment in both pulp and froth phases is dependent on the hydrophobic/hydrophilic ratio of surface species on individual mineral particle surfaces.^[1] If this ratio is too low for the value mineral particles, recovery will be low and flotation kinetics too slow. In reality, the surface of each individual sulphide mineral particle in flotation is a complex, distinctly non-uniform array of hydrophobic collector molecules and precipitates competing with hydrophilic oxidation products (ie, oxyhydroxides and sulfoxy species), adsorbed ions, precipitates, and attached fine and ultra-fine particles of other mineral phases.^[2] Hence, this ratio varies widely between different particles of the same mineral. Some

nonvalue (gangue) mineral phases may also have adsorbed hydrophobic collector from solution in metal precipitate form (eg, Cu-xanthate) giving inadvertent metal ion activation (as in copper ions activating pyrite and silicate flotation)^[2] contributing to gangue recovery and lower grades.

This hydrophobic/hydrophilic ratio may seem an esoteric measure to plant operators, but this has been shown^[3] to determine whether particles of both value and gangue report, correctly or incorrectly, to concentrate and tail. To understand and improve poor flotation recovery and/or grade, it is first necessary to separate whether this is being caused by primary preparation of the feed, poor hydrophobic/hydrophilic conditioning of the value mineral surfaces, or inadvertent hydrophobic conditioning of gangue minerals. Primary preparation would include initial analysis of any limitations in mineral liberation by grinding, particle size distributions, flotation cell parameters (eg, gas flow/hold-up and sparger/bubble size), pulp density, reagent addition and mixing, pH/Eh, and other parameters in models of

* Correspondence to: Roger St. C. Smart, Minerals Science and Technology, School of Natural and Built Environments, University of South Australia, Mawson Lakes, SA 5095, Australia.
E-mail: roger.smart@unisa.edu.au

a Minerals Science and Technology, School of Natural and Built Environments, University of South Australia, Mawson Lakes, SA, 5095, Australia

b Blue Minerals Consultancy, Middleton, SA, 5213, Australia

c Surface Science Western, University of Western Ontario, 999 Collipe Circle, LL31 (Lower), London, ON, N6G 0J3, Canada

flotation control, eg, Ralston et al.^[4] Surface analysis for problems in control of flotation performance is normally only done after the more primary control factors have been considered and failed to improve the flotation sufficiently.

To understand and improve poor flotation recovery, where it is due to surface chemistry, we need to know the variation of hydrophobic (flotation) and hydrophilic (dispersed) species on different particles of the same mineral phase and as a statistical distribution between different mineral phases across a flotation circuit from feed to (collected) concentrates and (rejected) tails that we need to know. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) can analyse detailed differences in surface chemistry by mineral phase across a flotation circuit. It is then possible to define the reasons for the unacceptable performance before useful changes can be made to mechanical or chemical conditioning to change the surface species and surface layers.

These techniques are equally applicable to recovery of metals from minerals by hydrometallurgical processes such as leaching, where leach kinetics and selectivity can be cost limiting, and rate-determining surface species and surface layers evolving during leaching may limit access of reactants to the surface and of reaction products to the solution. The limiting actions of complexants, oxidation products, fine gangue interference, precipitates as colloidal products, and thick surface layers (amorphous and crystalline) need to be defined in these systems before the subprocesses requiring change can be usefully addressed, eg, Weisener et al.^[5,6] However, statistical ToF-SIMS analysis has not yet been extensively used or developed in application to acid leaching, uranium and gold extraction, and electrostatic separation in heavy mineral separation where it may be valuable in defining these interferences.

The majority of the development and applications using ToF-SIMS analysis in minerals processing have been flotation related. The parallel development and application of ToF-LIMS, combining laser ionisation of small samples with time-of-flight mass spectrometry, by Chryssoulis and colleagues, reviewed in Smart et al,^[7] is also acknowledged. This paper will review the development of ToF-SIMS measurements, their current applications, and future prospects.

The requirement for statistical analysis of surface species

The analysis needed is the variation of hydrophobic/hydrophilic species on particles of a mineral phase and as a statistical distribution between different mineral phases across a flotation circuit (eg, feed, successive concentrates, and tails). This requires surface analysis of a large number of particles with high spatial resolution and chemical speciation. Analyses of a few individual larger particles carries the risk that they may not be representative of the surface chemistry that is causing low value recovery or interfering gangue flotation.

Until the development of direct surface analytical methods, studies of the actions of collectors, activators, depressants, and other chemical reagents used in the flotation process were largely based on indirect methods such as adsorption from solution and changes in average macroparameters including contact angle, zeta potential, and electrochemical methods mostly in idealised systems under laboratory conditions. The introduction of surface-specific techniques of XPS, SAM, FTIR, AFM, and STM to studies of single minerals and laboratory flotation systems reviewed previously^[2]

gave much more insight to the factors affecting recovery and grade. Most of the hydrophobic, including both reagent and reaction (eg, polysulfide) products, and hydrophilic species affecting flotation were defined in these studies. But the development of ToF-LIMS and ToF-SIMS, in particular, has provided the statistical basis for identification of surface species determining the hydrophobic/hydrophilic ratio and interfering with flotation performance. These techniques, together with mineral structure techniques, and the information they have given on the behaviour of different minerals in the flotation process have been extensively reviewed in the SME Centenary of Flotation volume.^[7] In this review paper, we will focus on ToF-SIMS because it is now the most advanced technique for this statistical analysis.

This technique can rapidly, statistically analyse detailed differences in surface chemistry by mineral phase across a flotation circuit to identify the location and extent of a problem (such as inadvertent activation, galvanic interactions, poor selectivity, and hydrophilic coatings) in operating plants. Its unique advantages are in being able to analyse the first few molecular layers on a mineral surface for both chemical species (eg, oxidation products, reagent adsorption, and surface layer formation) and spatial distribution (<0.1 μm). The 3 main forms of information from this technique are selection of mineral particles and their distribution by imaging for specific mineral-identification elements; statistical analysis of hydrophobic and hydrophilic species by comparison of intensities from selected mineral particles between feed, concentrates, and tails; and full statistical analysis by principal component analysis (PCA) of all species on particular mineral phases. This type of surface analysis can now be conducted with samples from operating mineral processing plants.

Brief history of development

Some examples of the first use of ToF-SIMS help to explain the current development. Early studies by Brinen and co-workers at Cytec^[8,9] and by Chryssoulis and his AMTEL group (eg, Stowe et al^[10] and Chryssoulis et al^[11]) confirmed that this technique can identify parent and fragment ions from collectors and map their distribution on single mineral grains. Brinen and co-workers^[9] found the distribution of dithiophosphinate collector on galena particle surfaces to be distinctly non-uniform, an important observation in understanding the mechanisms of bubble-particle attachment. Collector adsorption is generally not found to be in uniform monolayers but in hydrophobic patches on sulphide mineral surfaces. Chryssoulis et al^[11] showed that sphalerite particles lost to scavenger tails have less amyloxanthate and isobutyloxanthate collectors compared to sphalerite recovered to the zinc final concentrate confirming the ability of the ToF-SIMS to discriminate surface chemical species between flotation streams. Xanthates were detected on the surface of sphalerite particles inadvertently recovered into a copper/lead final concentrate. Time-of-flight SIMS was also used by Chryssoulis and colleagues^[11] to image a mixture of amyldithiophosphate and amyloxanthate on laboratory-treated mineral surfaces. The distribution of these reagents was again distinctly non-uniform between minerals. Carboxymethyl cellulose (CMC), commonly used as a depressant for talc-like gangue minerals, studied in the imaging mode using CMC fragments by Parolis et al,^[12] showed that CMC coverage of the talc particles was homogeneous after initial adsorption. Subsequent desorption in distilled water and partially restored floatability could be related

to an inhomogeneous CMC distribution on the talc surface. Addition of Ca^{2+} ions re-established homogeneous CMC redistribution and depressant action.

Hence, procedures to provide a statistical analysis basis to define differences in collectors and other species between different mineral phases and between different flotation streams were required.

Sample preparation requirements in application

Time-of-flight SIMS is an ex situ analysis technique. It is therefore essential that the sample is introduced to the spectrometer with the surface chemistry as close as possible to that in the flotation cell or operating plant at the time of sampling. This requires that the sample is representative of the flotation stream, does not oxidise or react in the tube (i.e. frozen) after sampling, and that these conditions are maintained until delivery to the spectrometer. Protocols for these requirements have been developed^[13] and verified by correlation with flotation response over more than 2 decades.

Calibration, quality control, and processing response

Calibration standards to identify single and molecular ion fragments have been recorded for all the main sulphide and gangue minerals (synthetic and natural), collectors, pH modifiers, activators, and depressants so that files of characteristic ions can be selected from the myriad (up to 1000) recorded in a mass scan. This is essential for statistical and PCA analysis modes to focus on the discriminating species.

The ultimate quality control is, however, in the correlation of the ToF-SIMS findings on surface species causing good or poor flotation with the flotation recovery and selectivity response. The technique has now been applied to both operating plant and lab float samples over more than 20 years. The main application and validation has been in first diagnosing surface species inhibiting recovery or selectivity, and then recommending changes to reagents and/or operating conditions to reduce this interference. In this mode, ToF-SIMS analyses have produced relatively straightforward, practical recommendations for many plants. Time-of-flight SIMS analysis in these modes to identify surface chemical reasons for losses in recovery or selectivity at SSW, IWRI, and the University of South Australia has now been applied to samples from operating plants including Mount Isa Mines (MIM), BHP Billiton Cannington Operation, Ok Tedi Mining Ltd. (Papua New Guinea), Cominco Red Dog Alaska Mine, Falconbridge (Strathcona, Canada), Anglo Platinum (South Africa), Mineracao Caraiiba (Brazil), Inco Matte Concentrator (Sudbury, Ontario, Canada), and Kennecott Utah Copper (KUC). Many other results from analyses by others on samples from other plants have not been published for commercial protection. There are many potential control factors, discussed in the last section, to address the identified limitation.

We will now turn to development and examples of ToF-SIMS analysis in statistical modes that have provided the information for these process changes.

Statistical comparisons by mineral phase

A method developed at the Ian Wark Research Institute first provided a statistical comparison of differences in surface species between feed, successive concentrates, and tails streams by mineral phase.^[14] Imaging for specific signals and combinations of signals (eg, Pb, Zn, Cu, Fe, and Ni) is used to identify the particles of a specific mineral phase (eg, galena, sphalerite, covellite, chalcopyrite, pyrite, and pentlandite) for specific analysis. Sufficient particles of each mineral phase are selected for reliable statistics and the full mass spectrum from each bounded particle recorded and stored. The statistical analysis^[14] then determines a mean value for each atomic and molecular species with 95% confidence intervals for each signal. This analysis was first applied to the effects of calcium ion depression on a laboratory galena flotation^[14] using collector adsorption of both isobutyl xanthate (IBX) and diisobutyl dithiophosphate (DBPhos). Linear regression and mean analyses of surface species on galena particles in the first concentrate and tail (26 particle sets) were used to estimate normalised hydrophobic (eg, $\text{IBX}^-/\text{SO}_3^-$ and $\text{DBPhos}^-/\text{SO}_3^-$) and hydrophilic (eg, Ca/Pb , Al/Pb , PbOH/Pb , and $\text{SO}_3^-/\text{S}_2^-$) indices. The results correlated closely with the flotation response. Hydrophilic species indices such as calcium (approximately 200%), but also aluminium and metal hydroxides, were statistically higher on tail than on concentrate particle surfaces. The method suggested that it was possible to quantitatively assess conditioning of sulphide surfaces for optimum selectivity. A second statistical study^[11] of the effect of iron hydroxide oxidation products and collector, IBX, on galena and pyrite flotation separation at pH 9 confirmed a clear separation of IBX normalised intensities with galena in concentrate 5 ± 1.5 times higher than those in feed or and tail. A hydrophobicity/hydrophilicity index, based on a ratio of signals from the hydrophobic collector (IBX) to ions from hydrophilic sulfoxy products (SO_3) and iron hydroxide (FeOH), gave a value for the concentrate of 44.7 ± 13.7 compared with 7.1 ± 2.4 for the tail. In this statistical analysis, separation of galena and pyrite using DBPhos collector also has approximately 7 times more collector on galena compared to pyrite (but some on gangue pyrite). Galena particles reporting to the concentrate have less calcium, lead hydroxide, and oxy-sulphur species on their surfaces compared to tail particles.

In the flotation sequence of a galena/pyrite separation using IBX collector between successive Concentrates 1, 2, and 3 (abbreviated to Con 1, 2, and 3) and Tail,^[15] differences in some hydrophobic indices (IBX/S , PbIBX/Pb , and $(\text{CH} + \text{IBX})/(\text{Pb} + \text{S})$) and hydrophilic indices (SO_3/S and PbOH/Pb) on galena particles were explored (Figure 1). Isobutyl xanthate decreased from Con 1 to Con 3, but there was no statistical difference between Con 4 and Tail although the combination of IBX with the hydrocarbon CH fragments decreased from Con 4 to Tail. Hydrophilic sulphide oxidation product (SO_3) increased from Con 1 to Con 3 again with no difference between Con 4 and Tail. The hydrophilic oxidation product PbOH, however, increased from Con 1 to Con 4 and Tail. The specific metal-collector precipitate PbIBX, which can form both on surfaces and in solution producing increased activation, appeared to be largely effective in Con 1 only. In general, these indices show that the hydrophobic/hydrophilic ratio systematically decreases across the flotation sequence and can be used to diagnose parts of the circuit in which this ratio is not effective for bubble-particle attachment therefore requiring changes to conditioning procedure.

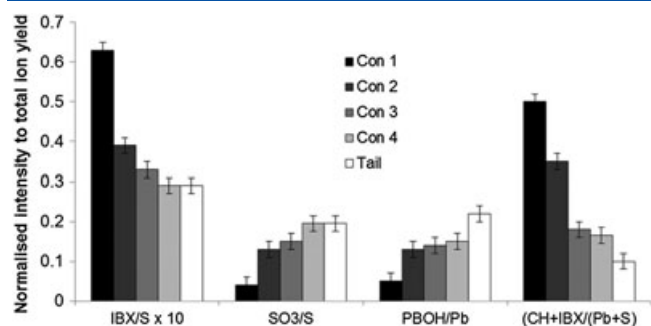


Figure 1. Comparison of normalised hydrophobic and hydrophilic indices of galena (20 particles; bars 95% confidence intervals) across successive concentrates (Con 1, 2, 3, and 4) and Tail from a galena/pyrite lab separation (d_{90} 50 μm ; IBX 100 g/t; pH 9; % recoveries C1 = 57.8, C2 = 25.4, C3 = 7.3, C4 = 4.4, T = 5.1)^[15]

An example of identification of residual surface layers in comminution relates to recovery of gangue pyroxene and chromite in platinum group metal (PGM) flotation plants. In Merensky (Bushveld Complex, South Africa) ore flotation, normally more than 2% of the gangue minerals, principally orthopyroxene with minor chromite, which constitute more than 60% of the ore, reports to the concentrate diluting the PGM recovery and contributing to subsequent processing costs. The ore is processed by bulk PGM and sulphide mineral flotation maximising valuable minerals' recovery and gangue minerals' rejection. Flotation of silicate gangue can occur through chemical interactions, principally inadvertent copper-collector complexation, but this mechanism does not account for the true flotation of large pyroxene (20–150 μm) particles. Statistical comparison of ToF-SIMS analysis of pyroxene particles from concentrate and tails at 2 similar pH values (Figure 2)^[16] reveals no significant difference in Cu and collector (IBX and DTP) signals, but surface exposure of Mg, Si, and O is favoured in the concentrate (Figure 2). Conversely, statistically significant surface species on pyroxene in the tail include the hydrophilic Na, Al, Ca, OH, and SO_3 (oxidation) ions as might be expected. Flotation of pyroxene without collector has confirmed this statistical discrimination. The Mg/Si/O association (normally expected to be hydrophilic as adsorbed ions) is explained by areas of hydrophobic talc-like residual layers, probably from partial serpentinisation of the pyroxene, which can be imaged in ToF-SIMS. These ultra-thin (<10 nm) residual layers result from shearing in autogenous grinding through the relatively soft talc-like material. The talc-like structure was verified in bulk XRD of concentrates and some thicker areas imaged using scanning

electron microscopy (SEM).^[17] A similar mechanism of residual talc-like layers has also been found in flotation of chromite in the UG2 Bushveld ores.^[18] Plant control through effective depressant action for talc (eg, Parolis *et al*^[12] and Lotter *et al*^[19]) has been extensively tested.

We have also observed thin residual layers of soft chalcocite on pyrite surfaces causing excessive misreporting to copper concentrates requiring resort to hydrothermal leaching rather than flotation.

The use of this information in sampling from real ore processing will be illustrated next. Three examples are discussed here: Others can be found in Smart *et al*^[2,7,20] and the recent review by Chehreh Chalgani and Hart.^[21]

A Brunswick Mines plant survey found sphalerite reporting excessively to the copper-lead concentrate. Plant samples were taken in the copper-lead circuit from the rougher feed, rougher bank A concentrate (Con A) and tail (TI A), and rougher bank F concentrate (Con F) and tail (TI F). Sphalerite particles were selected using mineral phase imaging to give reliable statistics.^[20] Increased Cu and Pb intensities in the Con A/Tail A pair and Con F relative to sphalerite in the feed (rougher feed) suggested dissolution/adsorption processes in conditioning. TOF-SIMS normalised intensities (Figure 3) shows the range and distribution of both Cu and Pb on the surface of sphalerite grains. The solid horizontal line in each box identifies median Cu or Pb content of the sample. The solid horizontal line across the entire plot identifies the mean Cu or Pb content in the sample group and is used as a base line.

The data suggest that for the Con/Tail pairs at A and F, Cu on the surface of sphalerite grains is discriminatory. Pb on the other hand does not show any significant discrimination between Con A and Tail A, and intensities are only slightly higher on sphalerite particles from Con F relative to the tail but there is large variation in the Pb content on the surface of the sphalerite grains reporting to Tail A. This kind of detail from surface analysis has been used to assess changes to conditioning, residence time and Cu deactivation reagents.

In a second example, Zn activation control in an industrial Cu flotation circuit treating a complex Cu-Pb-Zn-Au-Ag sulphide ore at the LaRonde Division of Agnico-Eagle Mines Limited (Quebec, Canada) was investigated through COREM.^[22] The action mechanisms of ZnSO_4 , TETA (triethylenetetramine), and NaHSO_3 , used as depressants to limit ZnS activation, were examined. A combined TOF-SIMS/XPS examination of grain surfaces from the tests was performed to evaluate the surface chemical response of sphalerite to the various depressants. The TOF-SIMS analyses were

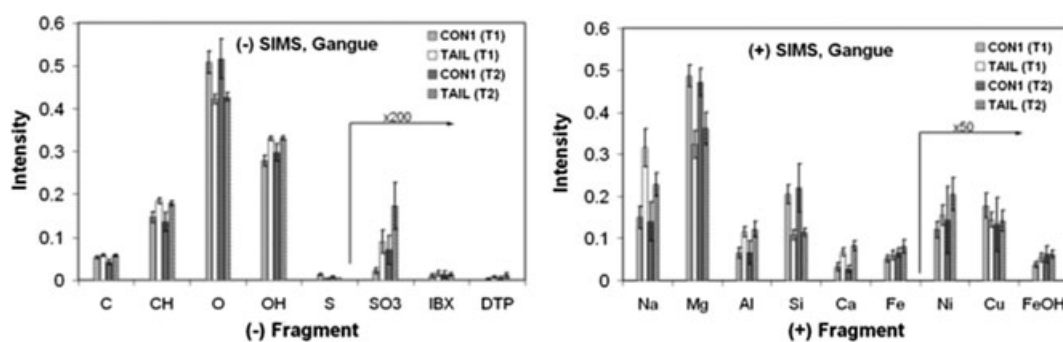


Figure 2. Statistical comparison of ToF-SIMS normalised intensities with $P = 95\%$ confidence intervals (bars) from positive (+) and negative (–) mass spectra of pyroxene gangue particles from Merensky ore flotation.^[16] Left to right: Concentrate1, Test 1; Tail, Test 1; Concentrate1, Test 2; Tail, Test 2. ToF-SIMS, time-of-flight secondary ion mass spectrometry

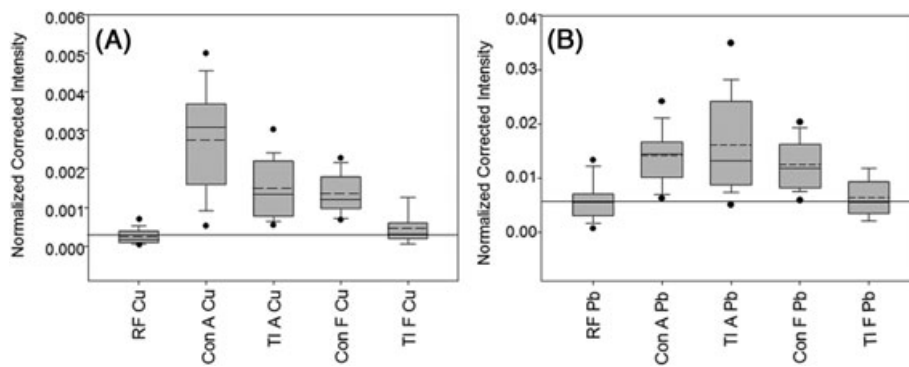


Figure 3. ToF-SIMS analyses of sphalerite surfaces from Con and Tail samples Brunswick Mines. A, Cu distribution and B, Pb distribution (adapted from Smart et al^[20]). ToF-SIMS, time-of-flight secondary ion mass spectrometry

on grains from the mill discharge sample, the first concentrate and reject samples of 4 tests: baseline, ZnSO₄ (25 g/t), TETA (25 mg/L), and NaHSO₃ (500 g/t), all with Cu²⁺ addition. The data revealed that copper transfer occurred under all test conditions (Figure 4).

Higher Cu intensities were recorded for the concentrate samples relative to the paired rejects. The greatest paired differences were noted for the baseline and the NaHSO₃ addition tests, where loading of Cu on the sphalerite grains from both concentrates is very similar. The smallest difference was observed in the ZnSO₄ test. The lowest degrees of Cu loading were observed in the ZnSO₄ and TETA tests. The intensity distribution of Cu in the samples mirrored that of the collector (3418A; data not shown). These data indicate that flotation was in response to collector attachment and, given that all sphalerite grains in the concentrate samples had some degree of Cu on their surface, the attachment was facilitated by Cu adsorption.

Both the ZnSO₄ and TETA test samples indicate that Cu was partially inhibited from attaching to the surface of the sphalerite grains. The operational mechanisms however were probably

different, the former likely related to the development of oxidative species on sphalerite grains as in Khmeleva et al^[23] and the latter to the chelating capacity of TETA.^[24,25] The data from the NaHSO₃ tests show a surprisingly significant loading of Cu on the surface of the sphalerite grains in the concentrate. This contradicts the recovery data that shows a decrease in Zn reporting to the Cu concentrate. Possibly more significant however is the collector response that did not correspond to the surface Cu distribution. Collector intensity data (not shown) for the concentrates and rejects from the NaHSO₃ test were the same as that for the rejects in the ZnSO₄ and TETA tests. Collector attachment in this case was not facilitated by the presence of Cu, consequently a greater proportion of the sphalerite reports to the rejects.

The surface of the sphalerite grains was examined for potential species acting as Cu inhibitors. Sphalerite grain surfaces in both the ZnSO₄ and NaHSO₃ tests reported the highest proportion of species indicative of oxidation such as Zn(OH)₂ and SO₃. It is possible that a greater development of sulfoxy and hydroxide species on the surface of the sphalerites, as identified by TOF-SIMS,

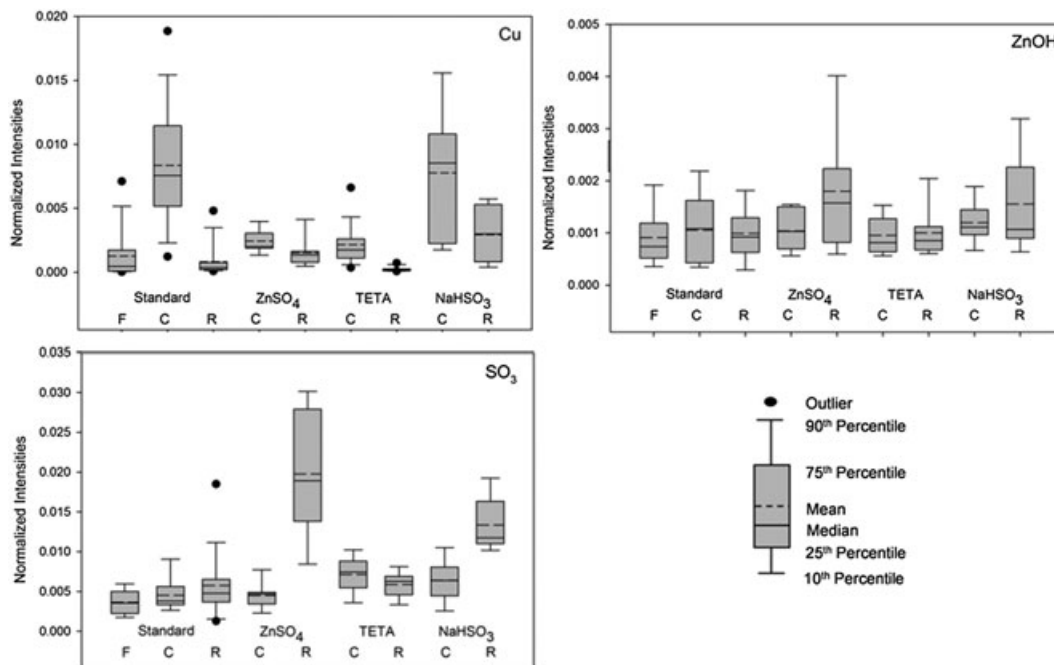


Figure 4. ToF-SIMS normalised intensity of Cu, ZnOH, and SO₃ measured on the surface of sphalerite grains from the feed (F), concentrate (C), and reject (R) samples in the baseline, ZnSO₄, TETA, and NaHSO₃ flotation tests.^[22] ToF-SIMS, time-of-flight secondary ion mass spectrometry

may inhibit collector attachment, produce hydrophilic surfaces, and, in combination, result in poor flotation.^[23,24]

In a Niobec Mines pyrochlore flotation plant survey,^[26,27] the composition of the pyrochlore grains reporting to the tails was identified as having a higher concentration of Fe than those reporting to the concentrate. A statistical compositional analyses of some +200 grains from the concentrate and tails samples showed that the Fe content was not related to Fe-rich inclusions but rather occurred in the mineral matrix, substituting for Na or Ca. Time-of-flight SIMS surface chemical analyses identified that the grains reporting to the tail (higher matrix Fe content) had a higher content of FeOH (along with other FeOx species) (Figure 5 A) and significantly less tallow diamine (TDM-1) collector on their surface (Figure 5B). The TOF-SIMS surface analyses established a link between mineral Fe content, the degree of surface oxidation, collector loading, and the observed poor recovery of high Fe pyrochlore grains.^[26,27]

To verify the relationship between pyrochlore matrix Fe content and the identified surface chemical variations, a series of bench conditioning tests were set up to determine the effect of accelerated oxidation on pyrochlore grains of different Fe content. XPS broad scan data and high-resolution scans for Fe revealed that, under controlled lab conditions, a greater proportion of oxidative Fe species developed on the surface of the pyrochlore grains with higher matrix Fe content (Figure 5C vs D). These data support the hypothesis reached from the TOF-SIMS analyses, which suggest that the development of surface oxides favours pyrochlore grains

with higher Fe content, ultimately impeding collector adsorption and reducing recovery.

PCA of TOF-SIMS data

The most recent advance in the statistical analysis of ToF-SIMS data is the use of multivariate PCA, first applied at the Surface Science Western Laboratories in 2006.^[28] A 256 × 256 pixel ToF-SIMS image data set obtained over a mass range of 1000 amu contains over 6.5×10^7 data points or variables. With such a large data set, extracting and analysing the relevant data, in this case, surface species from separate mineral phases, becomes a major issue. The multivariate PCA, using PLS_Toolbox 2.1 from Eigenvector Research Ltd. (Manson, Washington) running on Matlab 6.0, has been shown to improve image contrast, mineral phase recognition, and separation of topographic from chemical effects and identify related surface species on particular mineral surfaces. In PCA, the surface species are usually correlated such that the most important information is contained in a few specific, correlated components.

In essence, ToF-SIMS positive and negative secondary ion signals are the variables to be correlated. The analysis identifies relationships between these variables and reduces the data to those secondary ions that are major contributors to the variation in surface chemistry between minerals and between flotation streams, ie, feed, concentrates, and tail. The secondary ions are transformed into a set of linear combinations (principal

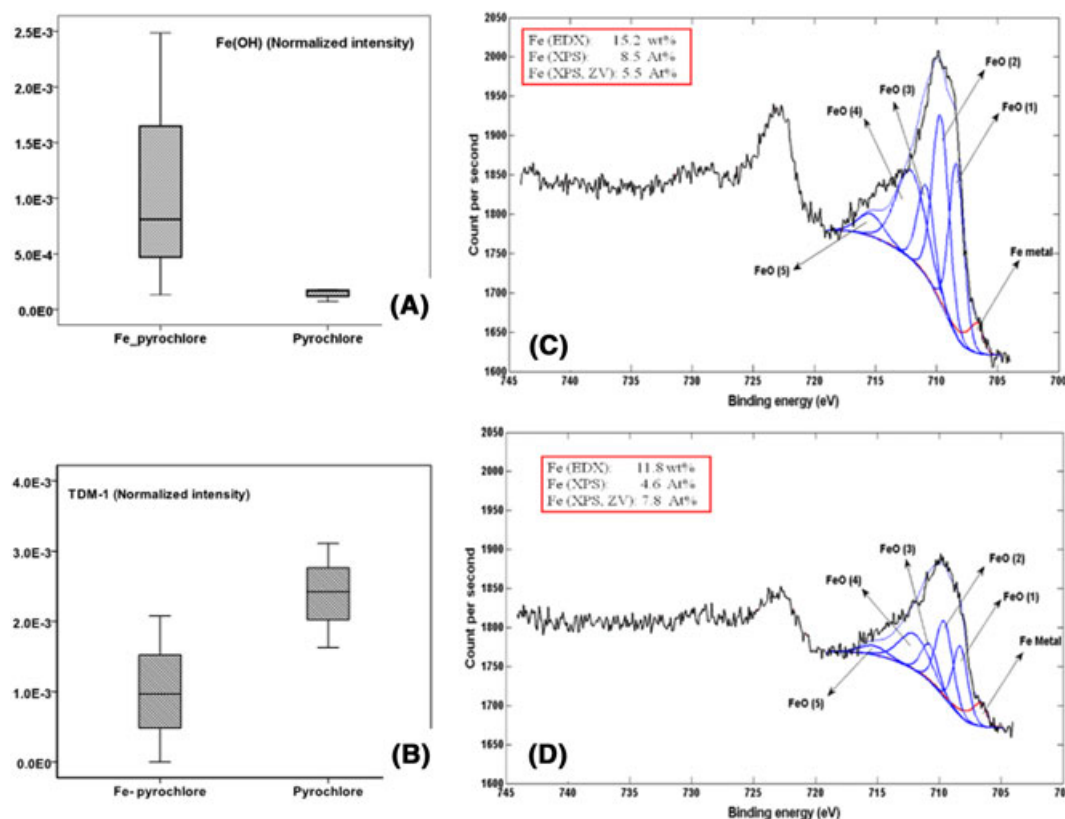


Figure 5. A and B, Vertical box plots of ToF-SIMS normalised intensity for FeOH and collector (TDM-1) on the surface of high Fe (Fe-pyrochlore) and low Fe pyrochlore (pyrochlore) grains from the Niobec flotation plant.^[26,27] C and D, High-resolution XPS spectra for grains with high Fe content (Fe-pyrochlore, C) vs low Fe content (pyrochlore, D) after conditioning for 30 minutes in oxygen over saturated water. Included for each grain examined is the weight % Fe (EDX) along with the relative atomic proportion (at %) of surface oxidised Fe (FeO) and Fe metal (XPS ZV) as determined by high resolution XPS scans. ToF-SIMS, time-of-flight secondary ion mass spectrometry

components [PCs] of the original signals representing surface species correlated with each other presented in (correlation) factor loadings. The first PC (PC1) represents the largest correlation in the data primarily corresponding to topography variations. After this is (usefully) removed, as in normalised intensities, subsequent PCs are automatically corrected for these variations. Each subsequent PC represents decreasing variation in the data but contains more explicit recognition of specific mineral phases and the surface species correlated with each mineral phase. This PCA processing is done in software in a few minutes. The PCA analysis immediately reduces the data to those secondary ions that are major discriminating contributors to the variation in surface chemistry between minerals and between flotation streams, ie, feed, concentrates, and tail, in PC sets.

To illustrate the type and value of the detailed information from these PCs, the case study of the Cu-Mo bulk flotation circuit at KUC^[29] can be used. Figure 6 shows a PC selected from the first concentrate (Con 1) from 2 different KUC ores. For the monzonite (MZ) ore, which separates Mo well but Cu poorly in flotation, in MZ Con 1 (left), a very strong correlation of all 3 Mo isotopes (at masses 92, 95, and 98) is found. It is important to emphasise that the bars in PCA sets are not intensities but correlation factors (since the Mo isotopes have very different relative intensities). The hydrophobic molybdenite particles identified from PCA in this first concentrate were remarkably clean with only small correlations of these surfaces with Cu (isotopes ⁶³Cu and ⁶⁵Cu) and collector (S8989 mass fragments), probably adsorbed hydrophobic Cu-collector complexes formed in solution. The negative set of factor loadings in Figure 6a represent correlation of Na, Mg, Al, Si, K, Ca, CaO, and CaOH with iron oxyhydroxide (Fe, FeO, and FeOH) from hydrophilic gangue in this concentrate. In other components from MZ Con1, selection of Cu and Fe (chalcopyrite/bornite) surfaces was correlated with FeO, FeOH, K, Mg, and collector fragments. In later concentrate (MZ Con 4) and MZ Tail, no surfaces correlated with Cu and Fe were identified indicating that chalcopyrite and bornite surfaces were obscured by adsorbed and oxidation species, correlating with poor Cu recovery.

Flotation separation of both Cu and Mo is poor in the limestone skarn (LSN) ore with which the MZ ore was previously blended before this case study. For comparison, a PC from Con 1 of this LSN flotation in Figure 6 (right) selects the 3 isotopes of Mo in the negative correlation set but the correlation factor loadings are much lower (near -0.10) than in the MZ Con 1 (near 0.4). Other components from LSN Con 1 select distinct Cu and Fe (chalcopyrite/bornite) mineral surfaces, but these areas are nearly equally correlated with hydrophilic Na, Mg, Al, Si, K, Ca, CaO, CaCH₃, FeO, FeOH, PO₃, and collector mass fragments indicative of mixed hydrophilic and hydrophobic surface species coverage, and the presence of either fines or colloidal precipitates on the chalcopyrite/bornite particles. These adsorbed hydrophilic species are likely to result in the reduced chalcopyrite flotation rate as observed in the LSN ore flotation test. In later concentrates, weak statistical recognition of Cu and Fe is strongly correlated with hydrophilic Ca, CaO, CaOH, and PO₃ species. For the LSN tail, no significant correlations for Cu and Fe were identified so that chalcopyrite/bornite particles lost to tail have obscured surfaces. The principal surface contamination of the concentrate minerals for the blended ores, which increased in severity from Con 1 to Con 4, was from Ca and Fe hydroxides, phosphates, and Ca and Mg aluminosilicate gangue. This is in agreement with the observed mineralogy with the LSN ore containing considerably greater proportions of the Mg containing minerals pyroxene, amphibole, and talc, and the Ca containing minerals, calcite, and andradite than the MZ ore. Based on this and other process information, KUC decided to stop blending these ores.

In a valuable application of PCA by Brito et al,^[30,31] the method has been used in single mineral studies of water contact angles in chalcopyrite flotation. They have used geometrical representation of the observations in 2D scatterplots relating successive PCs for identifying patterns within the data and potential outliers. This method has shown that the contact angle of chalcopyrite can be predicted from 3 secondary ions alone: oxygen, sulphur, and a thiol collector fragment, extending the use of the DTP/S and the (CH + S)/(O + OH) ratios used in the earlier contact angle study of

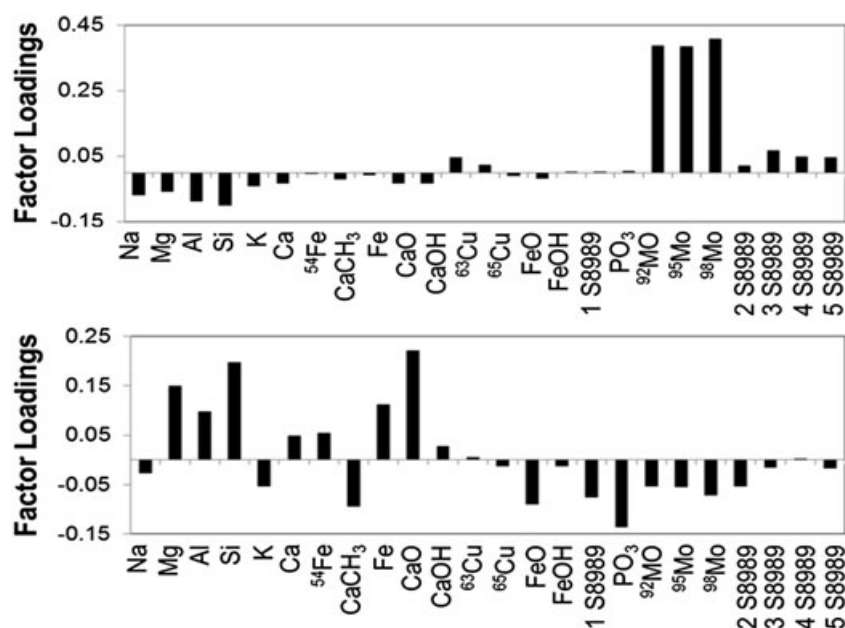


Figure 6. Principal component comparison of PC2 positive ion factor loadings for left, MZ Con 1; right, LSN Con 1 ores from KUC case study^[29]

chalcopyrite in the Ok Tedi ore.^[32] In these studies,^[30] differences in surface species and contact angles with particle size (20-38, 75-105, and 150-210 μm) were also determined. They found a considerable spread of contact angles within each size range from 20° to 90°. For low contact angles, no apparent difference in surface chemistry between particle sizes was found but particles with high contact angles show decreasing S and collector signals with increasing hydrophilic gangue signals (eg, Al, Na, and K) as the particle size increases. This combination of factors has been used in an analysis of contact angles from DTP flotation of chalcopyrite in a KUC ore.^[31] Two models were developed to predict the concentrate and tail department of particles, one targeting fine and intermediate particle sizes and the other for the coarse particle size. These models were tested using cross-validation giving 88% prediction accuracy for fine and intermediate particles and 77% for coarse particles. The models, tested on feed samples, show that they can be used as a predictive tool to estimate the maximum recovery expected based on the surface chemistry of particles under specified hydrodynamic conditions.

In the latest development of the PCA ToF-SIMS approach,^[33] positive and negative ion fragments are collected in the same pixels from the same surface area enabling PCA statistical analysis of all mass fragments simultaneously. Previously, this was not attempted with the positive and negative ion species from different areas subject to PCA examination separately. By performing these measurements on the same area, the 2 sets of data can be concatenated in the third dimension, ie, vertically, in the species

listing for each pixel. This PCA analysis significantly enlarges the potential for species correlation. In the latest methodological incarnation, all species are examined and those correlations that are significant are highlighted by ranking the resultant PC factor loadings. Applying this concatenation to previously obtained data, on the proviso that positive and negative ions data are taken on the same area, it is apparent that considerably improved and more holistic analyses result.

The value of directly combining both signals can be illustrated in analysis of silver particles lost to tails in flotation. Silver is commonly mined and produced as a by-product of Cu, Pb, and Zn, which are extracted from base metal sulphide minerals, or as a by-product of gold containing Fe sulphides. The extraction of Ag from base metal ores initially involves the separation of the Ag minerals together with the valuable base metal minerals from gangue minerals through flotation. The low recovery of Ag, often in the order of 50%, by traditional flotation and leaching process strategies is closely related to the complicated and heterogeneous nature of Ag-bearing minerals with Ag typically being associated with numerous minerals within any given ore body. To design cost-effective Ag-bearing mineral flotation and leach recovery strategies, it is firstly necessary to characterise the speciation of Ag and its correlation with other elements and surface species within the ore matrix and process streams.

ToF-SIMS images of Ag-containing particles from the zinc circuit tails^[33] are clearly correlated to positive secondary ions of Cu and Zn but also negative ions of S, its oxidation products, and CN

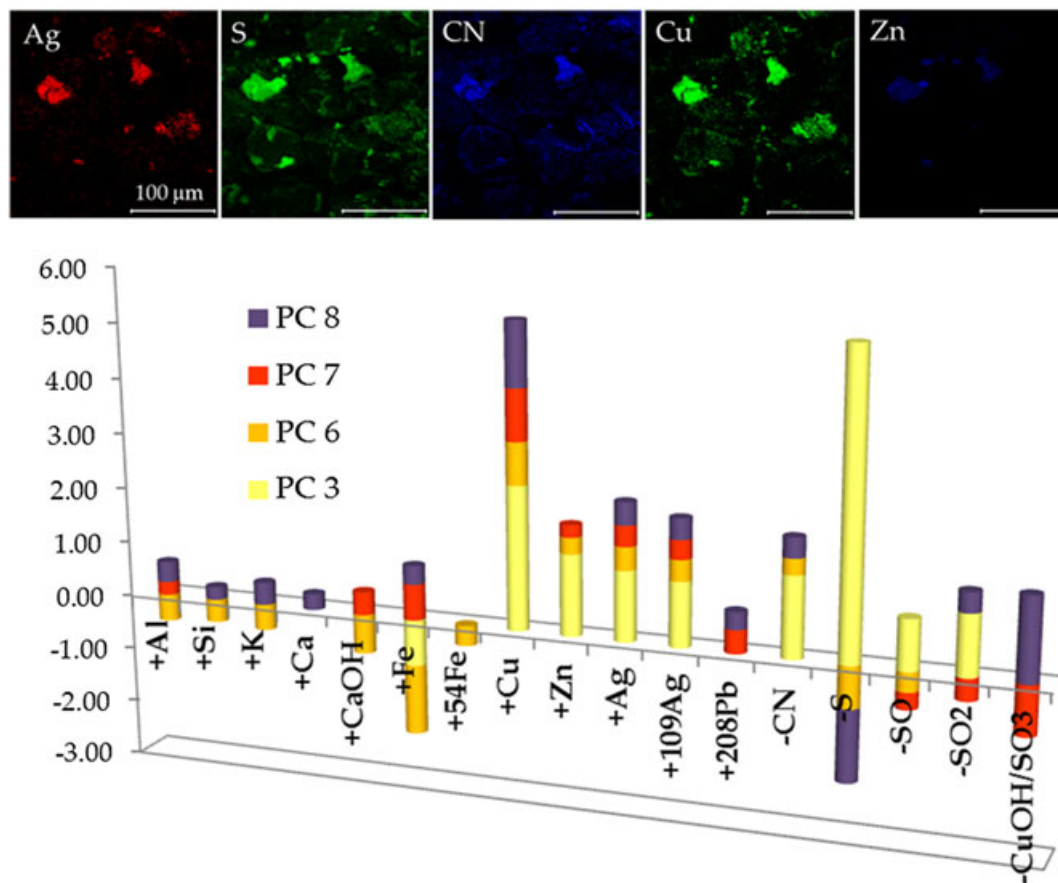


Figure 7. Study of particles SG > 4.05 lost to tails from a plant flotation sample. ToF-SIMS images (250 × 250 μm) for Ag, S, CN, Cu, and Zn with PCA factor loadings for 10 areas of ToF-SIMS data.^[33] Principal component 3, in particular, shows clear statistical correlation of Ag to CN (and Cl) as well as Cu, Zn, and S, suggesting flotation depression of these value components. PCA, principal component analysis; ToF-SIMS, time-of-flight secondary ion mass spectrometry

(Figure 7). This visual correlation is confirmed by factor loadings in PCA statistical analysis with added correlation to chloride. Cyanide was added to the lead circuit to depress sphalerite flotation. The mineralogy shows Ag in the Zn circuit tail mainly associated with sulfosalts, possibly pearceite, and as a minority element within sulphide phases. The ToF-SIMS and mineralogical analyses^[33] combined confirm Ag losses in copper-activated, oxidised sphalerite related to the surface adsorption of cyanide on these Ag-containing phases.

A strategic approach to flotation losses due to mineralogy and surface chemistry

The use of statistical ToF-SIMS is now part of a complete strategy developed for identification of the reasons for losses in recovery and/or grade, due to changes or complications in mineralogy and in mineral surface conditioning, and their subsequent correction.^[3] The sequence of methods starts with comparison of mineral phases between QEMSCAN/MLA (compositional) and Rietveld XRD (crystalline diffraction) with bulk assay reconciliation. This methodology has recently led to identification of unrecognised amorphous content (12–40 wt.%), previously attributed to crystalline phases, in the fine fraction (<35 µm) of some problematic flotation feeds. Attached amorphous silica, talc- and chlorite-like fines have direct influence on the hydrophobic/hydrophilic ratio on value mineral surfaces adversely affecting flotation. SEM is used in the backscattered imaging mode with energy dispersive spectroscopy to determine possible problems with liberation (eg, remnant local locking), not detected in standard liberation analysis, resulting in gangue flotation. Ethylene diamine tetra acetic acid extraction is used to assess bulk feed preoxidation and sequential oxidation product loading through the circuit. Changes in circuit solutions are assayed with speciation modelling of precipitates and potentially adsorbing species. Time-of-flight SIMS with PCA is then used to correlate surface species with specific minerals and can be used to assess the effectiveness of specific reagents particularly collectors. This approach identifies unwanted activating species and interference with value surfaces by adsorbed hydrophilic ions, precipitates, and fine particles. Its value is most effective as part of the problem-solving strategy to look at all aspects of the poor flotation as evidenced in the KUC case study. When the interference or ineffective reagents are specifically identified, remedial action can be targeted.

The results of this strategy can point to changes that can be made in a very wide variety of parameters in the operating processing, reviewed in previous studies.^[2,20,34] Interferences and control factors previously found can include consequences of changes in mineralogy of ores requiring comminution and/or reagent change; blending/mixing/storage to control reactivity before processing (eg, preoxidation and dissolution); grind size to limit gangue (eg, sulphide, sulphate, and talc) fines; cyclone cuts sizes (narrower); effects of shear in comminution, attritioning and/or high intensity conditioning to control residual and precipitated surface layers; surface oxidation control in aeration and residence time after grind to reduce oxidation products and inadvertent activation; water recycle quality to remove activator or depressant ions; Eh/pH measurement and control for oxidation control and effective collector adsorption; surface cleaning actions by collector choice, dosages, and time after addition and in cyclones, high intensity conditioning and attritioning; activation

by copper ions for monolayer coverage only with critical activation/oxidation time; inadvertent activation and control of Cu, Pb, and Ag ions in oxidation/dissolution; and water recycle. Other examples of applications in grinding, hydrophobicity, and contact angle estimation, as well as detection of reactions on mineral surfaces during flotation, are described in the review by Chehreh Chalgani and Hart.^[21]

Conclusions

The development of ToF-SIMS/PCA has provided direct identification of surface species interfering with and discriminating in processing as well as inadequacies in surface conditioning for the most effective recovery. In this respect, it has become central to the application of this strategy in improvements in mineral processing operations.

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