Innovations in Measurement of Mineral Structure and Surface Chemistry in Flotation: Past, Present, and Future

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ABSTRACT: This paper surveys the development of surface analytical methods that have contributed fundamental understanding of the flotation process and the ability to measure changes in mineral structure, surface chemistry and reagent uptake in single minerals and now between flotation feeds, concentrates and tails in synthetic and real plant samples. The early applications and past development of new techniques, i.e., XPS (or ESCA), Auger spectroscopy, scanned probe microscopies (STM, AFM), ion beam techniques (ToF-LIMS, ToF-SIMS) and vibrational spectroscopies (FTIR, Raman) to mineral processing are briefly surveyed. In current practice, further innovations in methodologies and principal component analysis applied to ToF-SIMS, contact angle estimation and vibrational spectroscopies (ATR FTIR, TIR Raman, SFG) with examples are reported including cases where the techniques have been combined with electrokinetic and electrochemical analyses (i.e., spectroelectrochemistry). Differences in hydrophobic/hydrophilic surface species on specific mineral phases, which can control recovery and grade, can now be analysed statistically using ToF-SIMS to diagnose problems in grinding, conditioning (physical and reagent) and interfering species on surfaces of value minerals. In future, new methods based on synchrotron techniques offering information on surface structure, amorphous phases and analysis of diffraction and composition on single particles (<2 μm) are being developed for location of toxic and penalty impurities.

INTRODUCTION

In froth flotation, the chemistry of the top few monolayers of different mineral surfaces determines the recovery and grade in operation. Attachment of a collector-conditioned mineral particle to a bubble and the stability of this attachment in both pulp and froth phases is dependent on the hydrophobic/hydrophilic ratio of surface species in the outermost molecular layers (1–2 nm) on individual mineral particle surfaces (Piantadosi & Smart 2002). In practice, adsorption of the

hydrophobic collector molecules to surfaces of the valuable mineral phase particles can be compromised by the presence of many hydrophilic oxidation and other surface species with preference for water attachment. In reality, the surface of each individual value mineral particle is a complex, distinctly non-uniform array of oxidation products (i.e., oxyhydroxides, oxy-sulphur species), adsorbed ions, precipitates, collector molecules and attached fine and ultra-fine particles of other mineral phases. In order to understand and improve poor flotation recovery, it is first necessary to know whether this is being caused by poor hydrophobic/hydrophilic conditioning of the value mineral surfaces (or inadvertent hydrophobic conditioning of gangue minerals). It is then possible to define the reasons for this before changes to mechanical (e.g., grinding, agitation, fines separation) or chemical (e.g., redox control, reagent doses, addition points, water quality) conditioning can be usefully made. Hence, ideally, we would like to know the hydrophobic/hydrophilic ratio by particle and as a statistical distribution between different mineral phases across a flotation circuit from roughers, scavengers, cleaners to tail. This is a difficult proposition but surface analysis has come a long way towards this goal. This paper will briefly review the development of these measurements, their current applications and future prospects.

These techniques are equally applicable to recovery of metals by hydrometallurgical leaching, where leach kinetics and selectivity can be cost-limiting, rate-determining surface species and surface layers forming 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 before the sub-processes requiring change can be usefully addressed. We will focus on the flotation applications in this paper.

THE PAST: DEVELOPMENT OF METHODS

Until the introduction 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. Fuerstenau and Chander (1982) noted in their early review "Industrial Applications of Surface Analysis" that "mineral processing research has extensively involved determination of electrokinetic behavior, voltammetry, gas adsorption, aqueous-phase adsorption, infrared and UV-VIS spectroscopy, measurement of contact angles, and, more recently, ESCA analysis to delineate surface composition. Lack of techniques to study solid/liquid interfaces *in-situ* has led to the development of many ex-situ and indirect methods for surface characterization. The results of such measurements are often interpreted through use of models requiring various underlying assumptions. It has been often necessary to use a combination of two or more techniques to delineate the physico-chemical interfacial phenomena."

The introduction and evolution of direct surface analytical techniques in their application to fundamental aspects of mineral structure and surface chemistry has provided the mineral processing industry with valuable tools to better understand factors involved in process control. Advances in these techniques and instrumentation have produced new tools and procedures for the comprehensive statistical analysis of ore samples and process stream products. These techniques, together with the mineral structure techniques, and the information they have given on the behaviour of different minerals in the flotation process have been extensively reviewed by experts in each technique in the SME Centenary of Flotation volume (Smart et al. 2007). The significance of these techniques is that they provide not only a compositional analysis of the surface layers but also information

on chemical states (e.g., oxidation, bonding), spatial and statistical distribution of adsorbed species between individual particles and mineral phases in complex mixtures as a function of depth through the surface layers. Nevertheless, Fuerstenau and Chander (1982) remain correct in that the combination of these ex-situ techniques with adsorption and solution modelling provides the most complete information on surface chemical conditioning and interferences in flotation. It is recognised that, since they are ex-situ techniques that operate in ultra high vacuum, validation of the relationship between the measured surface compositions or chemical states and those prevailing in the original pulp solution in the flotation cell or circuit, is required. Sampling methodologies have been developed and tested in extensive sets of correlated surface analysis/solution analysis/flotation response testing in major projects over more than 20 years (Smart et al. 2003a, 2007).

Two of the complementary techniques now widely used with the direct surface analysis techniques are EDTA extraction and solution speciation modeling.

EDTA Extraction

This technically much-simpler chemical-based analysis dissolves oxidised metal ions (i.e., Cu^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Pb^{2+}) as EDTA (ethylene diamine tetraacetic acid) complexes from in situ surface reaction layers, adsorbed colloids, precipitates and ions to give solution assays that provide a bulk estimate of the extent of oxidation of all minerals. Comparison with the chemical information (i.e species and composition) from specific minerals in the surface sensitive analyses of the top 1–10 nm can then provide a more complete picture of the hydrophilic species likely to be interacting with the bubbles and potentially interfering with flotation. Examples of the methodology and its use in this way can be found in early work (e.g., Grano et al. 1990) and more recently in Gerson and Jasieniak (2008).

Solution Speciation Modelling

Basic determination of solution speciation (i.e., predicted relative abundance of specific dissolved and precipitated chemical species) is readily accessible from solution assays but is often neglected. While there are numerous examples of the use of such simulation programs for environmental studies, particularly for adsorption and examination of oxidation states for toxic elements (e.g., Halim et al. 2005), there are surprisingly few applications for mineral flotation studies. Speciation simulation programs, e.g., GEOCHEM-EZ (Shaff et al. 2010), PHREEQC (Toran and Grandstaff 2002), MINTEQ (Allison et al. 1990) and others are available, often free to download. Solution concentrations of all cation and anions, pH, temperature and particularly E_H or ORP (often not measured) are required input. Gas partial pressures and the presence of specific solids phases can be specified in the estimates. The programs come with their own databases of equilibrium constants, solubility products and redox couples, including collector and complexant species, but data on more obscure species may need to be added to the data base.

The value of these simulation programs for minerals processing is to take a 'snap-shot' of the system, assuming equilibrium, so that under-saturated but potentially adsorbing species and precipitating supersaturated solids may be identified. This can again be compared with the surface analyses to extend the correlation of indirect and direct information on hydrophobic and hydrophilic species. An example of the value of this correlation of solution modelling and surface analysis can be found in defining correct procedures for copper activation of sulphide flotation (e.g., pentlandite) (Malysiak et al. 2002) avoiding precipitation of hydrophilic $Cu(OH)_2$. A recent example of

combined information from solution modelling with zeta potential, X-ray photoelectron spectroscopy (XPS) and EDTA extraction is in the flotation study on Cu and Pb speciation as a function of contrasting Eh and pH conditions during grinding (Peng et al. 2012).

XPS or ESCA

The technique of electron spectroscopy for chemical analysis (ESCA), later renamed more specifically X-ray photoelectron spectroscopy (XPS), was developed by Kai Siegbahn for study of atomic, molecular and solid state structure (Siegbahn et al. 1967) for which he received the Nobel Prize in 1981. In XPS, the sample surface is irradiated with mono-energetic x-rays producing photoelectrons analysed to determine their binding energy. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and percentage of an element in the top 2–10 nm are determined. Two-dimensional imaging can now provide species mapping of surface chemistry with a practical spatial resolution of 10–20 µm but the data collection is relatively slow. In minerals processing research, again for practical collection times, it has mostly been used in larger area-average mode (100 µm–1 mm) applied to single mineral or pure mineral mixture studies with limited application to statistical analysis of plant samples. The first studies of copper and copper oxide were made in 1958 (Siegbahn et al. 1967). The technique appears to have been first used in studies applied to mineral processing by Clifford, Purdy and Miller (1975) and Brion (1980). A series of seminal studies by Buckley and Woods across 1984–1994, combining XPS and cyclic voltammetry, reviewed in Buckley (1994), initially defined many of the surface oxidation products, including oxidised sulphur species (from sulphide, disulphide, polysulphide, elemental sulphur, to thiosulphate, sulphite and sulphate) and adsorbed xanthate species on the major base metal sulphide surfaces as single minerals. Later work on oxidation, collector, activator and other adsorption mechanisms as well as interfering species, reviewed by Smart et al. (2003a), extended the studies of single minerals and laboratory flotation systems giving more direct insight to the factors affecting recovery and grade. Most of the hydrophobic, including both reagent and reaction (e.g., polysulphide) products, and hydrophilic species affecting flotation were defined in these studies. The mechanisms and products of in-pulp oxidation and the actions of collectors in partial removal of oxidised species and hydrophobisation of the surfaces were studied using XPS combined with other surface analytical methods summarised in the two reviews (Smart et al. 2003a, 2007). The mechanisms of copper sulphate as flotation activator in sphalerite, in ion exchange with Zn^{2+}, reduction in situ to Cu^+ with collector attachment, and adjacent oxidation of sulphide to polysulphide-like species were revealed by these species seen in XPS (Gerson et al. 1999). Inadvertent activation by species such as Pb^+ and Ag^+ were first seen in these studies. Actions of depressants, such as cyanide and bisulphite (e.g., Khemleva et al. 2006), on this surface chemistry were also defined in XPS studies of single minerals. XPS has probably contributed more understanding of mechanisms of surface chemical actions in flotation than any other surface analytical technique.

Auger and Scanning Auger Spectroscopy

Auger electron spectroscopy, first suggested for surface analysis by Lander (1953), was also introduced to analysis of mineral surfaces in the same period as XPS (e.g., Eadington 1974, 1977). This is an analytical technique that uses a nm-focussed primary electron beam, similar to scanning electron microscopy (SEM), to probe the surface of a solid material. Electrons emitted as a result of the quantum-specific Auger process are analysed and the identity and quantity of the elements determined from the kinetic energy and intensity of the Auger peaks. Like X-ray photoelectrons, Auger

electrons can only escape from the outer 2–10 nm of a solid surface at their characteristic energy. The finely focused electron beam can be scanned to create secondary electron and Auger images, or the beam can be positioned to perform microanalysis of specific particles but surface charging (i.e., low-conductivity minerals) can limit applicability of this technique. In mineral mixtures after grinding and conditioning, scanning Auger spectroscopic images and analysis first illustrated the complexity of hydrophilic oxidised layers, adsorbed species and attached fine particles on mineral surfaces that can interfere with bubble-particle attachment (e.g., Smart et al. 2003a).

FTIR Spectroscopy

Just as XPS and Auger spectroscopy contributed to the greatest increase in our understanding of mineral surface chemistry of relevance for flotation, Fourier-transform infrared (FTIR) spectroscopy has contributed the most to our understanding of the adsorption mechanisms of reagents on those mineral surfaces. FTIR spectroscopy, with its ability to record high resolution spectra rapidly and with high signal to noise, revolutionised the structural determination and identification of organic molecules when introduced in the late 1960s. However, the application of infrared spectroscopy to surface adsorbed species pre-dates the advent of the FTIR spectrometer, with dispersive instruments being used to obtain spectra of monolayers of material on reflective surfaces through the sampling method of reflectance-absorbance infrared spectroscopy (RAIRS—also known as external reflectance infrared) (Francis and Ellison 1961; Greenler, 1966, 1969). In addition, dispersive instruments were used to study the adsorption of flotation collectors to metal sulphide surfaces (Greenler 1962). That being said, it was the introduction of FTIR instruments that resulted in a widespread uptake of infrared spectrometers in labs world-wide, and thus facilitated a step-change in our understanding of adsorption phenomena.

As mentioned above, external reflection infrared spectroscopy, which relies on the alteration of surface optical properties by adsorbed layers of molecules (and more importantly, specifically at energies that correspond to vibrations of the adsorbed molecules), has the sensitivity to detect monolayer and sub-monolayer quantities of adsorbing molecules. It has been used to great effect to elucidate binding mechanisms and orientation of flotation collectors on metallic reflective surfaces (gold, silver, copper, etc.) and on non-metallic surfaces (Mielczarski 1993; Mielczarski and Leppinen 1987). However, the general requirement to analyse samples dry (i.e., outside of the flotation-relevant solution environment) limits the relevance of the methodology for flotation studies, in spite of it being applied to real mineral surfaces (Mielczarski et al. 1993). RAIRS has been applied to metal surfaces in electrochemical cells whilst the electrode surface has been immersed in liquid, in studies of relevance to flotation (such as xanthate adsorption on copper metal (Bozkurt et al. 1996). The addition of surface potential control increases the usefulness of the methodology, but it is still one step removed from the analysis of real mineral surfaces.

A second infrared sampling methodology that is particularly useful for analysing real mineral particles is diffuse reflectance FTIR (termed DRIFT). The methodology requires that conditioned mineral particles be dried and mixed with a non-absorbing medium (potassium bromide, KBr), placed in a sample cup, irradiated with an IR beam, and diffuse (i.e., multiple non-specular reflections) are collected. DRIFT was shown to be useful in gaining some insight into binding mechanisms for collectors and polymers (Gärd et al. 1997; Khemleva et al. 2006; Raju et al. 1997), although the need to dry samples prior to analysis means that its use for analysing polymer adsorption is not without complications, and studies of adsorption kinetics are not possible.

A more routine FTIR sampling methodology that is suited to analysing adsorbates on surfaces immersed in liquid (in addition to dry surfaces) is ATR (attenuated total reflection) in which IR radiation is internally reflected in a reactive IR-transparent crystal and adsorbing molecules are probed by interactions with an IR evanescent wave at the solid-liquid interface (Harrick 1967). ATR combines the sensitivity and structure determination characteristics of RAIRS while enabling the study of reagents adsorbing from solution directly. The one caveat is that the routine application of the methodology is limited to adsorption substrates that are IR transparent (e.g., ZnS, CaF_2, NaCl, KCl, Al_2O_3, $CaCO_3$, germanium, silicon). The technique has been used to study collector adsorption, including studies of orientation (Larsson et al. 2000) and co-adsorption (Larsson et al. 2001). The in situ nature of the techniques also allows for the determination of collector adsorption kinetics (Fredricksson and Holmgren 2007). ATR using crystals as substrates suffers from the same limitations as RAIRS in terms of connecting directly with real flotation systems and real mineral particles. As will be discussed later, studies have also been done *in-situ* on mineral particles by pressing them as a bed against the ATR crystal, and then controlling the bed potential as needed. In addition, D_2O is usually used in all of these ATR/FTIR techniques to minimize the interfering signals from normal water (H_2O). However, a series of studies at The University of Utah with Jan Miller using reactive ATR crystals are particularly noteworthy and discussed in the following.

Kellar et al. (1990, 1991) examined fluorite (CaF_2)/oleate system and confirmed that oleate not only chemisorbed at the fluorite surface but also formed a near complete monolayer. As the monolayer formed, they found that the CH-stretching vibrations would change depending on the amount of surface coverage as well as temperature. Noting that it was similar to conformational/structural changes observed in the literature for liquid crystals, they likened it to the formation of coagel/gel phases as opposed to hemi-micelles. At high oleate concentrations, a small amount of calcium dioleate surface precipitation was also observed but would decrease when the solution concentration exceeded the critical micelle concentration (CMC).

Similarly, Young and Miller (2002a,b) investigated the calcite ($CaCO_3$)/oleate system. In their case, the ATR calcite crystal was fashioned from a natural specimen and required the study to be done using the Near-IR (NIR) as opposed to Mid-IR (MIR). They observed the same behaviour as for fluorite but found that chemisorbed oleate only gave submonolayer coverage equivalent to no more than approximately 25% of the maximum observed at fluorite surfaces. Surprisingly, thermodynamic analysis showed that the free energy for chemisorbed oleate formation was the same at both surfaces but enthalpic and entropic contributions varied significantly and were attributed to differences in hydration of the two surfaces prior to adsorption and therefore the desorption of water that had to occur in order for oleate adsorption to take place. By likening the chemisorbed oleate to a "protective coating" and comparing it to fluorite, they noted the lower amount of chemisorbed oleate on calcite allowed significantly more calcium dioleate surface precipitation to occur. Calculations showed that both surface precipitation events correlated well to the mineral solubility and Free and Miller (1996) suggested earlier that the mechanism was caused by the formation of calcium dioleate in solution followed by its transport back to the surface and not nucleation and growth at the surface. Likewise, the amount of chemisorption was related to the spacing between calcium adsorption sites with fluorite being able to accommodate the size of the oleate molecule at every site whereas calcite could not.

By comparison, Cross et al. (1993) used the ATR/FTIR technique to examine the alumina (Al_2O_3)/sodium dodecyl sulphate (SDS) system. They found similar conformational changes and concluded that the adsorbed species went through four stages of adsorption until maximum

adsorption occurred. During the initial stages, the surface species resembled cylindrical micelles in solution but transitioned into a coagel-like phase at higher adsorption densities. At increased temperatures, the coagel phase developed conformations similar to hexagonal liquid crystals. In this case and in agreement with the literature, adsorption was physisorption and therefore dependent on surface charge. Finally, Free and Miller (1994) used many of the same synthetic ATR crystals and observed the same characteristics when the collectors were transferred as Langmuir-Blodgett films. Their work revised the ATR adsorption density calculation and helped improve our understanding of the ATR techniques and flotation.

Laser Doppler Electrophoresis

On the other hand, Miller et al. (1992) and Yalamanchili et al. (1993) extended the ATR/FTIR studies at The University of Utah to halite (NaCl) and sylvite (KCl) in the presence of dodecylamine hydrochloride (DAH). As expected and in accordance with the literature (Fuerstenau and Fuerstenau 1956), they found DAH had minimal adsorption on halite and maximum adsorption on sylvite. However, through the use of laser-Doppler electrophoresis, they were able to surprisingly show that sylvite particles exhibited a negative surface charge as they dissolved in a near-saturated solution and halite yielded a positive charge, neither of which should occur according to classical DLVO theory via compression of the double layer. With this technique, particles with a surface charge are set in motion in a conductive fluid by applying a voltage across the fluid. Particle velocity and direction are instantaneously measured by laser Doppler and used to calculate the electrophoretic mobility and zeta potential based on traditional electrokinetic equations. By comparison, the cumbersome microscopic technique used previously by numerous authors for a variety of mineral/collector flotation systems would take several minutes to complete and simply would be impossible to use for studying soluble salt minerals. To explain how sylvite can be floated from halite, they found that DAH would form a positively charged colloid that adsorbed at the negatively charged surface of sylvite. Furthermore, they observed the opposite phenomenon when the solution pH was adjusted above the pzc of the colloid as well as when negatively charged laurate was used as the colloid/collector. Although they confirmed this surface-charging phenomenon by simultaneously studying other alkali halides, there were a few exceptions which led to subsequent studies that revealed how the interfacial structure of water also plays a role. In this regard, Hancer et al. (2000) showed that, depending on the soluble salt, the ions in the brine would either facilitate hydrogen bonding and thereby promote water structuring or disrupt it and thereby promote water breaking. They concluded that flotation would only be possible if the soluble salt was a structure breaker. Overall, these studies showed that there was significantly more to soluble-salt flotation than the size of the amine head group being able to accommodate the sylvite structure/lattice spacing as opposed to that of halite.

Perhaps the most significant contribution from this research campaign at the University of Utah was the colloid/coagel/gel extensions to the Hemi-Micelle Theory of Adsorption (Gaudin and Fuerstenau 1955). In essence, because it was understood that liquid crystals like coagel/gel phases would transform into micelles at temperatures above the Krafft point in bulk solution (Cross et al. 1992), the same must be true for adsorbed species, depending on the type of collector.

Laser Raman Spectroscopy

Young and Miller (1999) extended their studies on fluorite and calcite with oleate using Laser Raman Spectroscopy (LRS) and found that the carbon-carbon double bond would react between

neighbouring chemisorbed oleate molecules on fluorite but not on calcite. This phenomenon was attributed to epoxide formation that polymerized the surface by cross-linking the chemisorbed oleate helping to explain fluorite's enhanced hydrophobicity under certain conditions. The spacing between chemisorbed oleate on fluorite was close enough to allow the cross-linking to occur but not on calcite. This work was done *in-situ* by reflecting the laser beam off a bed of mineral particles and was among the first to use LRS for studying flotation systems.

Spectroelectrochemistry

Since then, most LRS studies have concentrated on examining sulphide minerals in the absence and presence of collector and often in conjunction with ever-improving sensitivity of electrical measurement and control associated with advancements in galvanostats/potentiostats. These "spectroelectrochemical" studies with voltammetric, galvanostatic and impedance techniques required the mineral to be prepared as the working electrode with a fresh surface being created by polishing in between tests. Greg Hope's research groups at Griffith University in Brisbane have been leading the charge in this area having studied a variety of sulphides ranging from simple to complex minerals including galena (PbS), pyrite (FeS_2), covellite (CuS), chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_6), tetrahedrite ($Cu_{12}Sb_4S_{13}$) and tennantite ($Cu_{12}As_4S_{13}$). Woods et al. (1998, 2000), Asbjornsson et al. (2003a,b), Parker et al. (2003) and Jeffrey et al. (2005), for example, examined a variety of collector types and lengths (xanthate, thiourea, mercaptan and dithiophosphinate) as well as collectorless flotation (often with additional application to hydrometallurgical leaching). Results typically showed direct evidence of collector bonding with the metal of interest such as Pb and Cu in a chemisorbed state (as opposed to inferred evidence). Results were often compared to E_H-pH (Pourbaix) Diagrams. Their latest efforts have included researchers at Montana Tech (Gow et al. 2012 and 2013) involving, for example, enargite (Cu_3AsS_4) electrochemistry and the use of mass-balanced diagrams determined with StabCal software (Huang et al. 2005 and 2012). In these studies, the utility of LRS for determining reaction products has been critical and even forced particular species to be excluded from and others included in the calculations. They stress the importance of mass-balanced calculations, particularly in systems involving at least three elements (e.g., Cu, As and S).

As alluded to earlier, spectroelectrochemical studies have also been conducted using ATR/FTIR by packing a bed of mineral particles against an inert ATR crystal, often with potential-control. Jaako Leppinen, Jerzy Mielczarski, and Roe-Hoan Yoon have been leaders with this technology, often with their own research groups but periodically in collaboration with one another (Basilio et al. 1988 and 1992; Laajalehto et al. 1999; Leppinen et al. 1988, 1989 and 1990; Mielczarski et al. 1979, 1986, 1987 and 1993; Talonen et al. 1991). They commonly used cyclic voltammetry and constant-potential control to study sulphide mineral flotation systems including the interaction of xanthate, thionocarbamate, mercaptobenzothiazole and dithiophosphate with galena (PbS), chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), marmatite [(Zn,Fe)S], pyrrhotite ($Fe_{1-x}S$) and pyrite (FeS_2) with and without copper activation. Depending on the system being examined and often with polarized IR, their results showed the collectors oriented at the sulphide surface depending on whether it chemisorbed as a monodentate or bidentate structure or, in the case of xanthate, additionally formed dixanthogen or a surface-precipitated metal xanthate. Different results were observed if contaminants were present in varying amounts, particularly if oxidation products were present prior to collector adsorption. In an innovative electrochemical

study, Woods et al. (1990) used cyclic voltammetry to determine xanthate chemisorption isotherms as a function of potential, plotted them on E_H-pH diagrams, and fit the charge-transfer isotherms to a Frumkin adsorption model. By comparing the chemisorption isotherms to flotation recoveries of chalcocite measured with a Hallimond tube, they respectively showed that 50% and 90% recoveries were obtained with surface coverages of 20% and 50%, specifically showing that flotation could be achieved with submonolayers.

Clearly, the amount and presence of hydrophobic-inducing species can vary with potential control. Research like this has ultimately lead to methods of controlling potential in industrial flotation practices including, for examples, using nitrogen gas as a flotation carrier to minimize oxidation, redox reagents to control pulp potentials, and specific types of steel as grinding media to control galvanic interactions. These concepts have even led to successful sulphide flotation operations in the absence of collector and, in this regard, arguments about whether the sulphide mineral surfaces become metal-deficient or sulphur-enriched (Buckley and Woods 1994).

The increasing hydrophobicity of some sulphide surfaces in initial oxidation in solution has been attributed to polysulphide S_n species in which the loss of metal ions to solution (metal-deficiency) results in some in situ S-S bonding (Buckley and Riley 1991). Using the correlation of XPS S2p signals from the oxidized sulphide surfaces with ToF-SIMS mass markers reflecting increased S-S bonding, has given confidence in the XPS assignment to hydrophobic polysulphide species. For instance, freshly-cleaved galena (PbS) surfaces reacted in pH 8 aqueous solution for increasing periods of time have shown a systematic increase in S_n/S ratios with increasing% of oxidised S2p species from XPS spectra (Smart et al. 2000). The identification of S2p species in oxidized sulphide surfaces was summarized in Smart et al. (1999).

Scanned Probe Microscopies: STM and AFM

The introduction of the scanned probe microscopy techniques of scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) to study surface structure at the nm scale in solution has revealed sometimes astonishing detail on oxidation and adsorption reactions. STM was invented by Binnig et al. in 1982 for which Binnig and Röhrer were subsequently awarded the Nobel Prize for physics. In STM, an atomically sharp tip is moved towards a reasonably conductive surface in sub-nm steps using piezoelectric crystal drivers until a tunnelling current is first observed between the tip and surface atoms. It can then be moved across the surface to produce atomic images and some identification of chemical structure in ST electrochemical mode. The AFM, was first demonstrated in 1986 by Binnig et al. (1986). AFM can image insulating surfaces, cannot chemically identify atoms, but can give information on particle–particle and even particle–bubble interactions and changes with reaction and adsorption in force–distance (approach–retract) mode (Ralston 1994). In AFM, the force between a piezo cantilever with attached tip or bubble and the surface is detected by deflection of the cantilever using a laser reflection device. For example, Eggleston and Hochella (1992) observed STM images of galena surfaces in which individual atoms react on contact with air-equilibrated water for 1 min. On oxidation, the tunnelling intensity maximum from single surface sulphur atoms disappeaed due to alteration of the local chemical structure. The apparent vacancies are in fact the sites of individual oxidised sulphur atoms. From their work, and from another study described below, it is clear that, when a surface S atom is oxidised, S atoms in adjacent sites are activated, thus promoting further reaction rather than initiating new oxidation reaction at S sites further away leading to development with time of pits of sub-nm dimensions. The

z-dimensions of these pits corresponded to half or full unit cell parameters of the PbS crystal structure (Smart et al. 2003a, 2007). XPS and AFM studies of the same surfaces with closely similar development of pits confirmed that congruent dissolution of Pb and S occurs with unaltered Pb 4f and S 2p spectra releasing lead and sulphate ions to solution. The rate of formation of dissolution pits was strongly dependent on the concentration of impurities, on pH, and on the gas (air, O_2, N_2) used to purge the aqueous solution. *In-situ* STM images of a freshly cleaved galena in air-equilibrated 10^{-4} M ethyl xanthate solution show colloidal particles of lead ethyl xanthate, confirmed by XPS, formed at the surface corresponding to multilayer surface coverage. In-situ STM studies of ethyl xanthate treated preoxidized galena surfaces have also shown the removal of oxidized lead species and the formation of colloidal lead ethyl xanthate particles as flattened spheres with diameters of 10–20 nm and average heights of 6 nm (Kim et al. 1995). Other examples of the fundamental understanding generated from these atomic-level techniques are reviewed in Smart et al. (2003a).

Ion Beam Mass Spectrometry: D-SIMS, ToF-LIMS, and ToF-SIMS

But the development of the ion micro-beam techniques based on secondary ion mass spectrometry (SIMS), and time of flight laser ionisation mass spectrometry (ToF-LIMS) and time of flight secondary ion mass spectrometry (ToF-SIMS) in particular, have provided the statistical basis for identification of surface species determining the hydrophobic/hydrophilic ratio and interfering with flotation performance. The development and applications of these techniques has been recently reviewed by Nessett (2012). Early applications of dynamic SIMS in quantitative trace element analysis in geological materials (e.g., Lovering 1975, Shimizu et al. 1979) required complex correction factors inherent to the technique. Calibration using selected ion-implanted standards was developed by Chryssoulis et al. (1986). Using this method, the concentration of Ag in various sulphides from Brunswick base metal ore, Au in common sulphides and As bearing sulphides from refractory ores were measured (Chryssoulis et al. 1987). The capacity of dynamic SIMS to image the distribution of sub-microscopic Au within the sulphides was also demonstrated. An analytical program developed in the AMTEL labs has become an industry standard for quantification of sub-microscopic (invisible) gold and other precious metals and their deportment in mineral phases (Chryssoulis and Cabri 1990).

The advent of the highly focussed (90 nm), highly sensitive (7 decade intensity range), highly mass resolved (m/Δm up to 10,000 times) time of flight mass analysers heralded the ability to determine all surface species on a specific mineral phase comparatively between feed, concentrates and tails in flotation. The use of the ToF-LIMS technique, using laser pulses to produce secondary ions for mass analysis, in minerals process analysis was pioneered by Clarke et al. (1986) and extensively developed by Chryssoulis (e.g., Chryssoulis et al. 1995) producing valuable new insight to flotation separation processes in plant operation. This work is reviewed in Smart et al. (2007) and Nesset (2011). This technique produces surface species in the first two laser pulses but has the disadvantage that the laser energy may destroy information from some organic reagents. In an early review of spectroscopic techniques to study the interactions between minerals and reagents in froth flotation by Giesekke (1983), it is noted that static SIMS using a focussed ion beam (i.e., ToF-SIMS) operates in a non-destructive mode analysing only the top-most monolayers of the sample surface and that this is the most appropriate tool for ion beam surface analysis.

In this short paper, we will focus on ToF-SIMS because it is now the most advanced technique for statistical analysis of the hydrophobic/hydrophilic surface chemistry directing flotation

response. In ToF-SIMS, a focussed (90 nm), pulsed primary beam of Ga, Ar, Cs or, more recently, Bi ions and Au ion clusters, is directed at the mineral surfaces in fixed, rastered or pixellated mode. A fixed beam will analyse a chosen area in the practical range from 90 nm to 1 mm diameter. A rastered beam produces lateral images for secondary ion products selected from the total mass spectra collected in the scan. In the pixellated mode, a full mass spectrum is recorded in each pixel (up to 256×256 pixels) in a chosen area giving more than 10^7 data points. Images for any ion can then be selected from this stored data but, importantly, the data can be statistically analysed for correlation of surface species within and between mineral phases. In static analysis mode, a very low flux of the heavy ions impacts surface layers so that, in the time of routine measurement, less than 5 surface atoms in 1,000 are impacted. The secondary ions, both positive and negative, ejected from these impacts are mass analysed by charge (m/z) with reversed polarities using their time of flight (t) to the detector in the relationship $m/z = at^{1/2} + b$. The very high mass resolution $m/\Delta m$ in the range 7,000–10,000 is able to easily separate almost all closely similar ion masses, e.g., O_2^- from S^-. Secondary elemental ions and molecular fragment ions detached from the first two molecular layers of the surface provide a very detailed set of positive and negative mass fragments from simple ions, e.g., Na^+, OH^- through to large molecular ions of specific reagents, e.g., isobutyl xanthate $(CH_3)_2CHOCS_2^-$. This data collection generally takes less than one hour.

There is a strict protocol for sample collection, storage, transfer and instrument introduction from either laboratory or operating plant flotations that preserves the surface chemistry at the time of sampling (Smart 1991). Validation tests of the method are described in the Centenary of Flotation volume (Smart et al. 2007).

Some examples of the first use of ToF-SIMS in mineral processing help to explain the current development. Early studies by Brinen and co-workers at Cytec (Brinen & Reich 1992, Brinen et al. 1993) and by Chryssoulis and his AMTEL group (e.g., Stowe et al. 1995, Chryssoulis et al. 1995) confirmed that this technique can identify parent and fragment ions from collectors and map their distribution on single mineral grains. Brinen and co-workers 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.

Mineral Phase Imaging: Hydrophobic/Hydrophilic Ratios

A method developed at the Ian Wark Research Institute first provided a statistical comparison of differences in surface species between streams by mineral phase (Piantadosi et al. 2000). Imaging for specific signals and combinations of signals (e.g., Pb, Zn, Cu, Fe) is used to identify the particles of a specific mineral phase (e.g., galena, sphalerite, covellite, pyrite, chalcopyrite) for specific analysis. Sufficient particles of each mineral phase are selected for reliable statistics and the full mass spectrum from each particle recorded and stored. The statistical analysis (Piantadosi et al. 2000) 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 galena flotation (Piantadosi et al. 2000) using collector adsorption of both isobutyl xanthate (IBX) and diisobutyl dithiophosphinate (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 hydrophobic (e.g., $DBPhos^-/SO_3^-$) and hydrophilic (e.g., Ca/Pb, Al/Pb, PbOH/Pb, SO_3^-/S_2^-) indices. The results correlated closely with the flotation response. Hydrophilic species indices such as calcium (~2×), but also aluminum 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 (Piantadosi and Smart 2002) 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 oxy-sulphur 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. A similar differentiation was found using DBPhos collector. These hydrophobic/hydrophilic indices systematically decreases across the flotation sequence between concentrates 1, 2, 3 and tail (Smart et al. 2003b) 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 procedures.

THE PRESENT: NEW METHODS

ToF-SIMS: Statistical Analysis of Real Ores

ToF-SIMS analysis is now applied to ore samples from lab floats and operating plants. Currently, this statistical diagnosis of surface chemical factors affecting flotation recovery and grade is used in two forms: direct comparison of intensities of surface species on selected mineral phases through feed, concentrates and tail; and principal component analysis (PCA) of all surface species correlated with specific mineral phases. An example of each mode is presented.

ToF-SIMS: Comparison of Intensities

In a Brunswick Mines plant survey, sphalerite was reporting to the copper–lead concentrate providing an opportunity for improvement of Cu-Pb-Zn separation. Plant samples were taken in the copper-lead circuit from the rougher feed (RF), rougher bank A concentrate (Con A) and tail (Tl A) and rougher bank F concentrate (Con F) and tail (Tl F). Sphalerite particles were selected using mineral phase imaging to give reliable statistics. TOF-SIMS normalized intensities (**Figure 1**) show the range and distribution of both Cu and Pb on the surface of sphalerite grains. Both Cu and Pb intensities in the con A/tail A pair and Con F relative to sphalerite in the feed (RF) suggesting dissolution/adsorption in conditioning. 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 sphalerites from Con F relative to the tail but there is extreme variation in the Pb content on the surface of the sphalerite grains reporting to Tail A. The down-bank increase in Pb activation may indicate a decrease in solution Cu. These data fit the early observations of Ralston and Healy (1980) who showed in adsorption studies that sphalerite surface uptake for the metal ion Cu occurs before that of Pb and the later observations that Cu activation is favoured 3–4 times over Pb at pH >9 (Sui et al. 1999).

This kind of detail from surface analysis can suggest changes to conditioning, residence time and Cu deactivation reagents. For instance, 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 (Olsen et al. 2012). The action mechanisms of $ZnSO_4$, TETA (triethylenetetramine) and $NaHSO_3$ used as depressants to
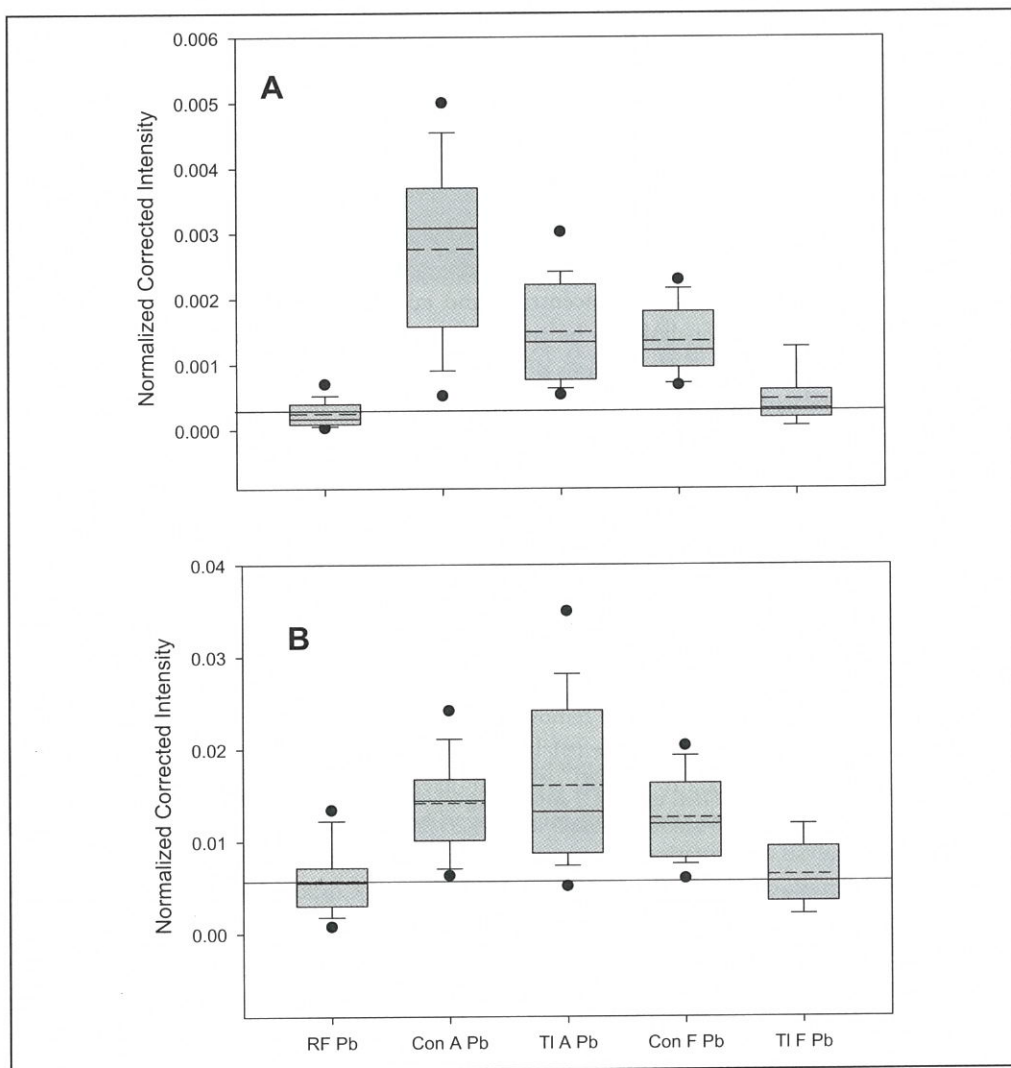
Figure 1. Vertical box plots for ToF-SIMS analyses of sphalerite surfaces from Con and Tail samples Brunswick Mines. (A) Cu distribution and (B) Pb distribution. Solid horizontal line in each box identifies median Cu or Pb content of the sample. The solid horizontal line across the entire plot identifies the mean Cu or Pb content in the sample group and is used as a base line.

limit ZnS activation were examined. A combined ToF-SIMS/XPS examination of sphalerite surfaces in copper plant samples with Cu^{2+} addition was performed to evaluate the response to the three depressants. Although copper transfer occurred under all test conditions, both the $ZnSO_4$ 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 (Khmeleva et al. 2006), the latter to the chelating capacity of TETA (Tukel et al. 2010). Sphalerite surfaces in both the $ZnSO_4$ and $NaHSO_3$ tests reported the highest proportion of species indicative of oxidation such as Zn

$(OH)_2$ and SO_3. It is possible that a greater development of sulfoxyl and hydroxide species on the surface of the sphalerites, as identified by ToF-SIMS, may inhibit collector attachment, produce hydrophilic surfaces, and, in combination, result in reduced sphalerite flotation (Khmeleva et al. 2006, Chandra & Gerson 2006).

ToF-SIMS: Principal Component Analysis (PCA)

In the most recent innovation, multivariate PCA an identify statistical relationships between secondary ions from species that contribute to variation in surface chemistry between minerals and between flotation streams, i.e., feed, concentrates and tail (Hart et al. 2006; Brito e Abreu & Skinner 2011). This form of analysis can be applied to an entire mapped area of ToF-SIMS data without the need to manually define regions of interest. As each set of correlated components are identified, this correlated data is removed from further analysis to enable further correlations to be defined. Each set of correlations is termed a principal component (PC) while the degree of correlation of each species within a given PC is termed the 'factor loading' (in both positive and negative sets in the PC). The factor loading is not a measure of the amount or intensity of that species present but of its correlation with other species in that PC. Many of these PCs immediately identify specific minerals with their associated, correlated surface species. An indication of the significance of a species identified in a given PC may be obtained by examining maps of the PC as compared to images of the actual mass fragment distribution (e.g., **Figures 2a**, b and c). In practice, the first PC 1 is found to be associated with topographic effects (like an SEM image) and does not hold any chemical information. This appears, after removal of the topography, in PC 2 onwards. This analysis can be processed in much shorter time (<1 h) compared with other techniques. Examples from PCA applied to ToF-SIMS data to provide chemical diagnosis capabilities illustrates the value of the method, The full set of data, combining mineralogy, liberation, solution speciation, microscopy (SEM), surface analysis and flotation testing, can be found in Gerson et al. (2012).

The initial flotation stage in the Kennecott Utah Copper Corporation (KUCC, Rio Tinto) concentrator flotation circuit is the bulk recovery (maximised) of copper and molybdenum sulphides, which are then separated via subsequent flotation steps. The Bingham Canyon porphyry copper deposit, the source of the ore, is geologically complex (Triffett and Bradshaw 2008) but can be simplified into limestone skarn (LSN) ore, containing economic concentrations of Cu sulphide minerals, and monzonite (MZ) ore, containing economic concentrations of both Mo and Cu sulphide minerals. It had been proposed, as a result of plant-based flotation observations that that blending of these two ore types leads to 'poisoning' of the flotation response. Laboratory flotation demonstrated that chalcopyrite and bornite recovery was near pro-rata in the blend but molybdenite recovery was substantially adversely affected (Gerson et al. 2012). PCA ToF-SIMS on the laboratory concentrates and tails from MZ, LSN and blended (70:30 respectively) feeds was used to explain these differences in behaviour.

PCA factor loadings from the MZ float experiments found a very strong correlation of all three Mo isotopes in PC 2 from Con 1 specifically identifying molybdenite surfaces (**Figure 2**d). The lack of significant correlation to other species, except a minor correlation to hydrophobic Cu-collector fragments (dicresyldithiophosphate), shows very clean molybdenite surfaces. In contrast, significant correlation of Cu isotopes with Fe, suggesting identification of bornite and chalcopyrite, is only obtained in PC 4 where this is correlated to both hydrophobic collector fragments and hydrophilic FeO, FeOH, K and Mg species. MZ Con 4 still displayed a very strong correlation of the
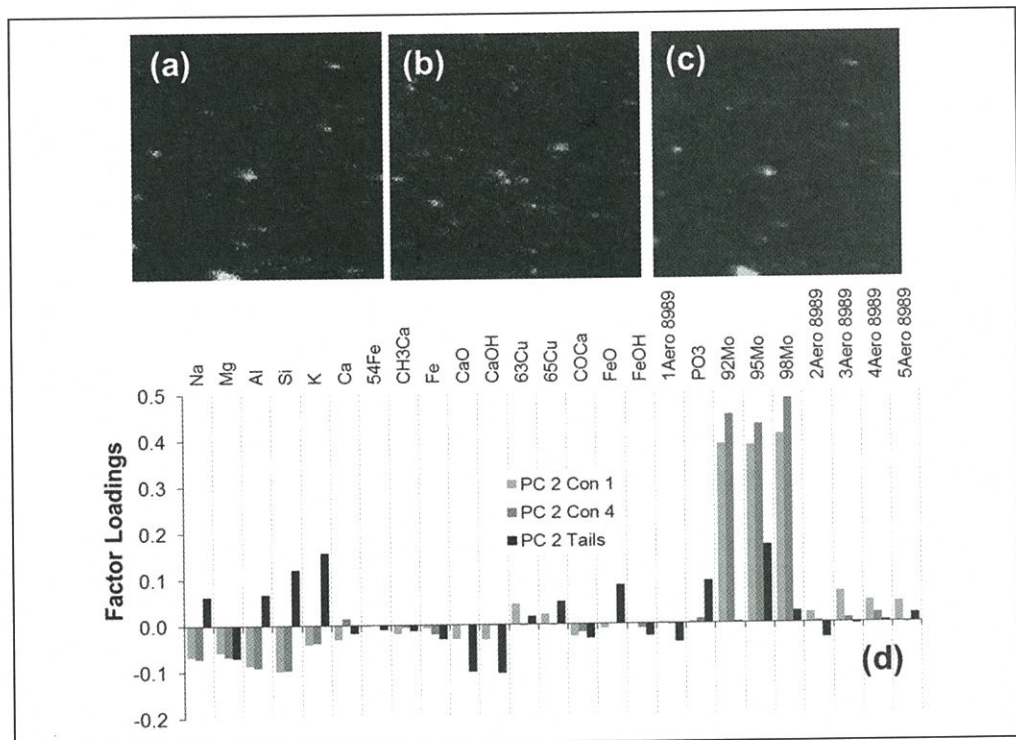
Figure 2. 500 × 500 mm images of MZ Con 1: (a) ToF-SIMS ^{98}Mo data; (b) ToF-SIMS ^{63}Cu data; and (c) PC 2 showing areas of positive factor loadings as pale. It is clear that there is a high degree of correspondence between PC 2 and ^{98}Mo. (d) PC 2 factor loadings for MZ float Cons 1 and 4 and tails.

Mo isotopes in PC2 (Figure 2d). In this later concentrate, no PCs identifying strong factor loadings for Cu and Fe were found suggesting that the surfaces of the copper containing minerals were largely obscured by oxidation and/or attached particles. For the MZ tail, all Mo isotopes were not found in PC2 (Figure 2d) and were only weakly selected in PC 4 but no Cu and Fe association were observed. These statistical correlations show that, while the

Table 1. Absolute factor loadings for PC 4 MZ flotation experiment

Species	Con 1	Con 4	Tails
^{63}Cu	0.37	0.17	0.07
Fe	0.20	0.04	0.01
Ca	0.10	0.13	0.28
CH_3Ca	0.01	0.07	0.13
CaO	0.06	0.07	0.21
CaOH	0.01	0.14	0.21

surfaces of molybdenite were relatively clean in Cons 1 and 4, the surfaces of the Cu containing minerals carried a much higher hydrophilic loading and were substantially obscured.

A similar trend was found for the Cu-containing components of the LSN ore. An increasing surface loading of Ca-containing and other hydrophilic components was observed as demonstrated in Table 1. For the blended ore, PCA ToF-SIMS from copper containing minerals in concentrates and tails was similar to that for the MZ and LSN ores with a relatively high hydrophilic species surface loading which increased through the flotation process, i.e., from Con 1 to Con 4 to tails. However, the ToF-SIMS PCA analysis for the blended ore after Con 1 did not select Mo in any PC

for either Con 4 or the tails, in contrast to the MZ ore analyses, showing either very low concentrations or high surface coverage of molybdenite.

These PCA ToF-SIMS analyses suggest that the copper-containing components within both the MZ and LSN ores were already associated with significant surface contamination so that, on blending, their flotation response was not significantly affected. However, the surface of the molybdenite component of the MZ ore was largely clean. On blending, partial transfer of the hydrophilic load in the LSN ore took place on to the MZ molybdenite resulting in apparent 'poisoning' of the flotation response of this component. Unless other factors apply, e.g., stock piling, throughput, there is no flotation benefit from blending these ore types.

In Situ Vibrational Spectroscopy

The combined limitations of traditional sampling methodologies (dry samples, or limited substates) in vibrational spectroscopy led current flotation researchers to adopt variations of FTIR sampling techniques and other forms of vibrational spectroscopy to enable information to be obtained from real mineral systems under flotation-related conditions (i.e., adsorption at the solid-liquid interface with control of solution conditions). The most widespread vibrational spectroscopy variant in this area is particle film ATR FTIR (McQuillan 2001). Rather than study the adsorption directly to the surface of an IR transparent crystal, layers of nano-sized mineral particles are deposited on the ATR crystal, forming a layer than is still thin enough to be probed by the IR evanescent wave (Cuba-Chiem et al. 2008; Beaussart et al. 2012). This procedure not only increases the range of substrates for analysis (including real mineral particles), it also increases the available surface area for adsorption, enabling detailed studies of surfactant (Khmeleva et al. 2006) and polymer adsorption (Kirwan et al. 2003) onto minerals.

In addition to particle film ATR FTIR, a similar variant of Raman spectroscopy, total internal reflection Raman (Woods and Bain 2012) has also been adopted for studies of flotation reagent adsorption (Beattie et al. 2006). The ability to minimize spectral interference due to water (water vibrations are much less intense in Raman than FTIR), and the electric field enhancements possible due to control of incident light angles, provides the technique with the ability to study complex systems such as collector mixtures (Beattie et al. 2006) and co-adsorption of surfactants (Woods et al. 2011). Surface enhanced Raman spectroscopy (SERS) has also been used to study collector adsorption on noble metal surfaces (with the same substrate limitations as RAIRS discussed above) (Woods et al. 2000), in addition to some novel studies using deposited metal nanoparticles to allow the study of collector adsorption on real mineral surfaces (Hope et al. 2007).

In addition to Raman spectroscopy, non-linear optical vibrational spectroscopic techniques (sum frequency generation spectroscopy—SFG) (Williams and Beattie 2002) are being applied to the study of adsorption on mineral surfaces (Wang et al. 2008). Although more complicated than Raman or FTIR (due to the need for advanced laser systems to generate tunable or broadband infrared light), the technique allows in situ analysis of adsorption to mineral-solution interfaces, is surface specific (i.e., no signal is generated from molecules in the bulk solution above the surface), and is highly sensitive to the presence of small amounts of adsorbates (detection limits of 1% of a monolayer). Given the low dosages/surface coverage of collectors in flotation circuits, the ability to probe adsorption and structure with higher surface sensitivity than FTIR and Raman is a distinct advantage. However, the power of the methodology is limited by a general requirement for analyzing flat surfaces (like RAIRS or traditional ATR FTIR).

Contact Angle Determination

The hydrophobic/hydrophilic ratio of species on each mineral particle determines the effectiveness of capture by the rising bubbles and, on average for a specific mineral phase, defines the three-phase (air/solution/gas) contact angle which is generally used in advanced flotation models to define the attachment and stability efficiencies (Ralston, Fornasiero & Grano 2007, Ralston et al. 2007, Eriksson & Yoon 2007). In the first use of hydrophobic/hydrophilic ratios to estimate contact angles on particular mineral phases (Piantadosi et al. 2001), contact angles on single mineral chalcopyrite, measured using the equilibrium capillary pressure technique across a packed bed of particles, were correlated with the amount of collector (dialkyl dithiophosphate, DTP) adsorbed from solution, the ToF-SIMS index DTP/S and flotation recovery at different collector dosages. These correlations were then used to estimate the contact angle of chalcopyrite particles in concentrates and tails from flotation of Ok Tedi ore at different collector dosages based on the statistical analysis of DTP/S ratios from 26 particles in the feed.

PCA ToF-SIMS has been used most recently by Brito e Abreu et al. (2010) and Brito e Abreu & Skinner (2011) to extend and simplify the estimates of contact angle in single mineral studies of 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 just three secondary ions: oxygen, sulphur, and a thiol collector fragment. In these studies (Brito e Abreu et al. 2010), differences in surface species and contact angles with particle size (20–38, 75–105, and 150–210 µm) were also determined with 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 (e.g., Al, Na, K) as the particle size increases. Estimates of contact angles using these statistical ToF-SIMS approaches have been incorporated into flotation model predictions of rate constants for mineral particles in operating plants (Ralston et al. 2007a, b; Muganda et al. 2012).

THE FUTURE: NEW TECHNIQUES AND ANALYSIS

The structure and composition of minerals in froth flotation can also compromise both grade and recovery in the process. The excellent primary tools for mineral structure and liberation analysis, QEMSCAN and MLA, are well known and widely used (Smart et al. 2007). They are based on compositional identification of minerals from EDS databases. They do not, however, separate crystalline from amorphous phases, identify different structures with the same composition (e.g., sphalerite, wurtzite) or different elemental substitution and are practically limited to >5 µm particles. Recent developments, to be described, have extended this structural analysis.

There are a number of emerging technologies and analytical approaches which are poised to play an important role in the understanding of the chemical processes occurring during mineral processing. We discuss here a few that are founded on the application of synchrotron radiation. Synchrotron X-ray radiation offers a number of technical advantages over laboratory based X-ray sources. For general purposes these can be roughly placed into three categories. The much greater brilliance, often by a factor of 10^{10} or more; enables the use of in situ or time resolved measurements not possible in a laboratory. The high degree of collimation, which enables focusing and

imaging with spatial resolution at times now reaching less than 10 nm (Ice et al. 2011), offers the opportunity to probe surfaces and structures with a resolution not before possible. The wide energy range offered by synchrotron radiation enables energy resolved or X-ray scanning experimentation thus offering new forms of analysis not practically possible in a laboratory.

Mineralogy can now be probed using synchrotron radiation with a spatial resolution routinely of 1–2 μm. By using synchrotron microprobe analysis it is possible to measure three different but complementary types of information using the same instrumentation. X-ray fluorescence (XRF) maps can be measured to enable location of elements of interest. This is particularly useful where high value elements at relatively low concentrations (low ppm or even ppb) are the focus of interest in tailings or leach residue samples as a means for process optimisation and improved recovery.

These areas may then be subject to micro-diffraction or entire micro-diffraction maps may be collected. This enables correlation of mineral phases to value elements that may be present as solid solution. Such elemental forms are often missed by techniques such as QEMSCAN and MLA. Furthermore application of these SEM-based techniques can result in error due to the assumption of crystal phase based on elemental quantification, the basis for these analyses, rather than on actual measurement of structure. Where crystallite size is larger than incident X-ray beam size, as is becoming increasingly the case, single crystal diffraction may arise rather than powder diffraction, resulting in very limited diffraction information from any particular voxel. However, this may be overcome by the application of Laue (broad bandpass) diffraction which enables sampling of many diffraction planes simultaneously. While the analysis of such data is more complicated than for monochromatic X-ray diffraction data, considerable effort is currently being directed into developing this approach into a rapid and accurate tool which will in the near future be able to be applied to mineral processing and earth sciences analyses (e.g., the development of the FOXMAS analytical software http://sciencestudioproject.com/foxmas.php).

These micro-XRF and –XRD measurements may also be coupled to micro-X-ray absorption spectroscopy. This enables the local spatial and/or electronic environment of an element to be examined. XAS measurements are carried out by scanning the incident X-ray energy across a specific electron excitation energy of a specific element. The photoelectron emitted then interacts with the local surrounding atoms, up to 5 Å away, giving rise to an interference fringe. The region of up to 50 eV above the edge energy is sensitive to the oxidation state of the element of interest and highly localised electronic environment. This region of measurement is commonly referred to as X-ray absorption near edge spectroscopy (XANES). The interference fringe arising from more than 50 eV above the edge energy, called extended X-ray absorption fine structure (EXAFS), is more sensitive to local spatial environment. These types of measurements enable the geochemical location of elements to be probed which is of particular application for examining surface adsorption mechanisms, and interstitial and substitutional environments of trace value elements. XAS can be measured in a number of different ways, e.g., total absorbance, fluorescence, partial or total electron yield. Each of these gives rise to varying probe depths and are described in detail elsewhere (Gerson et al. 2009). A recent example of the application of these three techniques applied to the mineralogy of nickel laterites can be found at Fan and Gerson (2011).

Two other emerging synchrotron-based techniques are worthy of mention. These are the related techniques of photoemission electron microscopy (PEEM) and scanning photoemission microscopy (SPEM). These are highly spatially resolved surface sensitive techniques that may be applied to the examination of the distribution of surface species on mineral samples. However, in

their current incarnation both techniques require flat mineral surfaces and in contrast to the previous techniques described in this section, both PEEM and SPEM require UHV environments. For both techniques the surface is subjected to photo-ionising radiation. For PEEM an entire surface area is irradiated simultaneously and the resulting excitation processes are imaged, whereas for SPEM the surface is raster scanned by a highly focused X-ray beam. Two approaches may be taken, with either the incident energy being varied with the intensity of the resulting emission intensity being measured, i.e., as for XAS, or the incident energy remains the same and a range of the kinetic energy of the excited electrons is measured as for X-ray photoelectron spectroscopy (XPS). Spatial resolution of less than 10 nm is now possible on the newest PEEM instrumentation. A recent example of the application of PEEM, coupled to synchrotron IR analysis deals with the examination of Cu activation of, and adsorption of xanthate onto pyrite (Chandra and Gerson 2012). In addition, PEEM has been used to study the evolution of surface chemistry on composite sulphide mineral surfaces, with direct evidence seen for galvanic interactions (Acres et al. 2010).

The improved sensitivity to structure and speciation coupled to high spatial resolution offered by synchrotron radiation based techniques offers potential for improved understanding of mineral flotation systems. Moreover with increasing accessibility, there are now more than 50 synchrotrons worldwide and costs (for IP restricted data collection only) that are competitive with top-end lab based analyses these approaches provide an as yet relatively untapped resource for minerals processing science and technology development.

SUMMARY

Poor flotation recovery or grade and misreporting losses can be caused by poor hydrophobic conditioning of the value mineral surfaces or inadvertent hydrophobic conditioning of gangue mineral surfaces. To define this surface chemistry, the hydrophobic/hydrophilic ratio by particle and as a statistical distribution between different mineral phases across a flotation circuit from roughers, scavengers, cleaners to tail is needed before changes to mechanical or chemical operation can be effective. Surface analysis using statistical methods in ToF-SIMS can now provide this information. Direct comparison of intensities and principal component analysis from hydrophobic (principally collectors) and hydrophilic species between feeds, concentrates and tails can identify surface species discriminating in bubble-particle attachment. In addition to MLA and QEMSCAN analysis, losses due to mineralogy (e.g., minor phases and solid solutions) can now be probed using both compositional and diffraction analysis in synchrotron radiation with a spatial resolution of 1–2 μm. These techniques open new opportunities for improvements in recovery and in unrealized value if they are used in plant surveys.

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