

TOF-SIMS studies of surface chemistry of minerals subjected to flotation separation – A review



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ABSTRACT

This paper reviews the applications of time of flight secondary ion mass spectrometry (TOF-SIMS) used for surface chemical analysis of mineral in the context of froth flotation. A wide range of applications are reviewed, including; interactions of reagents on the surface of mineral phases during flotation separation, determining the effects of various transferred ions from different minerals or the slurry, evaluation of hydrophobicity, identifying the relationship between mineral surface chemistry and contact angle, and evaluation of grinding effects. Conclusions indicated that TOF-SIMS, as a unique surface analysis technique, can potentially provide a direct determination of parameters which control the surface reactivity and consequently plays an important role in determining flotation behaviour of minerals.

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1. Introduction

Flotation is a complex process, partially governed by particle size and topography, the composition of the particle and the nature of the particle surface (edges and dislocations). Selective recovery however is driven by the chemistry of the top few monolayers of the mineral surface. The mineral particle–bubble attachment and its ensuing stability are governed by the balance of hydrophobic/hydrophilic species on the particle surface. Given that numerous

species can coexist on the mineral surface simultaneously, shifts in this balance can have significant consequences on recovery. For example, the promotion of mineral surface hydrophobicity through the adsorption of hydrophobic collectors is easily and commonly hampered by the presence of oxidation products (oxy-S-species, oxy-hydroxides), precipitates, adsorbed ions, depressants and fine particles of other mineral phases (Trahar, 1976; Stowe et al., 1995; Crawford and Ralston, 1988; Boulton et al., 2003; Malysiak et al., 2004; Smart et al., 2007; Shackleton et al., 2007; Muganda et al., 2012; Smart, 2013).

In order to optimize mineral beneficiation by means of froth flotation, a detailed evaluation of the surface chemistry of both value

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and non-value minerals by phase and stream in a process is essential. Ideally the surface evaluation must be weighed in context of the flotation (grade and recovery) along with other significant contributors to the recovery process: solution chemistry and speciation along with mineral chemistry and liberation data. The approach to process improvement then becomes integrated, potentially identifying recovery controls by linking various contributing factors prior to looking at opportunities for improvement, for example in grinding, water quality, reagent control and dosage. (Stowe et al., 1995; Piantadosi et al., 2000; Dimov and Chrysosoulis, 2004a; Ralston et al., 2007; Gerson and Napier-Munn, 2013).

For the identification of the surface chemical control factors in a flotation process, it is necessary to measure statistically, differences in surface species by mineral phase within the flotation circuit (feed, conditioners, roughers, cleaners and tails) (Hart et al., 2006; Gerson et al., 2012). Due to the complexity of the flotation procedure, the characterization of mineral grain surfaces from this process is a significantly challenging task. There have however been great advancements in the application of various surface analytical tools to flotation in the last 2 decades. An excellent review on a wide range of innovative surface analytical techniques, applied to the fundamental understanding of the flotation process is given by Smart, 2013. The article provides a short description on the development and application of the most common tools along with case studies and some insights to new techniques for analyses.

There are numerous spectrometric and spectroscopic techniques that can be employed to study both mineral bulk and surface chemistry (Cormia, 1992; Marabini et al., 1993). Some of these techniques are more applicable for identifying and understanding interactions between minerals and various components within the hosting pulp. The most sensitive and reliable method for surface analysis is secondary ion mass spectrometry (SIMS) which collects and analyzes the secondary ions that are removed from the surface after bombardment with an ion beam. The process, referred to as sputtering, results in the removal of surface material through the generation of positive and negative ions along with neutral fragments. SIMS is divided into two categories, dynamic and static, depending on the energy and nature of the primary ionizing beam. In the dynamic mode (D-SIMS), the high energy direct current ion beam continuously removes surface material creating a depth profile through the sample being analysed. The technique is considered destructive and provides information regarding the matrix composition of the sample (typical analytical sample depths are on the order of several microns). In the static mode (SSIMS or more commonly TOF-SIMS) a pulsed low energy ion beam removes surface material. In the time of analysis generally less than 0.1% of the samples atomic sites are involved in ion beam interaction. The ion interaction leads to a very low sputter rate, on the order of a fraction of a monolayer per hour and therefore the technique is considered non destructive. The SSIMS or TOF-SIMS technique is best suited for the analysis of surface materials, particularly organics, which may be present as thin over layers. Chemical imaging has been well established for both DSIMS and TOF-SIMS (Brinen et al., 1993).

TOF-SIMS is widely used to conduct qualitative surface chemical analysis. Properly identified secondary ions on the mineral surfaces can be characteristic of hydrophobicity functionalities. In the flotation context, an excess of "hydrophobic fragments" or "hydrophilic fragments" can be applied to identify the predominant surface chemical species contributing to the concentration (floated) or rejection (tail) of a particular particles (Trahar, 1976; Stowe et al., 1995; Crawford and Ralston, 1988; Piantadosi et al., 2000; Boulton et al., 2003; Ralston et al., 2007). Moreover, the intensity of TOF-SIMS signals from these surface chemical species as a qual-

itative indication tool can be used to estimate surface wettability of a mineral (Boulton et al., 2003; Piantadosi et al., 2000; Khmeleva et al., 2005).

TOF-SIMS signal intensities can be affected by (1) the concentration of ion species on the mineral surfaces, (2) sputter yield of species, (3) matrix effects (e.g., ion yield), and (4) the beam conditions (Benninghoven, 1969; Vickerman and Briggs, 2001; Hagenhoff, 2000; Piantadosi et al., 2000). Numerous studies have shown that TOF-SIMS has the required level of sensitivity for detection and analysis of mineral surfaces from flotation products (Chrysosoulis et al., 1995; Nagaraj and Brinen, 1996, 1997, 2001; Smart et al., 2008). However as the procedure is based on a comparative measurement of secondary ions generated from the surface of minerals (secondary ion yield, SIY), issues regarding matrix dependent variations in SIY, relative sensitivity factors (RSF) and surface component loading should be considered and incorporated into a separation method of minerals. For sulphides, comparative RSFs for various matrix components and several surface adsorbed reagents have been worked out (Hart et al., 2010). However for the various other value added minerals (for example rare earth element minerals), this task remains a work in progress.

It is the intent of this paper to provide a comprehensive review of the TOF-SIMS applications in the mineral flotation context. We hope to demonstrate how this technique has been applied to the various mineral processing applications including: the various testing strategies, grinding, hydrophobicity, contact angle, flotation which can reveal elemental and molecular information from the surface of different minerals during flotation, and the surface chemistry of single particles present in a mixture of mineral grains.

2. TOF-SIMS analyses in the mineral flotation context

In the flotation context, the surface chemistry of grains representing samples from the various points in the process stream are analysed by TOF-SIMS. The spectra are obtained by bombarding the surface of the grains with a pulsed primary ion beam to desorb and ionize species from the sample surface. Damage to the uppermost monolayer is minimized by applying extremely low primary ion fluxes (Gerson et al., 2012). The process results in the production of sputtered neutrals as well as positive and negatively charged ions. The most versatile ion beam for analysis of mineral surfaces from flotation process samples is Bi^{+1} which can be clustered into 3, 5 and 7 ion clusters, retaining the same kinetic energy while reducing or, spreading out, the ionization impact. The true value of the Bi^{+1} ion gun is in its capacity for minimizing fragmentation of larger molecules (collectors) allowing for significantly improved identification. Older generation ion beams include Au, Ga^+ , Ar^+ , O^- , Cs^+ , and SF_6 however with the advent of the new generation ion guns these have been phased out except for special circumstances (for example, Cs^+ depth profile sputtering, and Au cluster ions to enhance the sensitivity for molecular species).

As a result of the low primary ion current, the majority of the sputtered species are molecular in nature, both fragmented and parent, a feature which is exploited for reagent identification. The generated charged ions are separated according to mass in a time of flight (TOF) drift tube and detected by a sensitive dual channel plate analyser. By rastering the primary ion beam over a selected area on the sample, elemental and molecular distribution maps are obtained. From these maps, region-specific variability in atomic and molecular intensity can be established on a qualitative basis. Under the best conditions spectroscopic mapping at 0.2 μm spatial resolution is possible (Stowe et al., 1995).

All raw spectra are processed generally with instrument proprietary software (e.g., IONTOF or Wincadence-N). Peaks in the cal-

ibrated spectra are assigned to specific isotopes in accordance with their atomic mass. Peaks representative of specific materials (collectors) are defined based on spectral finger prints which are generated by analysing a small portion of the collector mounted on a specific substrate. For surface specie loading, comparative evaluation of the corrected ion intensity for each mass position, measured as the integrated area under each peak corrected for dead times, is calculated. In order to compare intensities between areas of different dimensions, corrected intensities are normalized to the total number of counts for the areas examined (Hart et al., 2006; Vizcarra et al., 2011).

Possibly one of the greatest challenges to studying the interactions between pulp and mineral surfaces in aqueous medium from flotation plants is sample collection. The key is to preserve the sample for analysis at a later date in a different facility. For this a method has been developed where surface reactions after collection are minimized by degassing the sample immediately after collection with de-oxygenated nitrogen and snap freezing with liquid nitrogen (Smart, 1991; Piantadosi et al., 2002; Hart et al., 2006, 2007). The sample must remain frozen during transport. In time delayed testing (when analysed within a 3 month period after collection) no differences in the surface characteristics in relation to the time of analyses have been identified.

3. Principal component analysis (PCA)

A major challenge associated with the application of TOF-SIMS analyses on the mineral flotation stream products is mineral phase recognition due to the composition complexity of minerals within multiphase ores and their surface chemistry. Principal component analysis (PCA) is a common technique applied to analyze multivariate data and has been applied in various disciplines (Jolliffe, 1986). PCA is generally utilized to reveal underlying information in the data (patterns and relationships among variables) and to decrease the dimension of data. Linear combinations of the original variables based on the covariance and correlation matrix are derived PCs. The test data of various analyses and the model of PC coefficients for different correlation matrixes can be compared based on the inter-correlations. The maximum possible variation in the database can be presented by the first principal component (PC1) data with the maximum variation in the uncorrelated data with PC1 represented by the second principal component (PC2). In this interactive fashion all the variations in the database are represented by PCs derived.

The first few PCs will represent the most variation in the database if the original variables show inter-correlation. In a two dimension plan, PC1 and PC2 are geometrically applied to indicate the structure of variables on PC1 x PC2 bi-plot and the observation patterns on a PC1 x PC2 scatter-plot. For more information, the interested reader is referred to the original work for a detailed description of this technique (Jolliffe, 1986).

One of the main advantages of PCA pattern is that this method can be applied for “the systematic examination and interpretation of the model outputs” (Kourti and MacGregor, 1995). It allows for classification of the ore into several phases, using all elements present (Smeink et al., 2005) and also reduces the number of secondary ions that would be useful to understand the variation of reactions without missing essential data (Brito et al., 2010).

Hart et al. (2005) have shown that for TOF-SIMS data analysis of flotation products, PCA is capable of providing useful information towards phase recognition and particle selection. They have demonstrated that in a complex multi-phase ore, mineral identification using PCA is a more reliable approach compared with elemental imaging and manual particle selection; as it can provide a clearer definition of particle boundaries using multi-variable recognition

(Biesinger et al., 2004; Hart et al., 2005; Hart et al., 2006). In particular, it allows for detection of different mineral phases and their surface species rather than manually focussing on one mineral for statistical analysis. This methodology is the subject of a patent (Smart et al., 2008).

PLS_Toolbox 2.1 from Eigenvector Research Ltd. (Manson, WA, USA) running on Matlab 6.0 (or 7.0) was the software used for PCA analysis. In processing TOF-SIMS images, PCA selects these correlations from the mass spectra recorded at each of 256×256 pixels in a selected area of particles (Hart et al., 2005). For each set of data as many significant mass peaks as possible were added to the peak list for analysis. Also included in the peak selection is the total remaining ion image (sum of ion intensity not selected as a specific peak) shown at mass zero in the loadings. Data was either “mean centred” or “auto scaled” prior to PCA (Hart et al., 2006). Mean centring is done by subtracting the column mean from each column, thus forming a matrix where each column has a mean of zero. For the “auto scaled” data, the data is first mean centred and each mean centred variable is then divided by its standard deviation resulting in variables with unit variance. This procedure puts all variables on an equal basis in the analysis. Thus, the less intense but more chemically significant higher mass peaks receive the same level of consideration in the analysis as the intense, low mass peaks (Hart et al., 2005; Gerson et al., 2012).

In the image mode, PCA has proved to be an applicable method of selecting particles by mineral phase with clearer definition of particle boundaries due to multi-variable recognition. Hart et al. (2005) have shown that intensities between the sphalerite and pyrite/chalcopyrite phases are clearly separated by statistical difference in copper (Fig. 1). The experimental results validate the selective transfer of Cu from chalcopyrite to sphalerite.

In another investigation, Hart et al., 2006 applied the PCA method on concentrate and tails samples collected from the Inco Matte Concentrator. The results indicate that the transfer of Cu and Ni between chalcocite (Cc) and heazlewoodite (Hz) results in the inadvertent activation of heazlewoodite and depression of the chalcocite. The data also provided evidence that the collector diphenyl guanidine (DPG) may be selectively attaching to hydroxylated Cu sites. The data revealed that there is a considerably higher CuOH signal on both Cc and Hz particles in the concentrate relative to the tails and higher CuO intensities on Cc and Hz particles from the tails. This finding is supported by the statistical analyses of all TOF-SIMS variables where Pearson product moment inter-correlations between CuOH and DPG (119) for Hz in the concentrate is 0.70 and for Cc in concentrate 0.96 where as for the tail samples, the inter-correlation for Cc in tails is significantly lower; 0.3, presumably due to the high surface concentrations of Ni ions.

Brito and Skinner (2011a) also used the PCA for TOF-SIMS images to examine the potential impact of surface chemistry on mineral recovery at constant hydrodynamic conditions. Results indicate that PCA can be applied on TOF-SIMS signals to differentiate chalcopyrite grains in the concentrate and tail, and on the quantified particle responses to the flotation process. Brito et al. (2010) applied PCA on TOF-SIMS outputs as a database to predict the contact angle of chalcopyrite particles according to their surface chemistry analyses. They used principal components to classify the surface species (secondary ions) into hydrophobic or hydrophilic categories. They have stated that “this approach is capable of determining the surface chemistry contribution to the contact angle of individual mineral particles and the distribution of contact angles within a large ensemble of particles” (Brito et al., 2010; Brito and Skinner, 2011a). The estimation of contact angle from TOF-SIMS surface chemical analyses of mineral surfaces was first investigated by Piantadosi et al. (2001). By comparison to single mineral studies using a variety of collectors, they were able to estimate the average contact angle for chalcopyrite from the sta-

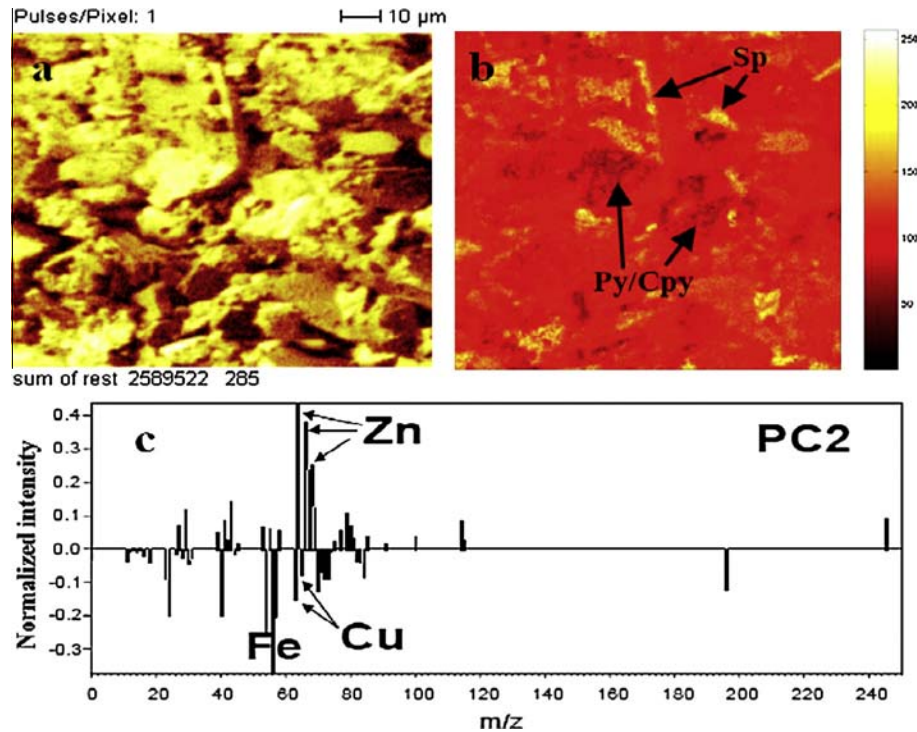


Fig. 1. TOF-SIMS total ion image of particles in pyrite, sphalerite and chalcopyrite mixture (a), reconstructed image (b), and mass loadings (c) for PC2 selected from the area (a) The image clearly differentiates Sp regions (high Zn) from Py/Cpy regions (high Fe) (Hart et al., 2005).

tistical analyses of the surface chemical data. However, in the study by Piantadosi et al. (2001), PCA analysis of the surface species was not performed.

Gerson et al. (2012) applied PCA on TOF-SIMS analyses in order to examine the surface species on both concentrates and tails samples from 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 sulfide minerals, and monzonite (MZ) ore, containing economic concentrations of both Mo and Cu sulfide minerals. It had been proposed, as a result of plant-based flotation observations that blending of these two ore types would lead to 'poisoning' of the flotation response. The TOF-SIMS PCA analyses indicate that copper-containing components within both the MZ and LSN ores showed 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 onto the MZ molybdenite resulting in apparent 'poisoning' of the flotation response of this component (Smart, 2013).

4. Grinding

Flotation separation of galena from pyrite was significantly affected by the oxidation of metal species on the surface of galena and pyrite throughout grinding. Iron hydroxide species on the surface of both minerals depressed their flotation, whereas lead hydroxide species can activate the pyrite surfaces with negligible impact on galena flotation. To optimize selective separation of galena from pyrite by flotation, grinding conditions should allow for the control of lead and iron oxidation (Peng et al., 2003; Chandra and Gerson, 2009).

Peng et al. (2003) used a specific type of mill which allowed for controlling the pH during grinding. It was utilized to study the

impact of grinding conditions on selective flotation of galena from pyrite. Two types of iron media were investigated: mild steel and 30 wt.% chromium (with ~70 wt.% iron). They used TOF-SIMS to identify differences in surface species occurring as a result of the different media and test parameters. The TOF-SIMS results revealed the highest intensity of oxygen and iron species on the surface of galena was observed during grinding with mild steel

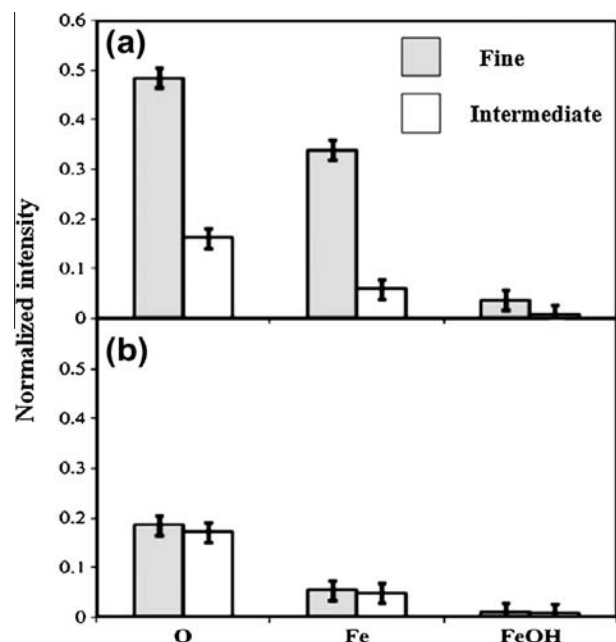


Fig. 2. TOF-SIMS normalized intensities of oxygen and iron on galena particles: (a) mild steel grinding media with oxygen purging and (b) chromium grinding media with nitrogen purging (Peng and Grano, 2010).

and oxygen purging. In flotation testing, these results correlated with the poor galena recovery.

In the same investigation TOF-SIMS analyses of pyrite surfaces also identified that the highest intensity of FeOH was observed during grinding with mild steel and oxygen purging. The intensity of lead and lead hydroxide species on the pyrite surfaces also had a positive correlation with low recovery of pyrite. Comparative analyses between EDTA extraction analyses and TOF-SIMS results suggest that on the surface of galena and pyrite, lead hydroxide could be covered by iron hydroxide. This explains the reduction of lead oxidation species in the presence of iron oxidation species, independent of whether lead oxidation species depressed galena flotation or activated pyrite flotation (Peng et al., 2003).

In another investigation on flotation of galena and chalcopyrite, by using a similar experimental procedure, it was shown that flotation of fine particles, in the order of $\sim 10 \mu\text{m}$, strongly depended on grinding conditions (Peng and Grano, 2010). Two hypotheses were suggested: (1) Fe contamination depressed flotation of particles; (2) various percentages of iron hydroxide species could be present on the surface of fine and intermediate size grains. These possibilities were examined by TOF-SIMS, using two types of grinding media: the tapered cylinder mild steel grinding medium $\sim 100 \text{ wt.}\%$ iron, supplied from Pasminco Mining Co., Elura, Australia) and the spherical chromium grinding medium (30 wt.% chromium, supplied from Magotteaux, Australia) (Peng and Grano, 2010).

The normalized intensities of selected ions on the surface of treated galena for various sizes under different conditions were shown in Fig. 2. TOF-SIMS analyses indicated that the surfaces of treated fine particles under grinding with mild steel medium and oxygen purging showed much stronger intensities of O, Fe and Fe(OH) compared with intermediate particles (Fig. 2a). The higher adsorption of iron hydroxide species on the surface of fine grains is consistent with the lower recovery of those particles. Also, the same intensities of O, Fe and Fe(OH) on the surface of both fine and intermediate grains were observed when grinding was done with 30 wt.% chromium medium with nitrogen purging (Fig. 2b). The same recoveries under this condition for different particle sizes were achieved (Peng and Grano, 2010).

The same procedure was conducted on the surface of chalcopyrite particles under different grinding conditions. Greater intensities of O, Fe and Fe(OH) were detected on the surface of fine particles compared with intermediate ones after grinding with mild steel medium and oxygen purging (Fig. 3a). These results explained the low recovery of fine chalcopyrite particles even when minimizing iron contamination from grinding conditions. The normalized intensities of O, Fe and Fe(OH) on the surface of fine grains for samples ground with 30 wt.% chromium medium with nitrogen purging show a relative decrease on O, Fe and OH loading relative to the mild steel with oxygen purge test. The later test conditions resulted in higher particle depression during flotation. These results demonstrated that mild steel medium and oxygen purging mostly showed an increase in iron hydroxide species on the fine particle surfaces (comparing Fig. 2a with b and Fig. 3a with b). From the distribution of the FeOH species, it is apparent that the finer particles have a greater proportion of Fe oxidative species, certainly in response to galvanic interactions and/or as a result of surface precipitation. In summary, the TOF-SIMS results identified that poor recovery of fine particles of both pyrite and chalcopyrite ground in conventional mills is partially linked to the presence of surface Fe-oxidation species. Therefore, minimizing iron contamination in the grinding condition when fine particles are targeted would be beneficial (Peng and Grano, 2010).

A similar study was conducted by Hyde et al. (2009) using TOF-SIMS analyses to investigate the preferential surface oxidation, and also copper activation (by pure chalcopyrite) of pyrite versus arse-

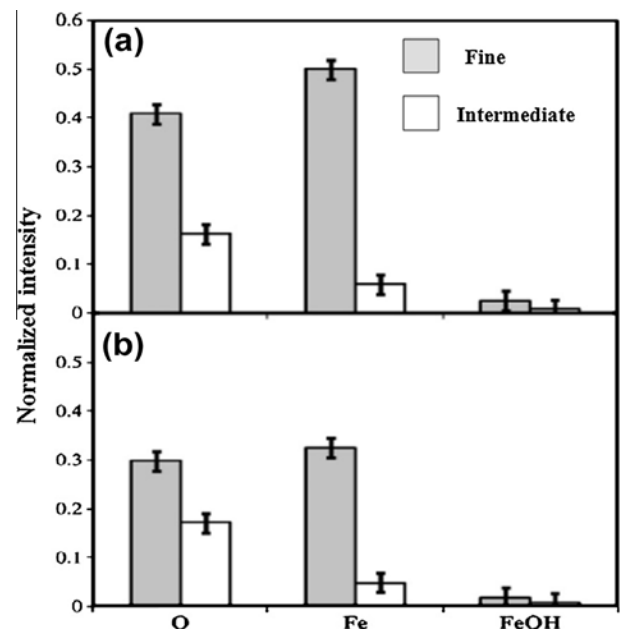


Fig. 3. TOF-SIMS normalized intensities of oxygen and iron on chalcopyrite particles: (a) mild steel grinding media with oxygen purging and (b) chromium grinding media with nitrogen purging (Peng and Grano, 2010).

nopyrite during milling with mild steel, stainless steel, 18% and 30% Cr steel grinding media. For pyrite, the development of surface oxidation products was greatest when using stainless steel and decreased when using mild steel, reflecting the preferential oxidation of the mild steel grinding media over pyrite. The more inert characteristic of stainless steel hinders Fe oxidation in the grinding media, preferentially promoting oxidation of the pyrite grains.

The TOF-SIMS data (FeO, FeOH and AsO) for arsenopyrite ground with 18% Cr and 30% Cr steel grinding media shows higher levels of all three species on grains ground with 18% Cr steel. The data agree well with those of Huang et al. (2006) who suggests that the increase is related to the more electrochemically active grinding media and a resulting transfer and precipitation of oxide species on the arsenopyrite surfaces. The investigation by Hyde et al. (2009) however also identified an increase in the proportion of As oxides on the surface of the arsenopyrite in the test with 18% Cr steel grinding medium. The implication here is that the surface oxidation products potentially also represent those developed in situ as opposed to solely transferred and precipitated species from the oxidation of the grinding medium.

Chapman et al. (2011) studied the effect of crushing by High Pressure Grinding Rollers (HPGR) in combination with rod milling (wet and dry) on the batch flotation test of Platinum-Group Minerals (PGMs). Results indicated a decrease in the recovery and grade of PGMs when HPGR-dry milling was used. TOF-SIMS was used to understand the mechanism of this reduction. The TOF-SIMS results demonstrated that the concentrate samples of both wet and dry grinding showed an increase in xanthate and dithiophosphate along with slightly lower levels of hydrophilic passivating species (calcium, magnesium, silicon and aluminium) when compared to the feed and tails samples (Chapman et al., 2011).

5. Contact angle

In mineral flotation, hydrophobicity is commonly determined by measuring the contact angle among the mineral surface and a bubble at the air/water/mineral three-phase system. There is no easy and reliable technique to measure the contact angle of a par-

ticular mineral in an ore. Capillary penetration is the recommended method to determine the contact angle of particles, using a powdered packed bed (e.g., the Washburn method). It is reported that this method provides the most accurate contact-angle values for a real mineral. Real minerals are non-ideal rough surfaces, with irregular size and shape, and can be chemically heterogeneous. In a real multi-mineral ore then, a wide range of contact angles can be obtained due to the complexity of mineral surfaces and the variety of minerals (Chau, 2009).

Duan et al. (2003) studied the possible correlation between the contact angle of chalcopyrite minerals and their surface analyses by TOF-SIMS. Also in 2008, Priest and his co-workers examined TOF-SIMS as a potential technique to predict surface wettability. They identified a correlation between the surface wettability and the relative intensity of secondary ions. These results suggested that TOF-SIMS analysis can be utilized as a predictive method for both advancing and receding contact angles on the surface of minerals (Priest et al., 2008).

Brito et al. (2010) used TOF-SIMS signals obtained from flotation experiments on a single-mineral, chalcopyrite (CuFeS_2), and found the correlation with their average contact angle, as measured by the Washburn method. In this study, PCA identified a set of seven secondary ions (Cu, O, S, $\text{C}_7\text{H}_7\text{O}$, FeO, FeOOH, and S_2) which describes the main variation in the chalcopyrite surface chemistry. The correlation between these secondary ions (SIs) and the contact angle of particles were examined and the intensity of total oxygen, total sulfur, and the collector fragment ($\text{C}_7\text{H}_7\text{O}$) were shown having a strong correlation with the contact angle. Using a multi-variable regression, a multi-variable linear equation of SIs was generated to estimate the contact angle:

$$\theta = 45.74 - 1.208I_{\text{O}} + 3.065I_{\text{S}} + 15.82I_{\text{C}_7\text{H}_7\text{O}} \quad (1)$$

Brito et al.'s results demonstrated that the presented model has several benefits over the conventional techniques such as the prediction of contact angles for different particle surfaces (small amount of samples) regardless of the particle size. Therefore, no pre-sizing of minerals is involved, and various mineral sizes/regions can be studied at the same time (Brito et al., 2010; Brito and Skinner, 2011b). Muganda et al. (2012) also found a good correlation between the advancing contact angle values predicted by TOF-SIMS and those determined from direct contact angle measurement on the 53–75 μm size fraction of chalcopyrite.

6. Hydrophobicity

In sulfide flotation, recovery and selectivity are fundamentally dependent on the relative rate constants of various mineral phases (Boulton et al., 2003). Therefore, an evaluation of the hydrophobicity balance by mineral particles requires accurate selection of the mineral phase. The hydrophobic–hydrophilic (hydrophobicity) balance by mineral phases and the relative statistical average require determination of the main species contributing to each category in surface layers. This determination is not a simple procedure in a flotation pulp containing diverse mineral phases, various mineral sizes, adsorption of various reagents, different products oxidation, precipitations (often colloidal), and polysulfide S_n^{2-} species (resulting from loss of metal ions, usually Fe^{2+}) on mineral surfaces (Smart et al., 2003a,b, 2007).

Numerous studies have been conducted to evaluate the hydrophobic–hydrophilic (hydrophobicity) balance by mineral phases (Vickers et al., 1999; Piantadosi et al., 2000, 2002; Duan et al., 2003). For adsorption studies in mineral flotation, quantification of surface species by TOF-SIMS and simply using the peak intensities of adsorbed and substrate signals are unsuitable (It does not take into account many of the matrix effects of mineral phases)

(Piantadosi et al., 2000). To generalize, in the case of adsorption, the ion ratio of interest can be expressed as:

$$\text{RPI} = \frac{I_{\text{ads}}}{I_{\text{ads}} + I_{\text{sub}}} \quad (2)$$

where RPI is the relative peak intensity, I_{ads} is the integrated peak area of the ion fragment characteristic of the adsorbed molecule, and I_{sub} is the integrated peak area of the ion fragment characteristic of the substrate. In principle, RPI is the relative peak intensity measured by TOF-SIMS, or RPI is the ideal parameter for adsorption studies since it has the character of θ , the traditional measurement of uptake (I_{ads}) function of monolayer capacity ($I_{\text{ads}} + I_{\text{sub}}$), and might be expected to vary regularly with the extent of coverage of the substrate adsorbent by the adsorbate (Vickers et al., 1999).

This method of quantification yields a clearer illustration of the differences between concentrates and tails (Piantadosi et al., 2002). It is required to use Eq. (2) for each index (Vickers et al., 1999). Piantadosi et al. (2000) investigated the coverage of potassium isobutyl xanthate (IBX) and sodium diisobutylthiophosphinate (DBPhos) adsorbed on the surface of galena by TOF-SIMS. They developed models which fully described both hydrophilic and hydrophobic indices of recovery of particles by flotation. An example of an initial development is described below:

$$\text{Hydrophobic} = \frac{\text{DBPhos}}{\text{S}} \left(\text{i.e. } \frac{I_{\text{ads}}}{I_{\text{substrate}}} \right) \quad (3)$$

$$\text{Hydrophilic} = \frac{\text{PbOH}}{\text{Pb}} \quad \text{or} \quad \frac{\text{SO}_3}{\text{S}} \quad \text{or} \quad \frac{\text{Ca}}{\text{Pb}} \quad (4)$$

Development of a more extensive hydrophobic/hydrophilic index may involve the ratios of a number of these indices, as shown above. For instance, the $\text{DBPhos}^-/\text{SO}_3^-$ indices may be chosen as a first attempt at a hydrophobic/hydrophilic ratio. An alternative hydrophobic/hydrophilic ratio has been chosen to form a more direct overall index (I), using the $I_{\text{ads}}/I_{\text{sub}}$ ratios.

$$I = \frac{\text{DBPhos}}{\text{S}} \cdot \frac{\text{Pb}}{\text{PbOH}} \quad (5)$$

Piantadosi et al. (2002) demonstrated that statistically, particles in the concentrate are more hydrophobic and separable than particles in the tail when both hydrophobic (collectors) and hydrophilic (oxidation products) species are combined (Piantadosi et al., 2002). Piantadosi et al. (2002) continued their surface analysis by TOF-SIMS with the aim of investigation on the particle-by-particle statistics of hydrophilic and hydrophobic species on the surfaces of mixed samples (galena and pyrite) under flotation-related conditions. Using a similar procedure, they found that in the concentrate the surface of galena have less Ca/Pb, PbOH/Pb and oxy-sulphur species (SO_3/S) compared top articles in the tail. In other words, they were less hydrophilic. These differences are statistically considerable. Statistical results obtained for other species, such as Mg/Pb species, did not show any significant difference. This technique identified the effective species that correlate with flotation. Using a similar method, Duan et al. (2003) predicted an advancing contact angle of 71 ± 2 (degrees) for the chalcopyrite particles in the Mount Isa Mines ore using the DTP/SO_3 ratio as measured by TOF-SIMS.

7. Detection of reactions on mineral surfaces during flotation

7.1. Platinum group metals (PGM)

Numerous studies have been conducted on flotation separation of minerals from the Merensky reef ore (Bushveld Igneous Complex, South Africa), containing platinum group metals (PGM), and also metal sulphides which mostly include pentlandite, chalcopy-

rite and pyrrhotite. The main gangue phases of the ore are pyroxene and feldspar as well as minor quantities of talc, chlorite and chromite. Bulk PGM and sulphide flotation are the main treatment methods to optimize the recovery of valuable particles and remove gangue minerals. Surface chemistry analyses have been used to understand the mechanism of maximizing the concentration of valuable minerals (PGM and sulphide minerals), and also minimizing the recovery of gangue phases (pyroxene, feldspar, talc and chlorite) in concentrates to reduce their adverse effects on smelting (Malysiak et al. 2002, 2004; Shackleton et al., 2003; Lotter et al., 2008; Jasieniak and Smart, 2009, 2010).

Malysiak et al. (2002) utilized TOF-SIMS in their study of potential interactions between collector (sodium isobutyl xanthate), and ionic activation (Cu ions) to demonstrate their effects on mineral surfaces in a pentlandite–feldspar flotation system. Analyses of the surface of feldspar particles indicated that the coverage of Cu species were lower in the presence of Ca ions compared with the presence of the collector ions. They revealed that the surface coverage of pentlandite by Cu species is hardly affected by the addition of Ca ions, and a higher proportion of Cu was detected on the surface of pentlandite particles compared with the feldspars. Also, TOF-SIMS data demonstrated that there is a positive correlation between the collector adsorption (xanthate) and the intensity of Cu species on the feldspar surfaces; xanthate ions were not observed on the feldspar surface in the absence of Cu. At pH 9 however, copper and xanthate were both identified on feldspar surfaces indicating inadvertent Cu–xanthate activation. In summary the results indicated that low copper concentrations limit inadvertent Cu activation of feldspar potentially improving the grade of concentrate (Malysiak et al., 2002).

The effect of the chelating agents (diethylenetriamine (DETA), ethylenediamine (EDA), triethylenetetramine (TETA), and ethylenediaminetetraacetic acid (EDTA)), to control inadvertent activation of Cu and Ni ions in the flotation separation of pentlandite from pyroxene was studied by Shackleton et al. (2003). TOF-SIMS results identified the presence of both Cu and Ni ions on pyroxene and pentlandite surfaces. Surface analyses of the same minerals in tests with the addition of EDA revealed a decrease in both Cu and Ni from the mineral surfaces however the decrease appeared to be more significant for pyroxene.

Malysiak et al. (2004) used TOF-SIMS to evaluate mineral surface changes from a series of microflotation tests performed to maximize the flotation of pentlandite while simultaneously minimizing the proportion of pyroxene reporting to the concentrate. The results revealed that inadvertent activation of pyroxene by Cu and Ni ions can be minimized by the addition of DETA. It was proposed that the decrease in these surface species is related to the development of soluble stable chelates and their removal from the mineral surface to the pulp.

Lotter et al. (2008) discussed the undesirable flotation behaviour of orthopyroxene showing talc rims in the processing of Bushveld Merensky deposits. TOF-SIMS surface chemical analyses of the grains with the talc rims did not show the activating Cu or Ni species on the surface, while Cu and Ni ions were identified associated with the non-talc rimmed coarse liberated orthopyroxene grains. The data reveal that the orthopyroxene is reporting to the concentrate either by the natural floatability of the talc rim or inadvertent activation by Cu or Ni.

Jasieniak and Smart (2009) compared the surface chemistry of pyroxene reporting to the concentrate and tail to understand parameters that affect floatability of Merensky ores. TOF-SIMS results did not reveal any significant variation in copper or collector species on the surface of pyroxene particles between those from the concentrate or tail. The essential difference on the particle sur-

faces was observed in the intensity of Mg and Si. Although these intensities may reflect the matrix components of pyroxene and possibly identify hence clean surfaces, pyroxene is inherently a hydrophilic mineral, and would not be expected to float. The Mg and Si intensity discrimination favouring the concentrate samples combined with XRD analyses identified that inadvertent flotation is in response to hydrophobic talc like layers present on the outer surface of the pyroxene grains. (Jasieniak and Smart, 2009). The layers, which represent partial serpentinization of pyroxene, have also been identified in the ultramafic Sudbury ores where a similar inadvertent recovery of pyroxene has been observed.

In Jasieniak et al. (2010) used TOF-SIMS to detect species that could possibly activate and effect on the surface of coarse chromite in the flotation process of Bushveld complex. The main purpose of the investigation was a comparison between the surface chemical properties of coarse chromite grains reporting to the concentrate and to the tail. TOF-SIMS images indicate a high intensity of magnesium and silicon-rich patches on the surface of recovered coarse chromite grains in the concentrate. A silicon to chromium intensity ratio from TOF-SIMS data identifies a discriminating floatability parameter for chromite in these samples (Jasieniak and Smart, 2009).

7.2. Sulfides

In Brinen et al. (1993) studied the reaction of a series of homologous collectors (dialkyldithiophosphinates) with the surface of natural galena using TOF-SIMS. The non-uniform distribution of the dithiophosphate adsorption on the surface of various grains was demonstrated by TOF-SIMS images. Results revealed a possible correlation with the non-uniform adsorption and oxygen rich areas on sample surfaces. Also TOF-SIMS analyses showed an approximate relationship between flotation data as a function of pH and the relative amounts of the collector on the surface of galena crystals (Brinen et al., 1993).

TOF-SIMS mapping was used by Stowe et al. (1995) to differentiate grains of sphalerite, pyrrhotite, galena and pyrite from the ore processed at the Geco Cu–Zn mine (Ontario, Canada) and to measure intensity differences for amyl xanthate and di-isoamyldithiophosphate on the surface of these sulphides. Using the relevant TOF-SIMS information, they could successfully detect collectors on the surface of mineral phases. More importantly, the intensity differences for activators and xanthate correlate and show that the relative difference in surface loading is related to recovery. The results also revealed that collector adsorption on the sulphide mineral grains were localized and non-uniform (Stowe et al., 1995).

Boulton et al. (2003) used TOF-SIMS surface analyses to examine factors controlling the recovery of sphalerite and pyrite through conditioning tests with copper sulphate and xanthate. They reported that the intensity of FeOH on the surface of sphalerite reporting to the concentrate is less than FeOH intensity on the surface of sphalerite particles reporting to the tail. They also reported that the pyrite partitioned to the tail has a significant proportion of surface FeOH, limiting Cu activation and xanthate adsorption.

TOF-SIMS has been used to identify the surface interaction mechanisms between sodium bisulphite (an effective depressant) ions and copper-activated sphalerite in the collector-less flotation. The results suggested that there is a significant change in the nature of the various sulphur species on the surface of grains which would partially account for the collector-less flotation (Khmeleva et al., 2005). This study was continued using TOF-SIMS to examine the interaction between sulphite ions, the collector (isobutyl xanthate) and the sphalerite surface. Analyses showed that sodium

bisulphite interacts with the surface of Cu activated sphalerite regardless of the collector. The postulated mechanism is that sodium bisulphite results in oxidation of the polysulphide species on the sphalerite surface, rendering it more hydrophilic and less floatable. In addition a greater proportion of ZnOH was observed on the surface of the sphalerite grains after sodium bisulphite addition (Khmeleva et al., 2006).

In a similar study by Olsen et al. (2012), both the TOF-SIMS and XPS analyses were used to identify the effect of ZnSO_4 and NaSO_3 on the inadvertent activation of sphalerite in a poly metallic ore. The data revealed that addition of sulfite ions through NaSO_3 dissociation adsorb to hydrophobic Cu coordinated S (polysulphide) generated as a result of Cu substitution for Zn. The sulfite ion decomposition of the polysulphides, generates thiosulfate, which is subsequently oxidized to sulfate. The effect is to remove the hydrophobic polysulphide while rendering the Cu ineffective for collector attachment.

In 2006, (Goh et al. (2006)) designed experiments to examine the ability of TOF-SIMS analyses to distinguished monolayer from multilayer species arising from the interaction between thiol collectors and metal sulfides. Results revealed that the analysis can provide valuable data complementary to that obtained by XPS, and for all the systems studied, they were able to differentiate monolayer from multilayer coverage. According to these results, Goh et al. (2008) attempted to understand the undiminished floatability of sulfide minerals observed for collector (Cu and Ag thiolate multilayers) coverage exceeding a monolayer. TOF-SIMS results provided valuable information on the formation of multilayer patches or islands on top of a chemisorbed monolayer and hence continued exposure of the monolayer in the presence of the multilayer. According to the results, it can be concluded that undiminished floatability of sulfides with multilayer collector coverage can probably be attributed to the patch-wise nature of the multilayer (Goh et al., 2008).

Zanin et al. (2009) applied TOF-SIMS to survey the surface chemistry of molybdenite in the concentrate from the bulk copper-molybdenum flotation circuit at Kennecott Utah Copper. Grains with the $+150 \mu\text{m}$ were subject for the TOF-SIMS analysis. To understand the possible relationship between differences in surface composition of particles with their floatability, the surface of fast and slow floating particles was studied. The surface chemistry analysis indicated higher concentrations of Ca, Fe, Mg and K on the surface of slow floating molybdenite minerals compared to the fast floating grains. The flotation response and surface chemistry can be correlated to the presence of specific gangue phases present in the typical limestone skarn (LSN) ore. This investigation was continued by Gerson et al. (2012), who analysed the surface chemistry of flotation stream samples to understand whether hydrophilic poisoning did actually occur on the chalcopyrite or molybdenite surfaces during the processing of monzonite ore (MZ) blended with LSN, as opposed to simply a pro-rata effect of

the individual ore types. TOF-SIMS data suggested that blending had little effect on chalcopyrite flotation, since both minerals already had similar levels of surface contamination within the two ore types. However, as a result of blending, the formerly relatively clean molybdenite surfaces from the MZ ore were contaminated, and the flotation response was dramatically reduced.

In flotation of galena by xanthate, the recovery of chalcopyrite can be depressed (selective depression) with chitosan (a natural polymer extracted from crustacean shells (Fig. 4)). TOF-SIMS studies indicated that with presence of both minerals in the separation process, chitosan is selectively adsorbed on chalcopyrite, and the adsorption on galena was negligible (Fig. 5) (Huang et al., 2012a).

Further studies were done to understand the mechanism of selective interactions of chitosan on chalcopyrite compared with galena. The dominant stable species of CuNH_3 was found by TOF-SIMS on the surface of chalcopyrite as a result of reaction with chitosan. The TOF-SIMS data suggest that the main mechanism of selective adsorption of chitosan on the surface of chalcopyrite is the chemical interaction between the surface copper atoms with the protonated amine and (to a lesser degree) the hydroxyl groups on the structure of chitosan; the identification of species indicative of this chemical interaction was not observed on the surface of galena (Huang et al., 2012b).

7.3. Other minerals

Talc: Talc, a common gangue phase in Ni sulphide deposits, is naturally hydrophobic and highly floatable. To reduce the floatability of talc, carboxymethyl cellulose (CMC) has been typically used as a depressant. TOF-SIMS was used to examine the characteristics CMC adsorption on the basal planes of New York talc. Surface analyses demonstrated that increased Ca in the pulp resulted in a more homogenous coverage of CMC and suggested that there was a link between surface Ca adsorption and CMC attachment (Parolis et al., 2007).

Studies have shown that even at low concentrations of Ca in an electrolyte solution at pH 9, CaOH^+ can be detected on the surface of talc. In tests with CMC, negligible adsorption of divalent Ca^{2+} ions was observed on the talc surface in the absence of CMC, however in the presence of CMC, Ca^{2+} uptake increased significantly. This information indicated that the main mechanism in the adsorption of CMC macromolecules on the surface of samples was the interaction between acid and metal hydroxyl species. TOF-SIMS data identified a positive correlation between CaOH^+ intensity and the rate of CMC adsorption indicating surface adsorption of CMC is facilitated by hydroxylated Ca ions (Burdukova et al., 2008).

Sylvinit (KCL): The flotation recovery of coarse KCl particles with an amine collector (Armac HT) from the Taquari/Vassouras mine (Companhia Vale do Rio Doce; CVRD, Aracaju, Brazil) is affected by several mechanisms. Several years of experience has

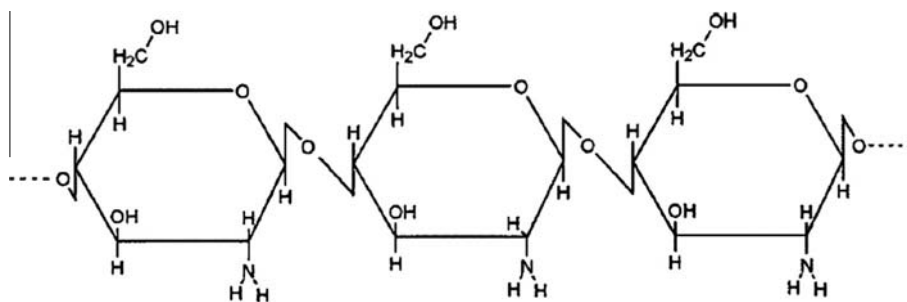


Fig. 4. Structure of chitosan (Huang et al., 2012a).

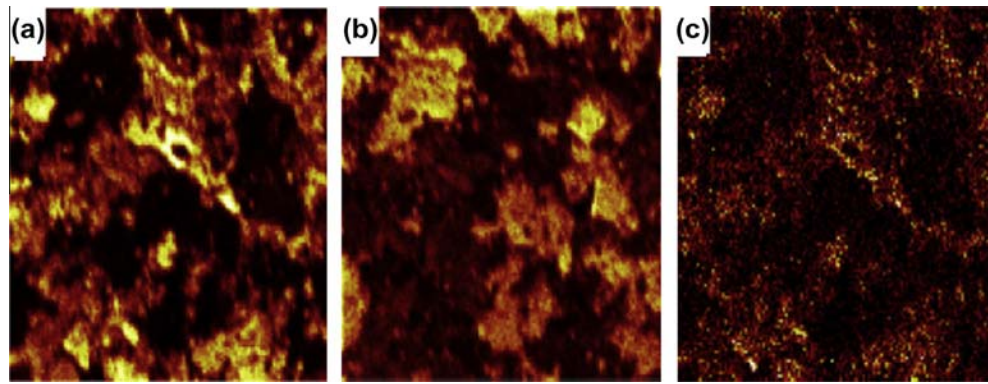


Fig. 5. Positive-ion images of the surface of a mixture of chalcopyrite and galena (weight ratio 1:1) after chitosan adsorption; (a) image of chalcopyrite (Cu^+); (b) image of galena (Pb^+); (c) image of chitosan signed molecule ($\text{C}_6\text{H}_{11}\text{O}_4\text{N}^+$) (Huang et al., 2012a).

shown that an increase in carnallite ($\text{KCl}\cdot\text{Ca}(\text{Mg})\text{Cl}_2\cdot 6\text{H}_2\text{O}$) content in the feed ore decreases the recovery of coarse KCl grains.

TOF-SIMS analysis was used to study the surface properties of coarse KCl particles from a series of flotation tests to understand the how the recovery of KCl is affected by the presence of high concentrations of carnallite. Analyses of laboratory tests indicated that an increase in solution Mg^{2+} concentration resulted in the nucleation and precipitation of fine NaCl (mostly) and KCl salt crystals on the surface of the coarse KCl grains. Their precipitation resulted in a diminished number of sites for collector adsorption and causing depression of the coarse KCl (Fig. 6). The recovery data linked the increase in Mg content to the increase of carnallite in the feed and explained the reduction in coarse KCl hydrophobicity and flotation recovery (Weedon et al., 2007a, 2007b).

Pyrochlore: Recent investigations on the mineralogy of samples from the rougher circuit at the Niobec plant (Quebec, Canada) have shown that high iron content pyrochlore grains appear to be less recoverable than those with a lower iron content (Chehreh chelgani et al., 2012a). TOF-SIMS was used to study the relationship between the matrix and surface properties of different pyrochlore grains, and their impact on collector (diamine) adsorption. Analyses revealed that the species indicative of the diamine molecules, favour the surface of low iron pyrochlore more than the iron rich samples. TOF-SIMS along with XPS analyses showed that higher surface oxidation in high iron grains reduces diamine attachment and yield low recovery (Chehreh chelgani et al., 2012b).

Free gold: TOF-SIMS was applied to identify factors controlling collector loading on gold particles towards optimizing the flotation scheme and improving gold recovery. TOF-SIMS analyses indicated that the collector loading (di-isobutyl dithiophosphate, DIBDTP) is

sensitive to changes in surface silver. Results indicated that silver would activate flotation of gold and there is a strong relation between concentration of silver on the surface of gold and the loading of certain collectors (Dimov and Chryssoulis, 2004a,b).

8. Summary

Mineral separation by flotation is a complex procedure. Establishing a chemical evaluation of a particular process requires a detailed, integrated examination of the flotation data in the context of the mineralogical, liberation, solution and mineral surface data from the various stream products. Given that the top few monolayers of mineral surfaces play the critical role in selective flotation, a detailed evaluation of the surface chemistry of both value and non-value minerals in the process, is essential. The time of flight secondary ion mass spectrometry (TOF-SIMS) technique is uniquely suited for mineral surface evaluation. Numerous studies have shown that TOF-SIMS has the required level of sensitivity for detection and analysis of mineral surfaces from the flotation process and, with the development and application of the modern day instruments, TOF-SIMS analyses is becoming more accessible and routine. The literature review indicates that TOF-SIMS analysis has a positive track record for evaluating factors effecting mineral recovery both in the laboratory and from industrial flotation systems.

The objective of this review was to examine and identify the various applications of the TOF-SIMS technique in the mineral processing context. There is significant information to indicate that a mineral surface from a flotation process is a patch work of different species, all of which can affect selective recovery. Examples of chemical transfer from one mineral phase to another affecting

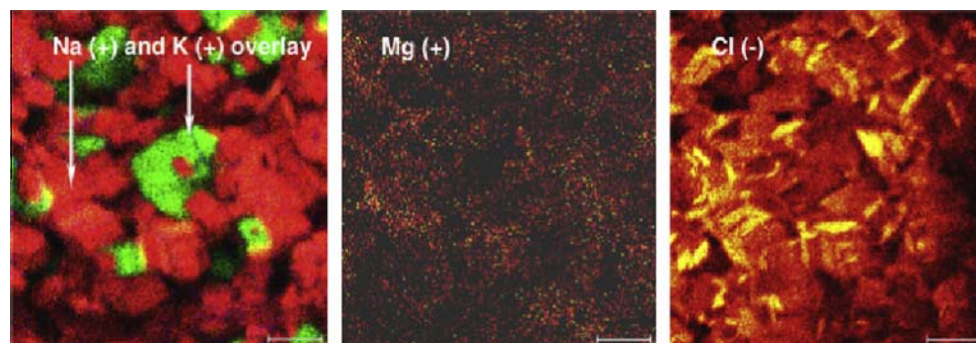


Fig. 6. TOF-SIMS images of mixed salt precipitates, the precipitation of fine grains of NaCl and KCl significantly decreased the recovery of coarse KCl, the increase of carnallite as a source of Mg^{2+} to the brine solution assisted in the deposition of fine salt crystals on the surface of the coarse KCl particles (Weedon et al., 2007).

the flotation outcome have been reported by numerous TOF-SIMS analyses. Copper has been commonly identified by TOF-SIMS as an inadvertent activator of various sulphides. Similarly, surface analyses of recovered gangue silicate phases from a flotation process showed a positive correlation between the collector adsorption and the concentration of Cu and Ni species on gangue surfaces. Both Cu and Ni are implicated as factors controlling inadvertent collector attachment and flotation.

TOF-SIMS studies on the flotation of sulfide minerals also revealed a correlation between the non-uniform adsorption of collectors and oxygen rich areas on sample surfaces. The surface analyses also showed a difference in the ratio of collector to oxygen rich areas between the coarse and finer grains. The fine and intermediate sized grains had a higher proportion of oxygen rich areas identifying their greater potential for surface oxidation, likely in response to residence time in the grinding process. The technique in combination with other analytical tools has been used to understand the operative process in response to various reagents added to promote flotation or depression. In the flotation of galena by xanthate, chalcopyrite can selectively depressed with chitosan. The stable species of CuNH_3 was identified on the surface of copper sulphide as a result of reaction with chitosan. Clearly mineral surface analysis by TOF-SIMS has the capacity to identify surface chemical factors controlling the partitioning of minerals to stream products.

Preferential oxidation of mineral surfaces during grinding and its relation to galvanic interaction has been well established for many years. TOF-SIMS has been used to validate and identify different reactions occurring on the surface of mineral phases during the grinding process. TOF-SIMS surface analyses of sulphides from a poly metallic ore ground with mild steel showed that iron hydroxide covered lead hydroxide on the surface of both pyrite and galena. This explained a reduction in recovery for both pyrite and galena when grinding in mild steel environments. In a similar study, TOF-SIMS analyses of pyrite and arsenopyrite grains ground with stainless steel balls and those of various Cr contents identified selectivity in the degree of mineral surface oxidation in relation to ball composition. The surface analysis by TOF-SIMS validated the previously identified relationship between mineral recovery and the electrochemical activity of both the minerals and grinding media.

TOF-SIMS investigations have also been conducted to evaluate the possible correlation between surface contact angle and surface chemistry. These studies suggested that TOF-SIMS analysis can be utilized as a predictive method for performing a hydrophobicity evaluation on the surface of minerals. A prediction of contact angle based on ion specie intensities has several benefits over the conventional techniques as the estimation can be carried out concurrently for different particle surfaces regardless of the particle size. Direct evaluation of the hydrophobic–hydrophilic balance based on a statistical evaluation of ion intensity on the mineral surfaces indicated that when both hydrophobic (collectors) and hydrophilic (oxidation products) species are combined, particles in the concentrate are more hydrophobic than those in the tail. The TOF-SIMS examination was able to clearly link contact angle to surface chemistry a thereby provide a recovery prediction evaluation.

Although the quantity of research carried out in this field is limited, the reports that have been published to date provide compelling evidence of successful applications of TOF-SIMS within the flotation context. The review identifies the capacity of the TOF-SIMS technique to provide reliable surface chemical data for evaluating factors controlling stream partitioning in various mineral flotation processes. Furthermore TOF-SIMS data can potentially be used to select the most suitable commercially available reagents to optimize selectivity and recovery, or to help design reagents

particularly suited to the mineral in flotation process. Ultimately, as part of an integrated approach, TOF-SIMS surface chemical analyses may become indispensable for evaluating and/or designing flotation processes.

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