

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

Roger Smart¹, Ning Xu¹, Rong Fan¹, Andrea Gerson¹ and Brian Hart²

1. *Mawson Institute, University of South Australia, Australia*

2. *Surface Science Western, University of Western Ontario, Canada*

ABSTRACT

A complete strategy has been developed for identification of the reasons for losses in recovery and/or grade, due to changes or complications in mineralogy and in mineral surface conditioning, and their subsequent correction. The sequence of methods starts with comparison of mineral phases between QEMSCAN/MLA (compositional) and Rietveld XRD (crystalline diffraction) with bulk assay reconciliation. This methodology has recently led to identification of unrecognised amorphous content (12-40 wt.%), previously attributed to crystalline phases, in the fine fraction (<35 µm) of some problematic flotation feeds. Attached amorphous silica, talc- and chlorite-like fines have direct influence on the hydrophobic/ hydrophilic ratio on value mineral surfaces adversely affecting flotation. SEM/EDS is used in the backscattered imaging mode to determine possible problems with liberation (e.g. remnant local locking), not detected in standard liberation analysis, resulting in gangue flotation. EDTA extraction is used to assess bulk feed pre-oxidation and sequential oxidation product loading through the circuit. Changes in circuit solutions are assayed with speciation modelling of precipitates and potentially adsorbing species. ToF-SIMS with principal component analysis is then used to correlate surface species with specific minerals and can be used to assess the effectiveness of specific reagents particularly collectors. This approach identifies unwanted activating species and interference with value surfaces by adsorbed hydrophilic ions, precipitates and fine particles. When the interference or ineffective reagents are specifically identified, remedial action can be targeted. This method has identified residual talc-like layers (<10 nm thick) inducing gangue flotation of pyroxene and chromite in PGM flotation. Recent case studies of application of the full methodology to losses of molybdenite at KUCC and to sphalerite activation in the Cu/Pb circuit at Brunswick Mines with remedial action are discussed.



INTRODUCTION

Losses of value in froth flotation have multiple possible causes as the multi-variable froth flotation models illustrate (e.g. Ralston et al. 2007a). After liberation, pulp density, bubble size, gas flow and holdup, agitation, froth control and other cell parameters have been adjusted with no further improvement, it is the attachment of a collector-conditioned mineral particle to a bubble and the stability of this bubble/particle attachment in both pulp and froth phases that determines recovery and grade. If this is still unacceptable, the reasons for losses likely lie in the mineralogy and surface chemistry of the conditioned feed. In froth flotation, the chemistry of the top few monolayers of different mineral surfaces determines the recovery and grade in operation. The collector addition is designed to adsorb to the valuable mineral particle surfaces making them selectively hydrophobic so that these surfaces prefer to attach to bubbles rather than to water molecules. In reality however, the surface of each individual mineral particle in the flotation pulp is a complex, distinctly non-uniform array of precipitates (e.g. CaSO_4), oxidation products from sulphides (i.e. oxyhydroxides, oxy-sulfur species), adsorbed ions, and attached fine and ultra-fine particles of other mineral phases including clays– all hydrophilic surface species – with hydrophobic collector and metal-collector complexes (see examples in Smart et al. 2003). This attachment is therefore largely dependent on the ratio of hydrophobic to hydrophilic surface species on individual mineral surfaces (Piantadosi & Smart 2002). If this ratio is too low for value mineral particles, recovery will be low and flotation kinetics too slow. This ratio varies widely between different particles of the same mineral and some non-value mineral phases will also have adsorbed hydrophobic collector in some form, contributing to gangue recovery and lower grades. This hydrophobic/hydrophilic ratio, or contact angle in the flotation models (Brito e Abreu and Skinner 2011) may seem esoteric measures to plant operators but they have been shown to determine whether particles of both value and gangue report, correctly or incorrectly, to concentrate and tail (e.g. Piantadosi et al 2000, Ralston et al. 2007b). In order to understand and improve poor flotation recovery, it is first necessary to know whether this is being caused by unrecognised interferences in the mineralogy of the feed or 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, return water quality) conditioning can be usefully made.

A complete strategy has been developed for identification of the reasons for losses in recovery and/or grade due to changes or complications in mineralogy and in mineral surface conditioning, and their subsequent correction. In feed mineralogy, in addition to particle size distribution and liberation of value minerals normally measured, interference from rapidly-soluble minerals, clays and amorphous phases (Forbes et al. 2014, Cruz et al. 2013, Xu et al. 2014) can seriously compromise recovery and grade. It is then essential to fully define the mineralogy to reduce or eliminate these interferences. In order to understand and improve poor flotation recovery where it is due to surface chemistry, it is the variation of hydrophobic/hydrophilic species by particle and as a statistical distribution between different mineral phases across a flotation circuit (e.g. feed, successive concentrates, tails) that we need to know. This requires surface analysis of a large number of particles with high spatial resolution and chemical speciation. A sequence of measurements in this strategy, with examples of outcomes, is summarised.

METHODOLOGY, RESULTS AND DISCUSSION

The methodology follows 6 successive stages. Results and discussion are included in each stage.

Mineralogy

Mineralogy of the flotation feed is normally assessed as part of the liberation studies and whenever the ROM changes significantly. 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 mineral structures with the same composition (e.g. sphalerite, wurtzite) or different elemental substitution and are practically limited to $>5 \mu\text{m}$ particles. The problems with mineralogy in low grade and recovery can be in unrecognised fractions of ultrafine ($<200\text{nm}$) clays and clay aggregates ($<2 \mu\text{m}$) (e.g. kaolin, smectites, illites) and in amorphous minerals (e.g. silica, talc- and chlorite-like fines) that surface-attach more readily than crystalline forms. Hydrophilic clays and amorphous minerals can be attached to value mineral surfaces with direct influence on the hydrophobic/hydrophilic ratio adversely affecting bubble attachment and flotation. High-clay ores are well known to be problematic often requiring higher collector dosages. The effects of clay aggregates on rheology, viscosity and flotation, particularly entrainment, are the subject of other papers in this conference (e.g. Xu et al., 2014).

Amorphous identification and content can be estimated using a combination of: quantitative XRD (e.g. Rietveld analysis using TOPAS) scaled to known (e.g. 15 wt.%) added corundum to give the amorphous wt.%; reconciliation of the XRD-identified phases with bulk assay; and comparison with compositional QEMSCAN or MLA analysis. Table 1 from a high-clay ore shows an example where, in addition to clays and minor minerals not detected in XRD, the amorphous material is found to be mainly hydrated silica with additional implications for slime coatings.

Liberation

The liberation classes by size and by mineral are well described in the automated QEMSCAN and MLA procedures. There can, however, be some forms of incomplete liberation that are not detected in these analyses that may require more specific SEM/EDS analysis. Residual locked particles below the size limit of liberation analysis can be responsible for incorrect reporting of gangue or value. For example, at Kanowna Belle Gold Mine, a bulk sulfide float for Au in pyrite and arsenopyrite from a predominantly sericite gangue with good liberation assessment was producing good gold recovery but too much sericite in rougher concentrate and consequent smelting issues. SEM backscattered electron (BSE) images of particles from the rougher concentrate (Fig. 1) explained this sericite flotation. The large ($>20 \mu\text{m}$) sericite (mica) particle in the centre foreground of Fig. 1 (dark in BSE imaging) has residual pyrite particles less than $3 \mu\text{m}$ (light in BSE image) attached to the surface. These pyrite particles would not be detected in the liberation analysis. With collector addition, they provide multiple hydrophobic points of attachment to bubbles and flotation of large sericite gangue. Results from this study resulted in plant changes to reduce pulp density and increase agitation to reduce recovery of this large sericite, an investment that was recovered in 18 months with on-going benefit.

Table 1 Comparison of mineralogy of a high-clay ore feed between Rietveld XRD, bulk assay and QEMSCAN analysis

Minerals	XRD-bulk assay reconciliation (wt.%)	Rietveld XRD (wt.%)	QEMSCAN (wt.%)	Differences between Rietveld and QEMSCAN results
Quartz	62	42	57.7	15.7
Kaolinite	12	18	11.5	-6.5
Smectite	-	-	4.5	4.5
Albite	15	20	15.9	-4.1
K-Feldspars		-	0.3	0.3
Muscovite	10	9	5.4	-3.6
Other Silicates	-	-	0.3	0.3
Carbonates	-	-	0.3	0.3
Ti(Fe) Oxides	-	-	1.1	1.1
Fe(Mn) Oxides	-	-	0.4	0.4
Pyrite	0.5	1	0.4	-0.6
Cu(Fe) Sulfides	-	-	0.3	0.3
Ca sulfates	-	-	0.0	0.0
Phosphates	-	-	0.0	0.0
Others			1.8	
Amorphous		11		-11

Other examples of residual, locked, hydrophobic surface layers less than 10 nm thick causing gangue flotation have been found using time of flight secondary ion mass spectrometry (ToF-SIMS) (Smart et al. 2007). These examples relate to recovery of gangue pyroxene and chromite in platinum group metals (PGM) flotation plants. The Merensky (Bushveld Complex, South Africa) ore is processed by bulk PGM and sulfide mineral flotation but normally more than 2% of the gangue minerals, principally orthopyroxene with minor chromite which constitute more than 60% of the ore, reports to the concentrate contributing to subsequent processing costs. Flotation of this gangue can occur through inadvertent copper-collector complexation but this mechanism does not account for the true flotation of large pyroxene (20-150 μ m) particles. Statistical comparison of pyroxene particles between concentrate and tails (Jasieniak & Smart 2009) revealed no significant difference in Cu and collector (IBX, DTP) ToF-SIMS

signals but surface exposure of talc-like Mg, Si and O is favoured in the concentrate. Flotation of pyroxene without collector confirmed this statistical discrimination. The hydrophobic talc-like residual layers, which can be imaged in ToF-SIMS, are likely from partial serpentinisation of the pyroxene. These ultra-thin (<10 nm) residual layers result from shearing through the relatively soft talc-like material in autogenous grinding. Some thicker areas have been imaged using SEM (Lotter et al. 2008). A similar mechanism of residual talc-like layers has also been found in flotation of chromite in the UG2 Bushveld ores (Jasieniak & Smart .2010). Plant control through effective depressant action for talc (e.g. Parolis et al. 2007) has been extensively tested.

We have also observed thin residual layers of soft chalcocite on pyrite surfaces causing excessive mis-reporting to copper concentrates requiring resort to hydrothermal leaching rather than flotation. This sometimes unrecognised liberation issue, requiring grinding, chemical, flotation or process changes, can be identified and understood, using information from both SEM and ToF-SIMS.

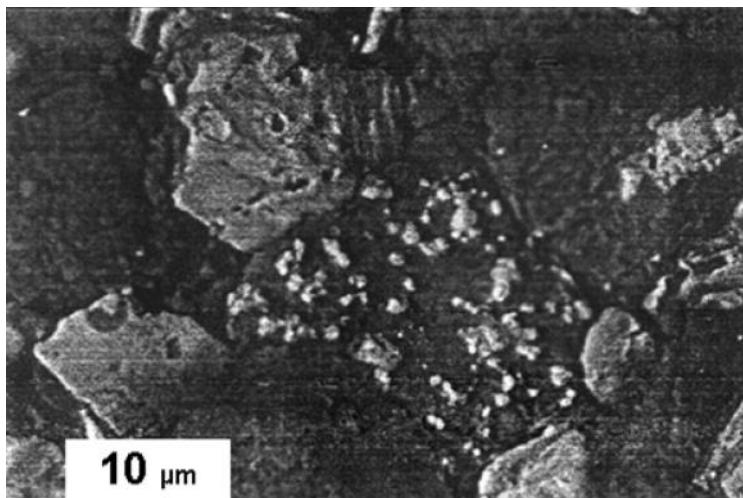


Figure 1 BSE image from a rougher concentrate. The large (>20 µm) sericite particle in the centre (dark) has pyrite particles less than 3 µm (light) attached to the surface (from Smart and Skinner, unpublished report)

Flotation

At this point, samples from feed, successive concentrates and tail are compared. Ideally, these are collected directly from operating plant using sampling protocols to keep the surface chemistry as close as possible to that in the flotation circuit at the time of sampling. This requires that the sample is representative of the stream, does not oxidise or react in the sample tube (i.e. frozen) after sampling, and that these conditions are maintained in delivery to the lab and analytical instruments. In plant, the feed is normally sampled after reagent addition, the concentrates by cutting the lip of the cell or in launder and the tail from the final cell using a splitter box in each case. Protocols for these requirements have been developed (Smart 1991) and verified by correlation with flotation response over more than two decades. Collection of samples from lab flotation experiments on problematic feeds requires similar rigorous

sample handling for correct analysis. The essential steps for sampling are specified to plant operators and described in Smart et al. (2007).

Comparison of the feeds, concentrates and tails where possible between conditions that give varied recovery and grades is a more direct way to recognise the mineralogical or surface chemical factors differentiating in the flotation selectivity.

EDTA Extraction

This technically simple chemical-based analysis can provide a bulk estimate of the extent of oxidation of all minerals in the feed before flotation and in the concentrates and tail after flotation. This is useful if oxidation products on value surfaces are restricting overall or kinetics of recovery. Prolonged storage of ore and/or aeration of feed are particular issues in some cases. EDTA (ethylene diamine tetraacetic acid) complexes and dissolves oxidised metal ions (i.e. Cu^{2+} , Fe^{3+} , Zn^{2+} , Ni^{2+} , Pb^{2+}) from in situ surface reaction layers, adsorbed colloids, precipitates and ions to give solution assays (i.e. identification and quantities) of these oxidation species. 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 equilibrium solution speciation (i.e. predicted relative abundance of specific dissolved and precipitated chemical species) from standard solution assays of feed and pulp solutions through a flotation circuit is readily accessible but not often used. This information, like the EDTA analysis, can indicate potentially adsorbing species and precipitating supersaturated solids, both hydrophilic (e.g. iron hydroxides, calcium sulphate) and hydrophobic (e.g. metal-collector complexes) that may interfere with surface chemistry and hydrophobic/hydrophilic ratios of value (lowering ratio) and gangue (raising ratio) minerals. Combined with EDTA analysis and surface analyses of the top 1-10 nm (ToF-SIMS; Surface Analysis section below), this can particularly provide a more complete picture of the hydrophilic species potentially interfering with flotation of value minerals. Speciation simulation programs, e.g. GEOCHEM-EZ (Shaff et al. 2010), PHREEQC (Toran and Grandstaff 2002), MINTEQA2 (Allison et al. 1990) and others are available free to download. Input required is solution concentrations of all cation and anions, pH, temperature and particularly E_H or ORP (often not measured). The presence of specific solids phases as minerals or existing precipitates can be specified in the calculations. These programs have their own databases of equilibrium constants, solubility products and redox couples, including collector and complexant species, but may require addition of more unusual minerals or reagents from literature.

This correlation of solution modelling and surface analysis has been used in defining correct procedures for copper activation of sulphide flotation (e.g. pentlandite) (Malysiak et al. 2002) avoiding precipitation of hydrophilic $\text{Cu}(\text{OH})_2$. Another recent example of combined information from solution modelling with EDTA extraction and surface analysis 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).

The full use of this modelling with mineralogy, liberation and surface analysis (Gerson et al. 2012) in defining reasons for reduced recovery and grade is illustrated in the flotation at KUCC of the problematic LSN skarn ore alone and in blends with the monzanite MZ ore. In flotation testing, Cu grade versus recovery for the blended ore (70% MZ : 30% LSN) was close to that predicted by pro-rata flotation of the separate ore fractions so that significant interference with MZ copper containing minerals was not occurring. In contrast recovery and grade of molybdenite, which is only present in significant quantities in the MZ ore, was significantly reduced compared to pro-rata prediction, indicative of a surface interference effect on molybdenite flotation performance induced by the LSN addition. In solution modelling, the predominant species in solution for samples (pre-, post-conditioning and tails) are similar: *i.e.* Ca^{2+} , $\text{CaCO}_{3(\text{aq})}$, Cl^- , CO_3^{2-} , HCO_3^- , K^+ , $\text{MgCO}_{3(\text{aq})}$, Na^+ , NaCO_3^- , SO_3^{2-} , SO_4^{2-} but the activities of the carbonate containing species are greater in the post-conditioning samples than in the pre-conditioning and the tail samples in all cases. Calculated saturation indices of possible precipitates indicated that the all post-conditioning samples are super saturated with respect to a range of Ca and Mg containing carbonates likely resulting from the adjustment of the slurry pH with lime. In calculations for the LSN samples (pre- and post-conditioning and tails) allowing precipitation to occur, calcite (predominantly) and dolomite were predicted to precipitate. This suggested that some precipitation of these species may have already occurred and that hydrophilic Mg and Ca oxide and carbonate species are likely to be widespread on the surfaces of the ores within the slurries. This also suggested that flotation with reduced lime addition may be desirable. However, these results did not explain the difference in flotation behaviour of the LSN and MZ ores, as the saturation indices were similar for the LSN, MZ and Blend assays these results or the impact of blending as effects of possibly solution precipitates would be expected to be closely equivalent in all these three cases.

Surface Analysis (ToF-SIMS with Principal Component Statistical Analysis)

In the final stage, it is the surface chemistry that we may need to examine in detail. *i.e.* it is the variation of hydrophobic/hydrophilic species by particle and as a statistical distribution between different mineral phases across a flotation circuit (e.g. feed, successive concentrates, tails) that we need to know. This requires surface analysis of a large number of particles with high spatial resolution and chemical speciation. Analyses of a few individual larger particles carries the risk that they may not be representative of the surface chemistry that is causing low value recovery or interfering gangue flotation. The technique of choice for this analysis is ToF-SIMS described in detail in Smart (2014) and Smart et al. (2007). This technique can rapidly, statistically analyse detailed differences in surface chemistry by mineral phase across a flotation circuit. Its unique advantages are in being able to analyse the first few molecular layers on a mineral surface for both chemical species (e.g. oxidation products, reagent adsorption, surface layer formation) and spatial distribution ($<0.1 \mu\text{m}$). The three main forms of information from this technique are: selection of mineral particles and their distribution by imaging for specific mineral-selective elements; statistical analysis of hydrophobic and hydrophilic species by comparison of intensities from selected mineral particles between feed, concentrates and tails; and full statistical analysis by principal component analysis of all species on particular mineral phases. This type of surface analysis can now be carried out with samples from operating plants. ToF-SIMS analysis in these modes to identify surface chemical reasons for losses in recovery or selectivity has now been applied to samples from operating plants including Mount Isa Mines (MIM), BHP Billiton Cannington Operation, Ok Tedi Mining Ltd. (Papua New Guinea), Cominco Red Dog Alaska Mine, Falconbridge (Strathcona,

Canada), Anglo Platinum (South Africa), Mineracao Caraiba (Brazil), Inco Matte Concentrator (Sudbury, Ontario, Canada), Kennecott Utah Copperton Company (KUCC). Two examples are discussed here: others can be found in Smart et al. (2003, 2007) and the recent review by Chehreh Chalgani and Hart (2014),

A Brunswick Mines plant survey found sphalerite reporting excessively to the copper-lead concentrate. Plant samples were taken in the copper-lead circuit from the rougher feed (RF), rougher bank A concentrate (Con A) and tail (TI A) and rougher bank F concentrate (Con F) and tail (TI F). Sphalerite particles were selected using mineral phase imaging to give reliable statistics (Smart et al. 2014). Increased Cu and Pb intensities in the con A/tail A pair and Con F relative to sphalerite in the feed (RF) suggested dissolution/adsorption processes in conditioning. TOF-SIMS normalized intensities (Figure 2) shows the range and distribution of both Cu and Pb on the surface of sphalerite grains. The solid horizontal line in each box identifies median Cu or Pb content of the sample. The solid horizontal line across the entire plot identifies the mean Cu or Pb content in the sample group and is used as a base line.

The data suggest that for the con/tail pairs at A and F, Cu on the surface of sphalerite grains is discriminatory. Pb on the other hand does not show any significant discrimination between Con A and Tail A, and intensities are only slightly higher on sphalerite particles from Con F relative to the tail but there is large variation in the Pb content on the surface of the sphalerite grains reporting to Tail A. This kind of detail from surface analysis can be used to assess changes to conditioning, residence time and Cu deactivation reagents. For instance, control of Zn activation in the Cu flotation circuit at the LaRonde Division of Agnico-Eagle Mines Limited (Quebec, Canada) was investigated using depressant action mechanisms of $ZnSO_4$, TETA (triethylenetetramine) and $NaHSO_3$ (Olsen et al. 2012). Both the $ZnSO_4$ and TETA test samples indicate that Cu was partially inhibited from attaching to the surface of the sphalerite grains due to increase in hydrophilic oxidation species ($ZnSO_4$) and chelation (TETA) mechanisms. (Khmeleva et al. 2006, Chandra & Gerson 2006).

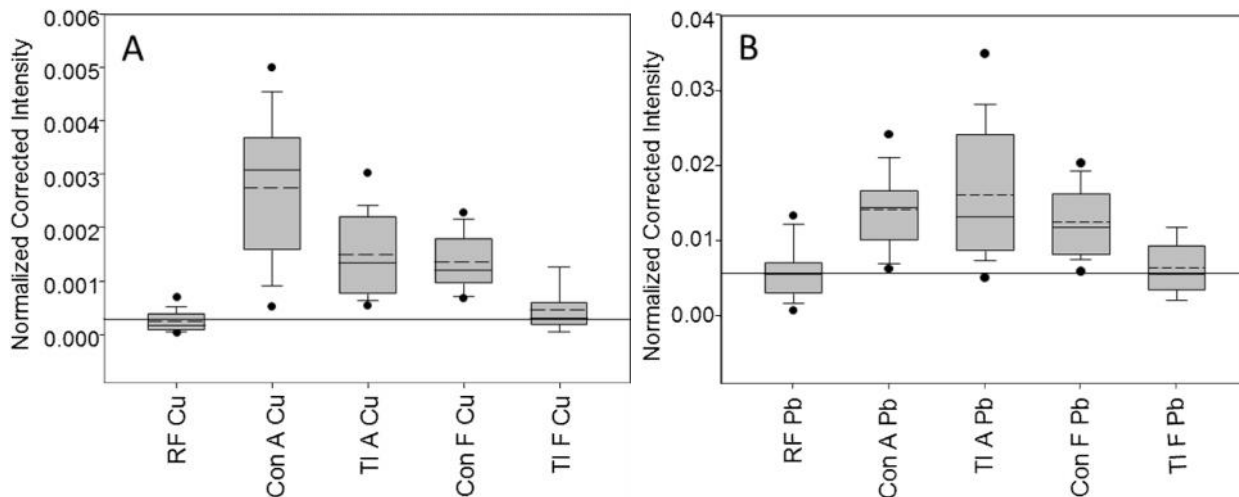


Figure 2 ToF-SIMS analyses of sphalerite surfaces from Con and Tail samples Brunswick Mines. A. Cu distribution and B. Pb distribution (adapted from Smart, Gerson et al. 2014).

The most recent advance in the statistical analysis of ToF-SIMS data is the use of multivariate principal component analysis (PCA) which has been shown to improve image contrast, mineral phase recognition, separation of topographic from chemical effects, and identify related surface species on particular mineral surfaces. The PCA analysis immediately reduces the data to those secondary ions that are major discriminating contributors to the variation in surface chemistry between minerals and between flotation streams, i.e. feed, concentrates and tail, in principal component sets. To illustrate the type and value of the detailed information from these principal components, the case study of Cu-Mo separation at KUCC, (Gerson et al. 2012), introduced in the Solution Speciation Modelling stage, can be used. Figure 3 shows a principal component selected from the first concentrate (Con 1) from two different KUCC ores. For the monzonite (MZ) ore, which separates Mo well but Cu poorly in flotation, in MZ Con1 (left) a very strong correlation of all three Mo isotopes (at masses 92, 95, 98) is found. It is important to emphasise that the bars in PCA sets are not intensities but **correlation factors** (since the Mo isotopes have very different relative intensities). The hydrophobic molybdenite particles identified from PCA in this first concentrate were remarkably clean with only small correlations of these surfaces with Cu (isotopes 63, 65) and collector (S8989 mass fragments), probably adsorbed hydrophobic Cu-collector complexes formed in solution. The negative set of factor loadings in Figure 3a represent correlation of Na, Mg, Al, Si, K, Ca, CaO, CaOH) with iron oxyhydroxide (Fe, FeO, FeOH) from hydrophilic gangue in this concentrate. In other components from MZ Con1, selection of Cu and Fe (chalcopyrite/bornite) surfaces was correlated with FeO, FeOH, K, Mg and collector fragments. In later concentrate (MZ Con4) and MZ tail, no surfaces correlated with Cu and Fe were identified indicating that chalcopyrite and bornite surfaces were obscured by adsorbed and oxidation species, correlating with poor Cu recovery.

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

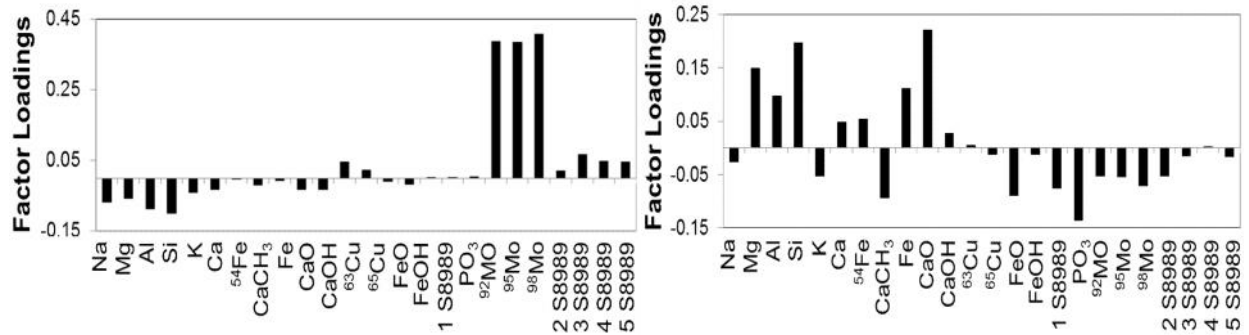


Figure 3 Principal component comparison of PC 2 positive ion factor loadings for: left, MZ Con 1; right, LSN Con 1 ores from KUCC case study (Gerson et al., 2012)

CONCLUSION

This strategic, sequential approach to identification and resolution of mineralogical and surface chemical factors limiting recovery and grade is much more powerful than the more usual single-technique or limited stages of analysis. It has only been used and reported fully in the KUCC case study but has the potential to be applied in plant studies to, first identify the discriminating mineralogical or surface chemical species, and then verify improved discrimination in parallel plant testing of potential solutions. Some of these solutions have been discussed and others are found in Smart (2014).

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