Development of a TOF-SIMS technology as a predictive tool for the needs of the mineral processing industry

Brian R. Hart,[a]* Stamen S. Dimov[a] and Roger St. C. Smart[b]

Recently, upgrades towards a semiquantitative approach to mineral processing applications using the time of flight (TOF) SIMS (TOF-SIMS) technique have been developed and implemented. Secondary ion yield at specific instrument parameters for matrix elements in the predominant ore minerals and their comparative normalization factors have been determined. Surface loading quantification for Cu on a variety of ore minerals has shown that signal intensity variability is related to the substrate matrix. Relative sensitivity factors for component loading have been determined and calibration curves for Cu loading on mineral surfaces have established with lower limits of detection in the range of 10 ppm.

Given the new semiquantitative approach for surface characterization of minerals, a new test was developed to be used as a predictive tool in mineral flotation separation. The test protocol involved a two-chamber ball mill where Cu transfer between the pulp and specimen surface was measured by the semiquantitative TOF-SIMS approach. The test was applied to 13 ores. The reported experimental data on these ores demonstrated the ability of this technique to differentiate Cu transfer over a large dynamic range. The data also demonstrated that the surface loading of Cu on pyrite can be correlated, in some cases, with mineralogy. In others, however, the surface Cu loading observed is not congruent with the mineralogical assessment of the ore sample, but still linked with flotation behavior. This shows that the test could be used with mineralogy to better benchmark a sample before embarking on a flotation flowsheet development programme. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: TOF-SIMS; surface copper quantification; chemical reactivity test; flotation chemistry; mineral processing

Introduction

In flotation separation, surface chemistry is the principal determinant for selective separation of the various mineral phases.[1,2] In essence, the chemistry developed as part of a flotation process is usually designed to create a hydrophobic surface on the valuable mineral, and a hydrophilic surface on all others (the converse is also sometimes sought). Historically, laboratory flotation flowsheet development has often been described as a form of 'black art' rather than by process defined by scientifically derived parameters. However, in the past 15 years, the use of surface analytical tools, most notably the time of flight (TOF) SIMS (TOF-SIMS) has emerged as a mechanism to derive the parameters.

In essence the TOF-SIMS is used to determine the hydrophobic/hydrophilic balance of particles in the flotation process. Crucial to the analyses is correct phase identification followed by a statistical analysis of particle surface chemistry with an estimation of the spread of values. Reliable mineral analyses have been accomplished by mapping ions specific to a mineral phase[2] and by principal component analysis (PCA) which identifies combinations of factors that are strongly correlated (positively or negatively) from sets of spectral data.[3,4]

For this surface chemical approach to be fully applicable in the mineral processing context, all aspects of the technique for comparative surface analyses on different minerals need to be fully clarified. As the technique is based on the measurement of secondary ions generated (secondary ion yield: SIY) from the surface of minerals, issues regarding mineral matrix dependent variations in SIY, comparative normalization factors and surface component loading quantification must be determined and

incorporated into a mineral processing applications model. To this end, this paper will focus on the following: i) recent advances towards the development of a semiquantitative approach; and ii) recent development of a predictive tool in mineral flotation.

Recent Advances

The following are factors peculiar to the TOF-SIMS technique which have been included and corrected for in the semiquantitative approach towards surface chemistry applications in mineral processing. This updated application is particularly relevant for the development of flotation flowsheets.

Matrix Effect and Mineral Indices

Secondary ion yield is a strong function of mineral matrix. The difference in SIY for an element of interest in any mineral is referred to as a relative sensitivity factor (RSF). In combination with other mineral identification techniques, this use of RSFs for specific

* Correspondence to: Brian R. Hart, Surface Science Western, University of Western Ontario, London, ON, Canada, N6A 5B7. E-mail: bhart@uwo.ca

a Surface Science Western, University of Western Ontario, London, ON, Canada, N6A 5B7

b Applied Centre for Structural and Synchrotron Studies, Building H, University of South Australia, Mawson Lakes Campus, Mawson Lakes, South Australia, 5095 Australia

Table 1. Mineral index values (m*l*) for Fe, S and Cu in selected ore minerals. The index for Fe is relative to pyrite, for S relative to pyrite and for Cu relative to chalcopyrite. The index factor is used as a normalization factor for inter mineral comparative analyses

Fe m*l*		S m*l*		Cu m*l*	
Arsenopyrite	0.74	Arsenopyrite	0.40	Bornite	4.60
Bornite	0.66	Bornite	2.31	Chalcocite	4.95
Chalcopyrite	0.71	Chalcocite	0.73	Chalcopyrite	1.00
Geothite	1.81	Chalcopyrite	0.81	Covellite	4.66
Hematite	0.91	Covellite	2.73	Enargite	5.70
Magnetite	1.48	Enargite	2.01	Tetrahedrite	0.92
Pentlandite	1.42	Galena	2.73		
Pyrite	1.00	Pentlandite	0.61		
Pyrrhotite	1.08	Pyrite	1.00		
Sphalerite	0.11	Pyrrhotite	0.28		
Tetrahedrite	0.02	Sphalerite	1.00		
		Tetrahedrite	1.14		

Figure 1. Mean normalized Cu counts on the surface of pyrite (Py), sphalerite (Sph), arsenopyrite (Apy) and pyrrhotite (Po) after loading at various Cu concentrations. The data are normalized to the total ion intensity for the area investigated. Inset (MI) median mineral index (m*l*) values for 5 concentrations of Cu measured in sphalerite (Sph), arsenopyrite (Apy) and pyrrhotite (Po). The index MI for Cu, is calculated relative to pyrite.

matrix elements between mineral phases enables a greater degree of confidence in their correct identification.

From the determined variability in SIY between minerals, normalization indices were created to perform comparative surface chemical analyses between mineral phases. The indices are created using the RSF data according to the following formula:

$$\text{Mineral Index } ml = \frac{\text{normalized counts for the specific element}}{\text{normalized counts for the specific element in a standard}}$$

For the Fe m*l*, all Fe counts are normalized to the Fe counts in pyrite, and for Cu and S m*l*(s), counts are normalized to the Cu counts in chalcopyrite and S counts pyrite. The calculated m*l*(s) are given in Table 1. The m*l*(s) will allow for comparative analyses between mineral phases given that the intensities are normalized.

Calibration of Cu on Sulphides

Calibration curves for selected surface modifiers were generated in order to semiquantitatively determine the amount of modifiers adsorbed on mineral surfaces. Figure 1 is a summary of the calibration data for Cu on the surface of pyrite, sphalerite, arsenopyrite and pyrrhotite. The data reveal a difference in Cu signal intensity between the various mineral phases at any specific Cu concentration, mostly related to factors influencing SIYs. Calculated mineral indices for Cu (Fig. 1 inset), provides information related to the enhancement or depression of surface Cu relative to pyrite and allows for comparison of Cu loading between these minerals.

Ball Mill Chemical Reactivity Test

The mill used in this study resembled a laboratory version of the simple two-compartment mills used in cement or slag milling, the compartments being separated by a screen of 140 micron aperture size. All the milling occurs in the 'active' compartment, neither balls nor ore are added to the 'passive' compartment, so only sub-140 μm material flows to the passive side. Specimen
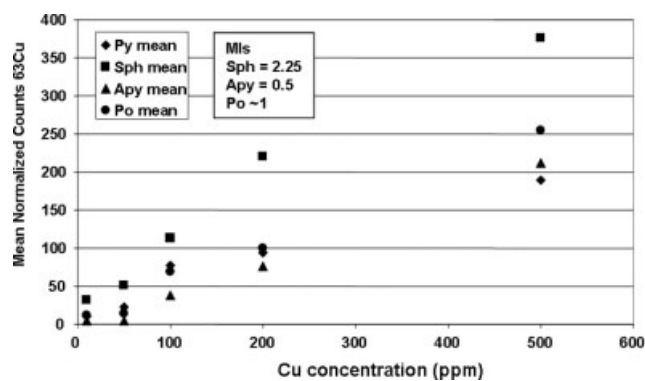
pyrites (+180 μm) placed in the passive side interact with the pulp during the grind. The pyrite specimens are easily separated by screening the material from the passive side of the mill after the test, at 150 μm.

The principal behind the mill is that if the grinding environment (media, shell, pulp density etc.) are consistent, then the single factor driving chemical activity is the ore itself. Chemical activity is measured by the degree of surface sorption taking place on a single mineral and should represent a true comparative measure of ore chemical activity and not any variable facet of the test itself.

The test data (Fig. 2) represents a summary of chemical reactivity tests from a number of ore samples with varying mineralogies in order to investigate the relative degree of Cu transfer from the ore minerals to the specimen pyrite surface during the grinding process. For comparative analyses, a baseline of Cu transfer was established by performing a number of tests under standard operating procedures (SOP) with pyrite and sand.

The variability of Cu on pyrite for the entire ore data set illustrates that the Cu content on mineral surfaces extends over a several orders of magnitude dynamic range. Curiously, some of the highest Cu loadings occurred when 'non-Cu'-bearing ores were milled. For example, ore samples 1 and 2 are from the same mine but exhibit significantly different flotation behavior. Mineralogical analysis of both samples identified a mass proportion of 0.02% undifferentiated Cu sulphides. Flotation testing has shown that ore 1 exhibited strong inadvertent sphalerite flotation and work elsewhere had indicated that copper activation was indeed playing a role. By comparison, ore 2 from the same deposit yielded excellent flotation separation, and no inadvertent sphalerite activation. The flotation behaviour of ore 1 would not have been predicted from mineralogical analysis alone, and demonstrates the value of conducting this test in parallel with automated mineralogy as a preliminary ore assessment tool ahead of flotation testing.

Conclusion

A new semiquantitative TOF-SIMS approach for comparative surface analyses based on the fundamentals of secondary ion generation has been developed. A new chemical reactivity test was developed that could be used as a predictive tool in mineral flotation separation. The data demonstrated that the surface
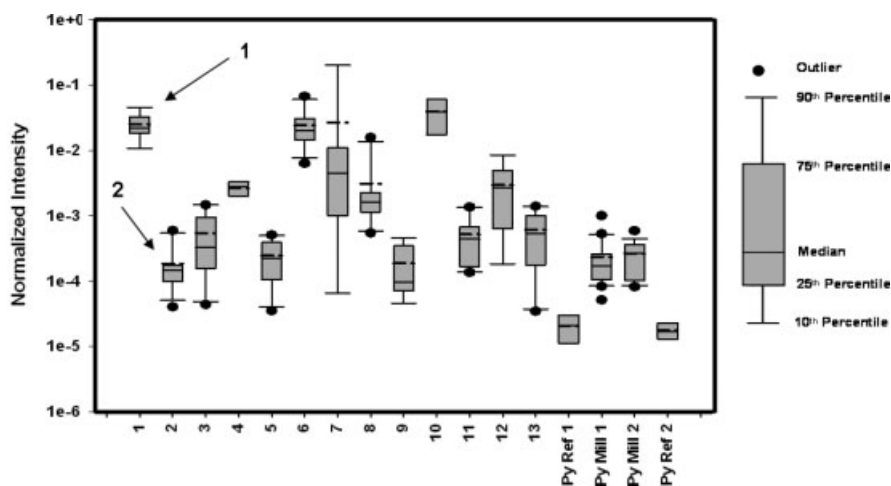
Figure 2. Vertical box plots showing TOF-SIMS data for Cu as measured on the surface of pyrite specimen grains from the chemical reactivity test for all ores investigated. The data for the Py reference represents the normalized Cu intensity on the as received pyrite reference samples and for the Py mill samples for Cu on the surface of the pyrite after milling with sand. The horizontal line through the plot is the estimated baseline for the testing program. Ore numbers 1 and 2 are indicated by the arrows.

loading of Cu on pyrite can be correlated, in some cases, with mineralogy. In others however, the surface Cu loading observed is not congruent with the mineralogical assessment of the ore sample, but still linked with flotation behavior, showing that this test could be used with mineralogy to better benchmark a sample before embarking on a flotation flowsheet development programme.

Acknowledgements

References

[1] S. R. Rao, *Surface Chemistry of Froth Flotation*, Kulwer Academic/Plenum Publishers, New York, **2004**, p 744.

[2] R. St. C. Smart, J. Amarantidis, W. M. Skinner, C. A. Prestidge, L. LaVanier, S. G. Grano, Surface Analytical Studies of Oxidation and Collector Adsorption in Sulfide Mineral Flotation, in *Solid-Liquid Interfaces* (Eds: K. Wandelt, S. Thurgate), Topics in Applied Physics, Springer-Verlag, Berlin, **2003**, 85, pp 3.

[3] B. Hart, M. Biesinger, T. St. C. Smart, *Improved statistical methods applied to surface chemistry in minerals flotation. Minerals Engineering*, **2006**, *19*, 780.

[4] R. St. C. Smart, B. R. Hart, M. C. Biesinger, J. T. Francis, T. Negeri, *Surface Chemical Control in Sulfide Flotation: Principal Component Analysis of ToF-SIMS Data, Proc. XXIV International Minerals Processing Conference*, (Eds: D. Z. Wang C. Y. Sun, F. L. Wang, L. C. Zhang, L. Han) **2008**, Beijing, China, September, ISBN 978-7-900249-54-8/TD 1 (Science Press: China), pp 1008.

View this article online at wileyonlinelibrary.com