

Experimental Study of Slag/Matte/Metal/Tridymite Four Phase Equilibria and Minor Elements Distribution in "Cu-Fe-Si-S-O" System by Quantitative Microanalysis Techniques

Jeff (Jiang) Chen¹, Charlotte Allen², Peter C. Hayes¹, Evgueni Jak¹

¹PYROSEARCH, School of Chemical Engineering, The University of Queensland, Brisbane, Australia

²Central Analytical Research Facility, Institute for Future Environments, Queensland University of Technology, Brisbane, Australia

Keywords: phase equilibria, trace elements, quantitative microanalysis

Abstract

Laboratory studies have been carried out to determine the slag/matte/metal/tridymite four condensed-phase equilibria in the "Cu-Fe-Si-S-O" system and the minor element distributions between the equilibrated phases at 1200°C. A combined quantitative microanalysis technique including electron probe X-ray microanalysis (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been developed to accurately characterize the equilibrated system for both major and minor elements. Analysis precision, estimated accuracy and current limitations are discussed. The resulting elemental distributions are plotted against matte grade and compared to FactSage predictions. It was found that the experimental results for major elements are in good agreement with FactSage predictions. The simultaneous distributions of Ag and Au between slag, matte and metal phases are reported for the first time.

Introduction

Current copper production via pyrometallurgical process involves: a smelting process in which copper sulfide concentrate is smelted to produce copper-rich matte and fayalite or calcium ferrite slag; and a converting stage in which copper matte is converted to copper metal. In order to optimize and improve present industrial practice for copper production, extensive laboratory scale studies have been carried out to obtain the fundamental data on phase equilibria, thermodynamic and physicochemical properties of complex multi-component slag/matte/metal systems. However, there are significant difficulties in conducting high temperature experiments and quantitatively analyzing samples using conventional experimental and analysis techniques. These difficulties arise from the fact that the samples contain many phases at micro-scale with presence of trace elements at concentration of ppm (part per million, or 0.0001wt%) levels. As a result, there are significant knowledge gaps and discrepancies in the existing scientific data for these systems.

This project is part of an integrated research program that combines both experimental and thermodynamic modelling studies to characterize the complex multi-component oxide/sulfide/metal systems at high temperature, of interest to pyrometallurgical production of copper. The specific aim of the present study is to

1. develop experimental and analytical methodology to characterize phase equilibria of the slag/matte/metal/tridymite systems;

2. determine the equilibrium distribution coefficients of minor elements between four condensed phases, slag/matte/metal/tridymite.

The experimental conditions in the present study are in some cases not directly relevant to the current industrial conditions for copper making, however, the fundamental data generated from this study is vital for the construction of a self-consistent thermodynamic database to model and to subsequently optimise industrial processes.

Experimental

Experimental technique for high temperature phase equilibria

The experimental technique used in present study was based on the technique previously developed at PYROSEARCH [1-2]. It involves the preparation of a chemical mixture sample of predetermined composition. The sample mixture is equilibrated at a fixed temperature. On rapid cooling the liquid phases convert to glass so that the phase assemblage that exists at high temperature is "frozen in". The compositions of the solid and liquid phases are then measured using microanalysis techniques.

In this system, the equilibrium is determined by the presence of the four condensed phases. The procedure used follows the sequence outlined below.

a. Determination of initial bulk composition

An estimation of the initial bulk composition of the mixture is carried by FactSage 6.2 [3] calculation at the temperature of interest. The initial chemical components used were Cu_2O , Cu, Cu_2S , Fe, FeO, FeS and SiO_2 . The criteria for composition selection in this case are

1. All slag, matte and copper metal three phases are present at equilibrium with tridymite;
2. Matte grade is within the composition range interest;
3. The proportion of slag, matte and copper metal is close to 50, 25 and 25wt% respectively.

High purity chemicals of Cu_2O , Cu, Cu_2S , Fe, FeO, FeS and SiO_2 were mixed at the selected ratios; Small amounts (<1wt%) of the minor elements of interest (e.g. Au and Ag) were doped into the mixture. The prepared chemical mixture of total weight approximately 0.3g was added into a silica ampoule before it was evacuated and sealed.

b. Equilibration

The sample mixture in the silica ampoule was equilibrated at 1200°C for 6 to 24 hours in a vertical tube furnace.

c. Quenching

Rapid quenching rate is crucial to ensure a quality sample for following microanalysis. Both the matte and copper metal require much faster quenching rates than slag in order to produce homogeneous phases for analysis. The much larger thermo-mass of silica ampoule (8-9g) compared to the actual sample (0.3g) would result in a decrease in cooling rate, which is undesirable.

In the quenching procedure previously used samples are dropped directly into a container that contains large amount of cold water. In present study, modification has been made to this by

placing a hard ceramic brick at the bottom of the container. The container then was filled with water to a height just about 20mm above the top level of the brick. During quenching, the silica ampoule dropped under gravity onto the brick and was found to disintegrate on impact so that sample inside the ampoule could be in direct contact with water almost instantaneously. Reducing the amount of water reduced the buffering effect and ensured the disintegration of the ampoule. Photos of samples before and after equilibration are shown in Figure 1

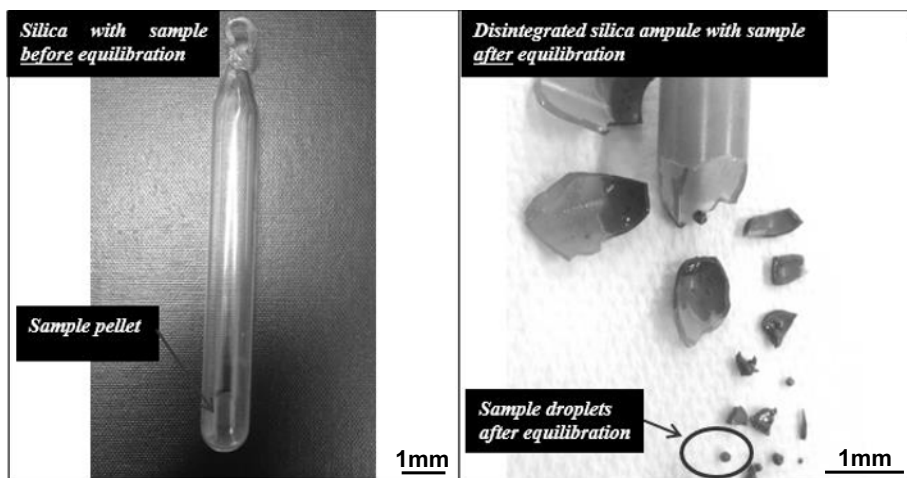


Figure 1 Photos of samples before and after equilibration

Development of analysis technique

EPMA

Electron Probe X-ray Microanalysis (EPMA) is a powerful microanalysis technique and has been increasingly used to quantitatively determine the composition of metallurgical samples including oxides, sulfides and metals. At PYROSEARCH efforts have been made to ensure accurate measurements by EPMA based on the understanding of its capability and limitation at fundamental level. The following issues were taken into account.

1. Identify and minimize background/peak interferences

The probability of background/peak interferences during EPMA measurement increases proportionally with increase of number of elements in the sample for analysis. Efforts have been made, and accurate background positions of each element have been determined for the measurement, to avoid/minimize the background/peak interferences.

2. Reduce minimum detection limit (MDL)

EPMA is generally used for quantification of elements with concentration greater than 1wt% with good accuracy and precision. However, complications arise when the concentrations of the elements of interest are below 1wt%. The concentration of an element below its limit of detection

cannot be measured with confidence. As part of the development of analysis technique, current procedure has been modified to enable the measurement of some of the minor elements of interest. An example is shown in Figure 2. It can be seen, according to current analysis procedure with 10 second counting time on background, the MDL of Ag is close to 1400ppm, by increasing background counting time during the measurement to 300 seconds, the MDL is decreased down to close 200ppm.

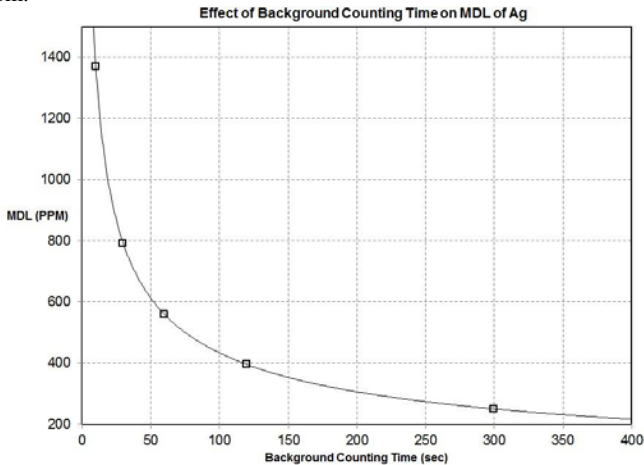


Figure 2 Relationship between MDL of EPMA measurement on Ag and background counting time on JEOL 8200 superprobe (probe current: 15nA, acceleration voltage: 15Kev, probe size: 0, X-ray measured: Ag $L\alpha$)

3. Reduce the effect of boundary secondary X-Ray fluorescence

Uncertainties in measurement as a result of secondary X-Ray fluorescence can occur when EPMA measurements are undertaken on material close to phase boundaries. Excited high energy X-Rays of a particular element in one phase can travel through to another phase and excite low energy X-Rays of another element and therefore influence the observed concentration. This effect can introduce significant error to the measurement results, especially when there is a significant concentration difference of an element in the two adjacent phases (e.g. Fe concentration in copper metal measured close to the interface with slag phase could be systematically higher than actual). In the present study this effect has been evaluated by simulation software CalcZAF and action has been taken during actual EPMA measurement to minimize its effect on the measurement results (i.e. taking measurements at a distance from phase boundary where the effect of boundary secondary X-Ray fluorescence is negligible).

Laser Ablation - Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS)

In present study, Laser Ablation - Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) has been used to quantitatively determine the concentration of trace/ultra-trace elements in the phases presented at equilibrium.

The technique begins with a laser beam focused on the sample surface to generate fine particles – a process known as Laser Ablation. The ablated particles are then transported to the secondary excitation source of the ICP-MS instrument for ionization of the sampled mass. The excited ions in the plasma torch are subsequently introduced to a mass spectrometer detector for both elemental and isotopic analysis.

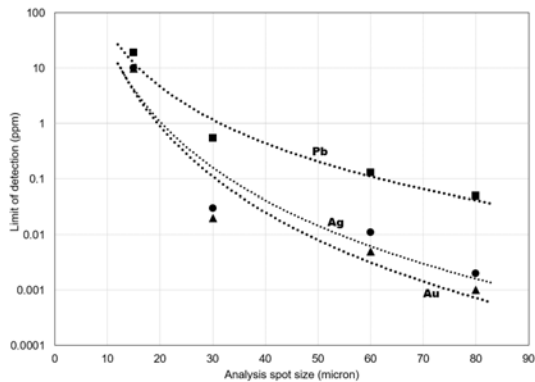


Figure 3 Relationship between analysis spatial resolution and limit of detection using LA-ICP-MS determined in present study

LA-ICP-MS can generally analyze an area of 20-100µm on the sample and provide an ultra-highly sensitive chemical analysis with limits of detection for many elements down to the ppb (parts per billion) level without much sample preparation work. The relationship between analysis spot size and detection limits for the minor elements of interests have been determined in the present study and an example is shown in Figure 3. Uncertainties in the measurement results generally come from mass interference (e.g. Cu⁶⁵ and Zn⁶⁵) and elemental fractionation occurred during laser-sample interaction. Figures 4a-b show examples of the crater left in a slag phase(4a) and a matte phase(4b) after laser ablation process. More significant melting effect observed in matte phase induced by laser generally leads to more elemental fractionation therefore makes accurate measurement more difficult. Efforts have been made to evaluate these uncertainties and introduce appropriate correction procedures to ensure the accuracy of the measurements.

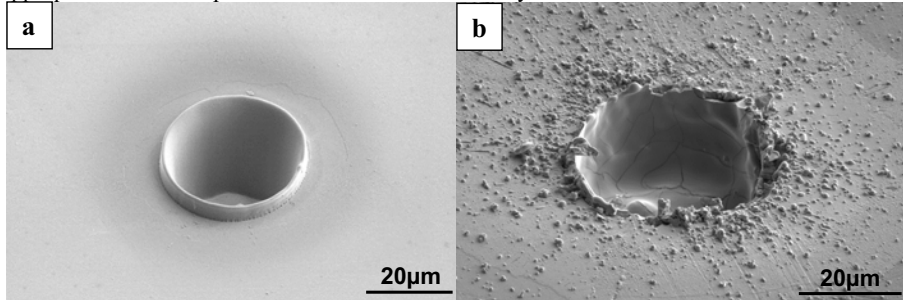


Figure 4a-b SEM micrographs of a crater left in a a) slag sample and in b) a matte phase after laser ablation process.

Results

Microstructures of equilibrated sample

Typical micrographs of samples from slag/matte/metal/tridymite experiments at 1200°C taken using scanning electron microscope with backscattered electron detector (SEM-BSE) are shown in Figures 5a-c. Three types of microstructures after equilibration have been identified.

TYPE I Metal-matte-slag 3 phases all in contact with each other

This type of microstructure is typically seen as Figure 5a. The spherical metal phase is seen surrounded partially by the matte phase and the rest by the slag phase. A slag/matte/metal 3 phase adjacent point can be observed. It is expected best equilibrium state is achieved with this microstructure. This microstructure is not commonly observed across the sample.

TYPE II Metal encapsulated by matte phase in contact with slag

This type of microstructure is typically seen as Figure 5b. The spherical metal phase is seen fully surrounded by the matte phase; while the matte phase is in good contact with the slag phase, it blocks the direct contact between metal and slag phase. This microstructure is more commonly observed across the sample.

TYPE III Individual metal or matte particles suspended in slag phase

Another type of microstructure which is more commonly observed in the sample consists of individual metal or matte particles that are suspended in the slag, which are shown in Figure 5c. There is no direct contact between matte and metal phases. Analysis on this type of microstructure should be avoided since equilibrium is unlikely to be achieved in this case.

In addition to the three typical microstructures described above, it is commonly observed that the matte phase contains some entrapped metal particles, this is probably due to the low interfacial tension between matte and metal phase that leads to a poor separation between the two phases. The metal phase may also contain some fine pores which might be formed when S is released during the quenching process.

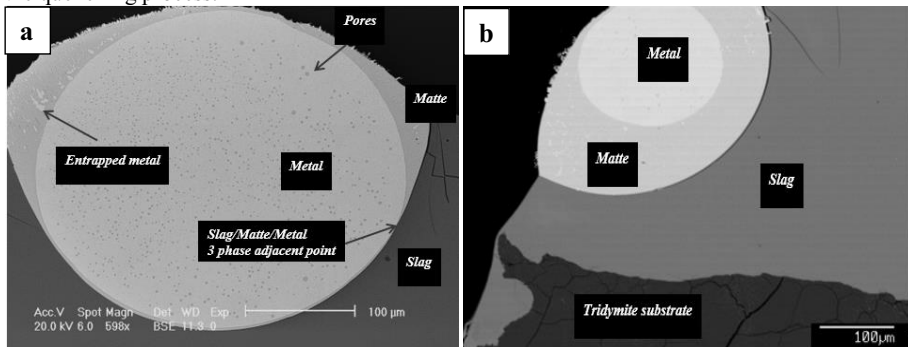


Figure 5a-b Typical Microstructures observed in slag/matte/metal/tridymite four phase equilibrium samples.

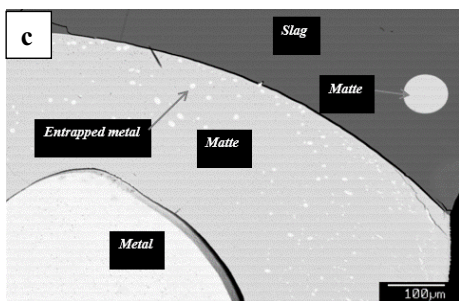


Figure 5c Typical Microstructures observed in slag/matte/metal/tridymite four phase equilibrium samples.

Slag/matte/metal/tridymite four condensed phase equilibria at 1200°C

The experimental results obtained in present study together with available literature data of the 4-condensed-phase Slag/Matte/Metal/Tridymite equilibria at 1200°C are given plotted against matte grade in Figure 6a-c together with FactSage predictions. It can be seen, the relationship between Cu concentration in the slag phase and matte grade is in good agreement with results obtained by Shimpo et al. [5] as well as the FactSage prediction; the measured S concentrations in the matte phase also agree well with the predicted values and reported data; S dissolved in Cu metal phase was found to be lower than predictions for about 0.2wt%;

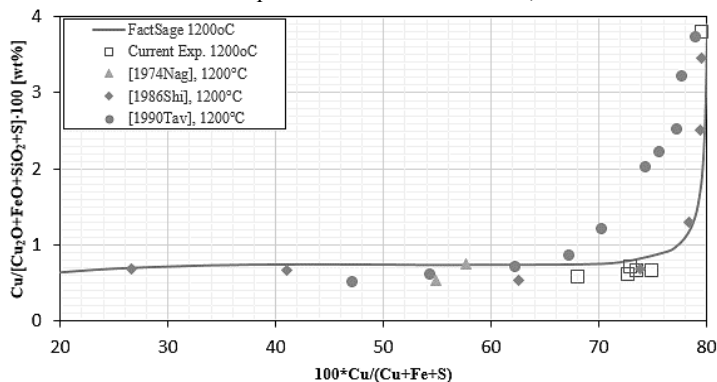


Figure 6a Concentration of Cu in slag wt% vs matte grade Cu/(Cu+Fe+S) wt% [4-6]

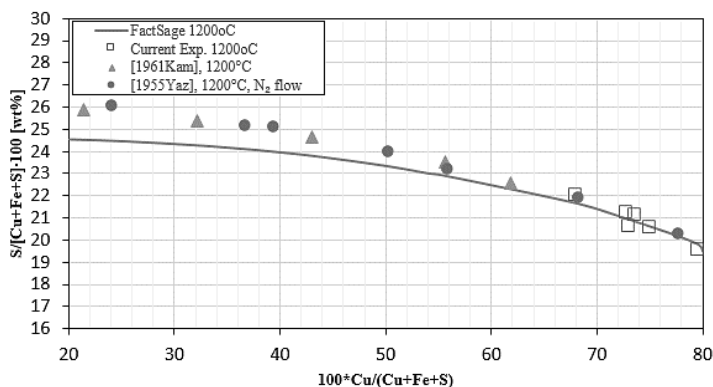


Figure 6b Concentration of S in matte wt% vs matte grade $\text{Cu}/(\text{Cu} + \text{Fe} + \text{S})$ wt% [7-8]

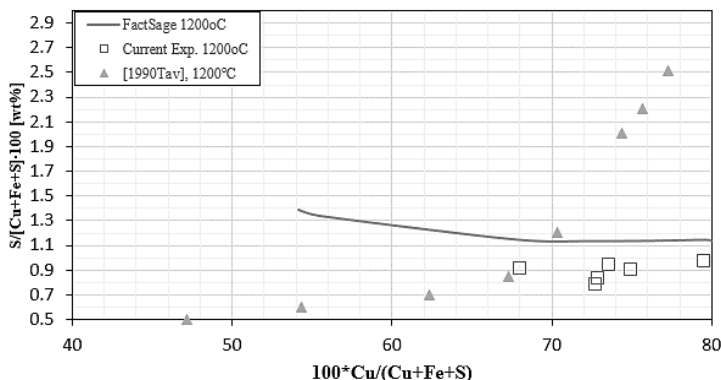


Figure 6c Concentration of S in Cu metal wt% vs matte grade $\text{Cu}/(\text{Cu} + \text{Fe} + \text{S})$ wt% [6]

Distribution of Ag and Au in slag/matte/metal/tridymite four condensed phase equilibria at 1200°C

The distribution coefficients of Au and Ag between slag and Cu metal at equilibrium have been determined for the first time by present study. The results together with FactSage predictions are plotted against matte grade in Figures 7a-b. Significant differences were found between predicted and experimentally determined values.

It can be seen from the results, the experimentally determined distribution coefficients of Au between slag and metal are about half order of magnitude lower than predicted values; in contrast, the distribution coefficients of Ag between slag and metal are found to be half order of magnitude higher than predicted values. The discrepancies between FactSage predictions and experimental results are expected due to the fact that no data on the distribution coefficients for both Au and Ag at four-phase equilibrium condition were available and FactSage database has not been optimized for this system.

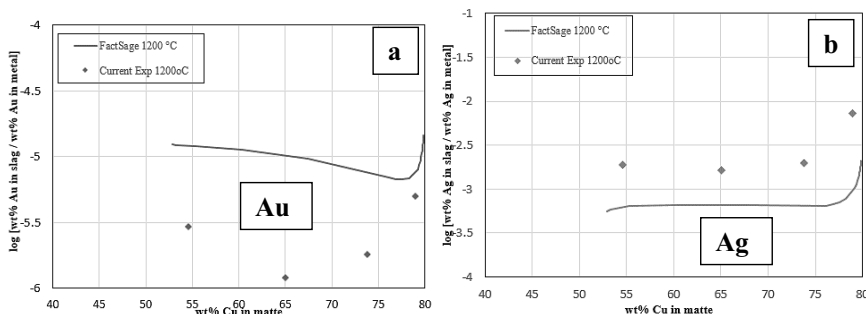


Figure 7 a: Distribution coefficients of Au between slag and metal vs matte grade wt %Cu/[Cu+Fe+S]; b: Distribution coefficients of Ag between slag and metal vs matte grade wt %Cu/[Cu+Fe+S];

Summary

Experimental and analysis techniques have been successfully developed for characterization of slag/matte/metal/tridymite four condensed phase equilibria in Cu-Fe-O-S-Si system and for the determination of minor elements distribution in the phases at equilibrium.

The phase equilibria results obtained in present study for major elements are found to be in good agreement with FactSage predictions for the range of conditions investigated. The distribution coefficients of Au and Ag between slag and Cu metal at slag/matte/metal/tridymite four condensed phase equilibria at 1200°C were reported for the first time.

The previously available data and the new experimental data for the system will be critically evaluated and used to optimize the current FactSage database for copper making applications.

Acknowledgement

The authors would like to thank Australian Research Council Linkage program, Altonorte Glencore, Atlantic Copper, Aurubis, BHP Billiton Olympic Dam Operation, Kazzinc Glencore, PASAR Glencore, Outotec Oy (Espoo), Anglo American Platinum, and Umicore for the financial and technical support.

References

- [1] Jak, E., Liu, N., Lee, H. G., & Hayes, P. C, "The Application of phase equilibria studies to describe behaviour of lead smelting slags." *6th AusIMM Extractive Metallurgy Conference*. Vol. 94. No. 4. Australasian Institute of Mining and Metallurgy, 1994, vol. 94, No. 4, pp. 261-268
- [2] E. Jak, "Integrated experimental and thermodynamic modelling research methodology for metallurgical slags with examples in the copper production field." In *Proceedings of IX International Conference on Molten Slags, Fluxes and Salts*, Beijing, 2012 paper 77.

- [3] C.W. Bale, A.D. Pelton and W.T. Thompson: "Facility for the Analysis of Chemical Thermodynamics" (FACT), Ecole Polytechnique, Montreal, Canada, 1996
- [4] F. J. Tavera and E. Bedolla, "Distribution of copper, sulfur, oxygen and minor elements between silica-saturated slag, matte and copper - experimental measurements," *Int. J. Miner. Process.*, 1990, vol. 29, pp. 289-309
- [5] R. Shimpo, S. Goto, O. Ogawa, and I. Asakura, "A study on the equilibrium between copper matte and slag," *Can. Metall. Q.*, 1986, vol. 25, pp. 113-121
- [6] M. Nagamori, "Metal loss to slag: Part I. Sulfidic and oxidic dissolution of copper in fayalite slag from low grade matte," *Metall. Trans. B*, 1974, vol. 5B, pp. 531-538
- [7] M. Kameda and A. Yazawa, "The oxygen content of copper mattes," in *Physical Chemistry of Process Metallurgy, part 2*, 1961, vol. 8, pp. 963-988
- [8] A. Yazawa and M. Kameda, "Fundamental studies on copper smelting. IV. Solubility of FeO in copper matte from SiO₂-saturated FeO-SiO₂ Slag," *The Technology Reports of the Tohoku Univ.*, 1955, vol. 19, pp. 251-261