Experimental study and thermodynamic modelling of phase equilibria in the FeO-$FeO_{1.5}$-$SbO_{1.5}$-SiO_2 system in equilibrium with metal

Hamed Abdeyazdan[1], *Maksym Shevchenko*[2], *Joe Grogan*[3], *Daniel Graf*[4] *and Evgueni Jak*[5]

1. Postdoctoral Research Fellow, The University of Queensland, Brisbane, Queensland 4072. Email: h.abdeyazdan@uq.edu.au
2. Research Fellow, The University of Queensland, Brisbane, Queensland 4072. Email: m.shevchenko@uq.edu.au
3. Chief Technology Officer, Gopher Resource, 685 Yankee Doodle Road, Eagan, MN 55121, USA. Email: Joe.Grogan@GopherResource.com
4. Principal Engineer, Gopher Resource, 6505 Jewel Avenue, Tampa, FL 33619, USA. Email: Daniel.Graf@GopherResource.com
5. Professor, The University of Queensland, Brisbane, Queensland 4072. Email: e.jak@uq.edu.au

Keywords: phase equilibria, FeO-$FeO_{1.5}$-$SbO_{1.5}$-SiO_2-Ag, Pb smelting, minor elements, slag

ABSTRACT

An integrated experimental and thermodynamic modelling study of the phase equilibria in the FeO-$FeO_{1.5}$-$SbO_{1.5}$-SiO_2 system in equilibrium with liquid Sb and Sb-Ag metal has been undertaken to develop thermodynamic model of the Na-Si-Fe-O slag system with S-Sn-Sb-Pb-As minor elements based on the experimental investigation of the selected sub-systems. New experimental phase equilibria data at 575-1600 °C were obtained for this system using high-temperature equilibration of synthetic mixtures with predetermined compositions in sealed silica ampoules, Fe_3O_4 basket in sealed silica ampoule, or Re foils, a rapid quenching technique, and electron probe X-ray microanalysis of the equilibrated phase compositions. Experimental results on phase equilibria in the Fe-Sb-Si-O + Sb metal system obtained helped to produce initial set of model parameters in the slag. The primary phase fields of quartz/tridymite/cristobalite (SiO_2), 2 high-SiO_2 immiscible liquids, olivine (Fe_2SiO_4), wustite (FeO_{1+x}), spinel (Fe_3O_4), schafarzikite ($FeSb_2O_4$) and valentinite/senarmontite (Sb_2O_3) were identified in the binary Sb_2O_3-FeO, Sb_2O_3-SiO_2 and ternary FeO-Sb_2O_3-SiO_2 systems. Further refinement, particularly the distribution of excess Gibbs energy among the "FeO"-Sb_2O_3-SiO_2 and "$FeO_{1.5}$"-Sb_2O_3-SiO_2 interactions, required the study at more oxidizing conditions. Oxygen potential was increased using an inert metal (Ag) rather than using the gas flow due to the high volatility of Sb-containing gaseous species. Liquid Ag-Sb alloys with low concentrations of Sb of a few percent were used. At these conditions, the concentration of $AgO_{0.5}$ in slag was below 1 mol.%, which had a small effect on observed phase equilibria in the system. In addition, important information on the solubility of silver in slags is produced, which can be valuable when treating electronic recycling materials or primary silver-containing ores through the Pb process. Two main areas were addressed: the spinel-tridymite boundary (40-70% SiO_2 in slag) and spinel liquidus near 15% SiO_2 in slag. This allowed to deconvolute the separate contributions of the FeO-Sb_2O_3(-SiO_2) and Fe_2O_3-Sb_2O_3(-SiO_2) systems.

INTRODUCTION

Antimony, tin, arsenic and other critical valuable as well as unwanted metals are found in a range of streams within primary and secondary smelters. These elements are typically concentrated in dusts and other streams, resulting in process challenges within industrial smelters. To improve the recovery of Sb, Sn and other critical metals, as well as to remove hazardous metals from the slag, fuming of these elements needs to be controlled and optimized. The fuming process depends on a number of factors including kinetics at the gas-slag interface, diffusive and convective mass transfer in the slag and gas phases at micro- and macro-scales, fluid flow pattern in the reactor as well as the properties of the slag, in particular thermodynamics (that determines the driving force) and phase equilibria (directly linked to thermodynamics).

To optimize the fuming of secondary lead slags, a detailed understanding of the thermochemistry of the slag system including phase equilibria, thermodynamics, fuming mechanisms and kinetics for these elements is required. Slags generated in these smelters typically belong either to the Ca-Si-Fe-O system or the Na-Si-Fe-O system, with the two systems behaving differently. The present research program is focused on the Na-Si-Fe-O system as it is most commonly used for the smelting of side streams and by-products from smelters, typically enriched in these critical metals.

The characterization and modelling of fuming mechanisms and kinetics requires reliable detailed knowledge of the thermodynamics (determining the driving force) and phase equilibria of the slag system. It is not possible to characterize kinetics without reliable knowledge on thermodynamics and phase equilibria. Preliminary review of literature on phase equilibria and thermodynamics indicated the lack of data. It is therefore recommended to focus the major part of this initial stage of the research in this area on the characterization of phase equilibria and thermodynamics followed up by study of the kinetics of fuming.

This research provides new phase equilibria in the FeO-$FeO_{1.5}$-$SbO_{1.5}$-SiO_2 system in equilibrium with liquid Sb and Sb-Ag metal to develop thermodynamic model of the Na-Si-Fe-O slag system with S-Sn-Sb-Pb-As minor elements based on the experimental investigation of the selected sub-systems.

METHODOLOGY

The experimental apparatus and technique used in this study have been detailed in previous publications (Hidayat et al. 2012; Jak, Hayes, and Lee 1995; Jak 2012). The initial chemical mixtures were prepared by blending selected proportions of high-purity powders of Fe_2O_3, Sb_2O_3, Sb and Ag metal (99.9 wt.% purity), SiO_2 (99.9 wt.% purity, pre-dried at 400°C for 1 h before mixing), supplied by Alfa Aesar, MA, USA. The mixtures were pelletized and divided into 0.2-0.4 g samples for the experiments. The initial compositions were selected to ensure that the liquid slag was in equilibrium with at least one crystalline phase, and the crystalline solid phase(s) fraction in the final sample at the equilibration temperature was preferably ~10 vol% and not greater than 50 vol% to promote the retention of the liquid as an amorphous phase during quenching. The substrates used for equilibration were i) vacuum sealed silica ampoules for high-SiO_2 mixtures that were in equilibrium with tridymite and cristobalite at the target temperature, and ii) Re foils for low-SiO_2 mixtures. In some cases, Fe_3O_4 (spinel) baskets (obtained by controlled oxidation of Fe foil), or MgO crucibles sealed inside SiO_2 ampoules, were used. The experiments were conducted in a high-temperature vertical tube resistance PYROX furnace using lanthanum chromite heating elements under air or argon atmosphere. The samples were suspended in the center of the uniform hot zone of the furnace on a Kanthal (Fe-Cr-Al alloy) wire (0.7 or 1 mm diameter), with 15-20 cm platinum wire added to the Kanthal wire for $T > 1450$ °C to avoid failure at high temperatures. The samples were first pre-melted at 20-50 °C above the target temperature for 5 min to support the formation of a homogeneous liquid. The samples with high antimony oxide partial pressure (low-SiO_2) area were not pre-melted to decrease the overall loss of Sb_2O_3.

Following equilibration, the samples were rapidly quenched in calcium chloride brine at -20 °C, washed with water and ethanol, dried, and mounted in epoxy resin. Polished cross-sections were prepared using conventional metallographic techniques. The samples were examined using optical microscopy and then carbon-coated. The compositions of the phases were measured using electron probe X-ray microanalysis (EPMA) (JEOL 8200 L EPMA; Japan Electron Optics Ltd., Tokyo, Japan). The EPMA was operated with a probe current of 20 nA and acceleration voltage of 15 kV. The Duncumb–Philibert atomic number, absorption, and fluorescence correction (ZAF correction) was applied. Wollastonite ($CaSiO_3$), hematite (Fe_2O_3), Sb metal and Ag metal (supplied by Charles M. Taylor Co., Stanford, CA, USA) standards were used for Si, Fe, Sb and Ag calibration of the EPMA, respectively. Only the concentrations of metal cations were measured with EPMA; the proportions of Fe^{2+} and Fe^{3+} were not measured directly, Fe^{2+} (“FeO”) is assumed to be predominant.

RESULTS

Typical microstructures for the selected experiments in the “FeO”-$SbO_{1.5}$-SiO_2 system are shown in FIG 1. Liquidus surface of the “FeO”-$SbO_{1.5}$-SiO_2 system according to the new experimental results and estimated with database developed for this system is given in FIG 2.

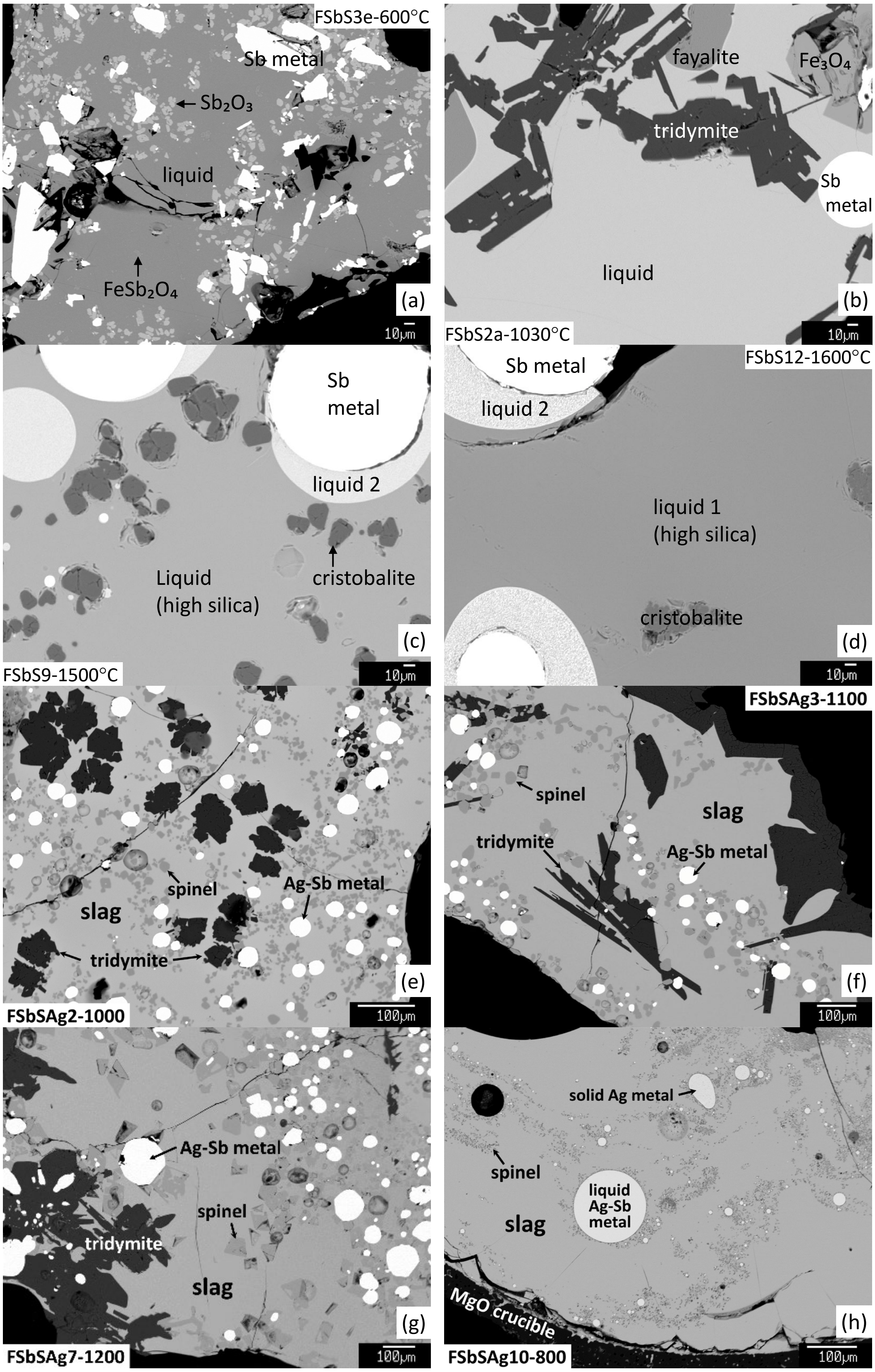


FIG 1. Typical back-scattered electron micrographs for selected samples in the “FeO”-$SbO_{1.5}$-SiO_2(-$AgO_{0.5}$) system in equilibrium with Sb-Fe(-Ag) metal, illustrating a) liquid slag, Sb_2O_3 (valentinite), $FeSb_2O_4$ (schafarzikite) and Sb metal (solid) at 600°C, b) liquid slag, Fe_2SiO_4 (fayalite), SiO_2 (tridymite) and Sb metal (liquid) at 1030°C, c) liquid slag 1, liquid slag 2, SiO_2 (cristobalite) and Sb metal at 1500°C, d) liquid slag 1, liquid slag 2, cristobalite and Sb metal at 1600°C, (e) liquid slag, Ag-Sb metal, Fe_3O_4 (spinel) and SiO_2 (tridymite) at 1000 °C, (f) liquid slag, Ag-Sb metal, spinel and tridymite at 1100 °C, (g) liquid slag, Ag-Sb metal, spinel and tridymite at 1200 °C, and (h) liquid slag, liquid Ag-Sb metal, solid Ag metal and spinel at 800 °C.

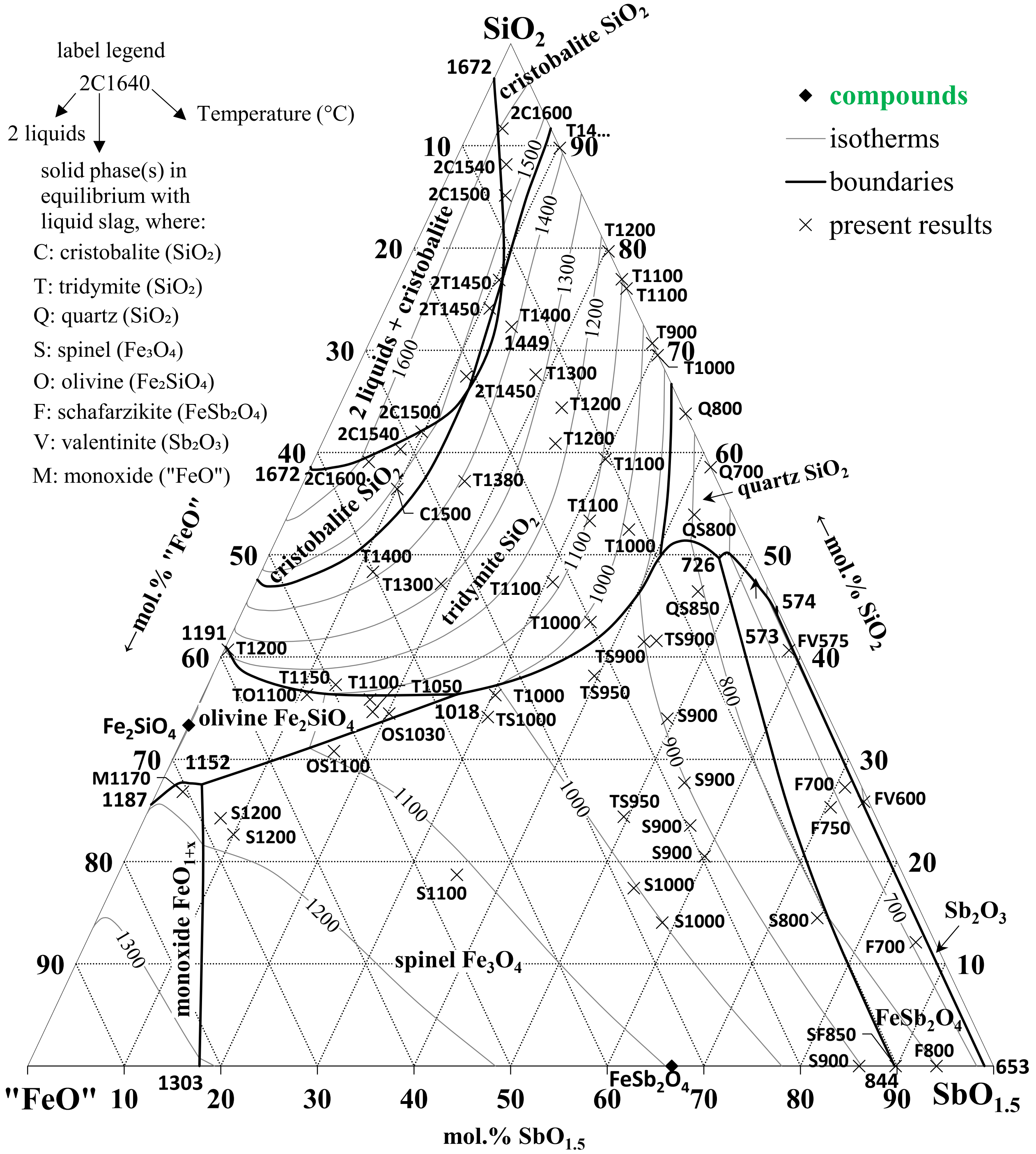


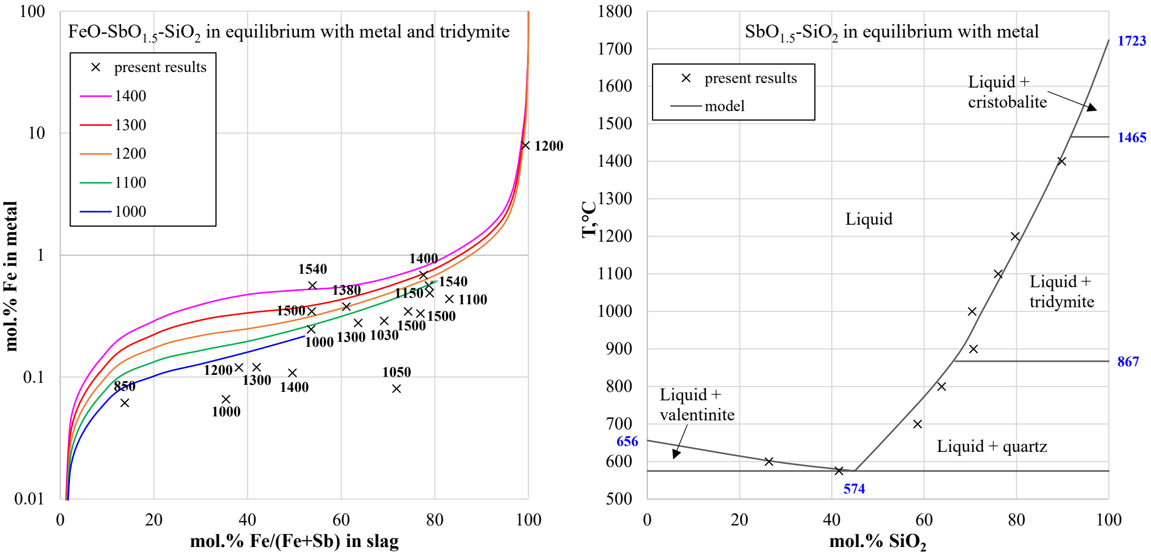
FIG 2. Liquidus surface of the “FeO”-$SbO_{1.5}$-SiO_2 system according to the new experimental results at 575°C to 1600°C and estimated with the thermodynamic database.

The “FeO”-$SbO_{1.5}$-SiO_2 liquidus is dominated by spinel and quartz/tridymite/cristobalite primary phase fields. The spinel-olivine-tridymite-slag-metal invariant point is located in the central part of the triangle at 1018 °C. Due to the “oxygen buffer” nature of this point, correct description of its composition and temperature by the present thermodynamic model indicates its good quality compared to initial versions of thermodynamic parameters (Shishin et al. 2019) (Shishin et al. 2020) that resulted in significantly underestimated temperature for this invariant point. This improvement was achieved through revision of thermodynamic properties of the $SbO_{1.5}$ liquid endmember.

An iron antimonite phase, schafarzikite $FeSb_2O_4$ ($FeO·Sb_2O_3$), was found at liquidus between the spinel and valentinite (Sb_2O_3) fields. This compound melts incongruently at ~844 °C in the “FeO”-

$SbO_{1.5}$ pseudobinary system in equilibrium with Sb metal. A significant area of two immiscible liquids was found over the cristobalite primary phase field, extending from the “FeO”-SiO_2 binary monotectic at 1672 °C (Wen et al. 2022) to a critical point at ~1449 °C and 13 mol.% $SbO_{1.5}$.

Prediction of the trend of mol% Fe in metal was carried out using the thermodynamic database and is given in FIG 3a. It can be seen that the trend of mol% Fe in Sb metal is consistent to the experimental results; however, the model overestimates the mol% Fe in metal. The eutectic of the $SbO_{1.5}$-SiO_2 binary (FIG 3b) estimated by thermodynamic database to form at 574 °C and ~45 mol% SiO_2. This system has not been studied before directly, most likely due to extremely high viscosity of slags, combined with Sb_2O_3 volatility, that caused significant scatter of observed quartz and tridymite points even in the present study despite multiple precautions. The miscibility gap in the low-SiO_2 area, predicted by (Kopyto et al. 2009), was not confirmed, although the $SbO_{1.5}$-SiO_2 system is characterized by small positive deviations from ideal solution.



(a) (b)

FIG 3. (a) Prediction of trend of mol% Fe in metal using the thermodynamic database, (b) the eutectic of the $SbO_{1.5}$-SiO_2 binary estimated by thermodynamic database.

Experimental results on phase equilibria in the Fe-Sb-Si-O + Sb metal system served well to produce initial set of model parameters in the slag. Further refinement, particularly the distribution of excess Gibbs energy among the “FeO”-Sb_2O_3-SiO_2 and “Fe_2O_3”-Sb_2O_3-SiO_2 interactions, required the study at more oxidizing conditions, compared to those typically observed during slag fuming. Often for systems containing iron, extremely oxidizing conditions (e.g. in air atmosphere) are used to provide the limiting case when most of iron is Fe^{3+}. In the present project, this type of study would not provide the necessary information for the “Fe_2O_3”-Sb_2O_3-SiO_2 interactions, because Sb can also exhibit higher oxidation state of Sb^{5+}. Thus, a study at moderately oxidizing conditions was designed, where significant amount of Fe^{3+} is expected, but Sb is still predominantly in a form of Sb^{3+}.

The flow of gas with fixed $p(O_2)$ cannot be used due to high volatility of Sb-containing gaseous species. Alternatively, the oxygen potential can be increased by the addition of an inert metal, silver or gold to liquid Sb. According to the equation Sb (metal) + $0.75O_2 = SbO_{1.5}$ (slag), for a fixed activity of $SbO_{1.5}$ in slag, decreasing the activity of Sb by dissolution in inert metal would cause an increase in $p(O_2)$. This method would not provide the value of $p(O_2)$ directly, but in combination with thermodynamic modelling, it will give the necessary data for the model. Silver (Ag) was chosen as an inert alloying metal due to its affordability and low melting temperature. Liquid Ag-Sb alloys with low concentrations of Sb of a few percent were used. At these conditions, the concentration of $AgO_{0.5}$ in slag is expected to be < 1 mol.%, which would have a small effect on observed phase equilibria in the oxide system. In addition, important information on the solubility of silver in slags is produced, which can be valuable when treating electronic recycling materials or primary silver-containing ores through the Pb process. Two main areas were addressed: the spinel-tridymite boundary (high-SiO_2

slag, FIG 4) and spinel liquidus (low-SiO_2 slag, FIG 5). The SiO_2-free slags were not attempted to study due to their extreme volatility.

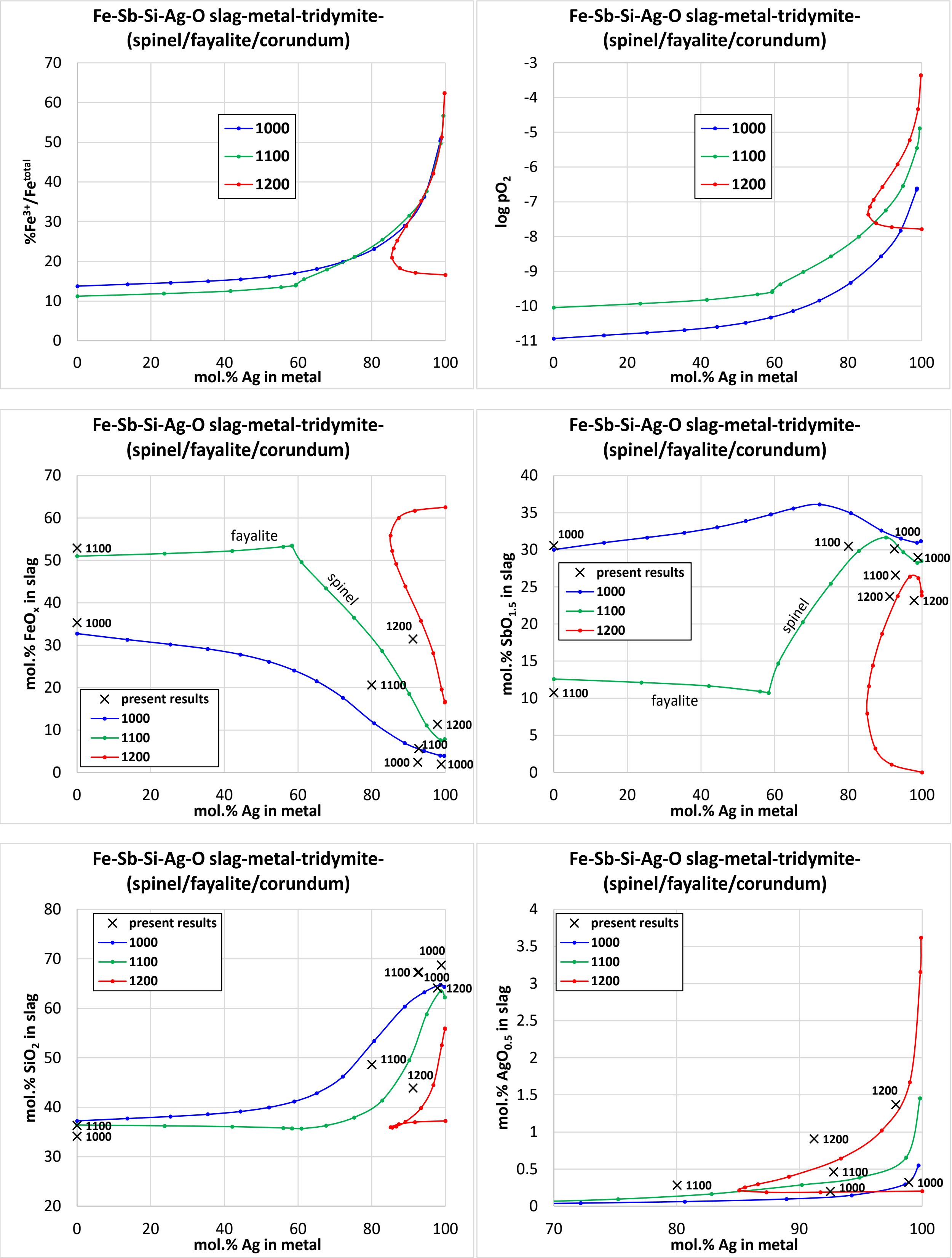


FIG 4. Phase equilibria in the FeO-$FeO_{1.5}$-$SbO_{1.5}$-SiO_2-(Ag) system. Composition of slag and $p(O_2)$ in equilibrium with Ag-Sb metal, tridymite and either spinel, or fayalite, or corundum at 1000, 1100 and 1200 °C are shown as a function of Ag in metal (the rest is Sb with traces of Fe). Lines are calculated using the thermodynamic model of the present study, black squares are experimental results, obtained in this study.

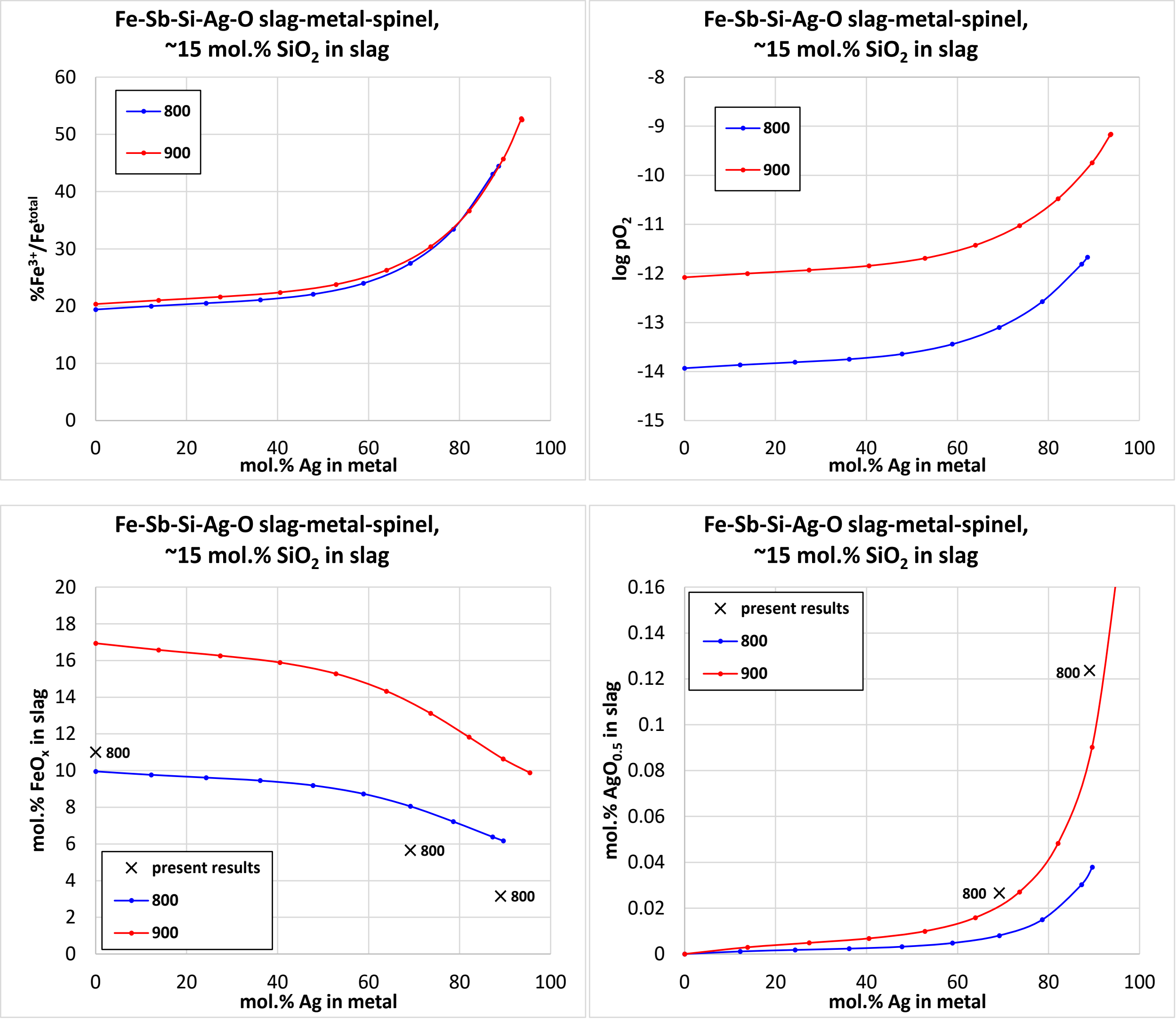


FIG 5. Phase equilibria in the FeO-$FeO_{1.5}$-$SbO_{1.5}$-SiO_2-(Ag) system (low-SiO_2 slag). Composition of slag and p(O_2) in equilibrium with Ag-Sb metal and spinel 800 and 900 °C are shown as a function of Ag in metal (the difference is Sb). Lines are calculated using the thermodynamic model of the present study, black squares are experimental results, obtained in this study.

As can be seen, the studied area covers a significant range of Fe^{3+}/Fe^{total} (from 10-20% in the Fe-Sb-Si-O system in equilibrium with Sb metal, to 60-70% in equilibrium with high-Ag, low-Sb metal. This allowed to deconvolute the separate contributions of the FeO-Sb_2O_3(-SiO_2) and Fe_2O_3-Sb_2O_3(-SiO_2) systems. The fact that total Fe solubility in slag at spinel liquidus dramatically decreases with replacing Sb by Ag in metal (more oxidizing conditions) means that there are positive interaction parameters (Gibbs energy) in the Fe_2O_3-Sb_2O_3(-SiO_2) system compared to FeO-Sb_2O_3(-SiO_2).

CONCLUSIONS

While no previous publication could be found on liquidus of the FeO-$FeO_{1.5}$-$SbO_{1.5}$-SiO_2 system in equilibrium with metal, this study provided experimental results and thermodynamic modelling of the liquidus in this system. There are minor discrepancies between the experimental tridymite(quartz)-spinel boundary and the line calculated with the thermodynamic model (overestimated SiO_2 by up to 5 mol.%). In this study, a new phase $FeSb_2O_4$ (schafarzikite) was found and added to the FactSage compounds list. No solid solutions (e.g. Sb in spinel, tridymite etc) were found in the system. Study of the $SbO_{1.5}$-SiO_2 binary system is challenging. This system is characterized by extremely high viscosity. Compositional gradients were observed in the samples at quartz/tridymite liquidus even after 1-2 weeks of equilibration. When amorphous SiO_2 (crushed ampoules) is used as a reagent, in all systems it usually instantly transforms to a crystalline phase on interaction with other components.

With $SbO_{1.5}$, however, it fails to crystallise for very long time. Instead, chunks of amorphous (supercooled liquid) SiO_2 remain surrounded by a continuum of slags with gradually increasing $SbO_{1.5}$ concentration. Further development of the technique is required to overcome this issue.

ACKNOWLEDGEMENT

The authors would like to thank Australian Research Council Linkage programs LP180100028 and LP190101020 as well as consortium of lead and copper producers: Aurubis, BHO OD, Boliden, Glencore Technology, Kazzinc Ltd. Glencore, Nyrstar, Peñoles, RHI Magnesita, Rio Tinto Kennecott and Umicore for the financial support for this study. The authors are very grateful to Prof. Peter Hayes for initiating and contributing in this research program. The authors would like to thank Mrs. Suping Huang and Mrs. Samaneh Ashjaa for assistance in the experiments and also the staff at the Centre for Microscopy and Microanalysis (CMM), University of Queensland for technical support.

REFERENCES

Hidayat, T., H. M. Henao, P. C. Hayes, and E. Jak. 2012. 'Phase Equilibria Studies of the Cu-Fe-O-Si System in Equilibrium with Air and with Metallic Copper', *Metall. Mater. Trans. B*, 43: 1034-45.

Jak, Evgueni. 2012. "Integrated experimental and thermodynamic modelling research methodology for metallurgical slags with examples in the copper production field " In *9th Intl. Conf. on Molten Slags, Fluxes and Salts*, 1-28. Beijing, China: The Chinese Society for Metals.

Jak, Evgueni, Peter C. Hayes, and Hae-Geon Lee. 1995. 'Improved methodologies for the determination of high temperature phase equilibria', *Korean Journal of Minerals and Materials Institute (Seoul)*, 1: 1-8.

Kopyto, M., W. Przybylo, B. Onderka, and K. Fitzner. 2009. 'Thermodynamic properties of Sb_2O_3-SiO_2 and PbO-Sb_2O_3-SiO_2 liquid solutions', *Arch. Metall. Mater.*, 54: 811-22.

Shishin, D., T. Hidayat, Jiang Chen, P. C. Hayes, and E. Jak. 2019. 'Combined Experimental and Thermodynamic Modeling Investigation of the Distribution of Antimony and Tin between Phases in the Cu-Fe-O-S-Si System', *Calphad*, 65: 16-24.

Shishin, D., T. Hidayat, U. Sultana, M. Shevchenko, and E. Jak. 2020. 'Experimental measurement and thermodynamic model predictions of the distributions of Cu, As, Sb and Sn between liquid lead and PbO-FeO-Fe_2O_3-SiO_2 slag', *International Journal of Materials Research*, 111: 733-43.

Wen, Xi Rui, Siyu Cheng, Maksym Shevchenko, and Evgueni Jak. 2022. "Experimental Study of the Cu_2O-FeO-Fe_2O_3-SiO_2 and FeO-Fe_2O_3-SiO_2 Slag Systems at fixed oxygen partial pressures." In *COPPER 2022*. Santiago, Chile.