Thermodynamic predictions and experimental investigation of slag liquidus and minor element partitioning between slag and matte in support of the copper Isasmelt smelting process commissioning and optimisation at Kazzinc

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Abstract: This experimental study is a part of a collaborative research program between The University of Queensland and Kazzinc metallurgists aimed at optimisation of the Isasmelt copper smelting process currently being commissioned. Thermodynamic modelling of the copper smelting process performed using the FactSage computer package is experimentally validated and calibrated. A number of key thermodynamic parameters, in particular, liquidus temperatures and minor elements distribution between copper smelting slag and matte in the range of conditions of interest to the industrial process are experimentally determined. The laboratory and thermodynamic modelling results are then validated and calibrated against actual industrial process through targeted sampling and expert analysis study.

The experimental methodologies are based on the use of high temperature equilibration at controlled temperatures and gas atmospheres followed by quenching and direct measurements of phase compositions using Electron Probe X-ray microanalysis (EPMA) with Wave-length Dispersive Detectors. This general experimental approach has been further significantly developed in this study to enable the slag / matte equilibria to be accurately measured at a given targeted matte grade. The slag / matte samples were equilibriated on a primary phase substrate (trydimite or spinel). The oxygen partial pressure P_{O2} was iteratively adjusted by mixtures prepared from pure gases to obtain the targeted matte grade close to the 60 wt pct Cu at fixed sulfur dioxide partial pressures P_{SO2}. Liquidus temperatures, compositions of the matte and minor elements distributions were obtained from direct EPMA measurements of phase compositions in quenched samples. Special procedures involving vacuumed silica ampoule were developed and applied for investigation of distributions of the volatile minor elements such as As and Pb.

The effects of variations of slag composition on slag liquidus temperature were evaluated using linear interpolation of the experimental results. The slag liquidus temperatures in the tridymite and spinel primary phase fields have then been constructed as binary plots vs Fe/SiO_2 at fixed CaO=3.3, Al_2O_3=0.9 and ZnO=2.0 wt % in equilibrium with a matte of 60wt pct Cu grade for temperatures 1160 to 1200 ^{0}C at P_{SO2} of 0.28 atm. Experimental results for the distribution of As, Pb and Zn between matte and slag as a function of P_{O2} were obtained. These data are essential for appropriate adjustments into thermodynamic model.

The next essential step is the implementation of the laboratory and theoretical thermodynamic modelling results into industrial process optimisation. This part of the research program is frequently overlooked, but is important and requires high level of research expertise to identify the actual conditions in the real process and relate them to the laboratory and theoretical tools. Both the industrial process analysis and the calibration relative to the results of the advanced research tools are crucial for the application to the actual copper smelting reactor. For this purpose, a series of quenching experiments directly from the tapped slag and matte streams were conducted with temperatures measured by disposable dipthermocouples at the time and in the place of sampling. Special precautions were made to ensure the slag and matte were not altered during sampling so that the quenched samples closely represent the compositions and phases in the slag and matte streams at the time just before the sampling. Expert analysis of the microstructures, phase morphologies, compositional profiles at microscopic level and other features in the industrial samples was performed with optical and scanning electron microscopy and with EPMA. This advanced analysis enabled the actual processes taking place in the reactor to be evaluated, examined and “de-convoluted”. This is an essential stage of the implementation of the laboratory equilibrium and theoretical thermodynamic research results that ensures that elemental reactions taking place in the actual process, non-equilibrium and kinetic aspects are evaluated and taken into account.

Keywords: copper smelting, slag, phase equilibria, liquidus, minor elements distribution

1. Introduction

Cu IsaSmelt smelting process is introduced at Kazzinc to treat complex concentrates containing high contents of minor elements and to produce (according to the design) 60 wt % Cu – containing matte. In order to optimise production and financial performance of the Cu treatment, a collaborative research program is undertaken that includes a) thermodynamic modelling using the FactSage computer package, b) laboratory experiments with synthetic samples on liquidus and partitioning of minor elements at precisely controlled conditions to verify or tune the theoretical predictions, and c) targeted plant slag and matte quenching tests followed up by advanced analysis aimed to identify and introduce relevant adjustments for differences between the theoretical predictions, results of laboratory experiments with synthetic samples and the actual conditions of the processes taking place in the Cu IsaSmelt reactor.

Liquidus temperatures directly determine the limits of optimisation of the main operating parameters of the pyrometallurgical operations such as temperature and the chemical composition of the slag, the latter is controlled by addition of fluxes. It is essential to know liquidus in order to precisely determine the limits within which is necessary to keep slag so that to optimise the process and to reduce amount of added fluxes (and therefore fuel consumption used to melt fluxes, overall volume of the slag and therefore Cu losses) at the same time to maintain the liquid slag, good separation of matte, eliminate excessive formation of deposits, reduce consumption of refractories, and to increase duration of the work of the lace and it’s tip, minimise contamination by dust of the uptake of the furnace and of the waste heat boiler. To date, only separate data was found on the liquidus temperatures that describe simplified chemical systems [1-18], however there are no accurate data on liquidus in complex multi-component slags with high levels of minor impurities such as CaO, Al_2O_3, MgO, PbO, ZnO in the presence of sulphur S and copper matte at conditions corresponding to the actual industrial process.

Partitioning of minor elements between matte, slag and gas (including dust formed on gas cooling) is one of the key issues for the efficient Cu production, optimum organization of recycling of materials, increased productivity and improvement of economic parameters. The list of minor elements particularly important for most of the copper smelters includes As, Pb, Zn, Au, Ag, Sb, Bi and Sn. Literature review [1-22] indicated that the data on distribution of minor elements exist, but have large scatter, are usually fragmentary and not in the range of conditions important for the Cu IsaSmelt process. Experiments reported in literature in general have large uncertainties, the metal oxidation states in slag and matte are frequently not accurately defined. Previous experimental techniques were based on the equilibration and quenching followed up by physical phase separation and measurements of the bulk phase compositions – these techniques have significant uncertainties due to the limitations in ability to physically separate slag from entrained matte or metal as well as from the oxide crystals formed in the slag due to interactions with the crucibles. Accurate information on the distribution between slag and matte phases and on the oxidation state of minor elements in slag and matte is essential for the thermodynamic modeling for the Cu smelting and for the overall improvements in the process.

The main reason for the lack of liquidus and minor elements distribution data is experimental difficulties that could not be resolved using research methodologies used previously. The combination of the present advanced modeling and experimental approaches enable these limitations to be overcome. Present paper outlines progress of collaborative research efforts of the University and plant specialists on the implementation of the thermodynamic modelling with computer package FactSage, experimental laboratory measurements of the liqudius temperatures of multi-component synthetic slags containing minor elements in the a range of Fe/SiO_2 ratios in equilibrium with matte at controlled SO_2 and O_2 partial pressures) in the range of conditions of interest to the copper smelting, distribution between matte and slag of minor elements important for copper operations as well as results of the quenching of the plant slag and matte.

2. Experimental Methodologies

2.1. General description of experimental approach

There are a number of difficulties in obtaining accurate chemical equilibrium data for complex slag systems at controlled laboratory environment. Experimental procedures for determination of phase equilibria have been developed by Pyrometallurgy Research Centre at the University of Queensland that have resolved a number of experimental difficulties; it is based on the high temperature equilibration of a synthetic slag samples of composition X (see Figure 1) in well controlled gas atmosphere and temperature followed up by quenching. The experimental conditions are planned to obtain liquid slag in equilibrium with crystalline and other phases. As a result of quenching the liquid slag phase is converted into glass, and crystalline solids (if present) are frozen in place. The quenched samples are then mounted in epoxy resin, polished and examined in scanning electron microscope. The compositions of all phases are directly and accurately measured with electron probe X-ray microanalyser (EPMA) equipped with wave-length dispersive detectors WDD. A point “a” in Figure 1 – is the composition of the liquid phase, and point “c” – composition of the solid phase directly measured with EPMA. The accuracy of temperature is within 5 degrees Celsius, and the accuracy of phase composition measurements is within 1 wt %. Particularly important is the fact that the accuracy of measurements does not depends on the change of bulk composition of the sample X since the compositions of phases (points “a” and “c”) are measured after the experiment. This enables to undertake measurements of complex multi-component systems with the bulk composition changing during experiment as a result, for example, of fuming, interaction with crucible or with gas and metal or matte. Moreover, this approach enables to develop a substrate method – when liquid phase is equilibrated on a substrate made of the primary phase instead of crucible. The application of this method (including equilibration of the primary phase substrate) enabled to measure the system having equilibrated slag and matte phases –

previously these measurements were practically impossible. For the measurement of the distribution of minor components, their concentrations in phases were also measured by EPMA in this study.

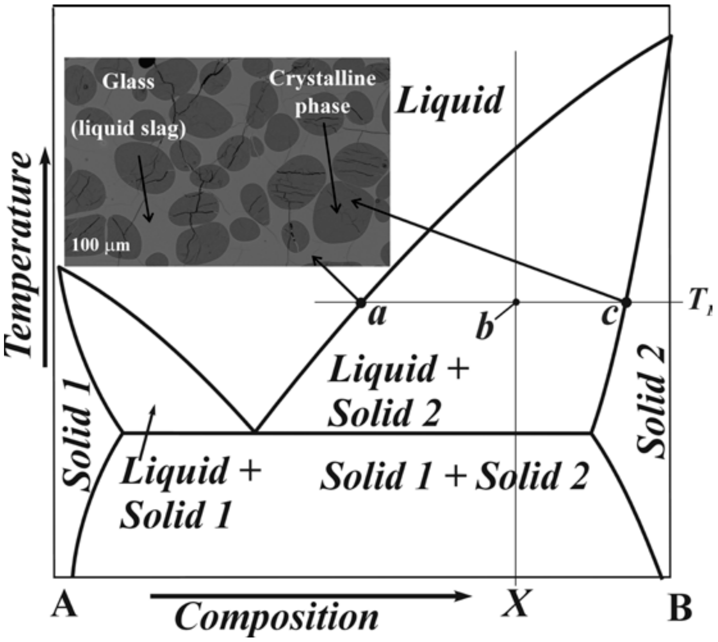

Figure 1: Experimental approach to phase equilibrium determination using sub-liquidus equilibration, quenching and EPMA

The starting mixtures were made from CaO, SiO_2, Cu, Cu_2O, Fe, Fe_2O_3, Al_2O_3, MgO, ZnO, SnO_2, As, PbO, Bi, ZnO and Sn powders (99.9 wt pct purity). The mixtures, selected for each sample were weighed and mixed with an agate mortar and pestle, and then pelletized.

All the equilibration experiments were conducted in a vertical reaction tube (impervious re-crystalized alumina, 30-mm i.d.) in electrical resistance silicon carbide (SiC) heated furnaces. The furnace temperature was controlled to ± 1K by an alumina shielded Pt/Pt-13wt pct Rh thermocouple placed immediately adjacent to the sample. This thermocouple was periodically calibrated against standard thermocouple (supplied by National Measurement Institute of Australia). The overall absolute temperature accuracy is estimated to be within 5K. The atmosphere within the reaction tube was maintained at fixed oxygen and SO_2 partial pressures of 0.28 atm using $CO/CO_2/SO_2$ (CO-99.5 wt pct pure, CO_2-99.99 wt pct pure, 99.9 wt pctSO_2) mixtures. The flow rates of gases to the furnace were controlled using glass capillary flow meters with the gas flowing from the bottom to the top of the furnace. The volumetric ratio of the gases used to achieve the selected thermodynamic oxygen partial pressure at a set temperature was calculated using the FactSage 6.2 thermodynamic package. The oxygen partial pressures were periodically checked with a partially stabilised zirconium oxygen probe ($SIRO_2$®, DS-type oxygen probe supplied by Australian Oxygen Fabricators (AOF), Melbourne, Australia). It was confirmed that the results of the measurements in the present study are at least within the accuracy of the DS-type oxygen probe, i.e. within log PO_2 of $\pm$ 0.1 units (PO_2 in atm) [22]. Later experiments indicated that the actual accuracy of the oxygen partial pressure control during experiments is even better.

The slag samples (synthetic and industrial) were mounted, polished, and examined using optical and Scanning Electron Microscopy (SEM). Measurement of the compositions of the various phases within the sample was undertaken using a JEOL JXA 8200L (trademark of Japan Electron Optics Ltd., Tokyo) electron X-Ray probe microanalyzer (EPMA) with wavelength dispersive detectors (WDD). An acceleration voltage of 15 kV and a probe current of 15 nA were used. The Duncumb-Philibert ZAF correction procedure supplied with the JEOL JXA 8200L probe was applied. The standards (Charles M. Taylor, Stanford, CA) that were used in the EPMA measurements; for the oxide phases - Cu_2O for Cu, wollastonite ($CaSiO_3$) for Si and Ca, hematite (Fe_2O_3) for FeO, Al_2O_3 for Al, Cr_2O_3 for Cr, PbO-SiO_2 glass for Pb, orthoclase for K and $5CaO.As_2O_5.SiO_2$ for As; for the sulphide and metallic phases - chalcopyrite ($FeCuS_2$) for Cu, Fe and S, PbS for Pb, ZnS for Zn and InAs for As.

An achievement of equilibrium was confirmed by carrying out experiment for different equilibration times, approaching equilibria from different directions, analysis of homogeneity of phases and consideration of reactions specific to the system. For example, a series of preliminary experiments was undertaken starting from the pure metallic Cu, metallic Fe and SiO_2 mixture on a silica substrate at 1180 ^{0}C, P_{O2} of $10^{-8.65}$ atm and P_{SO2} of 0.28 atm for different times; the resulting microstrucutres presented in Figure 2 indicate that homogenization of the liquid slag starting from the Cu, Fe and SiO_2 pure powders is reached after 4 hours, and that the 6 hours equilibration of the samples made from pre-melted slag and matte used for most of experiments was sufficient to achieve equilibrium.

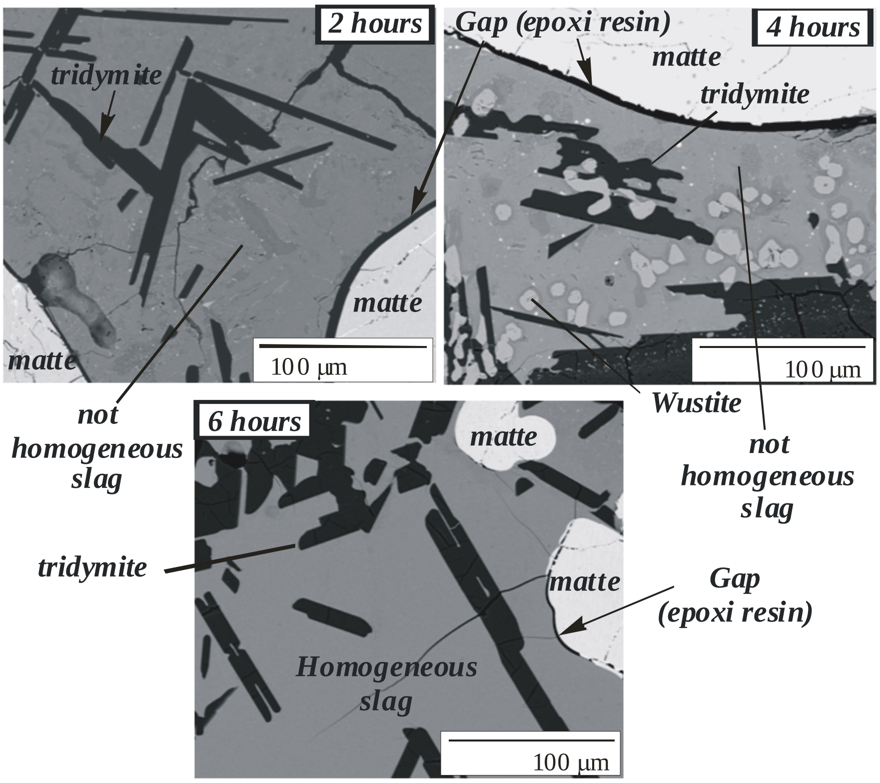

Figure 2. Scanning Electron Microscope images of liquid slag in equilibrium with tridymite at equilibrium times of 2, 4 and 6 hours.

2.2. Further developments of experimental methodologies

Although general experimental approach outlined above and applied to other simpler systems was established previously, present study required further development of the experimental methodology for to the conditions close to the Cu smelting since this project is the first time this advanced experimental approach of equilibrating slag with matte on a substrate at controlled O_2 and SO_2 partial pressures and temperature was applied to investigate both liquidus and minor element partitioning in the complex multi-component industrial system. This included several components such as geometry of substrate and the way slag samples were placed on substrate, matte formation, equilibration strategy (preheat and actual equilibration), direction of achievement of equilibria, equilibration time, strategy to obtain targeted matte grade, strategy to retain volatile elements in the sample (such as As, Pb and Zn), as well as health and safety As-related issues. Pt or Mo wires were selected to support of the substrates depending on the primary phase investigated. The EPMA composition analysis of slag included Pt and Mo in order to detect and reject samples with contaminations. The pre-melted slag and matte with higher Zn concentrations were used as starting materials to minimise Zn vaporisation during the final equilibration.

Minor elements Pb, As, Sb, Bi and Sn vaporise during the equilibration; closed-system technique was developed to characterise the distribution for these elements. A series of experiments was undertaken first to determine the oxygen partial pressure for the targeted matte grade of 60 wt pct of Cu at a given $P_{SO2} = 0.28$ atm and temperature. The master slag and matte were then prepared at the determined conditions by equilibration and fast quenching; slag and matte compositions were confirmed by EPMA. Minor elements were then added the slag phase and matte, and the mixture was sealed in a vacuumed silica ampoule with a welding torch. The ampoule is then equilibrated at a fixed temperature, then quenched and analysed similar to all other samples (see details above).

Since during experiment it was impossible to keep exact composition of slag and matte (those were measured after the experiment and changed during experiment), multiple repeating experiments were used to construct one diagram with fixed values of minor elements and fixed value of matte grade. The results for the liquidus temperatures were described with a simple polynomial expression as a function of minor components as well and Fe/SiO_2 and matte grade.

2.3. Industrial slag and matte quenching tests

The application of the advanced modelling and experimental results into industrial practice requires an implementation stage to identify possible differences between theoretical predictions, laboratory results on synthetic samples and the actual conditions in the reactor. For this purpose a series of the slag and matte samples were quenched directly from the taped streams together with the temperature measured directly in the corresponding slag or matte stream using the disposable dip R-type thermocouple (supplied by Heraeus). Slag and matte samples were taken at the same time. The sampling procedure was optimised to eliminate possible changes so that the quenched samples represent the phases in the slag and matte streams tapped directly from the reactor. The bulk compositions were analysed with XRF. The microstructures and phase compositions in the quenched slag samples were then analysed in the same way as the laboratory samples (see description above). The microstructural analysis by the expert researchers experienced in the analysis of both industrial and laboratory samples as well as in the high temperature phase equilibria and kinetics research is an essential stage to characterise the actual processes in the reactor and therefore to provide the basis for implementation of the advanced research outcomes in practice.

3. EXPERIMENTAL RESULTS

3.1. Effect of oxygen partial pressure on matte grade at fixed P_{SO2}

The number of degrees of freedom analysis indicates that the 5-component Cu-Fe-O-S-Si system with the 4-phase assemblage (gas + slag + matte + solid) has F=5+2-4 = 3 degrees of freedom; the system at fixed temperature, P_{SO2} and P_{O2} therefore is fully specified (this includes the matte grade). Addition of each further element such as Al, Ca etc and fixing it's concentration in the slag phase will keep the system fully defined. Series of experiments was undertaken to determine the P_{O2} corresponding to the 60 wt % Cu matte grade at fixed temperature and P_{SO2} of 0.28 atm. The results for the experiments at equilibrium with tridymite are given in Figure 3.

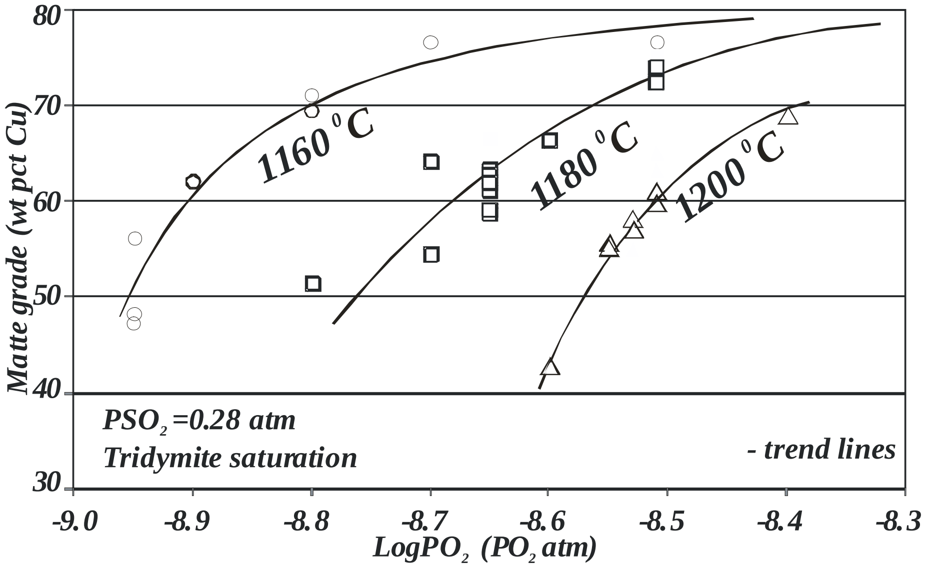

Figure 3 Relationship between concentration of copper in matte (matte grade) and oxygen partial pressure at temperatures of 1200, 1180 and 1160 °C (Equilibrium slag/matte/tridymite) .

The matte grade is extremely sensitive to the variations of oxygen partial pressure. For example, at 1200 ^{0}C the matte grade changes from 43 to 69 wt pc Cu for a variation of P_{O2} between $10^{-8.6}$ and $10^{-8.4}$. Note that the development and application of the methodology based on the experiments at targeted matte grade is the first research project of this kind. The approach indicated great capability, but also identified the need and directions for further improvements. For example, present series of experiments showed that the accuracy of the control of the oxygen partial pressure with capillary flowmeters is actually significantly better than the ± 0.1 logP_{O2} units. At the same time the large scatter in Figure 3 highlights the potential and the necessity to further improve the experimental accuracy and reduce uncertainties. The ranges of the oxygen partial pressures used for most of the experiments aiming the 60 wt % Cu matte grade are given in Table 1.

Table 1. Range of oxygen partial pressure to obtain 60 wt % Cu matte grade at P_{SO2}=0.28 atm

Temperature	Range of logP_{O2}
1160 ^{0}C	-8.9 to -8.95
1180 ^{0}C	-8.6 to -8.7
1200 ^{0}C	-8.50 to -8.53

3.2. Results of laboratory experiments on the liquidus temperatures of synthetic slags at fixed matte grade, P_{O2} and P_{SO2}

Experiments were carried out to obtain the slag liquidus in the "Cu_2O"-"FeO"-SiO_2-CaO-MgO-Al_2O_3-ZnO system for the equilibria gas/slag/matte with tridymite or spinel (on the corresponding substrates). Examples of the corresponding microstructures are presented in Figure 4.

Exact targeted values of the matte grade and minor CaO, MgO, Al_2O_3 and ZnO cannot usually be obtained since these are measured after the experiment and adjusted iteratively to obtain the values close to the targeted ones. For this reason a liquidus interpolation was used: the tridymite and spinel liquidus conditions were expressed as a polynomials of temperature, matte grade, Fe/SiO_2, CaO, MgO, Al_2O_3 and ZnO concentrations in the slag. The parameters of the polynomials were obtained by minimising the sum of squared differences between calculated and experimental values to obtain the best fit. The optimised parameters were then interpolated to calculate the tridymite and spinel liquidus at exact targeted CaO, MgO, Al_2O_3 and ZnO concentrations for the 60 wt % Cu matte grade. The use of these simplified mathematical expressions is justified by the relatively small range of compositions investigated.

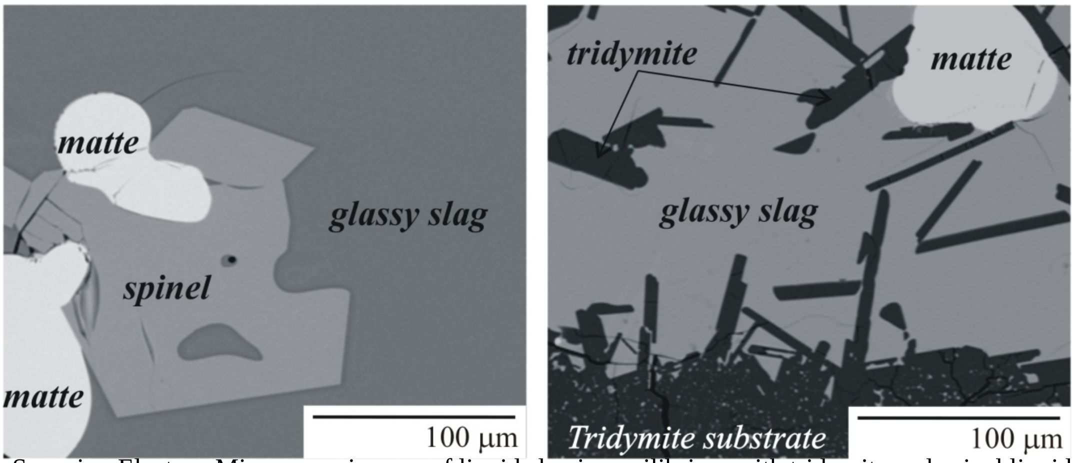

Figure 4. Scanning Electron Microscope images of liquid slag in equilibrium with tridymite and spinel liquidus and to construct the corresponding phase diagram projections.

Figures 5-A to 5-D show position of the liquidus lines for the selected targeted base case of 3.3 wt % CaO, 0.9 wt % Al_2O_3, no MgO and 2.0 wt % ZnO as well as effects of CaO , Al_2O_3, MgO and ZnO compared to the base case. The results indicate that the increase of the CaO, Al_2O_3 and MgO concentrations results in the significant increase of the spinel and decrease of the tridymite liquidus temperatures. Variation of the ZnO results in a relatively weak effect.

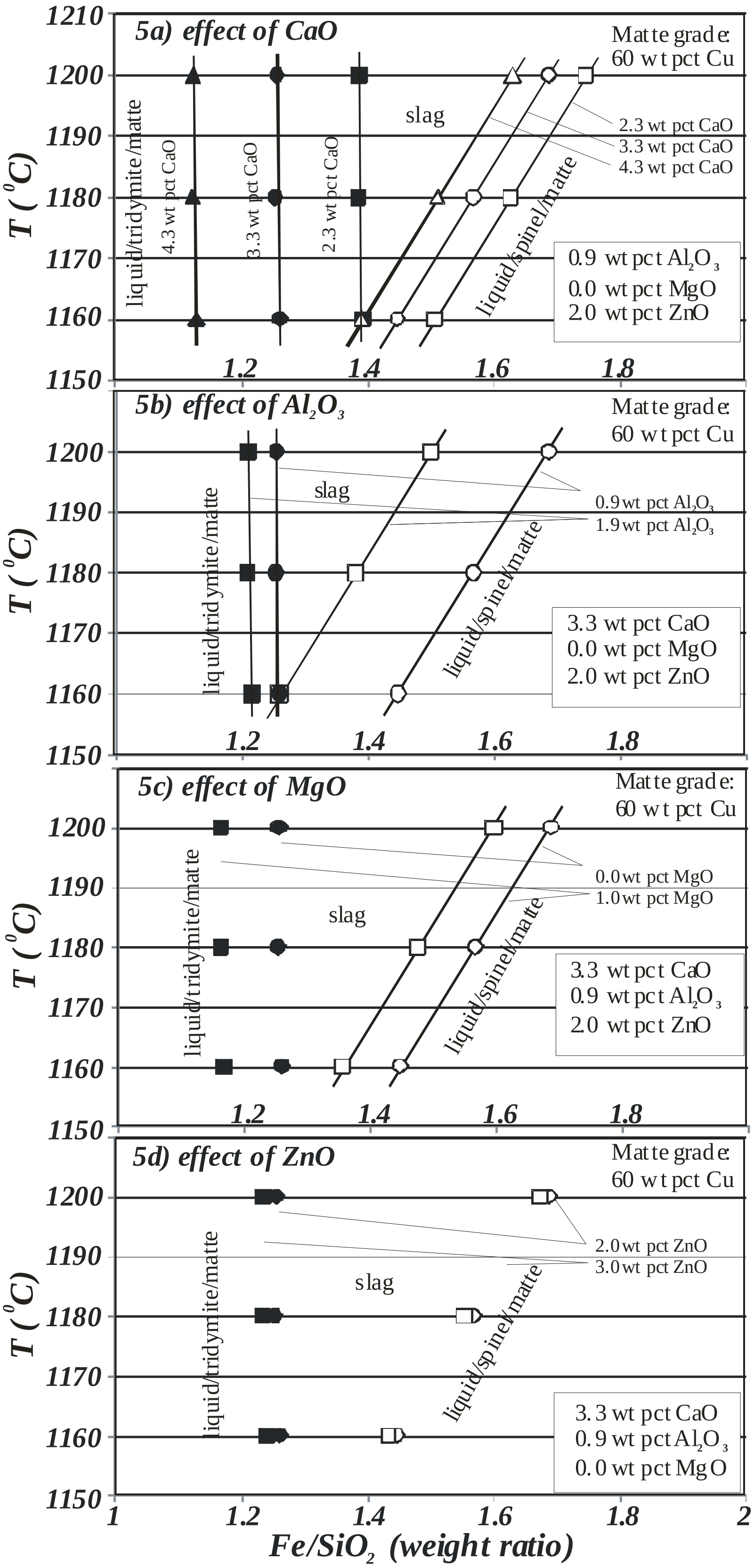

Figure 5. Experimental measurements liquidus trydimite and spinel boundary lines for the "Cu_2O"-"FeO"-SiO_2 slag at matte grade of 60wt % of copper and PSO_2 of 0.28 atm. for fixed concentration of CaO, MgO,

3.3. Results of the analysis of the quenched industrial samples

The expert analysis of the quenched industrial samples is particularly important for implementation of the outcomes of the advanced fundamental research methods into industrial operations; this analysis aims to identify differences between theoretical predictions, laboratory measurements and the behaviour of the industrial slag / matte system. The industrial samples are frequently heterogeneous, difficult to analyse and complex to interpret. The analysis of the quenched industrial slag undertaken by experienced researcher can provide information on the actual oxidation / reduction condition in the reactor through a number of indicators including S and Cu dissolved in the liquid slag in combination with the Cu concentration in the matte phase, the Fe^{2+}/Fe^{3+} ratio in spinel crystals if present, and many other features. Any unaccounted minor components are directly measured in the quenched industrial sample. Presence or absence of solids in combination with the morphology of the observed crystalline phases is an indicator of the relation of the actual slag to the liquidus. The kinetic aspects of the process can also be identified by searching for possible un-reacted particles such as sulphides, fluxes or phases related to the interactions with the refractory. It is important to anticipate particular microstructural features from the theoretical and practical knowledge of the industrial process as well as of the phase equilibria and kinetics foundations. In many cases the absence of a particular feature is important to confirm so that it is not necessary what is observed, but what is not observed enables to establish the actual condition, and in addition, some features can only be found in these complex industrial samples if a researcher is specifically looking for them based on the expert knowledge.

Microstructures of the slag samples with suspended matte and spinel are given in Figure 6; more detailed spinel and suspended matte morphologies are presented in Figures 7 and 8. The compositions of the phases in the quenched industrial samples measured with EPMA and the bulk analysis measured by XRF are given in Table 2.

Table 2. Bulk and phase compositions in the quenched industrial samples

##	Tem. (^{0}C)	Phase	Ana-lysis **	wt pct Normalized												Total	Fe/SiO_2 (weight ratio)	L_{Me} slag/matte		
				FeO /Fe	SiO_2	CaO	Al_2O_3	MgO	ZnO /Zn	PbO /Pb	Cu_2O /Cu	S	Cr_2O_3	K_2O	As_2O /As			Zn	Pb	As
1	1162	Slag	E	44.3	37.6	3.9	4.2	1.3	5.0	1.3	0.33	0.6	0.02	1.1	0.32	98.9	0.92	2.51	0.23	3.35
		Bulk slag	X	41.4	33.6	3.6	3.8	1.2	4.7	1.8	5.8	2.7	0.07	1.1	0.20	99.5				
		Matte*	E	14.4	0.0	0.0	0.0	0.0	1.6	0.0	58.8	25.1	0.00	0.0	0.06	99.3				
		Bulk matte	X	16.8	0.1	0.0	0.0	0.1	2.0	5.3	51.9	23.7	0.00	0.0	0.09	99.3				
		Low-Cr Spinel	E	94.5	0.1	0.0	1.2	0.4	2.8	0.0	0.0	0.0	0.9	0.0	0.0	95.8				
		High-Cr Spinel	E	81.4	0.5	0.0	4.2	0.5	4.1	0.0	0.0	0.0	9.2	0.0	0.0	94.3				
2	1161	Slag	E	44.2	38.0	3.9	4.2	1.3	4.8	1.1	0.38	0.7	0.04	1.2	0.26	99.3	0.90	1.67	0.18	2.37
		Bulk slag	X	40.0	31.1	3.2	3.5	1.1	4.3	1.8	9.3	4.4	0.07	1.0	0.16	100.5				
		Matte*	E	17.1	0.0	0.0	0.0	0.0	2.3	0.0	54.7	25.9	0.00	0.0	0.07	100.3				
		Bulk matte	X	14.0	0.1	0.0	0.0	0.1	1.8	5.7	54.8	23.4	0.00	0.0	0.10	100.4				
		Low-Cr Spinel	E	95.9	0.7	0.0	0.6	0.2	2.3	0.0	0.0	0.0	0.3	0.0	0.0	94.7				
		High-Cr Spinel	E	83.6	1.1	0.1	4.1	0.5	3.5	0.1	0.0	0.0	6.9	0.1	0.0	94.5				
3	1154	Slag	E	44.0	38.1	3.8	4.2	1.3	4.9	1.2	0.45	0.6	0.02	1.1	0.31	98.6	0.90	1.93	0.21	3.90
		Bulk slag	X	38.4	31.6	3.1	3.5	1.1	4.3	2.0	10.2	4.4	0.07	1.0	0.16	100.8				
		Matte*	E	16.1	0.0	0.0	0.0	0.0	2.0	0.0	56.3	25.5	0.00	0.0	0.05	97.4				
		Bulk matte	X	15.4	1.2	0.0	0.0	0.2	1.9	5.4	52.6	23.2	0.00	0.0	0.10	100.4				
		Low-Cr Spinel	E	88.8	3.6	0.3	2.3	0.5	2.9	0.2	0.0	0.1	1.1	0.2	0.0	95.3				
		High-Cr Spinel	E	77.6	3.5	0.3	4.4	0.6	4.4	0.1	0.1	0.1	8.8	0.1	0.0	95.3				

*Chemical composition of the matrix phase in the matte

** Analysis E=EPMA , X=XRF

All industrial quenched samples had three phases at the time of granulation including liquid slag, spinel (see Figure 7) and entrained matte (see Figure 8).

The samples contain well quenched areas in the liquid slag phase (see Figures 6 and 8). The analysis of the compositional profile as a function of distance from matte and from spinel phase indicated that the liquid slag phase is homogeneous. The Cu concentration in the slag phase is between 0.3 to 0.4 wt pct, and the S concentration is 0.6-0.7 wt % indicating quite reducing conditions. The reported concentration of copper in the bulk analysis of slag is between 6 and 10 wt pct due to the suspended matte (note that the samples were quenched from the stream tapped directly from the reactor before settling in an electric furnace).

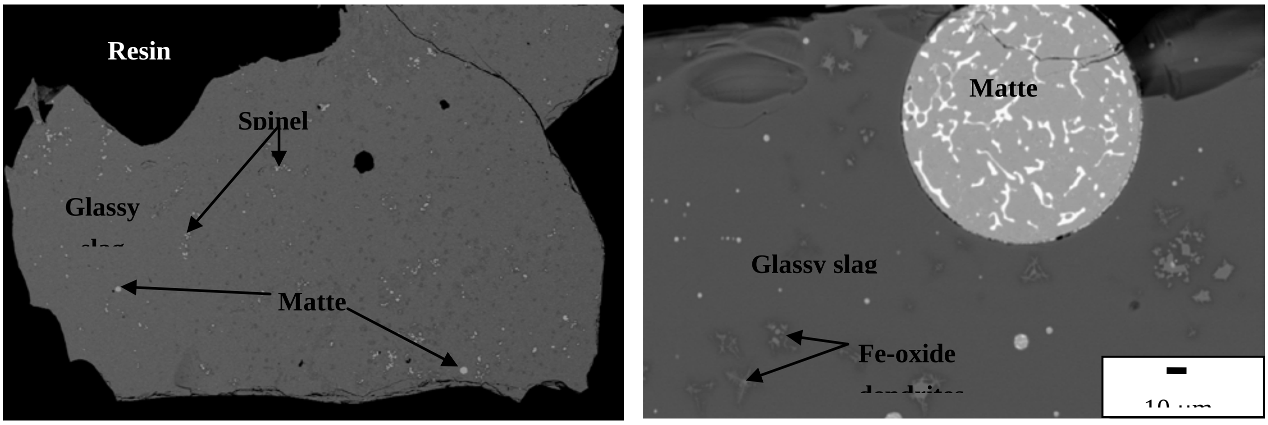

Figure 6. Scanning Electron Microscope images of the quenched industrial slag samples.

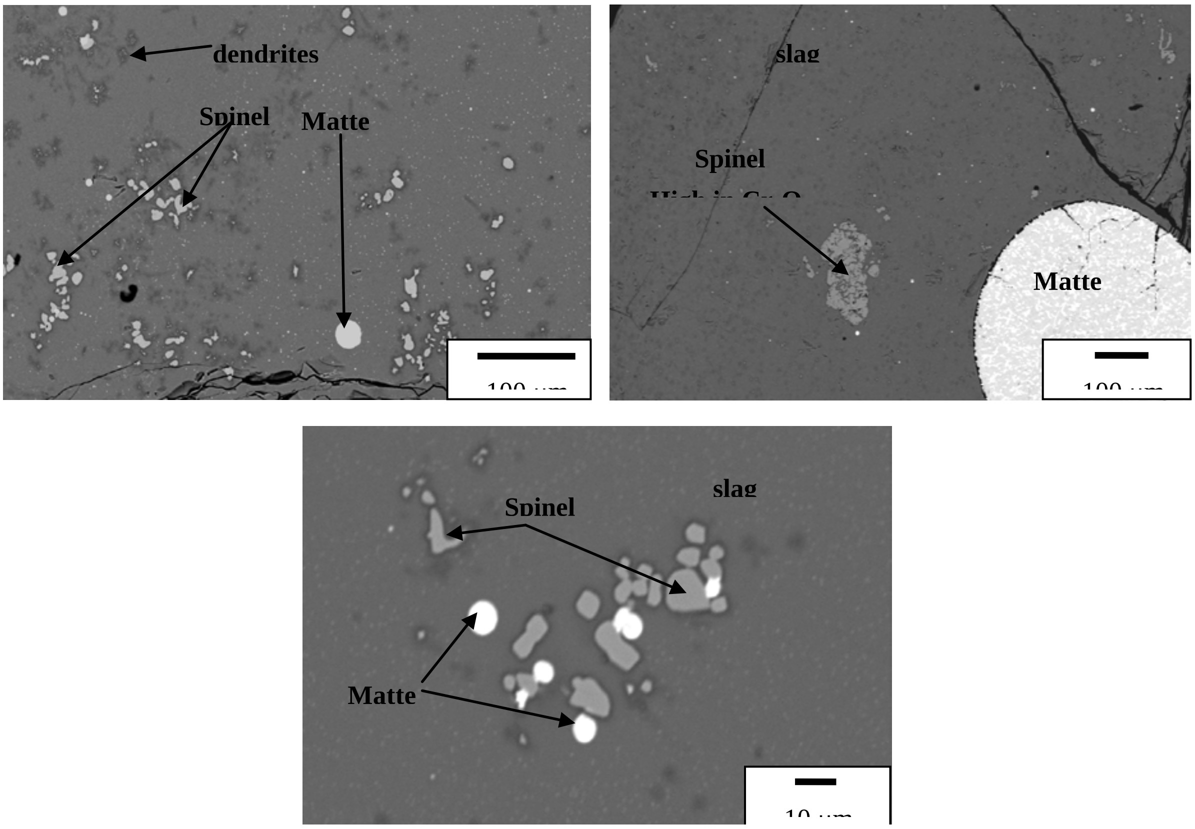

Figure 7. Scanning Electron Microscope images of spinel in the quenched industrial slag samples.

Small iron oxide dendrites (see Figure 6) most likely precipitated during quenching. The size of the observed crystals of spinel is 3 - 10 μm with euhedral or spherical shapes (see Figure 7). The morphology of the spinel crystals indicates they were present in the contact with the slag at the time of granulation; this observation in combination with the compositions of most of the spinet crystals indicate that the slag is in of close to the equilibrium with this phase; the composition of the quenched liquid slag in combination with the temperature just before the quenching measured with the dip thermocouple provides the liquidus of the industrial slag.

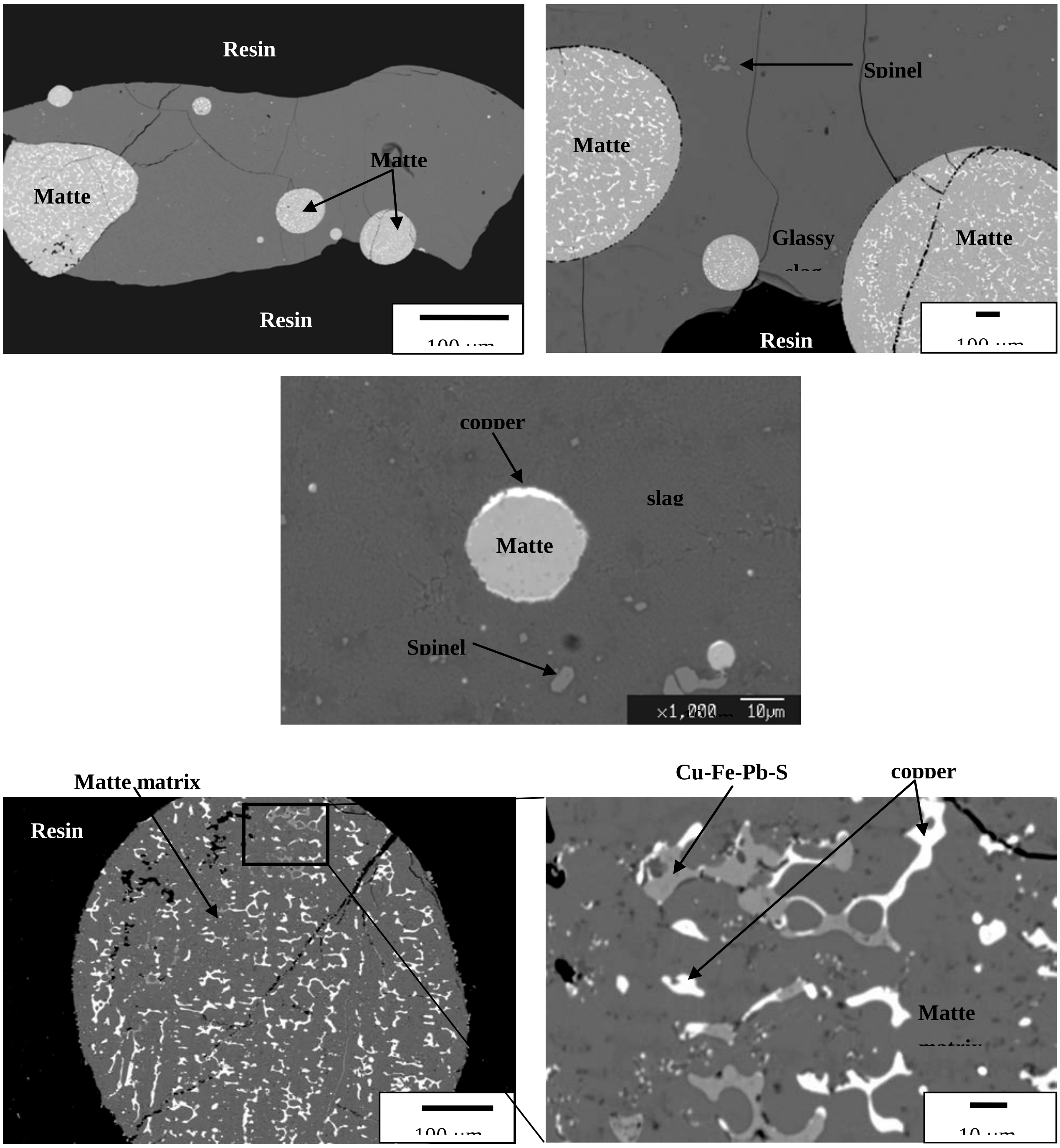

Figure 8. Scanning Electron Microscope images of matte phase in the quenched industrial slag samples.

The MgO, Al_2O_3 and Cr_2O_3 concentrations in different spinel particles vary significantly. Particularly large is the variation of chromium concentration in spinel particles ranging from a low values of less than 0.1 wt pct to as high as 12 wt pct. The high- Cr_2O_3 crystals are present as relatively large agglomerates (see Figure 7). The average high- and low- Cr_2O_3 spinel compositions are given in Table 2. The morphology and chemical compositions of the observed spinel crystals indicated possible different mechanisms including 1) erosion / dissolution of the Cr_2O_3–containing refractories and 2) precipitation/dissolution of crystals (the variable compositions of the observed low- Cr_2O_3 spinel crystals indicated at different condition at the time of formation of the crystals in terms of temperature, oxygen partial pressure and slag composition so that the observed crystals not necessary correspond to a condition of equilibrium with slag at the time of granulation). Un-dissolved crystals from the feed (for example corundum or un-melted silica) were not observed in the samples.

The suspended droplets of matte have variable size between few microns to1000 μm (see Figure 8). The matte phase segregated during quenching and incorporated Pb- rich and metallic copper phases in the matte phase matrix. The composition of the suspended matte droplets matrix measured with EPMA is relatively close to the matte samples bulk composition (see Table 2) indicating that only physical separation of the suspended matte droplets takes place. The matte droplet surrounded by a copper phase (see Figure 8) however indicates at the possible oxidation reaction through the slag phase being still in progress.

3.4. Comparison of the liduidus temperatures measured in the industrial slag, in laboratory experiments and predicted with FactSage 6.2

Liquidus temperatures determined in the laboratory experiments for the synthetic samples were calculated using the developed polynomials for the average levels of CaO, Al_2O_3, MgO and ZnO concentrations in the quenched industrial slag samples and are presented as the plot T vs Fe/SiO_2 for three levels of matte grade (see Figure 9). Predictions using FactSage 6.2 with the public thermodynamic databases [23] for the same average levels of minor elements for the 55 wt % Cu matte grade and P_{SO2} of 0.28 atm were also undertaken, reported in Table 3 and presented in Figure 9. Note that some other minor elements such as PbO, Cr_2O_3, K_2O present in the industrial samples were not taken into account in the polynomial nor in the FactSage predictions. The data presented in Figure 9 clearly indicates the necessary adjustments to the theoretical predictions of FactSage 6.2 compared to the laboratory measurements, and the differences between industrial slag sample and the liquidus determined from the laboratory study with synthetic samples. The liquidus temperatures predicted with FactSage 6.2 are lower compared to the laboratory experiments indicating at the need for possible further database improvements. The spinel liquidus temperatures of the industrial slag are lower than the liquidus determined in the laboratory for the synthetic samples indicating at a possible effects of other un-accounted minor elements or kinetic effects. The combination of these three sets of liquidus data including a) predicted with FactSage, b) laboratory experiments with synthetic samples and c) measured in the quenched industrial samples, is important valuable foundation for further possible optimisation of the process conditions.

Table 3. FactSage 6.2 predictions (using FToxid and FTmisc databases)

T[^oC]	logP_{O2}	logP_{S2}	P_{SO2}	Solid phases*	Matte [wt %]				Slag recalculated to oxides [wt %]								
					S	Fe	Cu	Zn	ZnO	Cu_2O	FeO	CaO	S	SiO_2	Al_2O_3	MgO	Fe/SiO_2
1160	-8.89	-2.08	0.28	Tr	25.9	18.7	53.0	2.4	4.9	0.21	43.5	3.9	0.76	41.2	4.2	1.3	0.822
1180	-8.73	-2.02	0.28	Tr	25.9	18.6	53.0	2.5	4.9	0.22	42.9	3.9	0.75	41.8	4.2	1.3	0.798
1200	-8.58	-1.97	0.28	Tr	25.9	18.5	53.0	2.6	4.9	0.24	42.3	3.9	0.74	42.4	4.2	1.3	0.776
1160	-8.80	-2.24	0.28	Sp	25.9	18.7	53.0	2.4	4.9	0.25	50.6	3.9	1.07	33.8	4.2	1.3	1.163
1180	-8.63	-2.24	0.28	Sp	25.8	18.6	53.0	2.6	4.9	0.28	52.4	3.9	1.19	31.9	4.2	1.3	1.277
1200	-8.45	-2.23	0.28	Sp	25.8	18.5	53.0	2.7	4.9	0.32	54.3	3.9	1.35	29.7	4.2	1.3	1.421

* Tr = tridymite, Sp=spinel primary phase field

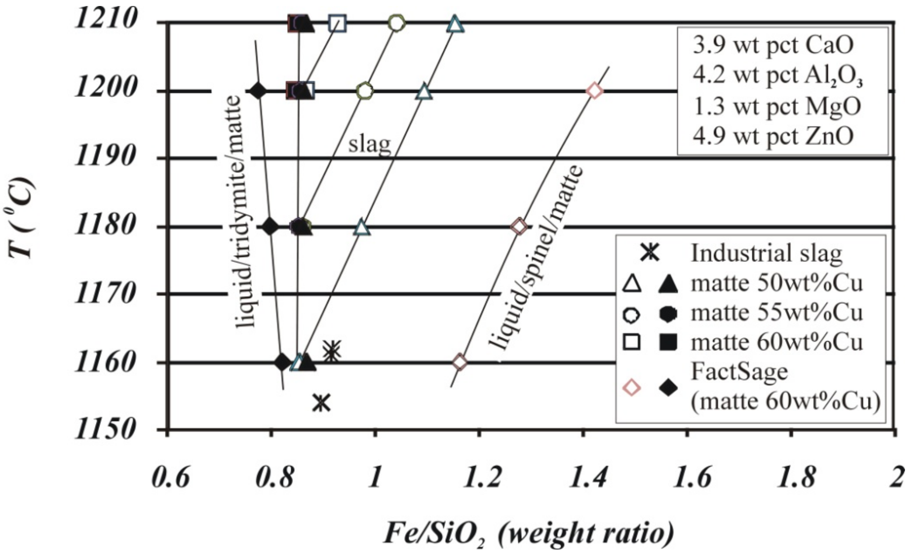

Figure 9. Experimental measurements liquidus trydimite and spinel boundary lines for the "Cu_2O"-"FeO"-SiO_2 slag at matte grade of 60, 55 and 50 wt %of copper and PSO_2 of 0.28 atm. for fixed concentration of CaO, MgO, Al_2O_3 and ZnO. (CaO=3.9, MgO=1.3, Al_2O_3=4.2, ZnO=4.9 wt pct). The figure also include measured liquidus of the quenched industrial samples taken from the Isasmelt Furnace and FactSage 6.2 predictions.

3.5. Results on distribution of minor elements between matte and slag

Detailed critical literature review on partitioning of As, Pb, Zn, Au, Ag, Sb, Bi and Sn, was undertaken and included over 150 sources; majority of the papers did not have relevant data (for example, many papers had information on only one phase, many papers repeated results). Only a few papers with reliable and relevant information therefore were selected (see references), the data were retrieved and rearranged for comparison so that the values are expressed in the same units, and the conditions are expressed using the same parameters (e.g. P_{O2}). In general, limited information was found on the slag/matte equilibrium distribution for all minor elements, and the available data are at conditions far from the Cu IsaSmelt process. Figure 10 reports present results of both a) laboratory experiments and b) measurements in the quenched industrial samples compared to the selected data from the literature (the oxygen partial pressure for the industrial samples was assumed to be approximately $10^{-8.5}$).

Figure 10 a) reports selected As distribution data [16, 17 ,18, 20, 21] for the equilibria a) slag/silver-As alloy at controlled oxygen partial pressure, b) slag/copper, and c) slag/ matte. The slag/metal or matte distribution ratios reported in the literature are between 0.001 and 10000 for a range of P_{O2} between $10^{-11.7}$ and $10^{-0.61}$ atm respectively. The slag / matte distribution ratio of arsenic measured in the present study at 1180°C, $P_{O2}=10^{-8.65}$ and P_{SO2} of 0.28 atm (corresponding to the matte grade of around 60 wt % Cu) is around 1.2. Present experimental results indicate that addition of CaO reduces the partitioning of arsenic into slag. The distribution ratio of arsenic measured in the quenched industrial samples is between 2.4 and 3.9 at temperatures around 1160 ^{0}C and matte grade from 52 to 55 wt pct Cu (see Table 2). The data reported in the literature are not sufficient for accurate determination of oxidation state of arsenic in slag. The slope of the relationship between the log$L_{As}^{s/m}$ and logPO$_2$ corresponds to an oxidation state of arsenic in slag between AsO and AsO$_2$.

Figure 10 b) reports selected Pb distribution data [4, 8, 16, 18, 20, 21] for the equilibria a) slag/copper and b) slag/matte at 1300 ^{0}C. The distribution ratios reported in the literature are between 0.06 and 10 for a range of PO$_2$ between 10^{-12} and $10^{-4.5}$ respectively. The slag / matte Pb distribution ratio measured in the present study at 1180^{o}C, $P_{O2}=10^{-8.65}$ and P_{SO2} of 0.28 atm (corresponding to the matte grade of around 60 wt % Cu) is around 0.4. The Pb distribution ratio measured in the quenched industrial samples is around 0.2 at temperatures around 1160 ^{0}C and matte grade from 52 to 55 wt pct Cu (see Table 2). The slope of the relationship between log$L_{Pb}^{s/m}$ and logPO$_2$ indicates the valence of lead to be PbO.

Figure 10 c) reports selected Zn distribution data [19, 20] for the equilibria a) slag/copper at controlled PO$_2$ and b) slag/copper at iron-saturation (in Fe crucible); no information for the equilibrium Zn slag/matte distribution was found in the literature. The slag / copper metal distribution ratios reported in the literature are between 0.05 and 100 for a range of P_{O2} between 10^{-12} and 10^{-5} atm. The equilibrium Zn slag/matte distribution measured in the present study at 1180^{o}C, P_{SO2} of 0.28 atm and P_{O2} from $10^{-8.6}$ to $10^{-8.7}$ atm corresponding to the matte grade of around 60 wt % Cu is between 2 and 10; the distribution ratio increases with increasing P_{O2} and decreasing temperature. The Zn distribution ratio measured in the quenched industrial samples is between 1.7 and 2.5 at temperatures around 1160 ^{0}C and matte grade from 52 to 55 wt pct Cu (see Table 2). The slope of the relationship between log$L_{Zn}^{s/m}$ and logPO$_2$ corresponds to the oxidation state of zinc to be ZnO.

6. Conclusions

The experimental methodology was developed for investigations of the slag and matte equilibria with fixed matte grade. Liquidus of the multi-component synthetic slag was measured at fixed matte grade, oxygen and sulphur dioxide partial pressures. Literature review on the distribution of minor elements was undertaken, significant uncertainties and the lack of information were identified. Experimental investigation on partitioning of minor elements between slag and matte has been undertaken. Present experimental results on the distribution ratios of minor elements (defined as $L_X^{slag/matte}$ = wt % Me in slag ⁄ wt % Me in matte) were compared with those reported in the literature. Targeted industrial slag and matte samples were quenched from the tapped streams; expert analysis of the industrial samples was undertaken. Predictions with thermodynamic computer package FactSage were performed. Data from all three sources including theoretical predictions with FactSage, laboratory experimentation and targeted industrial tests were compared. This work provided strong foundation for possible optimisation of the Cu smelting process and demonstrates the comprehensive systematic approach combining fundamental and applied research focused on the implementation into industrial practice.

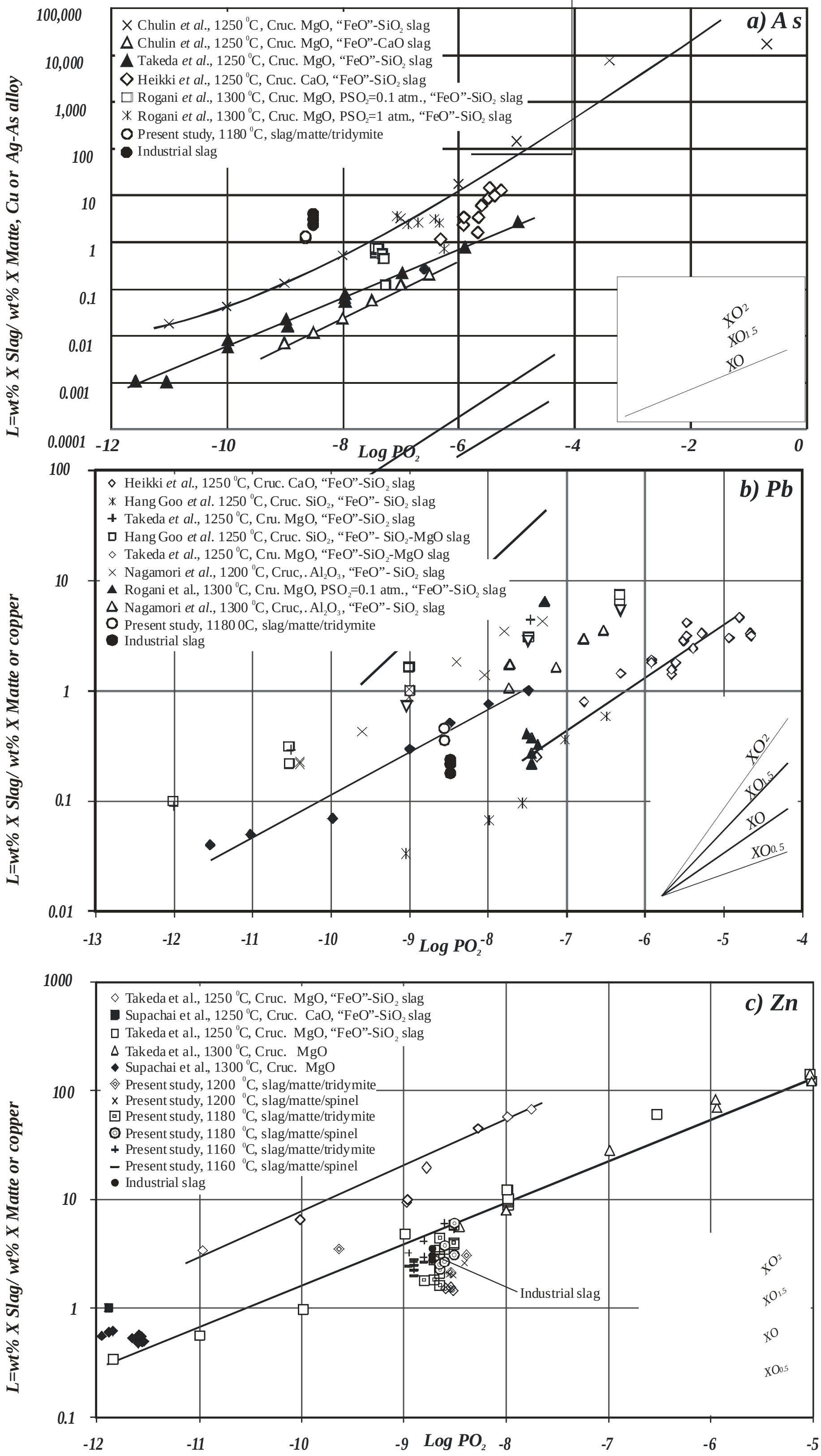

Figure 10. The distribution ratio of As, Pb and Zn between slag and matte or metal as a function of the oxygen partial pressure. Present results for the slag/matte/tridymite equilibrium are at P_{SO2}=0.28 atm and

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