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Slag-copper equilibria of selected trace elements in black-copper smelting.

Part I. Properties of the Slag and Chromium Solubility

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Abstract

The solubility of chromium in alumina- and lime-containing (≈ 5 wt-% Al_2O_3 and 0- ≈ 10 wt-% CaO) iron silicate slags saturated with chromium spinel have been measured experimentally at 1300 °C. In order to avoid contamination and the effects of further elements in the slag, the measurements were carried out in silica crucibles, i.e. in silica saturation. The solubility of chromium in the studied iron silicate slags was a function of oxygen partial pressure. At high oxygen partial pressures $P_{\text{O}_2} \approx 10^{-5}$ atm, the solubility was about 0.15 wt-% (Cr) and it increased to about 0.3 wt-% (Cr) in reducing conditions of $p_{\text{O}_2} \approx 10^{-10}$ atm. Alumina and lime seemed to increase the solubility slightly over the entire oxygen partial pressure range studied. The properties of iron silicate slags at silica saturation have also been measured.

Key words: Copper scrap, WEEE, iron silicate slag, alumina, lime, chromite

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Introduction

Black copper smelting is an optional route for the recovery of secondary copper resources, along with the copper primary smelting route utilizing feedstocks from sulphidic and oxidic ores (Graedel et al., 2002; Valero Navazo et al., 2014; Ghodrat et al., 2016). Typical secondary copper smelters are small and utilize local scrap of conventional origin, including end-of-life (EoL) electric appliances, cables and tubes. Their minor metal values are composed of iron, nickel and lead components following the copper scrap. The increasing volumes of e-scrap or WEEE (waste electric and electronic equipment) contain metals, which are both rare in Earth's crust (Nakamura, 2014), available only in limited amounts, and thus expensive. The reducing smelting-converting-electrolytic refining route is widely used in the copper scrap processing chain, but the operation lacks fundamental data on the trace elements in reducing and oxidising conditions. Therefore, the smelting and refining facilities must be redesigned, possibly also adjusted in terms of their operational point at each processing stage for the maximal metals recovery.

This detailed experimentation allows us to evaluate the thermodynamic properties of the substances in the various process streams and enables various process simulations for, e.g., optimization purposes. The thermodynamic features of the alumina containing iron silicate slags in copper smelting and refining conditions are not very well known (Klemettinen et al., 2017). Experimental observations of chromia solubility in iron silicate slags at oxygen partial pressures, typical to nickel and copper matte smelting, are rare. No experimental data are available in the literature on the solubility of chromium in slags of secondary copper smelting at 1250-1350 °C, but de Villiers & Kleyenstüber (1993) made equilibrations of chromium between iron mattes and alumina- and magnesia-bearing iron silicate slags at 1450 °C. Kwatara (2006) equilibrated copper mattes and slag under various oxygen and sulphur pressures at 1300-1500 °C. Du Preez (2009) did similar observations at 1550 °C. Wrigt et al. (2009) studied the chromium distributions between matte and Pt-alloys in reducing conditions in $p_{O_2}=10^{-9}$ atm and at 1400 °C.

In PGM extraction, excessive MgO and Cr₂O₃ concentrations of South-African nickel-copper concentrates from Bushveld Complex require much higher processing temperatures than nickel matte smelting and therefore design temperatures of their smelting vessels are close to 1600 °C (Nell, 2004; Andrews, 2005; Coezee, 2006; Eksteen et al., 2011). This may be also the case where the ore body has been formed next to a chromite mineralisation (Maier & Groves, 2011).

In spite of the industrial importance, very little fundamental data are available on the chemistry and phase equilibria of chromia in iron silicate slags, and the combined effect of chromia and magnesia. Murck & Campbell (1986) measured the solubility of chromium in iron silicate slags at 1300-1500 °C in various oxygen partial pressures. Roeder & Reynolds (1991) did the same for basaltic melts at 1200-1400 °C, extending the experiments to 10 kbar. They were later confirmed by Sattari et al. (2002). Eguchi et al. (1977) measured the solubility of chromia in iron silicate slags at 1230-1400 °C in equilibrium with solid iron. The solubility as Cr₂O₃ was 1.5, 3 and 5 wt-% at 1130, 1300 and 1400 °C, respectively. According to Nell (2004), the chromia solubility in iron silicate slags increases at low oxygen partial pressures and at 1550 °C it is >5 % (Cr₂O₃) below $p_{O_2} < 10^{-11}$ atm. Chen et al. (2005) measured the liquidus line at 1400-1600 °C, with 2 wt-% (Cr₂O₃) solubility in silica saturation. Ilyushechkin et al. (2015) determined twelve points at 1350-1490 °C in silica-spinel and silica-spinel-pyroxene saturation. Their EPMA data showed chromia solubilities of 0.2 to 0.5 wt-% in the molten oxide phase in oxygen partial pressures generated by CO₂-H₂ mixtures with the volumetric ratio CO₂:H₂ = 132:1. According to Somerville et al. (2004), a spinel of the type (Mg,Fe)(Al,Cr,Fe)₂(O)₄ was precipitated and the solubility of chromium at 1350-1630 °C in the molten silicate was between 0.3 and 1.3 wt% (Cr). They

also report chromium bearing olivine $(\text{Fe,Mg,Cr})_2\text{SiO}_4$ and pyroxene $(\text{Fe,Mg,Cr})\text{SiO}_3$ solutions to be stable below 1450 °C as primary phases. Henao et al. (2001) measured the distribution of chromium between a nickel alloy and $\text{FeO}_x\text{-MgO-SiO}_2$ slags at 1500-1600 °C at MgO saturation, which allowed calculation of the activity coefficient of chromia in the slag. Intensive experimental and modelling studies have been conducted in reducing conditions and iron-free slags related to ferrochromium smelting in the literature, e.g. Curr et al. (1988), Xiao & Holappa (1993), Pan & Eric (2004), Arnout et al. (2009) and Albertson et al. (2013). Several papers are also available on the $\text{Cr}^{2+}/\text{Cr}^{3+}$ and $\text{Cr}^{3+}/\text{Cr}^{6+}$ equilibria and speciation in various slags (Hanson & Jones, 1998; Farges, 2009).

The aim of this study was to measure experimentally the solubility of chromium in the iron-silicate slags containing alumina and lime, with the slag saturated by a chromium spinel, silica and metallic copper. The silica saturation boundary and properties of the molten slag were also determined. In order to avoid the effects of further elements in the slag, the measurements were carried out in silica crucibles, i.e. in silica saturation. The experimental domain covered the oxygen partial pressures from $p_{\text{O}_2} = 10^{-10}$ atm (slag cleaning conditions) to $p_{\text{O}_2} = 10^{-5}$ atm (copper refining step) at 1300 °C.

Experimental

A vertical Nabertherm RHTV 120-150/18 tube furnace was used in the experiments. It applied a Nabertherm model P310 temperature controller and the heating elements made of MoSi_2 . The furnace work tube was of pure impervious alumina supplied by Friatec (Germany). The details of the experimental set-up are available elsewhere (Avarmaa et al., 2015; Avarmaa et al., 2016 and Klemettinen et al., 2017).

The equilibrations were carried out at 1300 °C using flowing CO-CO₂ mixtures as the atmosphere, to generate controlled oxygen partial pressures of the system, according to reaction (1) and its β -function:

The thermodynamic data for calculating the oxygen partial pressures (β) was taken from the SGTE pure substance database (SGTE, 2012) of MTDATA software (Davies et al., 2002). The oxygen partial pressures generated by 1 atm CO-CO₂ mixtures with various CO:CO₂ volumetric ratios at 1300 °C are illustrated in Table 1. The volumetric flow rates of pure CO and CO₂ at room temperature and in 1 atm pressure used in the experiments are also shown in Table 1.

Table 1. The CO-CO₂ mixtures (STP) used for generating controlled oxygen partial pressures at 1300 °C.

$\dot{V}(\text{CO})/\text{mL/min}$	$\dot{V}(\text{CO}_2)/\text{mL/min}$	$\text{Log}_{10}p_{\text{O}_2}/\text{atm}$
1.4	298.6	-5.1
4.3	295.7	-6.0
13.0	287.0	-7.0
50.7	249.3	-8.3
177.0	123.0	-10.0

The raw materials used in this study for synthesizing the copper alloy and the iron silicate slag are shown in Table 2. The gases used were delivered by Aga-Linde (Finland) and their purities were CO (99.97 vol-%) and CO₂ (99.9993 vol-%). AALBORG DFC thermal mass flow controllers were used to regulate the gas flows. A 500 mL/min DFC controller was used for CO₂, while 10 mL/min, 20 mL/min or 200 mL/min units were used for CO, depending on the experimental point and the needed carbon monoxide flow rate.

Table 2. The chemicals used for synthetizing the alloy and slag.

Substance	Supplier	Purity (wt-%)
Cu	Alfa-Aesar, Germany	99.999
Al ₂ O ₃	Sigma-Aldrich, USA	99.99
CaO	Sigma-Aldrich, USA	99.9
Cr ₂ O ₃	Alfa-Aesar, Germany	99.9
Fe ₂ O ₃	Alfa-Aesar, Germany	99.99
SiO ₂	Umicore, Germany	99.99

The experimental slags were always saturated with silica. Their Fe:Al₂O₃ ratio was constant with the target of 5 wt-% Al₂O₃ in the slag in reducing conditions. The targeted lime concentrations in the slag were 5 and 10 wt-% CaO in reducing conditions. The slag and copper mass was 0.05 g each prior to the experiment. Concentration of chromia in the slag was initially 0.5 wt-%. The copper master alloy was prepared by weighting all the reagents in a fused silica tube. The evacuated ampoule was then placed inside a tiltable furnace and heated to 1200 °C. It was kept in the furnace for 120 h, and the furnace was tilted for mixing the alloy after 24 h and 72 h. The ampoule was quenched in ice-water mixture and a homogeneous alloy was recovered.

The fused silica crucibles (ϕ 10×h 6 mm) were delivered by Finnish Special Glass. Temperature of the sample was measured continuously using a calibrated Pt/Pt10Rh thermocouple (Johnson-Matthey, UK), in an alumina sheath next to sample, with an accuracy of ± 3 °C, see Fig. 1. The quenching medium was a water-ice mixture. Time needed to equilibrate the slag-copper alloy was determined by three pre-experiments of 12, 18 and 24 h duration carried out in $p_{O_2} = 10^{-8.3}$ atm, using the slag composition with no lime. 12 h was found to be enough for equilibration, as indicated in Fig. 2, and 18 h was selected for the entire experimental series.

Figure 1. Schematic arrangement of the sample and silica crucible in the equilibration furnace hot zone.

The quality of the slag-metal samples for EPMA measurements was examined using a LEO 1450 scanning electron microscope (SEM; Carl Zeiss, Germany) from polished and carbon coated specimens. The microstructure examinations were conducted with a TESCAN Mira3 SEM (Tescan, Czech Republic).

Figure 2. Development of the distribution coefficients in the time series in $p_{O_2}=10^{-8.3}$ atm; for some elements, the 24 h data were omitted due to concentrations below the detection limit of EPMA.

The phase compositions were measured from polished sections, made using conventional metallographical wet methods, by EPMA (Electron Probe X-ray MicroAnalysis). The EPMA equipment used was a Cameca SX100 (Cameca SA, France) microprobe equipped with five wavelength dispersive spectrometers (WDS). The number of EPMA analysis points in each phase of every sample was eight, and the detection limits for the elements were determined separately in each analytical series, Table 3.

Table 3. Detection limits of the EPMA measurement series with CAMECA SX100.

Detection Limit (Slag, ppmw)						
O	Al	Si	Ca	Fe	Cu	Cr
510	2780	200	90	190	280	50
Detection Limit (Copper, ppmw)						
O	Al	Si	Ca	Fe	Cu	Cr
1170	4590	280	110	180	350	80

The acceleration voltage used was 20 kV. 10-100 μ m spots were used for the glassy slag and 100 μ m for the metallic alloy with 60 nA emission current. The standard reference materials used for EPMA were Fe_2O_3 , Al_2O_3 , diopside, chromite and SiO_2 for iron, oxygen, aluminium, calcium, chromium and silicon in the oxidic phases, respectively. For the copper alloy phase, pure metals were used as standards. The detection limits calculated by Cameca are shown in Table 3 and the obtained concentrations below them are considered to be less reliable. PAP-ZAF matrix correction (Pouchou & Pichoir, 1986) by Cameca was used for the primary WDS data. Totals obtained with EPMA were typically within 98-100 % (see Supplementary Material).

Results

The microstructures of the slag-alloy samples indicated sufficient quenching rates for achieving glassy or microcrystalline slag and homogeneous copper alloy in all conditions with $p_{O_2} < 10^{-6}$ atm. Above that, the increasing copper solubility into the slag caused inhomogeneity in several parts of the slag phase, see Fig. 3,

and copper-rich precipitates segregated from the slag in quenching, due to insufficient cooling rate. The problem was eliminated by using a large electron beam for the slag analyses as described earlier.

The experimental EPMA data were normalised to 100 % in the slag and the molten alloy, and the average values were plotted as a function of the variables used in the study. The distribution coefficients of the trace elements Me between copper alloy and slag $L^{m/s}(\text{Me})$ were calculated from the following equation:

$$L^{m/s}(\text{Me}) \equiv [\text{wt-\% Me}]/(\text{wt-\% Me}) \quad (2)$$

where the brackets [] refer to Me concentration in the copper alloy and parentheses () to that in the slag as wt-%. The standard deviations of each experimental sample are shown as error bars in selected figures. Each experimental point in Figs 4-5 and 7 represents the average of two independent sets of experiments (see Supplementary Material).

Figure 3. Typical BSE microstructures of selected slag-copper samples after equilibration in CO-CO₂ mixtures and quenching in water from 1300 °C; secondary silica (#3) and spinel (#4) particles in slag; the other fields are copper (#1), slag (#2), epoxy (#5) and recrystallised silica crucible interface (#6).

Solubility of chromium in iron silicate slag

The experimental solubility of chromia in the slag (reported here as Cr concentration) is shown in Fig. 4 as a function of the prevailing oxygen partial pressure of the system. The slag composition is shown as parameter and the symbol (see Legend) refers to the targeted CaO concentration in reducing conditions. The initial concentration of chromia in the slag was selected so that the slags were always saturated with an iron (ferrous) chromite phase (a spinel) in all conditions. The oxygen partial pressure uncertainty in this study was estimated to be ± 0.1 log units in maximum, based on the accuracy of the thermal mass flow controllers given by the manufacturer and Eq. (1) relating oxygen partial pressure and the control variables of the study.

The solubility of chromium in the studied iron silicate slags, i.e. at silica saturation, is clearly a function of oxygen partial pressure, as can be seen in Fig. 4. At high oxygen partial pressures, the solubility was about

0.15 wt-% (Cr) and it increased to about 0.3 wt-% (Cr) in reducing conditions of $p_{O_2} = 10^{-10}$ atm at 1300 °C. Lime increased slightly the solubility over the entire oxygen partial pressure range studied. It seems to lower the activity coefficient of CrO_x thus allowing more chromia to dissolve, in spite of its obvious tendency of lowering the $CrO/CrO_{1.5}$ ratio [Wang et al., 2015]. The large uncertainty of the chromium analyses does not justify any conclusions about the possible minimum at high oxygen partial pressures, as shown in Fig. 4. The chromia spinel was analysed to be a ferrous chromite containing some dissolved alumina (as $Fe(Al_x, Fe_{1-x})_2O_4$).

Figure 4. Chemical solubility of chromium in the iron silicate slag at chromite saturation at 1300 °C; the data by Roeder&Reynolds (1991) are from iron-lean, sulphur-free basalts with $Fe:SiO_2 \approx 0.2$ and 6-16 wt-% MgO.

The experimental data of Roeder & Reynolds (1991) in 1 bar, at 1300 °C from silica-rich, iron-lean basalts are shown in Fig. 4 for comparison. The natural sulphur-free basalts contained also 10-15 wt-% alumina, some alkalis and 6-16 wt-% magnesia, and the system studied was not saturated with copper.

The copper-slag distribution coefficient could not be determined from the measured data as the chromium concentrations in copper were much below the detection limit of EPMA. The average value obtained was 9 ppm and that is about one order of magnitude smaller than the estimated detection limit, see Table 3. The trace element analysis of the copper alloy is currently not possible by LA-ICP-MS technique [Klemettinen et al., 2017].

The distribution coefficients of copper and iron

The direct quenching from elevated temperatures produced homogeneous, glassy or microcrystalline slag, except at $p_{O_2} = 10^{-5}$ atm where the equilibrium solubility of copper is large. Edges and corners with fast cooled phase areas were chosen in those cases for the EPMA analyses. In reducing conditions, segregations in the copper alloy were also identified in BSE (backscattered electron) micrographs and a large spot size was used for the analyses, as described earlier. The small chromite spinel volume fraction due to chromia saturation of the slag did not disturb the phase composition analyses.

The solubility of copper in the slag at copper saturation was strongly influenced by the prevailing oxygen pressure. Slag composition also plays a minor role in the dissolution of copper. The results of the current

experimental series in form of the distribution coefficients of copper according to Eq. (2) are shown in Fig. 5, as a function of oxygen pressure.

As can be seen in Fig. 5, the slope of the $\log L^{m/s}(\text{Cu})$ vs. $\log p_{\text{O}_2}$ plot is influenced slightly by the slag composition. The alumina and lime concentrations decrease the slope slightly so that in lime-free slags the slope was 0.31, in 5 wt-% CaO slags it was 0.29 and in 10 wt-% CaO slags it was 0.26. The slope obtained indicates that copper dissolved in the slag as an oxide species and is present in the current slag compositions at silica saturation as monovalent oxide $\text{CuO}_{0.5}$.

Figure 5. The distribution coefficient of copper between copper and slag at 1300 °C as a function of oxygen partial pressure of the system; the legend refers to the target lime concentrations of the slag in reducing conditions.

Figure 6. The metal-slag distribution coefficient for iron as a function of oxygen partial pressure at 1300 °C; the number in legend after lime concentration refers to the experimental series carried out in this study.

The distribution coefficient of iron between copper and the iron silicate slags were always much less than unity. The results obtained in different slags are summarised in Fig. 6 as a $\log L^{m/s}(\text{Fe})$ vs. $\log p_{\text{O}_2}$ plots. The slope of the lines, when omitting the highest oxygen partial pressure data, where iron concentration in copper alloy was below the detection limit of EPMA, is about 0.4 which is much less than expected based on the slag and its analysis in the studied oxygen partial pressure interval. Due to the large oxygen partial pressure range of this study, the properties of the slag and its iron oxides' activity coefficients varied significantly and the behaviour of iron in this respect is not as simple as those elements, which are present as trace elements in both phases.

Properties of the slag in copper and silica saturation

The silica saturation level of iron silicate slag increased with increased alumina and lime contents. This means that its $\text{Fe}:\text{SiO}_2$ ratio decreases with increasing alumina and lime concentrations in the molten slag, see Fig. 7. Here, the combined concentration of alumina and lime was used as variable in order to demonstrate their similar effects on the slag chemistry at low concentrations. The prevailing oxygen partial pressure was used as parameter in the figure.

This feature can be seen as an increase of silica concentration in the liquid slag at silica saturation, shown Fig. 8 when oxygen partial pressure of the system was varied through the operational window of copper scrap smelting. On the other hand, increasing oxygen partial pressure and hence copper solubility, decreased the concentration of silica in the molten slag at high oxygen partial pressures $p_{\text{O}_2} > 10^{-6}$ atm, where copper solubility in the slag exceeded 10 wt-%.

Figure 7. Development of the $\text{Fe}:\text{SiO}_2$ ratio of the slag in constant oxygen partial pressures with various Al_2O_3 and CaO concentrations in copper and silica saturated slags, as a function of alumina + lime concentration at 1300 °C; legend refers to oxygen partial pressures $\log_{10} p_{\text{O}_2}/\text{atm}$ of the measurements.

Figure 8. The effect of oxygen partial pressure on silica concentration of the liquid slag at silica and copper saturations at 1300 °C.

Discussion and conclusions

The measured chromium solubility in the iron silicate slags was in good agreement with the previous but scarce experimental data in the literature (Pan & Eric, 2004; Somerville et al., 2004; Chen et al., 2005; Ilyshechkin et al., 2015) at 1350 °C. The other observations available on simple slags are from higher temperatures (Henao et al., 2001; Pan & Eric, 2004; Zhang et al., 2009) relating to PGM matte smelting conditions, and from reducing atmospheres. The obtained chromium solubilities were also in agreement with the data from high-silica basalts (Roeder & Reynolds, 1991; Sattari et al., 2002) in spite of their lower iron concentrations and higher alumina and magnesia contents, see Fig. 4.

The low solubility of chromium (chromia) in iron silicate slags obtained in this study suggests that secondary copper smelters may prefer to restrict the use of such feed stock grades of WEEE, which are rich in stainless steel. This would generate a solid high-melting chromite precipitate in the smelting vessel from chromium present in excess of 0.1-0.3 wt-% (Cr) in the slag. The solid chromite spinel precipitate is denser than the slag but less dense than the metal (or sulphide matte), and will lead to its accumulation in the smelting vessel (Zhang et al., 2009; Avarmaa & Taskinen, 2018). This will limit the usable volume of the furnace by accretion formation in the hearth and side walls (Albertsson et al., 2013; Lennartsson et al. 2015; Avarmaa & Taskinen, 2018).

It is well known from the literature that additions of basic oxides in the iron silicate slags increase the solubility of silica in the slag (Turkdogan, 1983; Xu et al., 2012; Avarmaa & Taskinen, 2018). A simplified description of this is shown in Fig. 9 where the impact of dissolving copper oxide concentration has been eliminated, and the measured Fe:SiO₂ ratio of the silica saturated slag is presented as a function of the prevailing oxygen partial pressure of the system. The increasing silica solubility as a function of oxygen partial pressure and the Al₂O₃+CaO concentration in copper saturation was clearly visible for each oxygen partial pressure, as the Fe:SiO₂ ratio decreased in high oxygen partial pressures where the solubility and concentration of copper in the slag is the largest.

Figure 9. Development of the Fe:SiO₂ ratio of the molten slag with various Al₂O₃ and CaO concentrations at 1300 °C in copper and silica saturated systems as a function of the prevailing oxygen partial pressure.

The slag composition is not only affected by its CaO and Al₂O₃ concentrations, but also the prevailing oxygen pressure of the system and the simultaneous dissolution of copper oxide in the slag. Fig. 9 shows also the behaviour of the Fe:SiO₂ ratio at saturation with solid SiO₂ in the slag when the oxygen partial pressure was increased from $p_{O_2} = 10^{-10}$ to 10^{-5} atm.

The effects of simultaneous alumina and lime modifications of the silica and copper saturated iron silicate slag obtained in this study are summarised in Fig. 10. As can be seen, the silica saturation surface with 3-5 wt-% Al₂O₃ and up to 8-9 wt-% CaO in the slag at 1300 °C increased the solubility of silica from around 40 wt-% to around 50 wt-%.

Figure 10. The experimental silica concentration on the liquidus surface at 1300 °C as a function of lime and alumina concentrations in silica and copper saturation obtained in this study.

By using computational thermodynamics, the complex phase equilibria in the system $\text{CaO-Fe-O-Al}_2\text{O}_3\text{-SiO}_2$ can be simplified to a quasiternary diagram with suitable constraints as used in the experimental conditions of this study. Under constant oxygen partial pressure of 0.1 Pa (10^{-6} atm) and constant concentration of lime of 0 or 5 wt-% CaO the 5-component system is degraded into ternary. Its terminal phases of corners of the Gibbs triangle are thus Al_2O_3 or 95 wt-% Al_2O_3 +5 wt-% CaO, SiO_2 or 95 wt-% SiO_2 + 5 wt-% CaO and an iron oxide FeO_x or 95 wt-% FeO_x +5 wt-% CaO. A few isothermal sections of the system $\text{Al}_2\text{O}_3\text{-CaO-Cu-Fe-O-SiO}_2$ were calculated for monitoring the behaviour of the slag in copper saturation, using the Mtox database of MTDATA solver (Gisby et al., 2017). Figure 11 indicates that growing concentration of alumina in the slag continuously increases the silica concentration at the $\text{SiO}_2(\text{s})$ saturation boundary. In addition, an increase of more than 5 wt-% SiO_2 at silica saturation by 5 wt-% CaO can be found. Its shape in the CaO-bearing slags (black phase boundaries) and thus the distance of the silica saturation boundary from the lime-free case remain essentially constant when alumina up to about 20 wt-% is added into the slag. No major impact of lime is seen in the magnetite (spinel) saturation boundary, which is seldom of any interest in the copper smelting conditions, but highly essential to the matte converting slag and fluxing, when e-scrap is added in the converting stage.

Figure 11. An isothermal section of the system $\text{Cu-Al}_2\text{O}_3\text{-FeO-O}_2\text{-SiO}_2$ in a fixed $p_{\text{O}_2} = 10^{-6}$ atm at copper saturation without (—) and with 5 wt-% (CaO) (—); note the rapid increase of silica concentration at SiO_2 saturation by alumina and the formation of feldspar primary phase domain at high alumina concentrations in lime-containing slags (COR=corundum, FEL=feldspar, MEL=melilite, MUL=mullite, LIQ=Cu(I), OX_LIQ= molten slag, SP=spinel and TRI=tridymite).

In general, phase relations of the alumina modified iron silicate slags formed in secondary copper smelting are not very well known in the literature, in particular in high alumina concentrations (Zhao et al., 1999; Klemettinen et al., 2017b). Therefore, new experimental observations are needed on the saturation boundaries in the spinel, silica and mullite primary phase fields over the oxygen potential range used in the copper smelting, refining and slag cleaning, on the Fe-O-SiO_2 slags with >10 wt-% Al_2O_3 , in order to allow

validation of the available slag databases such as Mtox (Gisby et al., 2017). This is important in order to validate the correct oxygen partial pressure response of the copper bearing slags reproduced by computational thermodynamics.

The properties and thermodynamic descriptions of copper-rich slags in the slag databases, such as Mtox (Gisby et al., 2017), must be upgraded against the new information from copper saturated systems (Hamuyuni et al., 2016; Klemettinen et al., 2017 and 2017b; Avarmaa & Taskinen, 2018).

Summary

The poorly known chemical solubility of chromium (chromia) in the iron-silicate slags with alumina and lime, i.e. at a chromium spinel saturation, was determined. In order to avoid contamination and effects of the other elements in the slag, the measurements were carried out at silica saturation. The solubility of chromium in $\text{Al}_2\text{O}_3\text{-CaO-Fe-O-SiO}_2$ slags was a function of oxygen partial pressure. In high oxygen partial pressures the solubility was ≈ 0.15 wt-% (Cr) and in reducing conditions of $p_{\text{O}_2} = 10^{-10}$ atm it increased to ≈ 0.3 wt-% (Cr). Alumina and lime additions to the slag slightly increased the chromia solubility over the entire oxygen partial pressure range.

Addition of lime to Fe-O-SiO₂ slags with alumina, in reducing conditions below $p_{\text{O}_2} \approx 10^{-7}$ atm and at silica saturation, lowers slightly the metal-to-slag distributions of copper. This is in disagreement with the general concept and the impact of adding basic oxides to acidic silicate slags. The observations represent a constrained case where the slag is in equilibrium in a silica crucible, i.e. at saturation by solid SiO₂. Alumina and lime additions, therefore, did not shift the slag composition towards more basic composition domains, but in fact turned it more acidic when its silica concentration increased.

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