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Published in: Proceedings EMC 2019

Published: 01/01/2019

Document Version Peer-reviewed accepted author manuscript, also known as Final accepted manuscript or Post-print

Please cite the original version:

Hellsten, N., Taskinen, P., Jokilaakso, A., & Latostenmaa, P. (2019). Novel method to study volatile trace elements in electric furnace nickel slag cleaning. In *Proceedings EMC 2019* (pp. 557-570). GDMB Verlag.

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Novel method to study volatile trace elements in electric furnace nickel slag cleaning

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Keywords: Distribution, Iron silicate slag, Semi-closed ampoule, Equilibration experiments

Abstract

Experimental studies of the equilibrium behavior of easily vaporizing elements, such as As, Pb and Sb, at atmospheric pressures and in pyrometallurgical process temperatures is challenging. Previously, systems containing volatile elements have been studied using conventional methods with closed vessels or by adding sufficient amounts of the volatile materials to the starting mixtures to retain them in the system after experiment. However, some of these previously used techniques often lack sufficient accuracy and involve concentration gradients typical to non-equilibrium systems. In addition, external control of the gas atmosphere is difficult, which limits the use of these techniques. Thus, innovative experimental techniques to study the equilibria in systems involving volatile elements are needed.

Introduction

Raw materials of nonferrous metals, such as Cu, Ni and Zn, often contain various metals on trace levels, depending on and typical to the geological origin of the ore [1]. Generally, these traces are distributed into the material streams depending on the processing conditions. Elements, which have a tendency to volatilise, distribute into the gas phase. The tendency of an element to volatilise is governed by its vapour pressure and that of its stable compounds. When the equilibrium vapour pressure of an element in a condensed phase is greater than the equilibrium vapour pressure of a gas phase in equilibrium with the condensed phase (solid or liquid), it vaporises preferentially into the gas phase until saturation. Low melting elements, such as As, Hg and Pb, can have a high vapour pressure but the melting point is seldom the only factor determining the tendency of an element to volatilise. Traditionally, thermodynamic behaviour of volatile elements have been studied using conventional methods, such as equilibration and quenching in closed ampoules or by adding extra amounts of the volatile materials when using open containers [2].

Experimental determination of the distribution of important trace elements provides key information in managing process losses and consequently improving resource efficiency. In pyrometallurgical processing of major metals, such as nickel or zinc, trace concentrations of valuable and harmful metals are typically lost in the slag during oxidation of iron from the sulphides. In nickel processing, significant amounts of Ni, Cu and Co are lost in the smelting slag. For this reason, the slag is cleaned in reductive conditions in an electric slag-cleaning furnace by coke [3].

In this work, a semi-closed ampoule combined with an equilibration and quenching technique was tested and utilized to study the distributions of Ag, Au, Sb and Pb between a K₂O and MgO containing iron-silicate slags and Cu-Fe-Ni alloys at 1400 °C, in metallic Fe (s) saturation. These conditions resemble those of a nickel slag cleaning electric furnace and its end point [4]. Studies by Azakami et al. [5] suggest that Ag, Sb and Pb may be volatile in the experimental conditions of the current work. Previously, experimental data for the distribution of these elements in nickel slag cleaning is lacking. The advantage of the semi-close ampoule technique is that the gas atmosphere can be influenced externally by e.g. CO-CO₂ mixtures or allow the equilibration to progress internally in an inert atmosphere. This is due to the opening in the ampoule which allows the gas atmosphere from work tube to enter the ampoule. In contrast, there can be transfer of the volatile components from the ampoule decreases the exchange of the saturated gas phase with non-saturated flowing gas, effectively slowing down the depletion of volatiles and flattening their respective concentration gradients in the slag and metal alloy [6].

Experimental

Equilibration experiments were carried out to calculate distribution coefficients for the trace metals Ag, Au, Pb and Sb. The experiments included equilibration of a pre-mixed K₂O and MgO containing



iron-silicate slag with a pre-synthesized Cu-Fe-Ni alloy (referred to as 'EF matte' in Figs. 2-5) in pure Fe foil crucible so that metallic Fe is present in equilibrium (Fe saturation), in neutral and reactive gas atmospheres. All of the experiments in this study were conducted utilising the semi-closed ampoule method in conjunction with equilibration, quenching and EPMA and LA-ICP MS analysis of the chemical compositions of the phases as described by Hellstén et al. [6] The ampoules, foil envelopes, metallic alloys and the slag were prepared from high-purity chemicals (see Table I).

Chemical	Purity (wt-%)	Supplier
Cu	99.999	Alfa-Aesar
Ni	99.996	Alfa-Aesar
Fe	99.99	Alfa-Aesar
Fe foil, 0.25 mm (for crucibles)	99.99	Alfa-Aesar
SiO ₂	99.99	Umicore
MgO	>99	Sigma-Aldrich
Fused quartz glass (for ampoules)	99.99	Finnish Special Glass
Fe ₂ O ₃	99.99	Alfa-Aesar
K ₂ CO ₃ (as a source of K ₂ O)	99.5 - 100.5	Sigma-Aldrich
Ag	99.99	Alfa-Aesar
Au	99.96	Alfa-Aesar
Pb	99.999	Alfa-Aesar
Sb	99.999	Cerac

Table I. Purities and suppliers of the chemicals used.

Four Cu-Fe-Ni alloys of different compositions were prepared by melting respective powder mixtures in a protective Ar-H₂ atmosphere in a horizontal furnace at 1400 °C in Al₂O₃ crucibles overnight and then cooling to room temperature at a rate of 4 °C/min. Table I shows the targeted and EDS-analysed compositions of the alloys after synthesis. Starting mixtures for the slags were prepared by weighing and mixing powders of Fe₂O₃, SiO₂, K₂O and MgO in appropriate ratios using an agate mortar and pestle. After mixing, the homogenized mixtures were pelletised using a steel-die and a compressing machine. The targeted concentrations in the slag were 2 wt% of K₂O, 32 wt% of SiO₂ and 0 and 5 wt % of MgO, respectively.

Concentrations equal to 2 wt% of the total weight of the slag and metal of Ag, Au, Pb and Sb were added into the oxide mixture. The total sample weight was 0.4 g, consisting of 0.2 g of slag and the

Hellstén

metal alloy, respectively. To protect the iron foil crucible, pure metallic iron flakes were also added to the slag sample.

Table 2:	Measured compositoins	of the	synthesized	and	equilibrated	Cu-Fe-Ni	alloys.	Used
CO/CO ₂	$_2$ ratio was 50/50.							

Alloy target Fe/Ni	Gas	Fe/Ni original	Fe/Ni equili- brated	Fe (wt-%)		Ni (wt-%)			Cu (wt-%)			
				Initial	Equilib- rated	StDev	Initial	Equilib- rated	StDev	Initial	Equilib- rated	StDev
I (40/60)	N_2	43/57	65/35	30.9	55.4	±0.39	40.6	29.5	±0.30	28.6	15.1	±0.55
	CO/CO ₂		70/30		57.0	±1.48		24.2	±1.82		16.6	±0.34
II (50/50)	N_2	51/49	71/29	37.5	58.2	±0.39	35.3	23.4	±0.22	27.2	18.4	±0.48
	CO/CO ₂		80/20		72.4	±2.76		17.69	±1.82		8.10	±1.28
III (60/40)	N_2	60/40	74/26	45.9	59.1	±1.26	30.8	20.8	±1.44	23.2	20.1	±2.13
	CO/CO ₂		61/39		49.9	±0.58		31.5	±0.09		17.3	±0.42
IV (70/30)	N_2	70/30	77/23	46.7	58.7	±2.01	20.0	17.8	±2.66	33.3	23.4	±1.09
	CO/CO ₂		74/26		58.6	±3.76		21.2	±2.06		18.3	±5.61

Makeshift Fe crucibles (length 30 mm, outer diameter of 5.8 mm or less) were prepared from 0.25 thick pure iron foil by rolling and forming. Initially, 0.1 mm thick foil was tested, but it was observed that the slag and metallic alloy react strongly with the foil and penetrate it coming into contact with the surrounding SiO_2 ampoule.

To prevent volatilization of Ag, Pb and Sb, the Fe crucibles containing the samples were inserted into semi-closed quartz ampoules. These ampoules were manufactured from pure quartz tube (8 mm OD, 6 mm ID; Heraeus: HSQ 300) using a H_2 -O₂ torch. First, the bottom of the tube was formed by melting, then a 1.9 mm diameter hole was drilled into the ampoule 40 mm above the bottom using a dentist's drill (NSK Presto Aqua II, NSK, Japan) and a natural diamond ball point drill head (Intensiv, Switzerland). Then, the Fe crucible containing the sample was inserted into the ampoule and the top was closed by melting to form a hook for suspension leaving the drilled hole as the only opening to the ampoule. The small hole in the ampoule enables control of the atmosphere inside the ampoule by use of an external gas.



The gas phase inside the ampoule containing volatile components saturates with them and transport of the volatile components from the condensed phases ceases. Meanwhile the exchange of saturated gas with unsaturated gas outside the ampoule is much slower than volatilisation, which takes place on the surface of the condensed phases.

In this work, the equilibration experiments were conducted in a vertical tube furnace at 1400 °C. The furnace consisted of an Al₂O₃ work tube and six SiC resistance heating elements. Details of the method are describe elsewhere [6]. The gas atmospheres were obtained using N₂ and CO/CO₂ mixtures. In the case of N₂, the pO₂ inside the ampoule is determined by the reactions in the condensed phases, while in using CO/CO₂ mixtures the desired pO₂ in determined by their molar or volumetric ratio, as indicated by the reaction:

$$CO + \frac{1}{2}O_2 = CO_2 \tag{1}$$

The semi-closed ampoules containing the samples were inserted into the furnace work tube from below, suspended by a 0.5 mm thick Pt-wire, left in the cold end and the furnace was sealed using a rubber cork. The atmosphere inside the work tube was created by flowing the desired gas(es) for 30 minutes. Subsequently, the ampoule was raised to the hot zone of the furnace, equilibrated for four hours and quenched into an ice-water mixture with a temperature of 0 °C as measured by a thermometer prior to quenching. The quenched samples were dried, mounted into epoxy, polished and carbon coated for subsequent analysis. Chemical compositions of the phases in the quenched samples were measured by EPMA. Due to the small concentrations of the trace elements Ag, Au, Pb and Sb in the slag, the slag phase was also analyzed using LA-ICP MS due to its lower detection limits. The EPMA was operated using 20 kV accelerating voltage, 40 nA beam current and 50 - 100 μ m beam diameters. A PAP matrix correction program supplied by the manufacturer was used to correct the analytical results. The external standard materials and analysed lines used in the EPMA analysis were Fe K_a and O K_a (hematite), Si K_a (quartz), K K_a (sanidine), Cu K_a (Cu), Ni K_a (Ni), Ag L_β (Ag), Sb L_a (Sb-telluride), Au L_a (Au) and Pb L_a (galena).

LA-ICP-MS technique was used for analyzing Ag, Au, Pb and Sb in the slag, since their concentrations were mainly below the detection limits of EPMA. A Photon Machines Analyte Excite 193 nm 4 ns ArF laser ablation device (Teledyne CETAC Technologies, USA) coupled with a Nu AttoM single collector ICP-MS (Nu Instruments Ltd, UK), housed at Geological Survey of Finland, was utilized. The laser energy used was 30 % of 5.0 mJ, resulting in a fluence of 2.5 J/cm² on the sample surface. A spot size of 50 μ m and operating frequency of 10 Hz were selected. Details of the analytical technique used have been presented earlier [7].

Results and discussion

Equilibration experiments conducted in this work included two individual sets and a time series. In the two sets, a K₂O containing iron-silicate slag and a K₂O and MgO containing iron-silicate slag was



equilibrated with four individual Cu-Fe-Ni ternary alloys in metallic Fe saturation at 1400 °C under neutral gas or controlled pO₂. Each experiment was repeated to generate a campaign in total 16 experiments plus the time series.

The slag-molten alloy-solid iron system is univariant, according to the Gibbs phase rule, in isothermal and isobaric conditions, so that only the composition of the slag (e.g., the Fe:SiO₂ ratio) or that of the molten alloy (e.g., the Fe:Ni ratio) can be varied in the experiments.

Figure 1 shows micrographs of the quenched samples of (a) 0 wt% MgO in slag equilibrated under N_2 atmosphere and (b) targeted 5 wt% MgO in slag equilibrated under a CO/CO₂ atmosphere.



Figure 1. Micrographs of quenched samples with (a) 0 wt% MgO in slag equilibrated under flowing N_2 and (b) 5 wt% MgO in slag equilibrated under flowing CO/CO₂ mixture.

In Figure 1, the dark areas are slag and the lighter areas Cu-Fe-Ni alloy and metallic Fe. Any observable differences between these two samples quenched from different conditions are negligible to the naked eye. Elemental compositions of the Cu-Fe-Ni alloy and slag phases in all the quenched samples were analysed by EPMA. In addition, due to the extremely low concentrations of the Ag, Au, Sb and Pb in the slag phase, these were also analysed by LA-ICP MS. Each one of the analysed samples contained Ag, Sb and Pb as trace elements. These results suggest that the semi-closed ampoule method decreases the depletion of these volatile elements enough to enable their analysis from the samples. Table 2 shows the measured compositions of the Cu-Fe-Ni alloy phases after equilibration. Departing from similar initial compositions, when equilibrated using the CO/CO₂ gas mixture, the Cu-Fe-Ni alloys with a lower Fe content end up with higher Fe concentrations than what results in the N₂ atmosphere. In contrast, for the alloys where the initial Fe/Ni ratios are 60/40 and 70/30, the experiments conducted using neutral N₂ gas result with a higher Fe concentration in the equilibrated alloys. Corresponding EPMA measured average elemental compositions of Si, Fe, K and Mg from the slag phase from the samples equilibrated under N₂ and CO/CO₂ gases were calculated into SiO₂, 'FeO' and K₂O and MgO, respectively (Table 3). Totals in the EPMA measurements were 100%±2%. In addition, the slag in samples equilibrated under CO/CO₂ gas contained 1.10 – 2.08 wt% MgO.

Alloy	Gas	SiO ₂ (wt-%)	StDev	'FeO'	StDev	K ₂ O (wt-%)	StDev
I (40/60)	N_2	30.86	3.62	67.80	3,50	1.34	0.47
	CO/CO ₂	39.64	1.20	59.67	1.01	0.37	0.01
II (50/50)	N_2	36.64	4.10	61.85	5.17	1.51	0.61
	CO/CO ₂	41.76	1.59	56.94	1.78	0.56	0.08
III (60/40)	N_2	34.18	1.00	64.09	1.21	1.74	0.22
	CO/CO ₂	28.75	5.08	68.45	4.82	0.64	0.10
IV (70/30)	N_2	33.74	1.05	64.89	1.12	1.37	0.40
	CO/CO ₂	31.36	4.44	67.15	4.27	0.26	0.02

Table 3:EPMA analysed slag compositions.

For the slag equilibrated under flowing CO and CO₂, the analysed MgO and K₂O concentrations were lower than the targeted values of 2% and 5%, respectively. In addition, the analysed concentrations of SiO₂ for the samples vary more than for the samples equilibrated under flowing N₂. When the SiO₂ concentration of the slag is high enough, the system is saturated with it. Nevertheless, as metallic Fe was always present, the system was always in metallic Fe saturation. In the experiments with fixed pO₂, the reactions between the Fe foil, slag and the alloy appeared more aggressive. This can contribute to the chance of SiO₂ from the ampoule being dissolved into slag.

The differences between the two experimental sets demonstrates the effect of the gas selection and suggests that the atmosphere inside the ampoule can be influenced externally.

In these slag-nickel alloy experiments, the liquid alloy phase in the (s)-(l) two-phase domain where the copper concentration in the solid alloy is nearly constant at different Fe:Ni ratios. The activities of the components of the metallic alloy for copper vary from 0.55 to 0.75 referred to pure liquid copper, as shown in Figure 6, whereas the ranges of variation in iron and nickel activities are much larger.





Figure 6. Computational isothermal section of the Cu-Fe-Ni system at 1400 °C with (s)-(l) tie lines and the isoactivity contours superimposed (MTDATA with Mtox database, Gisby et al. 2017 [10]); (isoactivity contours: --- Cu, …Ni and … Fe)

From the analysed concentrations of Ag, Au, Pb and Sb in the slag and alloys phases, the distribution coefficients for these elements between the Cu-Fe-Ni alloy and slag were calculated for the samples equilibrated under flowing N₂. Distribution coefficients are a convenient way to assess the behaviour of trace elements. Their relation to thermodynamic properties was explained by Yazawa [8]. For a metal Me, they can be calculated using the formula:

$$L^{\frac{Al}{s}}(Me) = \frac{[wt\% Me]}{(wt\% Me)},\tag{2}$$

Where [] refers to the concentration of the element in the molten Cu-Fe-Ni alloy phase while () refer to its concentration in the slag, respectively. Figures 2-5 show the calculated distribution coefficients for the samples equilibrated under flowing N₂.



Figure 2. Distribution coefficient of silver between the molten Fe(s) saturated nickel alloy and slag at 1400 °C as a function of iron concentration of the molten alloy (EPMA and LA-ICP-MS data).

()



Figure 3. Distribution coefficient of gold between the molten nickel alloy and slag at 1400 °C as a function of iron concentration of the molten alloy in iron saturation.



Figure 4. Distribution coefficient of lead between the molten nickel alloy and slag at 1400 $^{\circ}$ C as a function of iron concentration of the molten alloy.



Figure 5. Distribution coefficient of antimony between the molten nickel alloy and slag at 1400 °C as a function of iron concentration of the molten alloy.

Based on the analysed metal concentrations and distribution coefficients calculated from them, in these conditions the metals distribute strongly to the liquid alloy phase. Furthermore, the effect of the Fe concentration of the alloy phase is the strongest for Ag and Pb, where the increase in the distribution coefficient is from 1 to 3 orders of magnitude when the Fe content of the alloy increases from 55% to 59%.

The scatter in the in the distribution coefficients calculated for the experiments conducted under similar conditions are attributed to the challenges in quenching when the molten samples are enclosed inside an Fe foil and a SiO_2 ampoule. In addition, the folds of the foil were often penetrated by the slag making it more difficult to find suitable areas of slag for analysis.

Nevertheless, the differing results from CO/CO_2 experiments testify that the gas phase enters the ampoule and prevails there as well. In light of the results from this work, the purging time of 30 minutes appears sufficient to remove air from inside the semi-closed ampoule. However, as the gas phase is unanalysed in these experiments, any deviations between the set pO_2 and prevailing pO_2 , when using CO and CO₂ to control pO_2 , can be only speculated. When inert N₂ was used, it can be assumed that all the oxygen has flushed out of the ampoule and the pO_2 is determined by the system and the only oxygen available comes from the slag. Use of Fe₂O₃ as a starting material may have contributed to the spreading of the slag inside the foil crucible. In addition, the slag wets the pure iron

foil well and may add to its tendency to penetrate into the folds of the foil. This is indicated by comparing the results of this work to those obtained using an iron crucible, drilled from pure Fe rod in the semi-closed ampoule method as described by Hellstén et al. [9].

Conclusions

The distributions of Ag, Au, Pb and Sb between FeO_x -K₂O-MgO-SiO₂ slag and a liquid Cu-Fe-Ni metallic alloy were studied using a new experimental method in nickel slag cleaning conditions at solid iron saturation. Due to the tendency of Ag, Pb and Sb to volatilize, the experimental technique applied included a semi-closed ampoule, which enables the study of the slag-metal system and external control by the prevailing gas atmosphere. The experiments were conducted at 1400 °C in metallic Fe(s) saturation using N₂ and CO/CO₂ atmospheres.

Application of the semi-close ampoule method to study the distribution of trace elements in nickel slag cleaning conditions was successful, as all the elements could be detected from the metallic alloy and slag phases post equilibration and quenching. Furthermore, the differing results between a neutral and reactive gas phases show that external control of the gas atmosphere is possible with this method.

The results show that the studied trace elements distribute preferentially to the metallic nickel alloy in these EF conditions close to the end point of slag cleaning. This means that they will be recovered from the smelting slag to the EF matte and transferred through that route to the nickel refinery.

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