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Urban mining of precious metals via oxidizing copper smelting

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Abstract
Recycling of precious metals from end-of-life electronics is a key factor for sustainable and efficient raw material usage. Simultaneously with the depletion of natural ore resources, the urban mines are storing increasing amounts of valuable and, more importantly, rare metals. To fulfill the targets of sustainability and move towards circular economy, the liberation of these valuables from wastes back to production and use needs to be improved. This study investigates the recoveries and behavior of gold, silver, palladium and platinum in copper smelting conditions at 1300 °C and pO2=10⁻⁵–10⁻⁷ atm. The investigated system includes a copper alloy with three different type of slags in silica saturation: pure iron silicate, iron silicate with 10 wt% alumina and iron silicate with 10 wt% alumina and 5 wt% lime, providing information on the influence of alumina and lime on precious metal recovery possibilities. A highly advanced equilibration-quenching technique, followed by EPMA and sensitive LA-ICP-MS analyses, has been adopted to execute the experiments. Results show that gold, platinum and palladium are recovered very efficiently in copper, as their distribution coefficients between copper and slag, L_Cu/s, were greater than 10⁴ under every experimental condition studied and with all slag compositions. Silver distributed 30–60 times more in copper phase than was lost to slag. The addition of alumina into the slag somewhat decreased the distribution coefficient of silver, whereas gold and palladium distribution coefficients were increased. Lime addition improved the recovery of every precious metal (Pt unclear) into the copper phase. The concentrations of platinum in the slags were mainly below the detection limit of the used LA-ICP-MS, providing a minimum distribution coefficient of 10⁶.

Keywords: sustainability, recycling, trace elements, black copper, LA-ICP-MS

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1. Introduction

Urban mining has arisen as a fundamental concept amongst environmentalists, industrialists, politicians and businesses (Brunner, 2011; Tesfaye et al., 2017). The term denotes the systematic reuse and recycling of anthropogenic resources from urban areas. These include all kind of anthropogenic stocks such as landfills, buildings, infrastructure, industries, products and emissions. Originally, as well as in this study, urban mining concentrates on WEEE (Waste Electrical and Electronic Equipment) utilization as modern urban ore. This is due to the high concentrations of valuable elements and short lifetimes, after which they are available for recycling. Fig. 1 represents simplified process sheets for urban mining of end-of-life copper in WEEE and for the primary copper production route from virgin ore.

![Figure 1. Analogy between urban mining for secondary copper production and ore-based primary copper production.](image)

As can be seen, both routes include similar steps: starting from the collection/mining of appropriate primary or secondary resources, followed by the beneficiation to a suitable feed mix for pyrometallurgical processing. The mineral processing of copper ore typically includes comminution and froth flotation steps, whereas the mechanical processing in secondary route includes different sorting, dismantling and mechanical separation processes. The smelting/refining processes vary, but typically primary pyrometallurgical processing starts with matte smelting followed by converting and hydrometallurgical refining. The secondary copper from WEEE can be fed into different process types or steps, depending on its composition and purity; some is fed into primary smelting/converting, some to ‘secondary’ matte smelting (Hagelüken, 2006) and some impure,
oxidized or complex copper fractions to black copper smelting (Ghodrat et al., 2017). The black copper smelting usually starts with a reducing smelting step, where oxidized copper and many other metals are reduced to ‘black copper’ metal. This metal alloy is further processed in oxidizing conditions to produce blister copper. However, if relatively pure, non-oxidized copper scrap is treated, the process may start with oxidizing smelting followed by the reduction stage (Knudsen process (European Dioxin Inventory, 2009)). After hydrometallurgical electrolytic refining, the final metal is produced.

Although the flowcharts (Fig. 1.) are drawn as linear, many internal and external flows and recycling routes exist in reality. Copper-containing scrap is produced in every step of its lifetime, from mining to production, and discarding of the products. Depending on what, where and when the scrap is produced, it can be treated with different procedures. Home and new scraps are produced during the production and manufacturing, and, depending on the manufacturing level, are recycled internally, i.e. directly to different steps of primary or secondary production including the smelter, converter and anode furnace. Old scrap category includes all end-of-life products, such as WEEE, which are more difficult to recycle efficiently compared to new scrap. As shown, they require multiple process steps before becoming feasible for smelting. Some end-of-life copper is processed in the primary route processes, although these materials have completely different mineralogy and composition compared to primary ores. This might cause problems and issues that are not prevalent and considered in traditional primary smelting. Thus, operations with high flexibility for feed morphology and composition, as well as advanced environmental control (such as TSL (Wood et al., 2011)), should be favored for WEEE based copper processing.

Metals in principle could be recycled infinitely, however, multiple factors make complete recycling impossible in practice. These type of limiting factors include product design, recycling technologies, social behavior, legislations and elemental thermodynamics. This study presents the recycling possibilities of gold, silver, platinum and palladium from the thermodynamic and industrial copper smelting perspectives.

Literature on precious metals in metallurgical slags

In general, the research concentrating on minor element behavior in WEEE smelting is a relatively new field of science, and very limited amount of literature and research is available. Some literature can be found on Ag, Au, Pd and Pt solubilities in metallurgical slags and their behavior in copper-slag systems, and these are reviewed next.

The silver equilibria in copper-slag systems have been examined in a few experimental studies (Hidayat et al., 2016; Mackey et al., 1975; Richardson and Billington, 1956; Takeda and Roghani, 1993; Takeda, 1983). Takeda and Roghani (1993) performed silver equilibria experiments between copper and CaO-SiO2-FeOx slag (%CaO/SiO2=0/1, ½, 1/1 and 1/0) in magnesia crucibles with pO2=10^{-8}–10^{-3.5} atm at 1300 °C. Distribution results varied around 10−10³ depending on the slag composition and oxygen partial pressure. In another study by Takeda (1983), the distribution behavior of silver between copper and calcium ferrite slag with pO2=10^{-11}–10^{-5} at 1250 °C was examined, with results consistent to those of Takeda and Roghani (1993). In two separate studies, Kashima et al. (1978) (matte-copper-slag equilibria) and Richardson and Billington (1956) (Ag/Pd alloy-slag equilibria) did not observe a dependency between silver solubility and oxygen partial pressure. Hidayat et al. (2016) investigated silver distribution in copper-silica-saturated iron silicate slag system in pO2=10^{-7}–10^{-9} atm at 1250 °C with an advanced experimental technique.

The solubility of gold in iron-silicate slags has been suggested to be ‘effectively zero’ in multiple previous studies (Altman, 1972; Geveci and Rosenqvist, 1973; Taylor and Jeffes, 1975; Toguri and Santander, 1972) and that approach has been used to detect mechanical copper or copper matte entrainment in the slag.
Interestingly, however, these studies reported gold concentrations of 40–80 ppmw (Taylor and Jeffes, 1975), 80 ppmw (Altman, 1972) and 0–800 ppmw (Toguri and Santander, 1972) (50–400 ppmw for most of the data points) in iron silicate slags. Additionally, Han et al. (2015) investigated gold dissolution behavior in the CaO-SiO₂-Al₂O₃-MgO sat. slag system at 1350–1500 °C with oxygen partial pressure of 10⁻⁸–10⁻⁹.5 atm. In Swinbourne’s study (2005), gold solubilities in iron-silicate (IS), calcium-ferrite (CF) and lead oxide (PbO) slags were determined. The IS and CF studies were performed at 1300 °C, in an oxygen potential range of 10⁻⁷–10⁻¹⁰ atm.

Mackey et al. (1975) presented operational distribution coefficients in the Noranda continuous Smelting process (T=1250 °C, 30% O₂ enriched air and Fe/SiO₂ ratio=1.4–1.9) of 250 for gold and 30 for silver. Nagamori and Mackey (1978) assessed distribution coefficients of 2.5×10⁵ for gold and 10⁴ for silver at 1250 °C, using an analytical thermodynamic method. Nakajima et al. (2011; 2009) calculated, using thermodynamic analysis, the minor element distributions, including Ag, Au, Pd and Pt, in copper converter with pO₂=10⁻⁶ atm at 1500 K (1226.85 °C). Han et al. (2015), Swinbourne et al. (2005) and Yang et al. (2017) have examined gold solubilities, whereas Park and Min (2000; 1999), Swinbourne (2005), Swinbourne and You (1999) and Ziolek et al. (1991) silver solubilities (mainly) in basic slags, and suggested that they would dissolve as complex anions in basic slags. Chen et al. (2016) investigated gold and silver distributions between copper and slag in copper - matte - silica-saturated iron silicate slag system, providing distribution values of 10⁵.5–10⁶ and 10²–10².7, respectively at 55–80 %Cu in matte.

Shuva et al. (2017) investigated palladium distributions between copper and a FeOₓ-SiO₂-CaO-MgO sat. slag at 1300 °C and pO₂=10⁻⁷–10⁻¹⁰ atm. Yamaguchi (2011) studied platinum and palladium distributions between Fe-Ni-(94 wt%)Cu alloy and CaO-FeOₓ slag in pO₂ range 10⁻⁸–10⁻⁵ atm at 1300 °C. Nishijima and Yamaguchi (2014) studied Pt and Pd distributions between copper and Al₂O₃-CaO-SiO₂-Cu₂O-MgO sat. slag in pO₂=10⁻¹⁰–10⁻⁵ atm at 1450 °C. All the aforementioned studies provided L⁰Cu/[Pt & Pd] values around 10³. Yamaguchi (2010) investigated the dissolution of platinum in FeOₓ-SiO₂ slag (pure Pt/Pt-Cu alloy – iron silicate slag) in MgO crucible at 1300 °C and pO₂ 10⁻⁶–10⁻⁸ atm, wherein the solubility varied between 3 and 30 ppm. Nakamura et al. (1998), Nakamura and Sano (1997), Morita et al. (2014) and Wiraseranee et al. (2014) have studied Pt solubilities in different types of liquid basic oxide systems. Sukhomlinov & Taskinen (2017) have investigated the distribution behavior of Ag, Au, Pd and Pt between copper and SiO₂-FeOₓ slag at 1300° C and pO₂ range 10⁻⁴–10⁻⁸ atm.

2. Experimental method

This study employs an equilibration-quenching-EPMA/LA-ICP-MS method to investigate the distribution behavior of precious metals between copper and slags. This technique has been used previously to investigate the behavior of minor elements at spinel saturation (Avarmaa et al., 2018a; Klemettinen et al., 2017) and in matte-slag system (Avarmaa et al., 2015). This study expands the investigation to silica saturation, and evaluates the influence of alumina and lime additions to iron silicate slag on precious metal recoveries.

The experiments were carried out in a vertical tube furnace manufactured by Nabertherm (RHTV 120–150/18) with MoSi₂ heating elements and a Nabertherm P310 temperature controller. The furnace temperature was measured with a calibrated S-type thermocouple (Johnson-Matthey, UK) and the cold junction compensation was performed by a PT100 resistance thermometer (SKS-Group, Helsinki, Finland; tolerance class B 1/10). They were connected to Keithley 2000 and 2010 DMM multimeters (Keithley Instruments, Inc., Cleveland, OH) and the data was logged with a Labview software. The gas atmosphere was created using CO 3.7 and CO₂ 5.3 gases (AGA, Finland), which were fed into the furnace through thermal mass
flow controllers (Aalborg DFC26, USA; accuracy ± 1% of full scale). The total flow rate was 300 mL/min (STP), and the CO₂/CO ratio was set to produce oxygen partial pressures of 10⁻⁷, 10⁻⁶ or 10⁻⁵ atm at 1300 °C (Avarmaa et al., 2018a).

The copper master alloy was prepared by melting and annealing copper cathode (Boliden Harjavalta, 99.999%) with approximately 1 wt % of each precious metal, silver, gold, platinum and palladium, in an alumina crucible at 1400 °C and under 99% Ar – 1% H₂ gas atmosphere for 12 h. All the precious metals were from Alfa Aesar with purity of 99.9% or better. The slags were prepared from SiO₂ (99.99%, Umicore), Fe₂O₃ (99.99%, Alfa Aesar), Al₂O₃ (99.99%, Sigma-Aldrich) and CaO (99.9%, Sigma-Aldrich). The pure iron silicate slag had an initial composition of 30SiO₂-70Fe₂O₃ for one series and 25SiO₂-75Fe₂O₃ for duplicate series. The slags containing alumina and lime had different initial starting compositions for each pO₂. The aim was to keep the alumina and lime concentrations constant along the varying pO₂ range. The correct initial mixtures were found with pre-experimental sets for both slags at each pO₂. Phase diagrams to predict slag composition and properties of FeO-SiO₂-Fe₂O₃ and FeO-SiO₂-Fe₂O₃-10 wt% Al₂O₃ systems have been presented previously (Avarmaa and Taskinen, 2018b). Fig. 2 presents the third slag system of-interest, FeO-SiO₂-Fe₂O₃-10 wt% Al₂O₃-5 wt % CaO, with oxygen activity contours superimposed at 1300 °C. The diagram was calculated with MTDATA software employing MTOX database (Gisby et al., 2017).

![Figure 2. Quasiternary phase diagram of FeO-SiO₂-Fe₂O₃-10wt% Al₂O₃-5wt% CaO slag with its oxygen activity contours at 1300 °C.](image)

This study follows the liquid-tridymite (OX_LIQ+TRI) phase boundary in Fig. 2. According to the phase diagram, increasing the oxygen partial pressure decreases the solubility of silica and increases Fe₂O₃ concentration in liquid oxide at tridymite saturation boundary. Dissolving copper will influence the liquidus boundaries, especially at high oxygen partial pressures, as shown previously (Avarmaa et al., 2018a).

Equal amounts of copper alloy and slag mixture, 0.08–0.1 g each, were pressed into pellets. The pellets were placed in silica crucibles (Heraeus, HSQ® 300) and the crucibles to platinum baskets. Each sample was
equilibrated for 16 h, after which they were quenched in brine or ice water mixture. The crucible-sample combo was cut in half or crushed, to get suitable sample pieces for epoxy resin mounting. The mounted samples were prepared with wet metallographic methods and coated with carbon. SEM-EDS technique (LEO 1450 with Oxford X-Max EDS) was used for preliminary phase composition analyses and sample imaging. Comprehensive composition analyses for copper and slag phases were executed with Cameca SX 100 Electron Probe Micro-Analyzer (Cameca SAS, France). The acceleration voltage, beam current and beam diameter were 20 kV, 60 nA and 100 μm for copper / 40 μm for slag, respectively, and the standards utilized were natural minerals (hematite for Fe and O, Al₂O₃ for Al, quartz for Si and diopside for Ca) and synthetic pure metals (Cu, Pt, Pd, Au and Ag). The copper alloy and slag were analysed from all samples with EPMA technique, by taking 8 points per phase.

The concentrations of trace elements (Au, Ag, Pd and Pt) in the slags were mostly below the detection limits of EMPA, and therefore they were measured using a Laser Ablation Inductively Coupled Plasma Mass Spectrometer. The LA-ICP-MS setup consisted of a Photon Machines Analyte Excite 193 nm ArF Excimer LA device (Teledyne CETAC Technologies, USA) and a NuAttom SC-ICP-MS instrument (Nu Instruments Ltd, UK). The laser spot size was selected as 110 μm, and eight spots were ablated from the slag phase of each sample. The laser was operated at 10 Hz frequency with 4 ns pulses. Laser operation was performed following a sequence of 5 pre-ablation pulses, 20 s pause, 15 s of gas background analysis, and 400 ablation pulses. The laser energy was set to 20% of 5.0 mJ, corresponding to a fluence of 1.67 J/cm². Time-resolved analysis (TRA) signals were acquired in Fastscan mode, with a low resolution (ΔM/M=300) for increased sensitivity. NIST 612 SRM (Jochum et al., 2011) was utilized as the external standard, and silicon as the internal standard. NIST 610 (Jochum et al., 2005), as well as USGS BCR-2G and BHVO-2G basaltic glasses (Jochum et al, 2005) were analyzed as unknowns for monitoring the analysis conditions and accuracy. The obtained time-resolved analysis signals were processed with a Glitter software (Griffin et al., 2008).

3. Results

The equilibrated samples were comprised of three phases - copper alloy, slag and tridymite - as shown in Figure 3.

![Figure 3. A backscattered electron micrograph of sample at 1300 °C and 10⁻⁷ atm, showing the copper alloy, slag and tridymite phases.](image)
3.1 Slag

Three types of silica saturated slags were employed in the experiments: pure iron silicate slag, iron silicate slag with ~10 wt% Al₂O₃ and iron silicate with ~10 wt% Al₂O₃ and ~5 wt% CaO. The measured alumina concentrations were 9.8–10.5 wt% and lime concentrations 4.1–4.4 wt%. According to these results, the aim of keeping these concentrations constant along the varying oxygen partial pressure range was reached. The iron-to-silica ratio, as a function of oxygen pressure, is presented in Fig. 4 (left side). The solubility of copper in slags is presented on the right side of Fig. 4.

As expected, the alumina and lime additions drastically increased the solubility of silica into the slags, thus lowering the Fe/SiO₂ ratio (Kim and Sohn, 1998). In addition, an increasing trend is observed along the decreasing oxygen partial pressure. The iron concentration in slag increased as the oxygen partial pressure decreased for all the samples, whereas silica behaved differently depending on the slag composition. In pure iron silicate slags, silica concentration increased as a function of decreasing oxygen partial pressure, whereas in alumina or alumina-lime containing slags, silica concentration decreased somewhat as the oxygen partial pressure decreased. According to phase diagrams, the silica content should increase as a function of decreasing partial pressure of oxygen in every slag investigated (Fig. 2 and phase diagrams in prior study (Avarmaa et al., 2018a)). However, they do not take into account the copper solubility in slags that modifies the slag composition, especially at high oxygen potentials (Avarmaa and Taskinen, 2018b).

The slopes of copper concentration in alumina-containing and alumina-lime-containing slags are -0.24 and -0.23, which strongly support dissolution as CuO₀.₅ (Cu⁺). For pure iron silicate slag, the slope is -0.34, which is closer to our earlier results in spinel saturation (Avarmaa et al., 2019).

3.2 Metal alloy

Precious metal concentrations in copper alloy as a function oxygen partial pressure, for each slag, are presented in Fig. 5. Pt, Pd and Au exhibit a similar type of behavior, since their concentrations increase as a function of oxygen partial pressure. This behavior is expected, as the amount of metallic copper phase decreases with increasing pO₂ due to increasing copper solubility in slag. The order of the slag trend lines can be explained with the decreasing copper solubility in slag when basic oxides are added (see Fig. 4, right side). This results in a higher amount of the copper alloy phase, lowering the precious metal concentrations in the alloy. Silver behaves differently and the concentrations after equilibration are lower than for Au, Pd and Pt in every experimental condition. Moreover, the order of the trend lines is different: the pure iron-silicate slag
has the lowest silver concentration, possibly due to stronger evaporation, when compared to slags containing basic oxides.

In order to maximize the precious metal recoveries in the secondary copper smelting, their behavior must be characterized in the process conditions. Moreover, the influence of different process parameters, such as oxygen partial pressure, temperature and slag composition, should be investigated in the sense of the recoveries. A practical thermodynamic parameter and tool for describing the behavior of a minor element (M) between two phases – copper and slag in this case – is the distribution coefficient:

$$L_{M}^{Cu/s} = \frac{[\text{wt\% M}]_{\text{copper}}}{[\text{wt\% M}]_{\text{slag}}}.$$  \hspace{1cm} (1)

It is independent of the scale of the system for minor elements (in dilute solutions), which means that experimentally determined distribution coefficients can be directly applied to large-scale industrial processes. Furthermore, as the analyses are executed with direct phase techniques, the results describe the distribution coefficients based on the real chemical solubility of each element in each phase, excluding the entrainments of other phases present in the sample. This provides valuable information for the industry; for example, if their industrially determined distribution coefficients are much lower than the ones presented here, it can be assumed that the most significant precious metals losses occur through mechanical copper droplet entrainment, instead of chemical dissolution. Thus, the following distribution coefficients will help to understand elemental behavior in different process conditions, and provide information for process development, e.g. how to improve the recoveries of elements into copper phase. Possible process

Figure 5. Precious metals in copper alloys as a function of \(-\log_{10}p_{O_2}\) at 1300 °C.
developments for improved recoveries can include for example slag chemistry modification, increased sub-process times for obtaining better settling, or the addition of a slag cleaning step.

The distribution coefficient can be calculated through thermodynamic approach (Yazawa et al., 1983; Anindya et al., 2013) if appropriate data exists. Moreover, if the (logarithmic) distribution coefficient is plotted against logarithmic oxygen partial pressure, the formed slope can be used to evaluate the oxidation state of the minor element in slag.

The distribution coefficients of silver between copper and the three investigated slags are presented in Fig. 6. In addition, the results at spinel saturation (Avarmaa et al., 2019) are presented in the same figure with red trend lines. The slopes of the plots, for all the silica-saturated slags investigated, are 0.28–0.29, indicating strongly to AgO_{0.5} (Ag^+) form for silver oxide in slag.

![Figure 6. Metal-slag distribution coefficients of silver as a function of oxygen partial pressure at 1300 °C. Black lines correspond to silica-saturated slag results, whereas the red trend lines correspond to a previous study: solid line for FeO_{x}-SiO_{2}-Al_{2}O_{3}^{sat.} slag and dashed line for FeO_{x}-SiO_{2}-Al_{2}O_{3}^{sat.}-5CaO.](image)

The distribution coefficients of silver with the pure iron silicate slag at silica saturation and the lime-containing slags at silica and spinel saturation are in the same range, whereas the alumina-containing iron- silicate slags seem to have lower distribution coefficients. The silver distribution coefficient decreases gradually with increasing alumina concentration in slag. Some interaction between silver and alumina could explain this phenomenon, for example AgAlO_{2} delafossites that can be produced with hydrothermal method at temperatures around 200 °C (Xiong et al., 2014; Sheets et al., 2008). However, the aforementioned compound has been shown to be stable only up to 800 °C (Xiong et al., 2014), although suggesting attractive interactions between silver and aluminum oxides.

The metal-slag distribution coefficients for gold and palladium as a function of oxygen partial pressure are presented in Figs. 7 and 8, respectively. The palladium concentrations in slags are the calculated averages of ¹⁰⁶Pd and ¹⁰⁸Pd isotopes, by employing the correction formula presented in detail in our other paper (Avarmaa et al., 2019).
As can be seen from Figs. 7 and 8, the addition of Al₂O₃ and CaO increases the distribution coefficients of gold and palladium. Thus, the recovery rates in oxidizing copper smelting conditions can be improved with the addition of basic (CaO) and/or amphoteric (Al₂O₃) oxides into acidic iron-silicate slags. The results for pure iron-silicate slag show a very good repeatability, whereas more scatter can be seen with the other slags by the duplicate experiment series.

The slopes of the plot for gold are around 0.5, indicating to dissolution oxide form AuO (Au²⁺) in slag. Slopes for palladium were between 0.24 and 0.3, indicating to PdO₁.₅ (Pd⁺) or a combination of different forms (Pd⁺ and Pd²⁺).
The minimum metal-slag distribution coefficients of platinum are presented in Fig. 9. They were calculated as the average detected values of isotopes $^{194}\text{Pt}$, $^{195}\text{Pt}$ and $^{196}\text{Pt}$, excluding the results below the detection limit of LA-ICP-MS.

Figure 9. Metal-slag distribution coefficient of platinum between copper and slags at 1300 °C.

Although most of the data points for platinum concentration in slags were below the detection limit, the results for pure iron silicate slags show good repeatability. For the other slags, the results show more scatter. Nevertheless, alumina or alumina-lime additions into iron silicate slag seem to lower the distribution coefficient, as opposed to how they influence the gold and palladium distributions. Previous (minimum) distribution results at spinel saturation were between $10^6$–$10^7$ (Avarmaa et al., 2019). Those result are in the same range as the ones obtained in this study. The slopes are 0.2–0.4 indicating to PtO$_{0.5}$–PtO, but for pure iron silicate slag, neglecting the $10^{-7}$ atm results, the slope is 1.1, indicating PtO$_2$ as the dissolving oxide. Nevertheless, these distribution coefficients represent rather the minimum distribution coefficients than the real ones.

The results show that in the oxidizing smelting conditions gold, platinum and palladium are distributed highly, i.e. extremely efficiently recovered, with $L_{\text{Cu/s}} > 10^4$, in the copper phase. Previous industrial results (Mackey et al., 1975; Shi and Ye, 2013; Kucha and Cichowska, 2001) for gold and experimental studies for gold and platinum group metals (PGMs) executed without the drop-quench technique and direct phase analyses (Shuva et al., 2017; Nishijima and Yamaguchi, 2014; Yamaguchi, 2010) show typically lower distribution coefficient values compared to ours. Exceptions that fit with our Pd, Pt and Au results are the previous studies (Chen et al., 2016; Sukhomlinov and Taskinen, 2017; Avarmaa et al., 2019) employing the same experimental technique with the sensitive LA-ICP-MS analytics. Our results are based on the real chemical dissolution values, whereas most of the previous results include physical separation of the phases before analyses, containing high risk of phase mixing and therefore incorrect solubility values. Thus, according to our results and compared to previous data, the main loss mechanism in the industrial conditions can be considered as mechanical entrainment of copper droplets. To improve the recoveries, the settling of copper and the copper-slag phase separation need to be optimized in terms of slag fluidity and surface forces, which may be sensitive to the slag assay. A slag cleaning (reduction) process step would improve silver recoveries to metal phase, although the distribution coefficient is at minimum 20 in the present experimental conditions. In the reducing
conditions with oxygen partial pressure $< 10^{-7}$ atm, the precious metal recoveries into copper alloy can be considered to be even higher than the presented ones. This consideration is based on the presented results and the trends they form, as well as the general oxidation of a minor element (M) via reaction $M + O_2 = MO_2$.

Fig. 10 represents an Ellingham diagram for the most ‘stable’ precious metal oxides of-interest, according to HSC (Roine, 2007). The figure includes also the nomographic scale of oxygen partial pressure (black lines) to clarify the stability range of precious metal oxides in the prevailing $pO_2$ conditions during copper smelting. All the precious metal reactions are normalized to consume one mole of $O_2$.

![Ellingham diagram for precious metals and oxygen partial pressures at temperature range 0-1500 °C according to values of HSC.](image)

This diagram supports the experimental results by showing that precious metals do not form oxides spontaneously under smelting conditions ($1300 ^\circ C$, $10^{-10}$-$10^{-5}$ atm). Somewhat surprising is the order of the curves in the diagram, as silver is above the PGMs, i.e. it forms much less stable oxides than the PGMs.

### 5. Conclusions

Today, WEEE is considered as a modern urban mine resource. WEEE and especially PCBs include higher concentrations of precious metals as their respective primary ores, making them highly valuable and economically viable for recycling. The main recovery path for precious metals is through metal smelting, where copper acts as the collector metal, as shown in the present study. This study was conducted to produce new precise data on the precious metals behavior in oxidizing copper smelting conditions at $1300 ^\circ C$. Moreover, the influence of alumina and lime additions to iron-silicate slag and to the precious metal distribution coefficients were investigated. According to the results of this study, copper smelting is a
powerful process for recovering precious metals into the copper phase, followed by further separation of 
these metals though electrolytic refining of copper cathodes and the subsequent anode slime treatments.

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