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Handling trace elements in WEEE recycling through copper smelting—an experimental and thermodynamic study

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ABSTRACT

Recycling of waste electrical and electronic equipment (WEEE) is attracting increasing attention, due to the presence of valuable metals and the risk of environmental emissions associated with WEEE disposal. In this study, the distributions of trace elements (Ag, Ni, Co, and Sn) between copper alloy and magnetite/wüstite-saturated iron silicate slags were investigated at 1200–1300 °C and PO2 of 10−10−10−6.5 atm, simulating the conditions of WEEE reprocessing through secondary copper smelting and converting. The high-temperature isothermal equilibration experiments were conducted in synthesized magnetite/wüstite crucibles under controlled CO-CO2 atmospheres followed by quenching in an ice-water mixture. The phase compositions and concentrations of the trace elements in copper alloy, magnetite/wüstite, and slag were determined by Electron Probe X-ray Micro-analysis and Laser Ablation-High-Resolution Inductively Coupled Plasma-Mass Spectrometry. The distribution coefficients of all investigated trace elements between copper alloy and slag increased with decreasing oxygen partial pressure and increasing temperature. Ag distributed strongly into the copper alloy at all conditions, whereas Co mainly deported into the slag phase. Ni and Sn were concentrated in the alloy at lower PO2 and in the slag at higher PO2. Varying concentrations of Ni, Co, and Sn were also dissolved into the solid magnetite/wüstite phase.

1. Introduction

The rapid development of the electronic information industry and the rapid upgrading of electronic devices have resulted in a surge of waste electrical and electronic equipment (WEEE) (Marinello and Gamberini, 2021). As the second largest WEEE generator after Asia, the production of WEEE in European Union is currently estimated to be approximately 11.6 million tonnes per year (Ibanescu et al., 2018). Motivated by stronger legislation, economic and environmental factors, efforts concerning recycling of WEEE are of high interest and in high demand (Directive, 2012; Messmann et al., 2018).

WEEE is a heterogeneous combination of metallic and non-metallic materials, including plastics, ceramics, copper, precious metals (Au, Ag, Pt, and Pd), heavy metals (Pb, Hg, Cr, and As, etc.) and other typical trace elements (Ni, Co, and Sn) (Zhang and Xu, 2016; Wang et al., 2017; Cesaro et al., 2018; Cui and Zhang, 2008; Zeng et al., 2018; Shuva et al., 2016), indicating WEEE can be an important raw material in many copper smelters (Lehner et al., 1999; Veldhuizen and Sippel, 1994; Hageliiken, 2006; Hageliiken and Corti, 2010; Lennartsson et al., 2018; Flores et al., 2014; Brusselaers et al., 2006; Khaliq et al., 2014) for recovering metal values. The route for WEEE recycling involves collection, dismantling, shredding and, crushing, followed by hydro-/pyrometallurgical processing. From the perspective of industrial practice, WEEE recycling, especially its copper-rich scrap fraction, is currently mainly performed through pyrometallurgical copper smelting routes (Tesfaye et al., 2017), due to the advantages of easy separation of precious metals from base metals, large capacity, high yields and convenient disposal of flue gas. Compared with available primary copper smelters, a wider variety of WEEE can be incorporated into the secondary copper smelters and subsequently produce copper as well as valuable side products of multiple precious and critical elements (Anindya et al., 2009). Among those secondary copper smelting routes, the processing of WEEE in TSL furnaces, like Ausmelt and Isasmelt technologies, are commonly used (Shuva et al., 2017). The precious and

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trace elements are introduced into the TSL furnace along with secondary materials like WEEE and the metals distribute in smelting and converting into metal, slag, and gas phases. The subsequent converting and refining operations in the same furnace are energy-saving and effective recovery routes for extracting metal values from the valuable metals-enriched copper. Fig. 1 shows the route for WEEE recycling through secondary copper smelting.

There is a wealth of data revealing the distribution of Ag in pyrometallurgical copper smelting processes. A detailed literature review for the distribution of Ag can be found in our previous studies (Chen et al., 2020; Chen et al., 2021). Table 1 summarizes the details of the most recent experimental studies (Anindya et al., 2013; Avarmaa et al., 2018a, 2019, Danzek et al., 2020, 2021; Derin and Yücel, 2002; Gortais et al., 1994; Kashima et al., 1978; Kho et al., 2006; Klemettinen et al., 2019; Nagamori and Mackey, 1977; Reddy and Healy, 1981a,b, Ren et al., 2020, 2021, Sukhomlinov et al., 2019a,b, 2020; Takeda et al., 1983; Tirronen et al., 2017; Wang et al., 1973; Klemettinen et al., 2018; Avarmaa and Taskinen, 2018b; Avarmaa et al., 2017; Sukhomlinov and Taskinen, 2017; Van den Bulck et al., 2018; Reddy, 1980; Louey and Swinbourne, & D.R., Lehner, T, 1999) for investigating the behavior of selected trace elements (Ni, Co, and Sn) in copper smelting processes. Apart from the above mentioned primary and secondary copper smelting routes, the distributions of trace elements in other pyrometallurgical processes and theoretical thermodynamic analyses have been reported by many researchers (Choi and Cho, 1997; Hellsten et al., 2019; Holland et al., 2019; Nakajima et al., 2011; Piskunen et al., 2018; Takeda et al., 1990; Teague et al., 2001; Wang et al., 1974; Xu et al., 2012, 2013; Yazawa, 1980; Nagamori and Mackey, 1978; Holland et al., 2018).

In those previous studies shown in Table 1, the behaviors of trace elements have been investigated extensively between metallic copper/sulfide copper matte and Al-Fe spinel/silica-saturated slags (Avarmaa et al., 2018a, 2019, Danzek et al., 2020, 2021; Derin and Yücel, 2002; Kashima et al., 1978; Klemettinen et al., 2019; Nagamori and Mackey, 1977; Reddy and Healy, 1981a,b, Ren et al., 2020, 2021, Sukhomlinov et al., 2019a,b, 2020; Wang et al., 1973; Klemettinen et al., 2018; Avarmaa and Taskinen, 2018b; Avarmaa et al., 2017; Sukhomlinov and Taskinen, 2017; Van den Bulck et al., 2018; Reddy, 1980), but none at magnetite/wüstite saturation. Moreover, the chemical analysis methods used in some earlier studies (Ren et al., 2021; Ren et al., 2020; Kashima et al., 1978; Reddy and Healy, 1981; Reddy and Healy, 1981; Reddy, 1980; Anindya et al., 2013; Kho et al., 2006; Gortais et al., 1994; Takeda et al., 1983; Louey and Swinbourne, & D.R., Lehner, T., 1999) may have caused inaccuracies when measuring the concentrations of trace elements in metal, matte, and slag, due to the incomplete phase separations. To overcome the difficulties of accurately determining the trace element concentrations in separate phases, direct phase microanalysis techniques were applied, thus avoiding distorted results caused by imperfect bulk sample separation.

This study aims to measure the distributions of Ag, Ni, Co, and Sn between copper alloy and magnetite/wüstite-saturated iron silicate slags, related to WEEE recycling in secondary copper smelting. The present results help to predict the conditions favorable for recycling valuable metals from WEEE into the copper alloy phase. The distributions of valuable metals between copper alloy and slag provide potential for improving recoveries of valuable metals from WEEE through adjusting the slag composition, temperature, and oxygen partial pressure. The trace element behaviors in the Cu-Fe-O-Si system have been investigated so far in slags at silica-saturation in previous studies (Sukhomlinov et al., 2019a,b; Sukhomlinov and Taskinen, 2017).

2. Experimental

High purity powders, shown in Table 2, were used for preparing the copper alloy and slag. The concentration of each trace element added into the copper alloy mixture was approximately 1 wt pct. The Fe2O3/SiO2 ratio of initial slag mixture was determined based on the prediction of the FeO-SiO2 phase diagram (Fig. 2) at copper saturation, simulated by MTDATA (Gisby et al., 2017; Davies et al., 2002) thermodynamic software using the MTOX database (Davies et al., 2002). Fig. 2 shows that the slag is saturated with wüstite (FeO) at 1200–1250 °C and P2O5 < 10–6 atm but is saturated with magnetite (Fe3O4) at higher P2O5. At 1300 °C, the slag is wüstite-saturated at P2O5 of 10–6 atm but is magnetite-saturated at P2O5 = 10–7–10–6 atm.

Approximately 0.2 g of copper alloy mixture was equilibrated with equal amount of slag mixture in each experiment. The copper alloy mixture and slag mixture were loaded into a mold and then pressed into a pellet using a hydraulic press under high pressure of five tons. Magnetite (Fe3O4) and wüstite (FeO) crucibles were used for holding the sample pellet. The type of crucibles used at different conditions was determined based on the prediction of slags predicted by MTDATA. The magnetite and wüstite crucibles were prepared by oxidizing the iron foil at 1250 °C and P2O5 of 10–7 and 10–10 atm, respectively. Before being oxidized, the iron foil was folded into a crucible shape and the bottom was formed into a bowl shape using a hemispherical stamping rod. The compositions of the crucibles were measured and validated by electron probe microanalysis. The atmosphere in the furnace was controlled by flowing CO-CO2 gas mixtures. The gas flow rates calculated by HSC Chemistry software (Roine, 2017) for each target P2O5 and the initial Fe2O3/SiO2 ratios are listed in Table 3.

A vertical tube furnace (Nabertherm, Lilienthal, Germany, RHTV 120–150/1) equipped with MoSi2 heating elements was used for conducting the high-temperature equilibration experiments. The
temperature of the furnace was regulated by a Nabertherm P310 temperature controller. A calibrated S-type Pt/Pt-10 wt pct Rh thermocouple (Johnson-Matthey Noble Metals, UK), placed next to the sample, was used for measuring the furnace hot-zone temperature. The platinum basket holding the crucible was hooked by a platinum wire which was inserted into the furnace from the top end of the guiding tube. The experimental set-up and the sample holding technique are displayed in Fig. 3. To verify that equilibration was attained, all samples were equilibrated in the furnace for at least 24 h (Daiczak et al., 2020; Daiczak et al., 2021; Avarmaa et al., 2019; Avarmaa et al., 2020) before being quenched in an ice-water mixture. The experimental procedure has been described in detail in our earlier publications (Klemettinen et al., 2017; Avarmaa et al., 2019; Avarmaa et al., 2020).

The quenched samples were dried and mounted in epoxy resin (EpoFix, Struers, Denmark). The sample surfaces were ground, polished, and then carbon coated using a carbon vacuum evaporator (JEOL IB-29510VET). The microstructures were obtained using a Scanning Electron Microscope (SEM; Tescan MIRA 3, Brno, Czech Republic) coupled with an UltraDry Silicon Drift Energy Dispersive X-ray Spectrometer (EDS; Thermo Fisher Scientific, Waltham, MA, USA).

Table 1
A summary table of most recent literature sources investigating the selected trace elements distributions in copper smelting.

| Equilibrium System                  | Slag                        | Log(PaO2/ atm) | T/ °C | Elements | Crucible | Analytical methods | Ref.                                              |
|------------------------------------|-----------------------------|----------------|-------|----------|----------|--------------------|--------------------------------------------------|
| **Al2O3/(Al-Fe) Spinel saturated slag**                             |                             |                |       |          |          |                    |                                                  |
| Copper alloy-slag                  | FeO,SiO2-(K2O)              | –10 to –5      | 1300  | Sn, Ni   | Alumina  | EPMA and LA-ICP-MS | (Klemmetinen et al., 2019; Klemmetinen et al., 2018) |
| Copper alloy-slag                  | FeO,SiO2-Al2O3-(MgO)        | –11 to –8      | 1300  | Sn, Ni, Co| Alumina  | EPMA and LA-ICP-MS | (Daiczak et al., 2020; Daiczak et al., 2021)      |
| Copper alloy-slag                  | FeO,SiO2-(Al2O3- CaO·K2O)  | –10 to –5      | 1300  | Sn       | Alumina  | EPMA and LA-ICP-MS | (Avarmaa et al., 2018a, 2019)                    |
| Copper alloy-slag                  | FeO,SiO2-Al2O3              | –10 to –5      | 1300  | Sn       | Alumina  | EPMA               | (Avarmaa and Taskinen, 2018b; Avarmaa et al., 2017) |
| Copper alloy-slag                  | FeO,SiO2-Al2O3              | –11 to –6      | 1200-1300 | Sn   | Alumina  | Polargraphic techniques | (Niemam and Mackey, 1977)                      |
| Copper alloy-slag                  | MnO·SiO2-Al2O3              | –12 to –10     | 1300-1350 | Co   | Alumina  | AAS                | (Ren et al., 2021)                              |
| Copper alloy-slag                  | FeO2-SiO2-Al2O3             | –10 to –8      | 1400  | Co       | Alumina  | Not reported       | (Derin and Yicel, 2002)                         |
| **SiO2 saturated slag**            |                             |                |       |          |          |                    |                                                  |
| Copper alloy-slag                  | FeO,SiO2-(Al2O3- CaO·K2O)  | –10 to –5      | 1300  | Sn       | Silica   | EPMA and LA-HR ICP-MS | (Avarmaa et al., 2019)                          |
| Copper alloy-slag                  | FeO,SiO2-Al2O3-(CaO)        | –10 to –5      | 1300  | Sn       | Silica   | EPMA               | (Avarmaa and Taskinen, 2018b; Sukhomlinov et al., 2020) |
| Copper alloy-slag                  | FeO,SiO2                   | –8 to –4       | 1250-1350 | Ni, Co | Silica   | EPMA and LA-ICP-MS | (Sukhomlinov et al., 2019a; Sukhomlinov and Taskinen, 2017) |
| Copper matte-slag                  | FeO,SiO2-(Al2O3- CaO)       | –8 to –7       | 1300  | Sn       | Silica   | EPMA and LA-ICP-MS | (Sukhomlinov et al., 2019b)                     |
| Copper alloy-slag                  | MnO·SiO2                   | –12 to –10     | 1350  | Co       | Silica   | AAS                | (Ren et al., 2020)                              |
| Copper alloy-white metal-slag       | FeO,SiO2                   | Not reported   | 1300  | Ni, Co   | Silica   | AAS                | (Kashima et al., 1978)                         |
| Copper alloy-slag                  | FeO,SiO2-CaO· SiO2         | Not reported   | 1300  | Sn       | Silica   | EPMA               | (Van den Buick et al., 2018)                   |
| Copper alloy-slag                  | FeO2-SiO2                  | –10 to –6      | 1250-1350 | Co   | Alumina  | Gravimetric technique and XRF AAS, XRD, and SEM-EDS | (Wang et al., 1973) |
| Copper alloy-slag                  | CuO·SiO2                   | Not reported   | 1200-1250 | Co   | Silica   | AAS, XRD, and SEM-EDS | (Reddy and Healy, 1981; Reddy and Healy, 1981; Reddy, 1980) |
| **MgO saturated slag**             |                             |                |       |          |          |                    |                                                  |
| Copper alloy-slag                  | FeO·SiO2-CaO               | –7             | 1300  | Sn       | Magnesia | ICP-AES            | (Aindiyar et al., 2013)                        |
| Copper matte-slag                  | FeO·SiO2                   | Not reported   | 1250  | Co       | Magnesia | ICP-AES            | (Dho et al., 2006)                            |
| Copper alloy-slag                  | CaF2·CaO-MgO-SiO2          | Not reported   | 1227  | Ni, Sn   | Magnesia | ICP and XRF        | (Gottais et al., 1994)                        |
| Copper alloy-slag                  | FeO·CaO                    | –12 to –5      | 1250  | Sn, Ni, Co| Magnesia | AAS                | (Takeda et al., 1983)                         |
| Copper matte-slag                  | FeO·SiO2                   | Not reported   | 1250  | Sn       | Magnesia | ICP-AES            | (Lousy and Swinbourne, & D.R., Lehner, T., 1999) |
| **Magnetite saturated slag**       | Copper alloy-copper matte-slag |               | 1200–1275 | Ni, Co | Silica   | EPMA and LA-ICP-MS | (Tirronen et al., 2017)                       |

AAS: Atomic absorption spectroscopy.
XRF: X-ray fluorescence spectroscopy.
XRD: X-ray diffractionmetry.
ICP: Inductively coupled plasma spectroscopy,
ICP-AES: Inductively coupled plasma atomic emission spectrometry.
LA-ICP-MS: Laser Ablation Inductively Coupled Plasma-Mass Spectrometry.
The concentrations of trace elements in the metal phase as well as the major element compositions of the metal, slag, and magnetite/wüstite phase were obtained with a CAMECA SX100 electron probe microanalyzer (EPMA) using wavelength dispersive spectrometry (WDS) technique. The accelerating voltage and beam current were 20 kV and 60 nA, respectively. A defocused beam diameter set to 20 μm for the magnetite/wüstite phase and 50 μm for the metal and slag phases was used. The standard materials used were obsidian for O Kα, quartz for Si Kα, hematite for Fe Kα, and metallic copper for Cu Kα, silver for Ag Lα, nickel for Ni Kα, cobalt for Co Kα, and tin for Sn Lα. Analytical results were corrected using the PAP on-line correction program (Pouchou and Pichoir, 1986). At least eight points were measured for the metal phase. A three-spot analysis technique was used for the slag and magnetite/wüstite phases, i.e., 24 analyzing spots were selected from the slag/magnetite/wüstite phase and the result for one point was determined by using the average of every three separate analysis spots next to each other. The analytical total of EPMA measurements was within 98–100.7 wt. pct. The analyses were taken from areas where all phases were present and in direct contact with each other, examples shown in Fig. 4.

Laser ablation single collector inductively coupled mass spectrometry (LA-ICP-MS) analyses of trace element concentrations in slag and magnetite/monoxygen phases were performed at the Geological Survey of Finland (GTK), using a Nu AttoM SC-ICPMS (Nu Instruments Ltd., Wrexham, UK) and an Analyte 193 ArF laser-ablation system (Photon Machines, San Diego, USA). The laser was run at a pulse frequency of 10 Hz and a pulse energy of 5 mJ at 30 % attenuation to produce an energy flux of 2.5 J/cm² on the sample surface with a 40 μm spot size. This spot size was chosen to provide the best compromise between adequate resolution, to allow spot analysis of individual phases determined by SEM imaging set at high contrast yet keeping limits of detection (LOD) as low as possible. Each analysis was initiated with a 20 s baseline measurement followed by switching on the laser for 40 s for signal acquisition. The trace element concentrations were obtained using time resolved analysis (TRA) with continuous acquisition of data for each set of points (generally following the scheme of primary standard, quality control standard, 20 unknowns). Both phase analyses of magnetite/wüstite and slag were conducted close to each other from the same well-quenched areas.

For the trace element analyses by LA-ICP-MS, GSE glass was used as the primary external standard, and GSD, BHVO-2G and BCR-2G glasses were used as reference materials for quality control. The isotope 57Fe was used as the internal standard for magnetite/wüstite and 29Si for slag by employing the EPMA measurement results for Fe and Si, respectively. The measurements were performed on isotopes 109Ag for silver, 60Ni for nickel, 59Co for cobalt, and 120Sn for tin at low resolution (ΔM/M = 300) using the fast scanning mode. Data reduction was handled using the GLITTER™ (Van Achterbergh, 2001) software which allows for baseline subtraction, signal integration over a selected time window and quantification using known concentrations of the external and internal standards. The detection limits of EPMA and LA-ICP-MS obtained for this experimental series are listed in Table 4.

![Fig. 2. The isopleths of the Cu-Fe-O-SiO₂ system calculated by MTDATA. Blue line-10⁻⁹ atm; green line-10⁻⁸ atm; red line-10⁻⁷ atm; black line-10⁻⁶ atm (MTOX database (Davies et al., 2002).](image-url)
3. Results and discussion

The microstructures of samples obtained at 1200–1300 °C and $P_{O_2}$ of 10$^{-8}$ atm are shown in Fig. 4. As can be seen in Fig. 4, the copper alloy was equilibrated with molten slag phase and solid magnetite/wüstite, depending on temperature and the prevailing oxygen partial pressure. The fraction of recrystallized magnetite/wüstite phase decreased with increasing oxygen partial pressure. The detailed primary phases of saturation in the slags can be seen in section 3.2.

3.1. Concentrations of trace elements in copper alloy

The concentrations of trace elements in copper alloy as a function of $P_{O_2}$ are shown in Fig. 5. Fig. 5(a) shows that Ag concentrations in the
copper alloy were somewhat scattered and had no significant change in the oxygen partial pressure range of $10^{-10}$-$10^{-8}$ atm at 1200–1250 °C, whereas it showed a slightly decreasing trend with increasing $P_{O_2}$ from $10^{-8}$ to $10^{-6.5}$ atm at 1250 °C. The results at 1300 °C fluctuated around 0.2 wt pct and at 1200 °C around 1 wt pct. The concentration of Ag in copper alloy decreased from around 1 wt pct to approximately 0.2 wt pct when temperature varied in the range of 1200–1300 °C, indicating a stronger vaporization of Ag at higher temperatures. The decreasing impact of higher temperature on the deportment of Ag into copper alloy was also observed by Sukhomlinov et al. (Sukhomlinov et al., 2019a).

The results by Avarmaa et al. (Avarmaa et al., 2020; Avarmaa et al., 2016) were almost constant at 0.9 wt pct at 1300 °C, whereas it showed a slightly decreasing trend with increasing $P_{O_2}$ from $10^{-9}$ to $10^{-7}$ atm at 1300 °C, indicating a stronger vaporization of Ag at higher temperatures. The decreasing impact of higher temperature on the deportment of Ag into copper alloy was also observed by Sukhomlinov et al. (Sukhomlinov et al., 2019a). The results by Avarmaa et al. (Avarmaa et al., 2020; Avarmaa et al., 2016) were almost constant at 0.9 wt pct at 1300 °C, whereas it showed a slightly decreasing trend with increasing $P_{O_2}$ from $10^{-9}$ to $10^{-7}$ atm at 1300 °C, indicating a stronger vaporization of Ag at higher temperatures. The decreasing impact of higher temperature on the deportment of Ag into copper alloy was also observed by Sukhomlinov et al. (Sukhomlinov et al., 2019a).

Fig. 5(b) shows that concentration of Ni in the copper alloy had a linearly decreasing trend with increasing $P_{O_2}$ at all temperatures investigated. With increasing temperature from 1250 °C to 1300 °C, the concentration of Ni in copper alloy increased by approximately 0.1 wt pct. The present results for Ni in copper alloy were lower than the observations by Klemettinen et al. (Klemettinen et al., 2018) and Sukhomlinov et al. (Sukhomlinov et al., 2019a) but showed similar decreasing trends.

Co displayed the lowest concentration in the copper alloy when compared with other trace elements investigated in this study, as shown in Fig. 5(c). Co concentration in the copper alloy had a downward trend with increasing $P_{O_2}$ as reported in previous studies (Daiczczak et al., 2020; Sukhomlinov et al., 2019a). However, the decreasing trend was less vigorous at higher $P_{O_2}$. The increase of temperature favored the deportment of Co in the copper alloy. The results by Sukhomlinov et al. (Sukhomlinov et al., 2019a) were within the range observed in the present study but were significantly lower than the data by Daiczczak et al. (Daiczczak et al., 2020).

The trend line for Sn in copper alloy exhibited a similar decreasing trend as Co. However, the impact of temperature was not as strong as for the other trace elements. The present results of Sn in copper alloy equilibrated with magnetite/wüstite-saturated slags were somewhat lower than the observations (Avarmaa et al., 2018a, 2019; Daiczczak et al., 2021; Hidayat et al., 2021; Klemettinen et al., 2019; Avarmaa and Taskinen, 2018b) obtained from copper alloy in equilibrium with silica/(Al-Fe) spinel-saturated slags, which showed different downward trends. However, the results by Avarmaa et al. (Avarmaa et al., 2019) determined from the copper alloy in equilibrium with silica-saturated slags were close to the present results at 1250 °C. The present results obtained at 1200 °C were slightly higher than the data by Nagamori and...
Mackey (Nagamori and Mackey, 1977) in the \( P_{O2} \) range of \( 10^{-10} \) to \( 10^{-8} \) atm, whereas the present results at 1300 °C were lower than their data (Nagamori and Mackey, 1977) by approximately 0.1 wt pct. The impacts of CaO, Al\(_2\)O\(_3\), and MgO on increasing the Sn concentration in copper alloy were reported in literature (Avarmaa et al., 2018a; Danczak et al., 2021; Avarmaa and Taskinen, 2018b).

3.2. Concentrations of trace elements in Magnetite/Wüstite

The loss of trace elements in the solid magnetite/wüstite primary phase in the copper-slag-magnetite/wüstite-gas equilibria system was investigated by LA-ICP-MS for the first time in the present study, as shown in Fig. 6. Fig. 6(a) indicates that the dissolution of Ag to the magnetite/wüstite phase was extremely low (<1 ppm), compared with the other trace elements. The results for Ni, Co, and Sn displayed a similar increasing trend with increasing \( P_{O2} \), wherein the loss of Ni and Co in the magnetite/wüstite phase were higher than that of Sn. The effect of higher temperature on decreasing the concentration of trace elements in magnetite/wüstite was evident for all minor elements, although less clear for Ag between 1250 and 1300 °C. The phenomenon of trace element dissolutions in solid phase, i.e., in magnetite/wüstite in the present study, was not observed in our previous studies (Avarmaa et al., 2019; Sukhomlinov et al., 2019a) focusing on the copper alloy/slag/tridymite equilibria system.

3.3. Concentrations of trace elements in slag

The concentrations of trace elements in the slag by LA-ICP-MS with their standard deviations (±1σ) against \( P_{O2} \) are presented in Fig. 7. Fig. 7(a) indicates the concentration of Ag in all magnetite/wüstite-saturated slags in equilibrium with copper alloy was lower than 70 ppm, suggesting a strong deportment of Ag into the copper alloy phase, when combined with above mentioned low Ag concentrations in magnetite/wüstite. The results at all temperatures investigated increased with increasing \( P_{O2} \). The increase of temperature reduced the loss of Ag in the slag to varying degrees, depending on the \( P_{O2} \). The data by Avarmaa et al. (Avarmaa et al., 2016) for silver at Al-Fe spinel saturation were higher than the present results and the observations in literature (Sukhomlinov et al., 2019a), but they displayed a similar increasing trend with increasing \( P_{O2} \). The Ag concentrations in slag reported by Hidayat et al. (Hidayat et al., 2019) had some scatter but were within the range of present observations. Additionally, it was reported in the study (Avarmaa et al., 2020) that the loss of Ag in slag can be reduced by adding CaO into the iron silicate slag.

The observed concentration of Ni in slag, as shown in Fig. 7(b), increased throughout the \( P_{O2} \) range investigated at all temperatures, as have been reported in literature (Danczak et al., 2021; Sukhomlinov et al., 2019a; Klemettinen et al., 2018). The present results for Ni in the slag decreased with increasing temperature at fixed \( P_{O2} \), contrary to the
findings by Sukhomlinov et al. (Sukhomlinov et al., 2019a). The discrepancies might attribute to the strong dissolution of Ni in magnetite/wüstite. The Ni concentration in slag measured by Klemettinen et al. (Klemettinen et al., 2018) and Dańczak et al. (Dańczak et al., 2021) at 1300 °C increased approximately from 300 ppm to 0.13 wt pct along with increasing \( P_{O_2} \), which is close to the present results obtained at 1250–1300 °C. They also reported that K₂O and MgO additions in the iron silicate-based slag decreased the loss of Ni in slag.

Fig. 7(c) indicates that the concentration of Co in the slag displayed a non-linear but increasing trend with increasing \( P_{O_2} \). However, the slope was steeper at \( P_{O_2} \) lower than 10⁻⁸ atm at 1200–1250 °C and at 1300 °C below 10⁻⁷ atm. The influence of higher temperature on decreasing the Co concentration in slag was more significant in the lower \( P_{O_2} \) range of 10⁻¹⁰ to 10⁻⁸ atm. A contradictory impact of temperature on Co loss in slag was observed by Sukhomlinov et al. (Sukhomlinov et al., 2019a). Reddy et al. (Reddy and Healy, 1981) reported that the solubility of Co in Cu₂O-CoO-SiO₂ slags increased with increasing ratios of Cu₂O/SiO₂, metal-to-oxide and the concentration of Co in the alloy, which fits well with the observations by Derin and Yücel (Derin and Yücel, 2002) for the solubility of Co in FeOₓ-SiO₂-Al₂O₃ slags. The concentrations of Co in the MgO-containing slag reported by Dańczak et al. (Dańczak et al., 2020) were around 30–70 ppm, which are much lower than the present results.

As shown in Fig. 7(d), concentration of Sn in the slag increased significantly with increasing \( P_{O_2} \) at 1200 °C. However, the results obtained at 1250–1300 °C had no significant changes over the entire \( P_{O_2} \) range studied. The increase of temperature from 1200 °C to 1250 °C reduced the Sn concentration in slag substantially at \( P_{O_2} \) higher than 10⁻¹⁰ atm, owing to its stronger volatilization at more oxidizing conditions (Avarmaa et al., 2019), whereas temperature influenced much less on the Sn concentration between 1250 °C and 1300 °C. The present results at 1200 °C were slightly higher than the data by Nagamori and Mackey (Nagamori and Mackey, 1977), but at 1300 °C the present results were on the lower side of their observations obtained in the same conditions. The results reported by Hidayat et al. (Hidayat et al., 2021) ranged from 580 ppm to 0.45 wt pct and 528 ppm to 1.33 wt pct, at 1250 and 1300 °C, respectively, which are on higher side of the present observations. It was also reported in literature (Anindya et al., 2013; Avarmaa et al., 2018a; Dańczak et al., 2021; Klemettinen et al., 2019) that additions of K₂O, MgO, and CaO into iron silicate slags depressed the loss of Sn into slags.

### 3.4. Distribution coefficients between copper alloy and slag

The high-temperature equilibrium reactions of a trace element \( Me \) between molten copper and slag in WEEE processing can be described using the following equation:

\[
Me + \frac{V}{2}O_2 = MeO,
\]
where the valence of trace element Me in slag equals to 2ν. The equilibrium reaction constant $K$ for reaction (1) can be defined as:

$$K = \frac{a(\text{MeO}_\nu)}{a(\text{Me})P_{O_2}}$$

where $a(\text{Me})$ and $a(\text{MeO}_\nu)$ refer to the activities of Me and MeO$_\nu$ in the copper alloy and slag, respectively. The distribution coefficient of Me between copper alloy and slag can be defined as:

$$L_{\text{Cu}/S}^{\text{Me}} = \frac{[\text{wt pct Me}]_{\text{incopperalloy}}}{[\text{wt pct Me}]_{\text{inslag}}}$$

where $[\text{wt pct Me}]$ and $[\text{wt pct Me}]$ denote the concentrations of trace element in copper alloy and slag, respectively. As suggested by Takeda et al. (Takeda et al., 1983), the distribution coefficient can be expressed further as:

$$L_{\text{Cu}/S}^{\text{Me}} = \frac{[\nu]_{\text{incopperalloy}}(\gamma_{\text{MeO}_\nu}P_{O_2})^{\nu/2}}{K[\nu]_{\text{inslag}}}$$

where $K$ represents the equilibrium constant of equation (1) and $\nu$

represents the total mole number of mono-cationic constituents in 100 g copper alloy and slag. $[\text{Me}]$ and $[\gamma_{\text{MeO}_\nu}]$ denote the activity coefficients of Me in copper alloy phase and MeO$_\nu$ in slag phase, respectively. By reorganizing equation (4), the logarithmic distribution coefficient can be represented as:

$$\text{Log}_{10}\frac{L_{\text{Cu}/S}^{\text{Me}}}{P_{O_2}} = \text{Log}_{10}\left(\frac{\gamma_{\text{MeO}_\nu}}{K[\nu]_{\text{inslag}}}\right) - \frac{\nu}{2}\text{Log}_{10}P_{O_2}$$

As the concentration of Me in the copper alloy and MeO$_\nu$ in the slag are quite low, thus obeying Henry’s law, the $\text{Log}_{10}\frac{L_{\text{Cu}/S}^{\text{Me}}}{P_{O_2}}$ can be regarded as a constant at a fixed temperature. $-\frac{\nu}{2}$ is the slope of the linearly fitted relationship between $\text{Log}_{10}\frac{L_{\text{Cu}/S}^{\text{Me}}}{P_{O_2}}$ and $\text{Log}_{10}P_{O_2}$ which can be used to determine the oxidation state of trace element Me in slag. The calculated logarithmic distribution coefficients of trace elements between copper alloy and slag as a function of logarithmic $P_{O_2}$ are displayed in Fig. 8. The present experimental results were also compared with the data from literature.

Compared with the other trace elements investigated in this study, the logarithmic distribution coefficient of Ag in Fig. 8(a) is rather

![Fig. 8. Logarithmic distribution coefficients of trace elements between copper alloy and slag vs. $P_{O_2}$ at 1200–1300 °C and FeO$_x$ saturation; Ag (a), Ni (b), Co (c), and Sn (d).](image-url)
scattered, ranging from 1.6 to 3.4 at 1200–1300 °C and $P_{O_2}$ of $10^{-6.5}$–$10^{-10}$ atm. This suggests that Ag was highly accumulated in the copper alloy. The present distribution coefficient values at 1200–1250 °C decreased with increasing $P_{O_2}$, as reported by Sineva et al. (Sineva et al., 2021); however, the results obtained in this study at 1300 °C remained almost constant around 2.6. The logarithmic distribution coefficient of Ag increased by approximately 0.2 units with increasing temperature from 1200 °C to 1250 °C. A depressing impact of higher temperature on $L_{Ag/C}$ was determined by Hidayat et al. (Hidayat et al., 2019), contrary to the observations by Sukhomlinov et al. (Sukhomlinov et al., 2019a). The present results at 1200 °C were on the high side of the data between molten copper and Al-Fe spinel saturated slag at 1300 °C determined by Avarmaa et al. (Avarmaa et al., 2016) at hercynite-magnetite saturation. The logarithmic distribution coefficients of Ag between copper alloy and silica-saturated iron silicate slags reported by Avarmaa et al. (Avarmaa et al., 2019) at 1300 °C were close to the present extrapolated results at 1250 °C. In another study by Avarmaa et al. (Avarmaa et al., 2020), the distribution coefficient of Ag increased with addition of CaO into slag. As for the dissolution mechanism of Ag in slags, some researchers suggested $Ag_2O_3$ (Ag$^+$) (Avarmaa et al., 2019; Kashima et al., 1978; Sukhomlinov et al., 2019a; Takeda et al., 1983; Park and Min, 1999) in slags. Avarmaa et al. (Avarmaa et al., 2020; Avarmaa et al., 2016) and Hidayat et al. (Hidayat et al., 2019) proposed a mixed valence of Ag$^+$ and Ag$^{2+}$. The slopes of the trend lines at 1200 °C and 1250 °C in this study were -0.40 and -0.39, respectively, giving an indication that Ag oxide dissolves in the slag with a combination valence of 1$+$ and 2$+$, similar to the observations by Avarmaa et al. (Avarmaa et al., 2016; Avarmaa et al., 2016) and Hidayat et al. (Hidayat et al., 2019).

The distribution coefficient of Ni in Fig. 8(b) decreased with increasing $P_{O_2}$ over the entire $P_{O_2}$ range studied. The increase of temperature from 1200 to 1300 °C favored the deportment of Ni into copper alloy, in good agreement with the observations by Sukhomlinov et al. (Sukhomlinov et al., 2019a). The present results at 1300 °C were slightly higher than the data by Klemettinen et al. (Klemettinen et al., 2018), which were determined between copper alloy and K$_2$O-free slags, but they fit well with their results for slag containing 3 wt% K$_2$O. The results by Daniczak et al. (Daniczak et al., 2021) were slightly higher compared with the present and other studies (Sukhomlinov et al., 2019a; Klemettinen et al., 2018). Klemettinen et al. (Klemettinen et al., 2018) observed that addition of K$_2$O into Al-Fe spinel saturated iron silicate slags increased the distribution coefficient of Ni between copper alloy and slag. The slope of the current trend lines at 1200–1300 °C was approximately -0.5, indicating that Ni dissolved into the slag as divalent oxide NiO, which agrees well with the results of previous studies (Kaur et al., 2009; Sukhomlinov et al., 2019a; Takeda et al., 1983; Wang et al., 1973, 1974). Reddy and Acholonu (Reddy and Acholonu, 1984) proposed that Ni dissolved in Al-Fe spinel saturated fayalite slags as a combination of Ni$^{2+}$ and Ni$^0$.

As shown in Fig. 8(c), the distribution coefficient of Co between copper alloy and slag decreased with increasing $P_{O_2}$ at all temperatures investigated. The logarithmic values of the present distribution coefficients were below zero, suggesting that Co was markedly accumulated in the slag phase. The distribution coefficient of Co decreased around 0.5 and 0.4 log units with increasing temperature from 1200 °C to 1250 °C and from 1250 °C to 1300 °C, respectively, at $P_{O_2}$ of $10^{-8}$ atm. Similar impact of temperature was also observed by Sukhomlinov et al. (Sukhomlinov et al., 2019a). The results by Daniczak et al. (Daniczak et al., 2020) were intermediate between the present results at 1250 °C and 1300 °C. The present results at 1250 °C generally fitted well with the trend line by Takeda et al. (Takeda et al., 1983). The slopes of the trend lines of the present results at 1200–1300 °C were around -0.60. This indicated that Co in the slag existed as a combination of Co$_2^{2+}$ and Co$_3^{2+}$, as the species CoO and Co$_2$O$_3$ would have slopes of 0.5 and 0.75, respectively. However, in most previous studies (Daniczak et al., 2020; Derin and Yücel, 2002; Kho et al., 2006; Reddy and Healy, 1981a,b, Ren et al., 2020, 2021; Sukhomlinov et al., 2019a; Takeda et al., 1983; Teagle et al., 2001; Yazawa, 1980; Sukhomlinov and Taskinen, 2017), Co was suggested to exist as a divalent oxide species of CoO.

Similar to the present results for Ni and Co, the distribution coefficient of Sn between copper alloy and slag displayed a decreasing trend with increasing $P_{O_2}$. Moreover, a higher temperature favored the deportment of Sn into the copper alloy phase, as reported by Nagamori and Mackey (Nagamori and Mackey, 1977). The results by Avarmaa et al. (Avarmaa et al., 2018a) at Al-Fe spinel saturation were close to the present data at 1250 °C, whereas the data between copper alloy and silica-saturated iron silicate slags by Avarmaa et al. (Avarmaa et al., 2019) are intermediate between the present results at 1250 °C and 1300 °C. It was reported by Daniczak et al. (Daniczak et al., 2021) at Al-Fe spinel saturation that the distribution coefficient of Sn increased with increasing the concentration of MgO in slags. Anindya et al. (Anindya et al., 2013) observed that the FeO/ $SiO_2$ ratio and CaO content in slags had strong impacts on the distribution coefficient of Sn. They found that the logarithmic distribution coefficient of Sn increased by approximately 0.8 with increasing the FeO/$SiO_2$ ratio from 1.0 to 1.1 and CaO content from 13.8 wt% to 21.9 wt% (Anindya et al., 2013). The slopes of the trend lines determined by Anindya et al. (Anindya et al., 2013) were close to -0.5 and they suggested that tin was present in slags as SnO. In the present study, the slopes of the trend lines at 1200–1300 °C were from -0.6 to -0.7, which suggested that tin in slags had a mixed valence of 2$+$ and 4$+$, since the species SnO and SnO$_2$ would have slopes of 0.5 and 1, respectively. Takeda et al. (Takeda et al., 1983) observed that tin preferred to concentrate in calcium ferrite slag when compared with iron silicate slag. In addition, they described that tin in calcium ferrite slags presented as SnO$_2$ at $P_{O_2}$ higher than $10^{-8}$ atm (Takeda et al., 1983). Avarmaa et al. (Avarmaa et al., 2018a) proposed that tin had a mixed valence in the Al-Fe spinel saturated FeO$_x$SiO$_{2-x}$Al$_2$O$_3$ slag but presented as SnO$_x$ in the FeO$_x$SiO$_{2-x}$Al$_2$O$_3$ slag at 1300 °C and $P_{O_2}$ of $10^{-7}$ to $10^{-8}$ atm. They also reported that tin presented as SnO in both slags over the $P_{O_2}$ range of $10^{-10}$ to $10^{-8}$ atm. Starykh et al. (Starykh et al., 2021) investigated the phase equilibria of the Fe-free Cu-Sn-Si-O system at 1180–1665 °C with tridymite/cuprite/cristobalite saturation in slags. They reported that tin existed as SnO and SnO$_2$ in slags and the total amount of tin oxide in slags decreased with increasing temperature. The loss of tin is similar to the present observations where more than 80 % was vaporized at high oxygen partial pressures at 1250 and 1300 °C during the equilibration.

3.5. Distribution coefficients between Magnetite/Wüstite and slag

As described in sections 3.2 and 3.3, trace elements dissolved into the solid magnetite/wüstite and molten slag phases to varying degrees. To have a deeper understanding of the trace element distribution mechanism in secondary copper smelting, the logarithmic distribution coefficients of trace elements between the solid magnetite/wüstite phase and molten slag were calculated and presented in Fig. 9 as a function of logarithmic $P_{O_2}$.

Fig. 9(a) indicates that Ag preferred the slag phase when compared with the solid magnetite/wüstite and the distribution coefficients at 1250–1300 °C decreased with increasing $P_{O_2}$. The logarithmic distribution coefficient results at 1200 °C showed constant value around -2. The increase of temperature from 1250 to 1300 °C increased the distribution coefficient of Ag by approximately 0.6 log units. As can be seen in Fig. 9(b), Ni distributed 2–4 times more in the solid magnetite/wüstite phase than in the molten slag. The distribution coefficients of Ni between magnetite/wüstite and slag at all temperatures investigated had a decreasing trend first and then increased with increasing $P_{O_2}$. Co displayed similar trends as Ni, however, Co distributed more into the slag phase at a certain $P_{O_2}$ which was dependent on the experimental temperature employed.

Fig. 9(d) suggests that the distribution coefficient of Sn increased with increasing $P_{O_2}$ at all temperatures. A higher temperature favored
The distribution of Sn into slag than into magnetite/wüstite. Furthermore, Sn distributed more into the molten slag phase at lower \( P_{O_2} \), depending on temperature.

The distribution of trace element between molten slag and solid magnetite/wüstite can be described by equilibrium reaction (6):

\[
(MeO_n) + \frac{v}{2}O_2 = [MeO_{n+v}]
\]  

(6)

where \((MeO_n)\) and \([MeO_{n+v}]\) represent the oxides of trace element in slag and magnetite/wüstite, respectively. Similar to the calculation for the logarithmic distribution coefficient of a trace element between copper alloy and slag, the logarithmic distribution coefficient of a trace element between magnetite/wüstite and slag can be expressed as:

\[
\log_{10}\frac{L_{Solid}}{L_{Slag}} = A + \frac{v}{2} \log_{10}P_{O_2}
\]  

(7)

where \(A\) is a constant at a given temperature. The slope, \(v/2\), of the trend line for the logarithmic distribution coefficient of a trace element between magnetite/wüstite and slag as a function of logarithmic \( P_{O_2} \) can be used to evaluate the change of valence for trace elements during their distributions between magnetite/wüstite and slag. If the trace element in slag is reduced to a lower valence state in magnetite/wüstite, the slope \(v/2\) should be negative, i.e., the logarithmic distribution coefficient of trace element between magnetite/wüstite and slag decreased with increasing logarithmic \( P_{O_2} \). On the contrary, if the trace element distributes increasingly into the magnetite/wüstite by further oxidizing the trace element species from slag, the slope should be positive, i.e., the logarithmic distribution coefficient of trace element increases with increasing \( P_{O_2} \).

Fig. 9(a) indicates that Ag was reduced to a lower valence state in magnetite/wüstite from the molten slag, independently of the slag saturation phase. In contrast, Sn was oxidized to higher valence states from the molten slag phase to magnetite/wüstite. It dissolves in iron spinels as Sn\(^{4+}\) in the octahedral sites (Berry et al., 1998). Thus, the mixed tetra- and divalent tin oxide in the slag (Avarmaa et al., 2018a, 2019; Klemettinen et al., 2019) is predominantly divalent in wüstite (FeO), and tetravalent in magnetite (Fe\(_3\)O\(_4\)). As for Ni and Co in the solid phases, both of them were reduced to lower-valent oxide species (MeO) from the molten slag when the slag was saturated with wüstite. However, they were oxidized further to higher valent species when the slag was saturated with magnetite which indicates the fact that cobalt and

![Fig. 9. Logarithmic distribution coefficients of trace elements between solid magnetite/wüstite and slag vs. \( P_{O_2} \) at 1200–1300 °C and FeO\(_x\) saturation; Ag (a), Ni (b), Co (c), and Sn (d).](image-url)
nickel (inverse spinels) in ferrite can dissolve both in octahedral and tetrahedral sites (Lu and Dieckmann, 1995; Salazar-Tamayo et al., 2019) as divalent and trivalent species. Fig. 9(b) and 9(c) suggest that a higher temperature favored the deportment of Ni and Co into wüstite but depressed their distributions into magnetite.

4. Conclusions

With a purpose of exploring the potential of recycling valuable metals from WEEE through secondary copper smelting and finding the optimal fluxing practices, the distributions of selected trace elements (Ag, Ni, Co, and Sn) between copper alloy and magnetite/wüstite-saturated iron silicate slags were investigated at 1200–1300 °C and P_{O2} of 10^{-10} to 10^{-6.5} atm using the high-temperature equilibration followed by drop-quench technique and in situ phase composition analyses.

It was found that silver was highly depleted into the copper alloy, however, cobalt markedly distributed into the slag and magnetite/wüstite phases. Nickel and tin mainly depleted into the copper alloy at lower P_{O2}, depending on the temperature. The distributions of all trace elements between copper alloy and slag investigated in this study were highly dependent on P_{O2} and temperature, and generally decreased with increasing P_{O2} and decreasing temperature which indicates that they dissolved in the slag as oxides.

By comparison of present results at magnetite/wüstite saturation in slag and the previous data (Avarmaa et al., 2018a; Katri Avarmaa et al., 2019; K. Avarmaa et al., 2019; Daitzak et al., 2021; Hidayat et al., 2019; Sukhominov et al., 2019a; Avarmaa et al., 2016) at Al-Fe spinel/silica-saturation, it can be concluded that the type of slag saturation has a small impact on the distribution coefficients of trace element between copper alloy and slag. Cobalt and nickel concentrations in magnetite and wüstite were high and they favored the solid phases compared to their dissolution concentrations in slag. The trace element distribution measurements in the magnetite and wüstite phases also indicated that their speciations are in the slag and the solid oxide primary phases. The present results indicate that the trace elements from WEEE can be effectively recovered into the copper alloy through secondary copper smelting route and their recoveries can be improved by increasing temperature and lowering P_{O2}.

From the perspective of industrial practices, e.g., the WEEE processing in a TSL furnace, the improvement of the recoveries of trace elements can be handled by adjusting the injection of fuel to air/oxygen ratio into the furnace through the submerged lance. The present observations also confirmed the substantial vaporization tendencies of some trace elements reported earlier (Avarmaa et al., 2019; Starykh et al., 2021).

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References

Marinelli, S., Gamberini, R., 2021. Multi-criteria decision making approaches applied to waste electrical and electronic equipment (WEEE): a comprehensive literature review. Toxics 9 (1), 13. https://doi.org/10.3390/toxics9010013.

Ibanescu, D., Cailean, D., Teodosiu, C., Fiore, S., 2018. Assessment of the waste electrical and electronic equipment management systems profile and sustainability in developed and developing European Union countries. Waste Manage. 73, 39–53. https://doi.org/10.1016/j.wasman.2017.12.022.

Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment, WEEE. Official Journal of the European Union L 197, 37-81. Accessed at: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32012L0019&from=EN.

Messmann, L., Helbig, C., Thorenz, A., Tumas, A., 2019. Economic and environmental benefits of recovery networks for WEEE in Europe. J. Cleaner Prod. 222, 655-668. https://doi.org/10.1016/j.jclepro.2019.02.244.

Zhang, L., Xu, Z., 2016. A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. J. Cleaner Prod. 127, 19–36. https://doi.org/10.1016/j.jclepro.2016.04.004.

Wang, M., Tan, Q., Chiang, J.F., Li, J., 2017. Recovery of rare and precious metals from urban mines-A review. Frontiers of Environmental Science & Engineering 11 (5), 1-17. https://doi.org/10.1007/s11783-017-0963-1.

Cesario, A., Marra, A., Kuchta, K., Belgıorno, V., Van Hullebusch, E.D., 2018. WEEE management in a circular economy perspective: An overview. Global Nest Journal 20, 743-750.

Cui, J., Zhang, L., 2008. Metallurgical recovery of metals from electronic waste: A review. J. Hazard. Mater. 158 (2-3), 228–256. https://doi.org/10.1016/j.jhazmat.2008.02.001.

Yazawa, A., 1980. Distribution of various elements between copper, matte and slag. J. Metall. Inst. 809. 795–809. https://doi.org/10.1080/09510080.1980.10865067.

Shuva, M.A.H., Rhamdani, M.A., Brooks, G.A., Masood, S., Reuter, M.A., 2016. Thermodynamics data of valuable elements relevant to e-waste processing through primary and secondary copper production: a review. J. Cleaner Prod. 131, 795–809. https://doi.org/10.1016/j.jclepro.2016.04.061.

Lehnert, T. (1999). Integrated recycling of non-ferrous metals at Boliden Ltd., Roslagskvarn smelter. In: Proceedings of IEEE International Symposium on Electronics and the Environment, Oak Brook, IL, USA, pp. 42-47.

Veldhuizen, H., Sippel, B., 1994. Mining discarded electronics. Industry and Environment. 17 (3), 7-11.

Hagelüken, C., 2006. Recycling of electronic scrap at Umicore’s integrated metals smelter and refinery. Enreslett 59 (3), 152-161.

Hagelüken, C., Corti, C.W., 2010. Recycling of gold from electronics: Cost-effective use through ‘Design for Recycling’. Gold Bull. 43 (3), 209-220. https://doi.org/10.1007/BF02414988.

Lennartsson, A., Engström, F., Samuelsson, C., Björkman, B., Pettersson, J., 2018. Large-scale WEEE recycling integrated in an ore-based Cu-extraction system. Journal of Sustainable Metallurgy 4 (2), 232-232. https://doi.org/10.1007/s40831-018-0157-5.

Flores, G.R.A., Nikolic, S., Mackey, P.J., 2014. ISASMELT™ for the recycling of E-scrap and copper in the US case study example of a new compact recycling plant. JOM 66 (5), 832-832. https://doi.org/10.1007/s11837-014-0965-5.

Brusselaers, J., Mark, F.E., Tango, L., 2006. Using metal-rich WEEE plastics as feedstock/fuel substitute for an integrated metals smelter. Plasteurope, Brüssel, Belgium.

Khalig, A., Rhamdani, M.A., Brooks, G., Masood, S., 2014. Metal extraction processes for electronic waste and existing industrial routes: a review and Australian perspective. Resources 3 (1), 152-179. https://doi.org/10.3390/resources3010052.

Tesfaye, F., Lindberg, D., Hamuyuni, J., Taskinen, P., Hupa, L., 2017. Improving urban mining practices for optimal recovery of resources from e-waste. Miner. Eng. 111, 209-221. https://doi.org/10.1016/j.mineng.2017.06.018.

Anindya, A., Swinbourne, D., Reuter, M., & Matusewicz, R. (2009). Tin distribution during smelting of WEEE with copper scrap. In Proceedings of the European Metallurgical Conference EMC 2009, Innsbruck, Austria, 28 June-1 July 2009; GDMB Verlag GmbH: Clausthal-Zellerfeld, Germany, 2009; pp. 555-566.

Shuva M.A.H., Rhamdani M.A., Brooks G.A., Masood S., Reuter M.A., & Firdaus M. (2017). Analysis for optimum conditions for recovery of valuable metals from E-waste through black copper smelting. In: 8th International Symposium on High-Temperature Metallurgical Processing (Ed. J.Y. Hwang et al.); TMS, Warrendale (PA), pp. 419-427. https://doi.org/10.1007/978-3-319-51340-9_41.
Avarmaa, K., Yliaho, S., Reddy, R.G., Healy, G.W., 1981. The Solubility of cobalt in Cu2O-CoO-SiO2 Slags in Reddy, R.G., Healy, G.W., 1981. Distribution of cobalt between liquid copper and copper...In: Proceedings of the European Metallurgical Conference EMC 2017, vol 4, June 25-28, Leipzig, Germany. GDBM, Clausthal-Zellerfeld, 2017, 1485-1500.

Nagamori, M., Mackey, F.A., 1973. The distribution of cobalt between Co-Cu alloys and Al2O3-SiO2-MnO slags. Metallurgical and Materials Transactions B 5 (1), 261.

Derin, B., Yücel, O., 2002. The distribution of cobalt between Cu-Cu alloys and Al2O3-Fe2O3-SiO2 slags. Scand. J. Metall. 31 (1), 12-19. https://doi.org/10.1080/03017040101651452.

Nagamori, M., Mackey, F.A., 1973. The distribution of cobalt between Co-Cu alloys and Al2O3-SiO2-MnO slags. Metallurgical and Materials Transactions B 5 (1), 261.

Derin, B., Yücel, O., 2002. The distribution of cobalt between Cu-Cu alloys and Al2O3-Fe2O3-SiO2 slags. Scand. J. Metall. 31 (1), 12-19. https://doi.org/10.1080/03017040101651452.

Nagamori, M., Mackey, F.A., 1973. The distribution of cobalt between Co-Cu alloys and Al2O3-SiO2-MnO slags. Metallurgical and Materials Transactions B 5 (1), 261.

Derin, B., Yücel, O., 2002. The distribution of cobalt between Cu-Cu alloys and Al2O3-Fe2O3-SiO2 slags. Scand. J. Metall. 31 (1), 12-19. https://doi.org/10.1080/03017040101651452.
Hidayat, T., Chen, J., Hayes, P.C., Jak, E., 2021. Distributions of As, Pb, Sn and Zn as minor elements between iron silicate slag and copper in equilibrium with tridymite in the Cu-Fe-O-Si system. Int. J. Mater. Res. 112 (3), 178-188. https://doi.org/10.1515/ijmr-2020-7857.

Hidayat, T., Chen, J., Hayes, P.C., Jak, E., 2019. Distributions of Ag, Bi, and Sb as minor elements between iron-silicate slag and copper in equilibrium with tridymite in the Cu-Fe-O-Si system at T = 1250 °C and 1300 °C (1523 K and 1573 K). Metallurgical and Materials Transactions B 50 (1), 229-241. https://doi.org/10.1007/s11663-018-1448-8.

Sineva, S., Shishin, D., Starykh, R., Hayes, P.C., Jak, E., 2021. Equilibrium distributions of Pb, Bi, and Ag between fayalite slag and copper-rich metal, calcium ferrite slag and copper-rich metal. In: thermodynamic assessment and experimental study at 1250 °C. Journal of Sustainable Metallurgy. https://doi.org/10.1007/s40831-021-00360-4.

Park, J. H., & Min, D. J. (1999). Quantitative analysis of the relative basicity of CaO and BaO by silver solubility in slags. Metallurgical and Materials Transactions B, 30(4), 689-694.

Kaur, R.R., Swinbourne, D.R., Nexhip, C., 2009. Nickel, lead and antimony distributions between ferrous calcium silicate slag and copper at 1300 °C. Mineral Processing and Extractive Metallurgy 118 (2), 65-72. https://doi.org/10.1179/174328569X38389C.

Reddy, R.G., Acholonu, C.C., 1984. Distribution of nickel between copper-nickel and alumina saturated iron silicate slags. Metall. Trans. B 15 (1), 33-37.

Starykh, Roman, Shevchenko, Maksym, Shishin, Denis, Jak, Evgeni, 2021. Experimental study and thermodynamic modeling of the Ca-Sn-Si-O system and sub-systems. Calphad 74, 102312. https://doi.org/10.1016/j.calphad.2021.102312.

Avarmaa, K., Yliaho, S., Taskinen, P., 2018a. Recoveries of rare elements Ga, Ge and Sn from waste electric and electronic equipment through secondary copper smelting. Waste Manage. 71, 400-410. https://doi.org/10.1016/j.wasman.2017.09.037.

Berry, F.J., Skinner, S.J., Helgason, O., Bilboeirov, R., Marco, J.F., 1998. Location of tin and charge balance in materials of composition Fe3-xSnxO4 (x < 0.3). Polyhedron 17 (1), 149-152. https://doi.org/10.1016/S0277-5387(97)00212-X.

Lu, F.H., Dieckmann, R., 1995. Point defects in oxide spinel solid solutions of the type Co, Fe, MgO4 at 1200 °C. J. Phys. Chem. Solids 56 (5), 725-733. https://doi.org/10.1016/0022-3697(94)00187-1.

Salazar-Tamayo, H., Garcia, K.E., Barrero, C.A., 2019. New method to calculate Mössbauer recoilless f-factors in NiFe2O4. Magnetic, morphological and structural properties. J. Magn. Magn. Mater. 471, 242-249. https://doi.org/10.1016/j.jmmm.2018.09.066.