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Recoveries of rare elements Ga, Ge, In and Sn from waste electric and electronic equipment through secondary copper smelting

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ABSTRACT

The recycling and recovery of valuable metals from waste materials is one of the key issues in maintaining the sustainability of base and rare metals. Especially WEEE (Waste Electric and Electronic Equipment) can be considered as a high potential resource for a number of valuable and critical metals like gallium, germanium and indium. During the mechanical processing of WEEE, these metals are primary separated into the non-ferrous scrap fractions, including copper fraction. As a consequence, the behavior of these valuable metals and the possibility of their recycling in secondary copper smelting are of great interest. This study experimentally investigates the distribution behavior of indium, gallium, germanium and tin between metallic copper and lime-free / lime-containing alumina iron silicate slags ($L^{Cu/s}[Me] = [Me]_{Copper}/(Me)_{Slag}$), as well as between solid Al-Fe spinel and slags ($L^{sp/s}[Me] = \{Me\}_{spinel}/(Me)_{slag}$). Moreover, the copper-slag-spinel equilibrium systems are examined. The experiments were executed simulating high alumina-bearing copper scrap smelting in typical black copper smelting conditions of $pO_2 = 10^{-10}–10^{-5}$ atm (1 atm = 1.01325 × 10^5 Pa) and T = 1300 °C. The experimental technique employed utilized a highly advanced equilibration-rapid quenching method followed by Electron Probe Micro-Analysis (EPMA).

The results show that tin and indium can be efficiently recovered into the copper phase in reducing process conditions (pO_2 below 10^{-7} atm), whereas gallium dissolved preferentially into the solid spinel phase in all conditions examined. Gallium dissolution into slag and spinel was found to occur as $GaO_{1.5}$, whereas indium in spinel was determined to be as $InO_{1.5}$. In addition, germanium was seen to distribute preferentially into the copper phase with $L^{Cu/s}[Ge] = 2–4$, although its concentrations in all phases present were relatively low. Thus, the main route for germanium can be considered to be vaporization.

1. Introduction

Currently, the mechanically separated and sorted copper scrap fraction of WEEE is treated mainly through pyrometallurgical processing followed by hydrometallurgical refining. One dominant pyrometallurgical method is black copper smelting, which is a commonly used and flexible technique for handling complex and impure raw materials in controlled metal-slag-gas conditions (Ghodrat et al., 2016; Outotec, 2011). While the metal produced by these methods is mainly copper and the slag is normally an iron silicate type, the exact compositions of these liquid phases are highly dependent on the raw materials and additives used in the process. Aluminum is one of the most common impurity metals in the copper scrap fraction and thus also in black copper smelting. The level of Al impurity can vary from less than 1 wt.% up to 10 wt.%, depending on the WEEE composition and the chosen processing methods (Andersen and Thomsen, 2012; Khaliq et al., 2014; Veit et al., 2006). Even with advanced techniques such as Eddy Current Separation (Meier-Staude et al., 2002), some portion of aluminum will end up in the copper fraction either as multi-metal pieces, wrapped inside another metal or through insufficient liberation. As aluminum easily oxidizes into alumina (Al_2O_3) during copper smelting, it becomes part of the slag phase and as a result influences the slag properties and minor element behavior in the slag (Kim and Sohn, 1998; Klemettinen et al., 2017b). This study focuses on the behavior of elements-of-concern and new in the black copper smelting circuits: gallium (Ga), germanium (Ge), indium (In) and tin (Sn).

The aforementioned elements are typical and highly critical metals for EEE (Electric and Electronic Equipment), e.g. tin in solders, germanium in fiber optics, indium in transparent electrodes and gallium in semiconductors. Overall, the main end-use-sector of Ga, Ge and In is in EEE, consuming over 90% of the total

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production of each metal (Licht et al., 2015; Paradis, 2015), whereas Sn in EEE utilizes between 50 and 60% of the total production (ITRI, 2011; USGS, 2014). Due to the natural scarcity of Ga, Ge and In and their crucial role in EEE production, they are currently ranked as some of the most critical elements in the EU (EC-European Commission, 2010; EU Commission, 2014). Tin has also been included in the newest report (EU Commission, 2014) and is alarmingly approaching a potential supply risk, while in the US, tin is listed as a conflict material (Anderson, 2017). Currently, the recycling rates of all these metals are extremely low (Reck and Graedel, 2012; Ueberschaar et al., 2017) and in order to meet the future demands, a systematic change in their recycling habits is needed.

Shuva et al. (2016a) have collected the existing trace element distribution studies concerning primary and secondary copper smelting in their review paper. They reported that only Anindya et al. (2014, 2013) have so far investigated trace elements (In and Sn) in the secondary copper smelting conditions. In addition, the authors have recently published data on minor element behavior in secondary copper smelting with alumina bearing slags (Avarmaa et al., 2017, 2016; Klemettinen et al., 2017a). Nevertheless, studies made in converting conditions (Cu–slag systems) can also be used as preliminary information.

In general, a very limited amount of literature and research exists on indium, gallium, germanium and tin behavior within the copper smelting process steps. Previous studies on gallium, tin and indium behavior in copper smelting have been presented in more detail elsewhere (Avarmaa et al., 2017; Shuva et al., 2016a). Germanium behavior was investigated by Shuva et al. (2016b) in the copper-FeO_x-SiO_2-CaO-$MgO_{sat.}$ system at temperatures between 1200 and 1350 °C with a pO_2 range of 10^{-10}–10^{-7} atm. Their distribution coefficient results show a dependency with the oxygen pressure, temperature and basicity of the slag. A computational study by Nakajima et al. (2011) defined $L^{Cu/s}$[Ge] (mol/mol) as 10^{-4} at 1300 °C and pO_2 10^{-6} atm, whereas also two experimental studies on germanium behavior in lead smelting can be found (Henao et al., 2010; Yan and Swinbourne, 2003). The results from both studies were quite similar as germanium was observed to distribute preferentially into the slag. However, Yan and Swinbourne (2003) suggested that the dissolution mechanism is the GeO form in slag, while Henao et al. (2010) proposed an oxidation state of GeO_2.

The purpose of the present study is to investigate, for the first time, the distribution behavior of rare elements gallium, germanium, indium and tin between molten copper and alumina-bearing iron silicate and iron-calcium-silicate slags under secondary copper smelting conditions ($pO_2 = 10^{-10}$–10^{-5} atm and 1300 °C). Furthermore, the equilibria within the copper-slag-spinel system are also examined.

2. Waste management in black copper smelting

Waste management is crucial at every step of copper production and approximately 80% of the total energy is utilized during the mining and beneficiation steps, depending on the ore grade (Marsden, 2008). Consequently, less than 20% of the related total carbon footprint results from smelting or other copper making operations, thus the opportunity to make use of secondary metallic raw materials is an attractive one, both in terms of waste reduction and overall environmental impact.

The new type of mixed secondary copper feed used in copper production is mainly based on WEEE, which contains a wide spectrum of metals as well as inorganic and organic components (Cucciella et al., 2015; Zhang et al., 2017; Wang et al., 2017). This complexity requires proper processing in order to maximize the metal value yields and to avoid formation of harmful or even poisonous side streams. One such issue – the illegal combustion of WEEE in order to burn its plastic residues – is commonly practiced in various locations around the world (Buekens and Yang, 2014; Sepulveda et al., 2010). Such operations do not involve either process control or treatment of the off-gases produced and are known to generate unknown and uncontrolled volumes of POPs (persistent organic pollutants), like dioxins and other related substances (Buekens and Yang, 2014; Hagelücken, 2006b).

A typical secondary smelting used for oxidized low-grade copper scraps is black copper smelting that corporates three stages: reduction, oxidation and fire refining. As previously shown by Ghodrat et al. (2016, 2017), multiple side streams are produced at every smelting stage with the most typical ones being slag, gas, dust and a possible solid phase. All of these side streams are treated and managed separately with their specific practices.

The main gas emission from the primary copper smelting is sulfur dioxide, which is treated, captured and recovered efficiently as sulfuric acid in modern copper smelting plants (Kojo and Storch, 2006). As black copper smelting is almost sulfur-free process, the sulfur dioxide production is much less than in primary copper smelting. However, WEEE based copper smelting has the potential to generate toxic emissions, such as aromatic hydrocarbons, dioxins and furans (Hense et al., 2015; Tsydenova and Bengtsson, 2011) that originate from plastics that contain chlorine or bromine (Yu et al., 2017). Nevertheless, if the smelting operation and its gas train are designed and controlled properly, the probability for these types of emissions is low (Hense et al., 2015; Kojo and Storch, 2006; Morf et al., 2005; Ni et al., 2012).

At typical copper smelting temperatures, the halogen-bearing organics are decomposed to their elemental form. The key question in secondary copper smelting is therefore the off-gas train, which must be capable to properly cool process gas and adjust its oxygen content so that the formation of POPs is not possible, independent of whether the WEEE feed is smelted separately (Lehner, 2007) or directly with the other feed components (Navazo et al., 2014).

The most voluminous side stream in the copper industry is the smelting and refining slag, which currently only has limited use as a construction material depending on the slag cleaning technology used (Piatak et al., 2015). In black copper smelting all slag passes through the reductive blast furnace or similar processing step (Ghodrat et al., 2017), a feature that improves the usability of copper slags.

Numerous rare and valuable non-ferrous metals, such as Au, Ag, PGMs, Ga, In and Sn, end up in the mechanically separated copper scrap fraction, which is further processed in the secondary copper smelter. Depending on their thermodynamic properties as well as the process conditions and practices, such metals will subsequently distribute between the existing process streams. The recoveries of valuable elements can be improved, if their properties are characterized, and they are systematically processed with state-of-the-art technologies (Hagelücken, 2006b).

3. Material and methods

Equilibria experiments between copper alloy, slag and gas were executed in a similar manner to those outlined in previous papers (Avarmaa et al., 2017; Klemettinen et al., 2017b). The technique is highly advanced, as the quenching occurs very quickly by dropping the sample from the hot zone of a vertical tube furnace directly into an ice water mixture. Moreover, the phase compositions were measured with direct phase analyzer EPMA. As a result, there was no need for bulk analyses or physical separation of the phases present, therefore the true chemical solubilities without possible inclusions could be measured from each phase.

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