



Distributions of lithium-ion and nickel-metal hydride battery elements in copper converting



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ABSTRACT

Waste batteries, such as rechargeable Lithium-ion and Nickel-Metal Hydride batteries, are important secondary raw materials. They contain considerable amounts of valuable metals, like Ni, Co, Cu, Mn, rare earth elements (REE) and Li. Recovery of these metals from waste streams is vital to decrease the primary production, increase resource efficiency and mitigate against future supply risk. Especially, as the consumption of rechargeable batteries is estimated to rise significantly and the current recovery rates are extremely low. Pyrometallurgical processing, such as secondary copper smelting, offers potentially an effective recovery route for a number of the key elements. Based on the fact that different trace elements have characteristic thermodynamic properties, they distribute in different material streams during pyrometallurgical processing, i.e. metal, matte, slag, magnetite, with different ratios. In particular, solubilities of trace elements in the primary magnetite phase have been properly investigated for the first time. Furthermore, fundamental data about the distributions of Li, Mn, and REE's in copper processing are also subject of speculation. The present study ascertains the distributions and deportments of battery elements during copper converting, between temperatures 1200 and 1275 °C. The thermodynamic data measured as a part of this study will provide basics and solid guidelines for the recovery of the studied trace elements in the industrial copper smelting and converting processes.

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1. Introduction

1.1. Overview

The increasing consumption of electronics, implementation of hybrid and electric vehicles into the daily life and the global transition from fossil fuels to renewable energy sources result in a significant rise of demand for electric storage devices in the future (Thackeray et al., 2012). In particular, secondary rechargeable batteries based on Li-ion and NiMH (nickel-metal hydride) chemistries appear to offer the necessary characteristics like manufacturability, power density, scalability and economic cost to meet the predicted future demand (Al-Thyabat et al., 2013; Sullivan and Gaines, 2010). Currently, pyrometallurgical processing, or smelting of battery

waste is a widely used method for the recovery of base metals like copper, cobalt and nickel. In many cases, pyrometallurgical steps combined with both mechanical separation and hydrometallurgical processing are used in order to improve the yields of recovery (Al-Thyabat et al., 2013; Granata et al., 2012). The waste material stream from Li-ion and NiMH batteries contains considerable amounts of recoverable metals including Ni, Co, Cu, Fe, Mn, Li and rare earth elements (REE, mostly La, Ce, Nd and Pr) (Granata et al., 2012; Reuter et al., 2013; Tang et al., 2013). Among these metals, cobalt and REE's are currently in the EU's list of critical raw materials, and REE's are classified as having the highest supply risk of all (EU Commission, 2014).

At the present, the base metals efficiently recovered from battery waste include Ni, Co and Cu by a combined pyro-hydro processing route (Al-Thyabat et al., 2013). In contrast, the recoveries of Li and REE's are virtually non-existent and consequentially, most of these valuable materials end up in the discard slag during smelting (Reuter et al., 2013; Cheret and Santen, 2007). Recovery of REE's

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from battery waste is highly important not only to lessen the potential supply risk for numerous high-end technologies, but also to minimise environmental impact of the primary REE extraction and to fix the current REE balance problem (Le et al., 2016; Heegn et al., 2003). Up to date lithium is not considered as a critical element of EU, however if the trend for lithium demand continues on the present level and recycling rates stay low, by 2050 lithium scarcity could be a major problem (Hanisch et al., 2015; Weil and Ziemann, 2014).

Pyrometallurgical methods just for Li-ion and NiMH batteries have been developed and today are applied successfully in the recovery of most their elements (Cheret and Santen, 2007). Nevertheless, battery waste is also widely used as a locally available, secondary raw material for primary smelters/refineries where the intention is recovery of only the main base metal or metals. The remaining materials are impurities allowed to distribute to the slag phase and thus removed from the metal stream. The reasoning for this is often related to low scrap volumes, transportation cost, low metals prices and high cost of developing specific technologies to deal with constantly changing battery waste stream assays. In addition, integrated batteries, i.e. those found in laptops or mobile phones, also often end up in WEEE (Waste Electronic and Electrical Equipment) recycling and are typically processed in the copper smelting route (Shuva et al., 2016).

1.2. Pyro-copper processing

In terms of pyrometallurgical recovery, it is most desirable that the valuable elements accumulate into the metal or matte for further extraction. Nonetheless, most of the trace elements of this study are generally dissolved in the slag, with the exception of silver, which has a high compatibility with copper. In the primary copper smelting, Cu-Fe-S concentrates (20–30 wt% Cu) are processed to copper matte (50–70 wt% Cu) by oxidising most of the iron and sulphur (Schlesinger et al., 2011). Silica flux is used for creating molten slag where iron and oxidised impurities dissolve. Copper making is done subsequently in Peirce-Smith converters where oxygen enriched air is blown to transform matte to blister copper (~99 wt% Cu), by oxidation of the remaining iron and sulphur. Secondary raw material such as copper rich battery waste is charged into the converter and it favorably cools down the overheated melt. During oxygen blow in copper converting, solid magnetite phase is frequently formed as a result of iron oxidation (Schlesinger et al., 2011). Thus, in the process conditions, the five condensed phases typically present in the final converting stage, where copper is formed, are metal, matte ('white metal'), slag in tridymite and/or magnetite saturation. The final distributions of trace elements between the phases in that stage determine which are in the end recovered to the metal phase, and which are lost in the slag (Johnson et al., 1979).

1.3. Previous literature

In general, only limited information is currently available as to the distribution characteristics of these trace elements between the different phases present in copper converting conditions. Overall, the copper converting process has been the subject of few scientific studies and to the best of authors' knowledge, there are currently no papers related to metal-matte-slag equilibria with simultaneous silica-magnetite saturation. There are several studies focusing on metal-slag (Hidayat et al., 2016) and matte-slag (Hidayat et al., 2016; Avarmaa et al., 2015; Takeda, 1997) equilibria and metal-matte-slag-tridymite equilibria (Chen et al., 2016; Kashima et al., 1978). Also, Elliott (1976) compiled a comprehensive review of the Cu-Fe-O-S-SiO₂ phase relations relevant to copper converting

conditions. A small number of distribution studies of Ni, Co and Ag as trace elements in closely related conditions, in magnetite or silica saturation, has been done, but the most relevant to this study has been performed by Kashima et al. (1978) with metal/matte/slag in silica saturated iron-silicate slags.

1.4. Aim of the study

The purpose of this study is not to outline entirely new recycling methods for Li-ion and NiMH batteries, but rather to provide accurate thermodynamic information of the battery trace element distributions (Ni, Co, Li, Mn, Nd and Ag) between different phases in the relevant copper converting process environments. The distribution behaviors of trace elements are fundamental for process development and accurate distribution data can be used in process evaluations and optimisation. Furthermore, the distributions of such trace elements between the slag and magnetite have not been studied previously and would provide valuable information in terms of copper slag beneficiation and the separation of magnetite from the fayalite-type slag (Fan et al., 2016; Guo et al., 2016).

2. Materials and methods

The experimental approach employed was comprised of equilibration of samples at 1200, 1225, 1250 and 1275 °C followed by rapid quenching, and compositional phase analysis using Electron Probe X-Ray Microanalysis (EPMA) and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). By this method, it is possible to study the high temperature compositions of the equilibrium phases at room temperature. The equilibrium composition remains unchanged by rapid quenching.

The experimental conditions used were controlled by temperature and the silica-magnetite double saturation of the slag and metal-matte saturation, which reduce the degrees of freedom of the system to nil. Thus, we have in isothermal conditions a fixed sulphur pressure and oxygen pressure in the base equilibrium system Cu-Fe-O-S-SiO₂, see Fig. 1. Each additional trace element introduced in the system to metal, matte or slag brings one new degree of freedom, which in this study is measured as distribution coefficients of the element between the phases.

2.1. Materials

Pure starting materials, see Table 1, were used to generate the thermodynamic system under the final copper converting conditions, where metal (copper) and matte ('white metal') phases are present together with an iron silicate slag that is double saturated with solid silica and magnetite. The samples prior to equilibration consisted of five main constituents: Cu powder, Cu₂S powder, a pre-melted iron-silicate slag, Fe₃O₄ powder and SiO₂. The starting composition of all samples was identical.

The trace elements in our experiments were selected for their relevance in the Li-ion and NiMH battery chemistries. The studied trace elements were introduced in the system in form of Ni, Co, MnO, Nd₂O₃, Li-silicate and Ag, as presented in Table 1. Silver was added to the sample on the level of ≈ 1 wt % determined from total mass of metal and matte, and all the others ≈ 1 wt % of the total mass of slag and magnetite.

Although silver is not present in Li-ion or NiMH batteries, it was selected as a trace element as it is one of the most studied trace element in copper processing and occurs naturally in copper ores. Furthermore, primary silver-oxide batteries' silver fraction can also be offered for recovery in traditional copper processing.

Neodymium (III) oxide Nd₂O₃ was chosen to represent REE's during high temperature processing in this study as the chemical

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