The selective alkaline leaching of zinc oxide from Electric Arc Furnace dust pre-treated with calcium oxide

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ABSTRACT

Zinc ferrite ($ZnFe_2O_4$), one of the major forms of zinc in Electric Arc Furnace (EAF) dust, is very difficult to chemically dissolve in aqueous solutions. In our previous work, a pretreatment process referred to as "CaO treatment" was proposed as a key technology for transforming the $ZnFe_2O_4$ in EAF dust to ZnO and $Ca_2Fe_2O_5$ without carbothermic reduction. Because this CaO treatment also enables the preferential removal of chloride, fluoride and heavy metals during heating with essentially no evaporation loss of zinc or iron, the CaO treated product, or "CaO treated dust", consists mainly of ZnO and $Ca_2Fe_2O_5$, and contains no chloride, fluoride or heavy metals. Zinc leaching, which involves dissolving ZnO into either acidic or alkaline solutions, makes it possible to recover zinc from the CaO treated dust. In this study, the feasibility of the alkaline leaching of CaO treated dust was investigated using a NaOH solution for the selective leaching of zinc over iron and calcium, and the effect of temperature, reaction time, NaOH concentration and solid/liquid (S/L) ratio were examined. It was found that significantly more zinc was extracted from the CaO treated dust than the as-supplied raw dust by the NaOH solution. Nearly complete zinc extraction from the CaO treated dust was achieved without any notable dissolution of iron and calcium, which remained as $Ca_2Fe_2O_5$ and $Ca_3Fe_2(OH)_{12}$ in the leach residue. These residues can be supplied to the steel making industry as flux for the dephosphorization of hot metal or a raw material for the blast furnace.

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1. Introduction

Iron scrap is melted at temperatures above 1600 °C during Electric Arc Furnace (EAF) production, and some iron together with metallic compounds, including volatile components such as zinc, lead cadmium and halides, are recovered in the gas cleaner system as EAF dust (Leclerc et al., 2003; Havlík et al., 2006; Pickles, 2010; Martins et al., 2008). While iron and zinc oxides are the main components in EAF dust, their content varies widely depending on the operating conditions, including the characteristics of scrap charged in the furnace, the operating period, and the specifications of the steel produced (Orhan, 2005; Salihoglu and Pinarli, 2008; Pereira et al., 2007). In general, approximately 10–20 kg of EAF dust is generated during the production of 1 ton of crude steel. As the volume of steel produced by EAF rises over time, the volume of EAF dust will also increase (Dutra et al., 2006; Oustadakis et al., 2010).

Because EAF dust is categorized as hazardous waste, dust treatment is important to recover zinc and to protect the environment. There have

been several different methods proposed for the recovery of zinc from EAF dust, including a pyrometallurgical process, a hydrometallurgical processes and a hybrid process (thermal reduction followed by leaching) (Leclerc et al., 2003; Ruiz et al., 2007). Among them, the method commonly employed worldwide is the pyrometallurgical Waelz process (Pickles, 2008, 2009). From both environmental and economic perspectives, this process has some problems: it requires carbon as the reducing agent and the use of relatively high temperatures to produce crude ZnO, which has little commercial value and requires further purification (Itoh et al., 2008; Nakajima et al., 2008; Tsubone et al., 2012).

The advantage of the hydrometallurgical process for the recovery of zinc from EAF dust is its low energy consumption (Leclerc et al., 2003). The leaching of ZnO is possible in either an alkaline or acidic media. On the other hand, the majority of zinc in EAF dust is in the form of $ZnFe_2O_4$. Because this compound is very stable and insoluble in alkaline or acidic media under moderate conditions, the zinc leaching efficiency using the hydrometallurgical process is very low (Langová et al., 2009). The zinc leaching efficiency from EAF dust by conventional leaching methods using NaOH solution has been reported as 9–85% while high concentration and high temperature are required to achieve high recovery ratio (Orhan, 2005; Dutra et al., 2006; Antrekowitsch and Antrekowitsch, 2001; Youcai and Stanforth, 2000a, 2000b; Xia and Pickles, 1999,

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2000; Caravaca et al., 1994). The conventional sulfuric acid leaching of zinc from EAF dust offers a low leaching efficiency of 75–80% (Pickles, 2010; Antrekowitsch and Antrekowitsch, 2001; Cruells et al., 1992; Havlík et al., 2005). It should be noted, however, that the chloride and fluoride in the dust are problematic (Leclerc et al., 2003).

A new, more efficient EAF dust treatment process based on CaO addition method for EAF dust treatment is proposed in the present study, which is more environmentally friendly and less costly, compared to the conventional process. The proposed CaO addition is conducted during pre-treatment step in which the $ZnFe_2O_4$ in EAF dust is reacted with CaO and converted to ZnO and $Ca_2Fe_2O_5$ without carbothermic reduction. The reaction proceeds at a relatively low reaction temperature of 900 to 1100 °C with a short treatment time of less than 3 h. Besides removing the zinc, CaO treatment also enables the preferential removal of chloride and fluoride and heavy metals during heating with no essential evaporation loss of zinc and iron (Itoh et al., 2008; Nakajima et al., 2008; Tsubone et al., 2012; Nagasaka et al.; Chairaksa et al., 2010; Chairaksa-Fujimoto et al., 2015, Miki et al., 2016). The conversion of $ZnFe_2O_4$ in the EAF dust to ZnO by CaO treatment is the key to solving the problem of insoluble $ZnFe_2O_4$ in the EAF dust in the hydrometallurgical process.

The principle flow sheet of the new approach for recovering zinc from EAF dust is given in Fig. 1. In this study, a thermodynamic analysis was carried out, and the feasibility of zinc alkaline leaching from the CaO treated dust with the aim of recovering zinc was investigated. Sodium hydroxide was chosen as the leaching agent for the selective dissolution of zinc (Eq. (1)), because it does not result in the dissolution of iron and calcium.
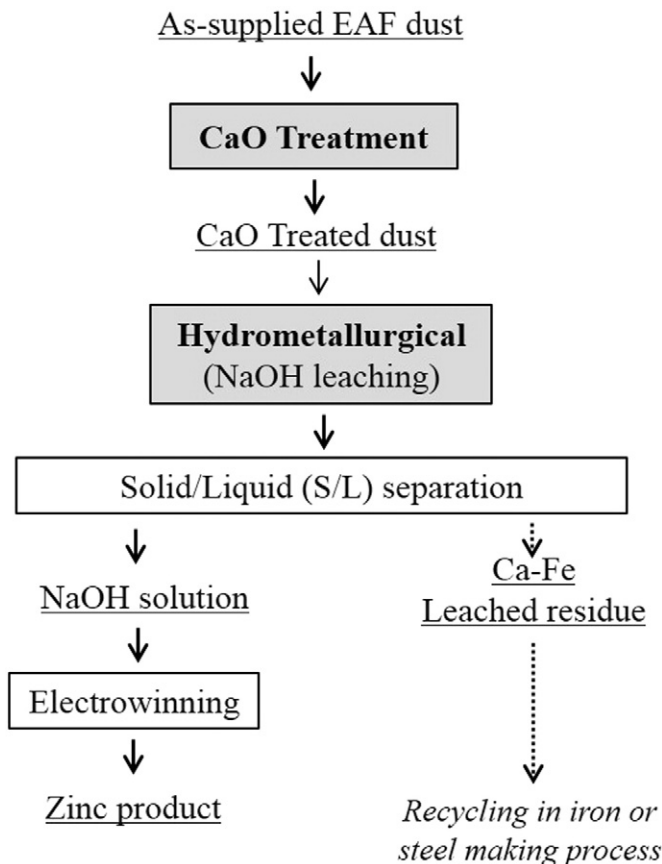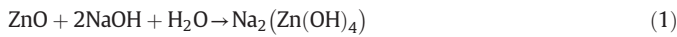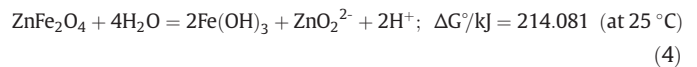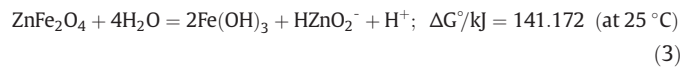
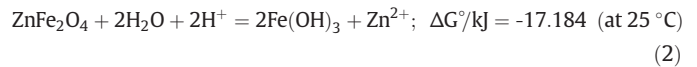$$ZnO + 2NaOH + H_2O \rightarrow Na_2(Zn(OH)_4) \qquad (1)$$

Fig. 1. Flowsheet of the new process to recover zinc from EAF dust.

The effect of reaction time, temperature, NaOH concentration and the solid/liquid (S/L) ratio were examined.

2. Theoretical background

The solubility of Fe_2O_3 or $Fe(OH)_3$ in water is much lower than that of ZnO (Pourbaix, 1966). Hence, it can be reasonably assumed that the Fe(III) concentration in water is at saturation level when iron is leached from $ZnFe_2O_4$ into water. The solubility of Zn(II) in water is calculated assuming that $ZnFe_2O_4$ and $Fe(OH)_3$ coexist.

The chemical potentials for $ZnFe_2O_4$, H_2O, H^+, $Fe(OH)_3$, Zn^{2+}, $HZnO_2^-$ and ZnO_2^{2-} as presented in Table 1 were taken from the equilibrium module of Outokumpu HSC Chemistry® 5.1 (Roine, 2002). For the solubility of $ZnFe_2O_4$ in water, the Gibbs free energy change for reactions (2)–(4) was calculated using the referred chemical potentials.

$$ZnFe_2O_4 + 2H_2O + 2H^+ = 2Fe(OH)_3 + Zn^{2+}; \ \Delta G°/kJ = \text{-}17.184 \ (\text{at } 25 \ °C) \qquad (2)$$

$$ZnFe_2O_4 + 4H_2O = 2Fe(OH)_3 + HZnO_2^- + H^+; \ \Delta G°/kJ = 141.172 \ (\text{at } 25 \ °C) \qquad (3)$$

$$ZnFe_2O_4 + 4H_2O = 2Fe(OH)_3 + ZnO_2^{2-} + 2H^+; \ \Delta G°/kJ = 214.081 \ (\text{at } 25 \ °C) \qquad (4)$$

The sum of concentration of Zn^{2+}, $HZnO_2^-$ and ZnO_2^{2-} was considered equivalent to the solubility of zinc ion in water. As seen from Fig. 2, ZnO solubility in a solution is much higher when compared with $ZnFe_2O_4$ solubility. Therefore, prior conversion of $ZnFe_2O_4$ into ZnO by CaO treatment is expected to improve the zinc leaching efficiency from EAF dust.

3. Experimental procedure

3.1. Raw materials and CaO treatment procedure

The EAF dust sample employed in this investigation was collected from a dust collecting system and provided by an EAF steel making company in Japan. The CaO treated dust was prepared by reacting the as-supplied raw dust with CaO (Ca/Fe molar ratio = 1.3) and heated in a muffle furnace at 1100 °C for 5 h in air. Prior to the leaching tests, the CaO treated dust was ground into a fine powder in an agate mortar. The particle size distribution of the CaO treated dust after grinding was measured with a Sympatec HELOS particle size analyzer.

3.2. Materials characterization and assays

The structural characterization of the as-supplied raw dust and the CaO treated dust was performed through a Rigaku-RINT2000 X-ray diffractometer. The X-ray diffraction patterns of sample powder were obtained with monochromated Cu-Kα radiation in the 2θ-range from 20° to 80° with scan steps of 0.02° at fixed intervals of 1 s per step.

Table 1
Standard enthalpy, entropy and free energy of the species used in the calculations.

Species	$\Delta H°$	$\Delta S°$	$\Delta G°$ (25 °C)
	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}
$ZnFe_2O_4$	−1179.05	153.30	−1224.76
H_2O	−285.83	69.95	−306.69
H^+	0	0	0
$Fe(OH)_3$	−836.00	105.00	−867.31
Zn^{2+}	−153.39	−109.62	−120.70
$HZnO_2^-$	−595.68	−66.94	−575.72
ZnO_2^{2-}	−552.71	−167.36	−502.81

Ref: Outokumpu HSC Chemistry® 5.1 (Roine, 2002).