**Supporting Information**

**Oxygen-assisted zinc recovery from electric arc furnace dust using magnesium chloride**

**Materials**

Reagent grade ZnO (99%, Aladdin), Fe2O3 (99%, Aladdin), MgCl2 (99%, Aladdin) and K2S2O7 (99.99% metals basis, Aladdin) were used. ZnO and Fe2O3 were blended in a 1:1 molar ratio and sintered in air at 1100°C for 24 h to produce ZnFe2O4. The XRD pattern of the sintered product (**Fig. S2**) matched the standard data for ZnFe2O4 (PDF# 04-002-0662). The as-prepared ZnFe2O4 was ground into particles ranging from 0.10 mm to 0.28 mm. The EAF dust sample was provided by a local EAF steelmaking company.

**Analysis and characterization**

The phase compositions of Solids-R and volatiles were analyzed using an X-ray diffractometer (XRD, Bruker, D8 Advance, Cu Kα radiation, λ = 1.54 Å, 5° min−1). The morphological properties of EAF dust and Solids-R were examined using a scanning electron microscope (SEM, Zeiss Gemini 450) equipped with an energy dispersive spectrometer (EDS, Oxford instrument). Raman spectra of EAF dust and Solids-R were obtained using a spectrometer (WITec, Alpha300R) with a laser source having an excitation wavelength of 532 nm, covering the range of 100−900 cm−1. X-ray photoelectron spectroscopy (XPS) analyses of volatiles were characterized using a Thermo Fisher Scientific Nexsa G2 instrument with a monochromatic Al-Kα X-ray source.

The metal contents of Rinse Solution-V, Rinse Solution-R, and Solids-R were determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES, ThermoFisher, ICAP PRO XP). For the chemical analysis of Solids-R, the solids were dissolved in 10 g of K2S2O7 at 550°C,[1] and then rinsed with distilled water before being measured by ICP-AES. The fractions (*F*M) of metals (Zn, Fe, Pb, and Mn) in Rinse Solution-V, Rinse Solution-R, and Solids-R were calculated by

(S1)

The contents (*C*M) of metals in volatiles were calculated by

(S2)

where represents the concentration of a metal ion in the solution (g L−1); *V* is the total volume of the solution (L); is the total mass of metals in initial ZnFe2O4 or EAF dust; is the total mass of volatiles. Since the quantities of Solids-V were negligibly small, the fractions of metals in Rinse Solution-V were defined as the chlorination percentage.**Mathematical interpretation of the effect of O2 partial pressure**

The equilibrium constants (*K*) for reactions (1), (2), (6) and (7) are

(S3)

(S4)

(S5)

(S6)

where is the activity of component A relative to pure substance, and are the activity coefficient and mole fraction of A in molten MgCl2, is the partial pressure of gas component B. The activities of MgO, ZnO and Fe2O3 are assumed to be unity as they exist in a pure solid state. The molar ratio of Zn to Fe in the melt at equilibrium can be calculated by

(S7)

Assuming that the activity of MgCl2 and the activity coefficients of ZnCl2, FeCl2 and FeCl3 are constant within a range of composition at a certain temperature, the molar ratio of Zn to Fe increases as a function of . Therefore, increasing the partial pressure of O2 is thermodynamically favorable for the selective chlorination of Zn in ZnFe2O4.

**Discussion of the chlorination kinetics**

The chlorination of Zn in solid ZnFe2O4 by molten MgCl2 is a solid-liquid reaction, proceeding from the surface of ZnFe2O4 particles to the inner part, as shown in **Fig.** 9. Therefore, a shrinking-core model was applied to evaluate the chlorination kinetics. **Fig.** **10**e plots the value of against *t* within 10 min for the cases of reacting MgCl2 with ZnFe2O4 (molar ratio = 4:1) at temperatures from 850°C to 1000°C in the Ar–air atmosphere containing 5.2vol% of O2. Two variables are linearly related at all temperatures, indicating the applicability of the shrinking-core model and the rationality of the diffusion control assumption.

Knowing the rate constants at various temperatures, the apparent activation energy () of chlorinating Zn in ZnFe2O4 can be determined by Arrhenius’s law

(S8)

where *A* is the pre-exponential factor; *T* is temperature; R is the gas constant (R = 8.314). Taking logarithm of both sides of Eq. (S8) yields

(S9)

According to the Arrhenius plot (**Fig. 10**f), the apparent activation energy of chlorinating Zn in ZnFe2O4 is calculated as 52 kJ·mol−1. The value is much less than the apparent activation energy of the reaction (134.85 kJ·mol−1) between MgCl2 and ZnFe2O4 in Ar, determined based on the weight loss curve in a prior study [2]. The difference indicates that the chlorination of Zn is the easier part in the overall reaction.



**Fig. S1****.** Standard Gibbs energy of the possible chlorinating reactions between ZnFe2O4 and different chlorinating reagents.

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**Fig. S2.** XRD pattern of the mixture of ZnO and Fe2O3 (molar ratio = 1:1) before and after sintering at 1100°C in air for 24 h.



**Fig. S3.** Chemical potential diagram of the Mg–O–Cl system at 1027°C (1300K).



**Fig. S4.** Fraction of MgCl2 in Rinse Solution-V (containing soluble phases in the volatiles) after reacting MgCl2 and ZnFe2O4 with different molar ratios at 1000°C for 40 min in the Ar–air atmosphere containing 5.2vol% of O2.



**Fig. S5.** Particle size distribution of the EAF dust.



**Fig.** **S6.**  The vapor pressures of different chlorides in the chlorination products.

1. R. Chairaksa-Fujimoto, Y. Inoue, N. Umeda, S. Itoh and T. Nagasaka, New pyrometallurgical process of EAF dust treatment with CaO addition, *Int. J. Min. Met. Mater.*, 22(2015), No. 8, p. 788–797.
2. J. Huang, I. Sohn, Y. Kang and X. Yang, Separation of Zn and Fe in ZnFe2O4 by Reaction with MgCl2, *Metall. Mater. Trans. B*, 53(2022), No. 4, p. 2634–2646.