**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

$F\_{M} \left(\%\right)=\frac{W\_{M}×V}{m\_{M}}×100\%$ (S1)

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

$C\_{M} \left(\%\right)=\frac{W\_{M}×V}{m\_{v}}×100\%$ (S2)

where $W\_{M}$ represents the concentration of a metal ion in the solution (g L−1); *V* is the total volume of the solution (L); $m\_{M}$ is the total mass of metals in initial ZnFe2O4 or EAF dust; $m\_{v}$ 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

$K\_{1}=\frac{a\_{MgO}P\_{Cl\_{2}}}{a\_{MgCl\_{2}}P\_{O\_{2}}^{1/2}} = \frac{P\_{Cl\_{2}}}{a\_{MgCl\_{2}}P\_{O\_{2}}^{1/2}}$ (S3)

$K\_{2}=\frac{a\_{Fe\_{2}O\_{3}}a\_{ZnCl\_{2}}P\_{O\_{2}}^{1/2}}{a\_{ZnFe\_{2}O\_{4}}P\_{Cl\_{2}}} = \frac{γ\_{ZnCl\_{2}}x\_{ZnCl\_{2}}P\_{O\_{2}}^{1/2}}{P\_{Cl\_{2}}}$ (S4)

$K\_{3}=\frac{a\_{FeCl\_{2}}^{2}P\_{O\_{2}}^{3/2}}{a\_{Fe\_{2}O\_{3}}P\_{Cl\_{2}}^{2}} = \frac{(γ\_{FeCl\_{2}}x\_{FeCl\_{2}})^{2}P\_{O\_{2}}^{3/2}}{P\_{Cl\_{2}}^{2}}$ (S5)

$K\_{4}=\frac{a\_{FeCl\_{3}}^{2}P\_{O\_{2}}^{3/2}}{a\_{Fe\_{2}O\_{3}}P\_{Cl\_{2}}^{3}} = \frac{(γ\_{FeCl\_{3}}x\_{FeCl\_{3}})^{2}P\_{O\_{2}}^{3/2}}{P\_{Cl\_{2}}^{3}}$ (S6)

where $a\_{A}$ is the activity of component A relative to pure substance, $γ\_{A}$ and $x\_{A}$ are the activity coefficient and mole fraction of A in molten MgCl2, $P\_{B}$ 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

$\frac{x\_{Zn}}{x\_{Fe}} = \frac{x\_{ZnCl\_{2}}}{x\_{FeCl\_{2}}+ x\_{FeCl\_{3}}}= \frac{\frac{K\_{2}}{γ\_{ZnCl\_{2}}}}{\frac{K\_{3}^{1/2}}{γ\_{FeCl\_{2}}P\_{O\_{2}}^{1/4}} + \frac{K\_{1}^{1/2}K\_{4}^{1/2}a\_{MgCl\_{2}}^{1/2}}{γ\_{FeCl\_{3}}}}$ (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 $P\_{O\_{2}}^{1/4}$. 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 $1-2/3x-(1-x)^{2/3}$ 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 ($E\_{a}^{c}$) of chlorinating Zn in ZnFe2O4 can be determined by Arrhenius’s law

$k\_{c}=Aexp⁡(-\frac{E\_{a}^{c}}{RT})$ (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

$lnk\_{c}=-\frac{E\_{a}^{c}}{RT}+lnA$ (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.

.



**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.