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Full length article

## Thermodynamic evaluation of elemental distribution in a ferronickel electric furnace for the prospect of recycling pathway of nickel

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## ABSTRACT

In this study, the elemental distribution of 26 elements in a ferronickel electric furnace was thermodynamically analyzed to determine the removability of impurities from secondary resources during smelting. Phosphorus was evaluated both thermodynamically and experimentally. It was found that Al, B, Ca, Ce, Cr, La, Mg, Mn, Nb, Si, Sr, Ta, Ti, U, V, and Zr were removed in slag phase, while Ag, Pb, and Zn were removed in gas phase. W and Mo could be removed in slag phase by increasing oxygen partial pressure. P was partially removed in a ferronickel slag that contained MgO. Most of the P was removed by the addition of CaO to the slag. In a case study, the recycling of secondary resources containing a large amount of P was found to be possible by the addition of CaO to the slag and by the adjustment of additive amount of secondary resources to the ferronickel ore.

## 1. Introduction

With the growth of human societies, particularly in Asian countries including China, the demand for products containing nickel, such as stainless steel, has increased drastically, and the nickel production has then increased drastically (Mudd, 2010). Nickel is selected for these uses because of its specific properties, such as high corrosion resistance, high toughness, high strength at high and low temperatures, and its range of special magnetic and electronic properties. At the same time, environmental risks and challenges are always attached throughout the life cycle of nickel-containing materials as reviewed in Nakajima et al. (2014), such as the huge energy consumption and environmental impacts (e.g. GHG emissions, sulfur oxide emission and solid waste) in cradle-to-gate nickel production (Norgate et al., 2007; Seppälä et al., 2002), and heavy metal pollution caused by the nickel industry (Norseth 1994; Moiseenko and Kudryavtseva 2001). The impact on biodiversity caused by mining nickel ore has received particular attention in recent years (Mudd 2010; Nakajima et al., 2014; Jaffré et al., 2010; Pascal et al., 2008), because mining activities have impacted on the removal of native vegetation and its destruction by the deposition of mine waste. On the other hand, Reck and Graedel (2012) have noted that in the anthropogenic cycle for nickel, about 48% of the nickel extracted worldwide is lost during the life cycle for nickel. Thus, avoiding the loss of nickel in its anthropogenic cycle and closing the loop for the material cycle of nickel would be expected to reduce the consumption of natural resources and contribute to the reduction of

negative impact on the environment and human health if they contaminate soil, water, and air.

For utilizing nickel metallurgy as an acceptor of secondary resource, phosphorus becomes a particularly crucial element affecting the product quality among many impurities. Phosphorus is a common impurity in Ni-bearing wastes (Nakajima et al., 2016), but plating sludge which is the typical waste particularly contains much phosphorus because phosphoric acid salt is used in nickel plating as a reductant. Phosphorous lower the strength, toughness and corrosion resistance of ferrous alloys, and typical market requirements for the phosphorous content must be less than 0.02% (Crundwell et al., 2011). Ferronickel smelters in Japan control the phosphorous concentration in products by strictly selecting raw materials containing a small amount of phosphorous. Ferronickel smelters in Dominica and Venezuela have an independent pyrometallurgical process for the removal of phosphorous after the electric furnace process mentioned later (Crundwell et al., 2011). The existence of independent removal process at high temperature naturally increases energy consumption and cost for production. A smelter without a facility of dephosphorization obviously has a limitation of acceptance of secondary resources. Not only phosphorous but also other elements are important. For instance, upper limits are set on Si, Co, Cu, and Cr in the standard for ferronickel (Japanese Industrial Standards Committee, 2000). If those elements are heavily mixed in ferronickel, mechanical properties of steel products are worsened. Besides, when secondary resource is used, elements which are not contained in natural resource could be mixed in. Therefore, many elements

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should be investigated.

Based on the background, the authors have investigated the material cycle of nickel in Japan and revealed the bottlenecks for closing the loop of nickel cycle (Nakajima, 2016). Not only the nickel content in the secondary resource, such as nickel plating waste liquids and sludge, but also the impurity level, particularly phosphorus concentration, is critical for recycling. According to refining companies in Japan, a nickel content to phosphorus content ratio (Ni/P) of 100 or greater (in one case, 800 or greater) has been declared for the permissible level with respect to phosphorus in ferronickel refining in order to cover a severe standard for customers' requirements. However, nickel contents of 30% or greater and phosphorus contents of less than 0.5% are the limits in nickel refining because there is a concern that the nickel production is disturbed by phosphorus associated in secondary resources. There is a wide gulf between the grades of materials demanded by refining industries and the grades of unutilized secondary resource.

In order to resolve the mismatch, it is important to understand the removability of impurities in smelting processes. Therefore, elemental distribution in a ferronickel electric furnace was thermodynamically analyzed in this study. A typical process flow of ferronickel production based on the reduction kiln-electric furnace process (the ELKEM process) is shown in Fig. 1. Potential recycling pathways are also shown in the figure. In the process, natural nickel ores are dried, calcined, partially reduced, and fed to an electric furnace. Since wastes containing nickel components are generally fed to the electric furnace, the furnace is targeted in the present study. The potential wastes are sludge/solid

formed in stainless steel production, plating industry, and consumer use. Phosphorus distribution that is crucial to ensure the product quality has been evaluated both thermodynamically and experimentally for quantitative discussion, and a way to enable nickel waste recycling has been discussed.

## 2. Materials and methods

### 2.1. Thermodynamic evaluation of the elemental distribution

Because the method of thermodynamic analysis used in the present study has been described in detail previously (Nakajima et al., 2009, 2010, 2011; Hiraki et al., 2011; Lu et al., 2012, 2016), only the important points are given below. In this analysis, the volatilization and oxidization of elements are considered. The distribution ratio of an element, M, can be obtained thermodynamically using the following equations:

$$M(l) = M(g) \quad (1)$$

$$L^{g/m} = \frac{p_M/p^\circ}{p_{\text{Solv}}/p^\circ} = \frac{a_M p_M^\circ}{p_{\text{Solv}}} = \frac{p_M^\circ \gamma_M x_M}{p_{\text{Solv}}} \quad (2)$$

$$M(l) + \frac{n}{2} O_2(g) = MO_n(\text{slag}) \quad (3)$$

$$K_3 = \frac{a_{MO_n}}{a_M (p_{O_2}/p^\circ)^{n/2}} = \frac{x_{MO_n} \gamma_{MO_n}}{\gamma_M x_M (p_{O_2}/p^\circ)^{n/2}} \quad (4)$$

$$L^{s/m} = \frac{x_{MO_n}}{x_M} = \frac{K_3 \gamma_M (p_{O_2}/p^\circ)^{n/2}}{\gamma_{MO_n}} \quad (5)$$

where  $p_M^\circ$ ,  $p_M$ ,  $p_{\text{Solv}}$ , and  $p^\circ$  are the partial pressure of the pure element M (Pa), the partial pressure of M dissolved in the solvent metal (ferronickel) (Pa), the partial pressure of the solvent metal vapor (Pa), and the conversion factor (1,01,325 Pa atm<sup>-1</sup>), respectively. The variables  $a_M$  and  $\gamma_M$  are the activity and the activity coefficient of M in the pure liquid standard state,  $x_M$  is the mole fraction of M in the solvent metal,  $a_{MO_n}$  and  $\gamma_{MO_n}$  are the activity and the activity coefficient of the oxidation product  $MO_n$  in the slag in the pure solid standard state,  $x_{MO_n}$  is the mole fraction of  $MO_n$  in the slag, and  $p_{O_2}$  is the oxygen partial pressure (Pa). The abbreviations *l*, *g*, and *slag* in parentheses in Eqs. (1) and (3) denote the state of the species: liquid solvent metal, the gas phase, and the slag phase, respectively.  $K_3$  is the equilibrium constant of Reaction (3) and is given by the Gibbs free energy change of the reaction  $\Delta G_3^\circ$  in Eq. (6).

$$K_3 = \exp\left(-\frac{\Delta G_3^\circ}{RT}\right) \quad (6)$$

Here,  $R$  and  $T$  denote the gas constant and the temperature (K), respectively. In the oxidation Reaction (3), a mono-cationic oxide species is assumed to be the oxidation product. For example, in the oxidation of phosphorus in the solvent metal, the product is  $PO_{2.5}$  rather than its general stoichiometric form of  $P_2O_5$ . The dissociation reaction of the general stoichiometric oxide to the mono-cationic oxide is represented in Eq. (7).

$$M_x O_y (\text{slag}) = x MO_n \quad (n = y/x) \quad (7)$$

The free energy change of this reaction is reasonably assumed to be zero. Therefore,  $\Delta G_3^\circ$  and  $K_3$  can be evaluated using general thermodynamic references. The distribution ratios  $L^{g/m}$  and  $L^{s/m}$  quantitatively show the removabilities by evaporation and oxidation, respectively. For slag/metal separation, a component is evenly distributed to slag and metal phases at  $\text{Log}(L^{s/m}) = 0$ . A component is removed to slag at  $\text{Log}(L^{s/m}) > 0$ . For gas/metal separation, a component is removed to gas at  $\text{Log}(L^{g/m}) > 1$ . A greater distribution ratio indicates easier removal to the gas or the slag phase.

For the calculation of  $L^{g/m}$  and  $L^{s/m}$  in Eqs. (2) and (5), the free

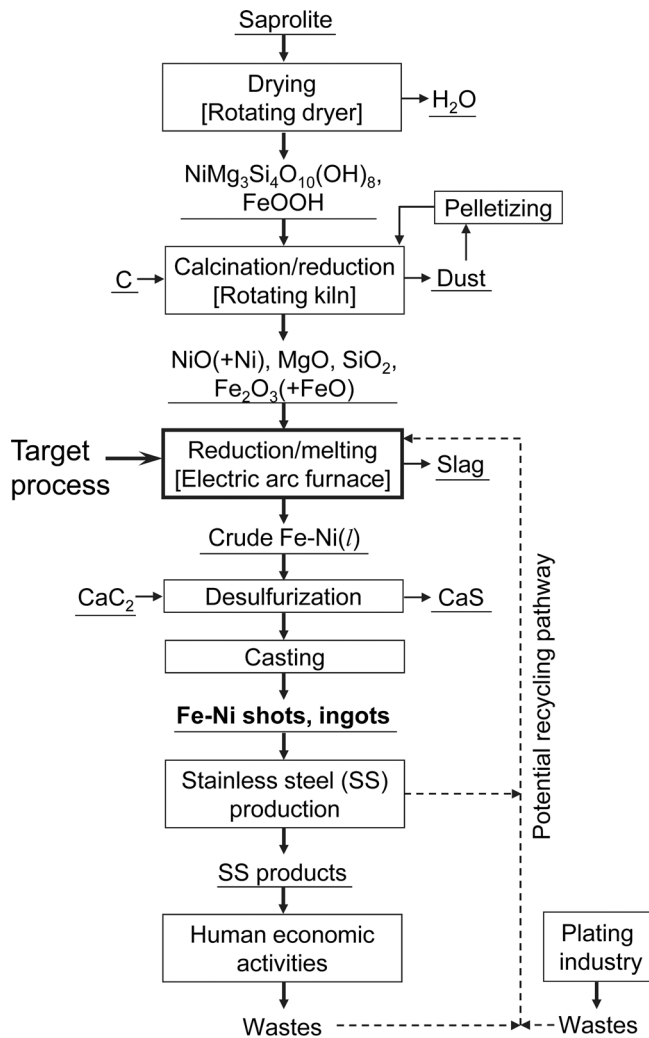


Fig. 1. Production process of ferronickel. Potential recycling pathways are also shown.

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