



Thermodynamic of selective reduction of laterite ore by reducing gases



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Abstract: As the sulfide ore deposits become less economical and environmental viable as a source of nickel, increasing attention is being paid to the laterite ores. But in the pyrometallurgical process of laterite, more efforts should be paid to control the reduction of iron oxide in order to get high nickel-content nickeliferous product. For these reasons, equilibrium condition of iron oxide when laterite ore was selectively reduced by CO_2/CO , $\text{H}_2\text{O}/\text{H}_2$ and CO_2/H_2 was studied from the perspective of iron activity with an assumption that the activities of FeO and Fe_3O_4 equal 1 in this work, and it well accounts for the inescapability of Fe metallization. Activity coefficient of iron in Ni–Fe binary solid alloy was calculated by Miedema model based on the known thermodynamics datum filed. According to Raoult's law, the relationship among the Fe/Ni ratio, reduction temperature and reduction gas composition was calculated when laterite ore was selectively reduced by the three different reduction systems. The calculation result was discussed and also compared with the experimental result. The trend of metal iron content in the reduction product of laterite ore varying with temperature and gas composition was well predicted by the calculation result.

Key words: selective reduction; laterite ore; activity coefficient; Miedema model

1 Introduction

Nickel, one of the most important strategic metals, is widely applied to stainless steel, electroplating, catalyst and petrochemical industry [1]. In recent years, more and more attention has been paid to the research about exploitation and utilization of nickel laterite ore rather than nickel sulfide ore, due to the factors such as resources, environment, and the cost aspects [2]. By regulating the reduction condition like reduction temperature and oxygen potential in the system, most of the nickel oxides in the ore are reduced to metallic state, while the reduction of iron oxides is minimized. Selective reduction of laterite ore, as explained before, plays an important role in the treatment process of laterite ore [3–6].

Reduction temperature and gas composition are two main factors which significantly affect the efficiency of the selective reduction of laterite ore [7]. And the metal Fe in the reduction production of laterite ore tends to combine with metal Ni, which is the reduction production of NiO in laterite ore, to be Fe–Ni alloy [8].

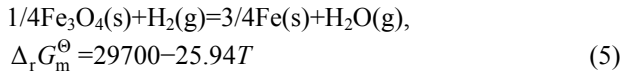
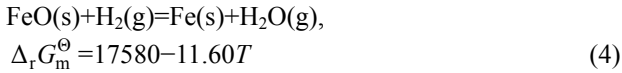
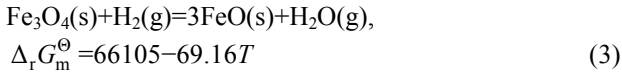
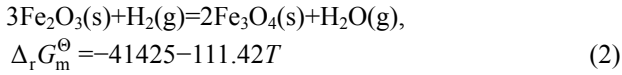
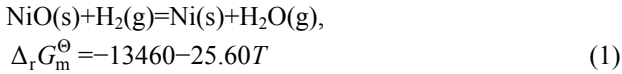
Thus, the varying activity of Fe will greatly affect the stability of iron oxide. In OLLI et al's study [9], the predominance programs for iron and its oxides in the presence of nickel when laterite ore was reduced by CO_2/CO and $\text{H}_2\text{O}/\text{H}_2$ mixed gas showed that the reduction of iron oxide could be affected by the variation of the activity of Fe. However, it cannot be used directly to predict the composition of nickeliferous produced from laterite due to the lack of the activity coefficient of Fe in Fe–Ni alloy. Based on their work, equilibrium conditions of iron oxide when laterite ore was selectively reduced by CO_2/CO , $\text{H}_2\text{O}/\text{H}_2$ and CO_2/H_2 was studied from the perspective of iron activity with an assumption that the activities of FeO and Fe_3O_4 equal 1 in this work. Activity coefficient of Fe in Fe–Ni alloy was calculated by Miedema model [10–12], which can well calculate the enthalpies of the formation of binary solid alloy based on the known thermodynamic data. Then, the relationship between the iron content in Fe–Ni alloy produced by the reduction of laterite Fe and reduction temperature as well as gas composition can be worked out by Raoult's law, when laterite ore was reduced by CO_2/CO , $\text{H}_2\text{O}/\text{H}_2$, CO_2/H_2 mixed gas respectively. The

calculation result was verified by reduction experimental result of Indonesia laterite ore with CO₂/H₂ mixed gas. A good interpretation of the inescapability of Fe metallization in the selective reduction process of laterite ore can be obtained in this work.

2 Analysis process

2.1 Calculation process of relationship of gas composition, temperature and activity of Fe in Fe–Ni alloy

Reactions as follows would take place when laterite ore was reduced by H₂O/H₂:



The reduction of iron complies with stepwise reaction mechanism. If the temperature is below 570 °C, reactions were carried out by two steps: Fe₂O₃ → Fe₃O₄ → Fe; otherwise, reactions were carried out by three steps: Fe₂O₃ → Fe₃O₄ → FeO → Fe.

Gibbs free energies of Fe₂O₃, Fe₃O₄, FeO, NiO and H₂O as a function of temperature are shown in Fig. 1. In the reduction system, the difficulty of Eq. (2), Eq. (1), Eq. (3), Eq. (4), and Eq. (5) increases successively. Therefore, virtually, selective reduction of the laterite ore is to inhibit the occurrences of Eq. (3), Eq. (4) and Eq. (5).

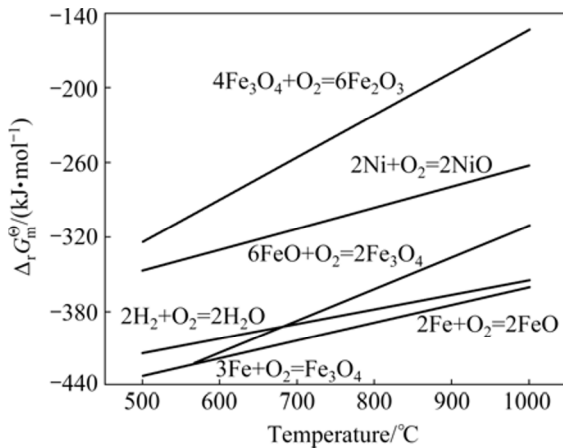


Fig. 1 Gibbs free energy of Fe₂O₃, Fe₃O₄, FeO, NiO and H₂O as function of temperature

For reactions from Eq. (2) to Eq. (5), the equilibrium constant expression can be stated as follows with an assumption that the activities of FeO, Fe₃O₄ and Fe₂O₃ equal 1.

$$K_2 = \frac{p_{\text{H}_2\text{O}} \cdot (a_{\text{Fe}_3\text{O}_4})^2}{p_{\text{H}_2} \cdot (a_{\text{Fe}_2\text{O}_3})^3} \quad (6)$$

$$K_3 = \frac{p_{\text{H}_2\text{O}} \cdot (a_{\text{FeO}})^3}{p_{\text{H}_2} \cdot a_{\text{Fe}_3\text{O}_4}} \quad (7)$$

$$K_4 = \frac{p_{\text{H}_2\text{O}} \cdot a_{\text{Fe}}}{p_{\text{H}_2} \cdot a_{\text{FeO}}} = \frac{p_{\text{H}_2\text{O}} \cdot a_{\text{Fe}}}{p_{\text{H}_2}} \quad (8)$$

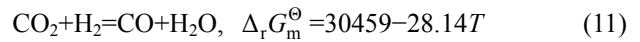
$$K_5 = \frac{p_{\text{H}_2\text{O}} \cdot (a_{\text{Fe}})^{3/4}}{p_{\text{H}_2} \cdot (a_{\text{Fe}_3\text{O}_4})^{1/4}} = \frac{p_{\text{H}_2\text{O}} \cdot (a_{\text{Fe}})^{3/4}}{p_{\text{H}_2}} \quad (9)$$

For Eq. (8) and Eq. (9), the activity of Fe depends on the corresponding equilibrium constant and the $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ ratio. According to Eq. (10), the relations between the partial pressure of hydrogen, the reduction temperature and the activity of Fe can be worked out based on the value of $\Delta_r G_m^\ominus$ at different temperatures.

$$\Delta_r G_m^\ominus = -RT \ln K \quad (10)$$

There is something different in the analysis process when laterite ore was reduced by CO₂/H₂ mixed gas compared with H₂O/H₂ mixed gas and CO₂/CO mixed gas.

Reaction as Eq. (11) may take place when CO₂/H₂ mixed gas is used to reduce the laterite ore.



The mole fraction of H₂ in initial mixed gas was supposed to be $x(\text{H}_2)^\ominus$. Thus, the mole fraction of CO₂ in initial mixed gas was $[1 - x(\text{H}_2)^\ominus]$. When the reactions were balanced, conversion amount of H₂ was supposed to be x . Then equilibrium constants can be stated as follows.

$$K = \frac{p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} \cdot p_{\text{H}_2}} = \frac{x^2}{[1 - x(\text{H}_2)^\ominus - x][x(\text{H}_2)^\ominus - x]} \quad (12)$$

So,

$$\Delta_r G_m^\ominus = -RT \ln K = -RT \ln \frac{x^2}{[1 - x(\text{H}_2)^\ominus - x][x(\text{H}_2)^\ominus - x]} \quad (13)$$

$$\ln \frac{x^2}{[1 - x(\text{H}_2)^\ominus - x][x(\text{H}_2)^\ominus - x]} = \frac{30459 - 28.14T}{-RT} \quad (14)$$

At the same time,

$$\frac{x(\text{H}_2\text{O})^\ominus}{x(\text{H}_2)^\ominus} = \frac{x}{x(\text{H}_2)^\ominus - x} \quad (15)$$

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