On Thermodynamics of Iron Reduction from Oxides

V. I. Berdnikov^a, * and Yu. A. Gudim^b

^a OOO Technology of Metals Industrial Company, Chelyabinsk, 454018 Russia
^b PJSC Magnitogorsk Iron and Steel Works, Magnitogorsk, 455000 Russia

*e-mail: berdnikov-chel@mail.ru

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Abstract—A computer simulation of the chemical process of direct iron reduction in aggregates is performed with the help of the MIDREX technology. Four variants of this technology, which differ by the type of raw material and working process temperature, are analyzed. It is determined that when the process temperature increases, the required consumption of natural gas decreases and the methane in the waste gas is completely removed. It is also noted that at a constant process temperature, the concentrations of all of the components of the system linearly depend on the flow rate of the reducing gas. This circumstance allowed us to record a single balance equation for all of the variants of the studied chemical process.

Keywords: chemical reactions, iron oxides, thermodynamic system, process modeling, direct reduction of iron, MIDREX process

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Usually, the direct reduction of iron from raw ore allows generating a half-product with a metallized (sponged) iron content of 80–95% for subsequent conversion in blast furnaces or steelmaking furnaces. About 70% of this iron worldwide are produced by the MIDREX technology [1–3]. In Russia, this technology has been adopted in steps since 1983 at the Oskol'ski Electrometallurgical Works (OEMW) [4].

In this process, iron-ore pellets are processed in a reducing gas a third of which is carbon oxide and the other thirds are hydrogen. This is why, the chemical composition of this gas is conventionally recorded as formulae CO(H_2)_2 or OCH_4. In the past, this gas was generated by the carbonic acid-vapor conversion of natural gas and later on—by the partial combustion of natural gas with oxygen [4].

The chemical process of reducing iron by this technology was modeled in the Terra software suite [5]. The Fe––O––C––H thermodynamic system with 1 mol of iron was analyzed. In this case, the following restrictions were imposed on the calculation method:

— the processed iron ores (hematite, magnetite) were recorded as pure oxides (Fe_2O_3, Fe_3O_4);
— the temperature of the furnace charge in the reaction zone was equal 750°C (in early aggregates) and 900°C (in modern aggregates);
— the gas pressure in the reaction zone was equal its maximal value of 0.2026 mPa (2 atm.), and at the minimal gas pressure of 1.3 atm. The design indicators of the processing changed less than by 1%;
— the processing was assessed by balance equations of type \( \text{oxide} + n\text{CO(H}_2\text{)}_2 = \text{reaction products} \), where \( n \) is the reducing agent consumption.

Then it was accepted that \( n_0 \) was the reducing agent consumption at the beginning of metallization and \( n_1 \) is the reducing gas consumption at theoretically feasible 100% metallization of iron. The numerical values of these quantities for the four variants of raw material processing are shown in Table 1. It is apparent that, during the recycling of magnetite and hematite, metallization begins right after the addition of the reducing agent and at gas flow rate \( n_0 = n_1/9 \) mol since at lower flow rates (\( n < n_0 \) moles) \( \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \).

As shown by the calculations, in all of the technology’s modifications mole fractions \( m \) of reduced iron linearly depend on reducing agent consumption \( n \) to an accuracy of 0.001, which is recorded as \( m = (n - n_0)/(n_1 - n_0) \). This allowed recording a single balance equation of the recycling process as

\[
(0.5\text{Fe}_2\text{O}_3 \text{ or } 0.333\text{Fe}_3\text{O}_4) + n\text{CO(H}_2\text{)}_2 = m\text{Fe} + 0.333(1 - m)\text{Fe}_2\text{O}_4
\]

\[+ n\eta_{\text{C}}\text{CO} + (1 - n\eta_{\text{C}} - n\eta_{\text{CH}})\text{CO}_2
\]

\[+ n\eta_{\text{CH}}\text{CH}_4 + 2n\eta_{\text{H}}\text{H}_2 + 2(1 - n\eta_{\text{H}} - n\eta_{\text{CH}})\text{H}_2\text{O}.\]

where \( \eta_{\text{C}}, \eta_{\text{CH}}, \text{and } \eta_{\text{H}} \) are the temperature-dependent characteristics of the underburning of carbon oxide, methane, and hydrogen. These parameters are formally defined as \( \eta_{\text{C}} = \text{CO/(CO + CO}_2 + \text{CH}_4) \), \( \eta_{\text{CH}} = \text{const} \), and \( \eta_{\text{H}} = \text{H}_2/(\text{H}_2 + \text{H}_2\text{O} + 2\text{CH}_4) \).
The numerical values of the parameters are shown in Table 1.

Thus, the reducing agent consumption necessary for having preset iron metallization level \( m \) during the recycling of hematite and magnetite are

\[
\begin{align*}
n &= m(n_1 - n_0) + n_0 = 0.889mn_1 + 0.111 \\
n &= mn_1 	ext{ moles.}
\end{align*}
\]

The parameters of the technology currently used at the OEMW are similar to variant 4 of Table. Thus, the reducing agent consumption at an average iron metallization of 90% \( (m = 0.9 \text{ moles}) \) is \( n = 0.93 \text{ moles} \). The balance equation of this process is

\[
0.333\text{Fe}_3\text{O}_4 + 0.93\text{CO(H}_2\text{)}_2 = 0.9\text{Fe} + 0.337\text{Fe}_3\text{O}_4 + 0.566\text{CO} + 0.364\text{CO}_2 + 1.023\text{H}_2 + 0.837\text{H}_2\text{O}. \tag{2}
\]

The specific natural gas consumption required for recycling magnetite with a molecular weight of 232 g/mol is \((0.93 \times 22.4 \times 10^3)/(0.333 \times 232) = 269\) cubic meters per ton of pellets, which is confirmed by the experience of OEMW.

CONCLUSIONS

This study suggests describing the chemical process of the reduction of iron by the balance equation of iron reduction which connects the reduced amount of iron and the composition of generated top gas on the flow rate of reducing gas.

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