

Thermodynamic calculation on the smelting slag of direct recycling of electric arc furnace stainless steelmaking dust

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Abstract: Thermodynamic calculation on the smelting slag of direct recycling of electric arc furnace stainless steelmaking dust was presented. An induction furnace was used to simulate electric arc furnace smelting to recover the metals from the dust. The elements of iron, chromium and nickel in the ingot and the components of metal oxides in the slag were analyzed. The thermodynamic model for FeO-Cr₂O₃-MgO-SiO₂ slag was set up and the active concentrations of substances in the slag at 1550 °C were determined by thermodynamic calculation according to the experimental data. The results show that the apparent equilibrium constant and quantitative distribution of chromium between slag and steel are unstable and affected by the mass ratios of pellets to start iron and metal reducing agent to the pellets. In order to get satisfactory chromium recovery from the direct recycling of electric arc furnace stainless steelmaking dust, it is important to ensure the mass ratio of pellets to the steel below 0.20 and the mass ratio of metal reducing agent to pellets over 0.18 in practical smelting runs.

Key words: thermodynamic calculation; stainless steelmaking dust; reduction; recycling

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1 INTRODUCTION

Electric arc furnace (EAF) dust has been classified as a hazardous waste due to its high content of some heavy metals leachabilities such as zinc, lead, cadmium and chromium, so it has been banned from landfills in many countries. An estimated 1%-2% mass fraction of the scrap charged to an EAF is converted to dust. And more dust is generated in the Argon Oxygen Decarburization (AOD) or in the Vacuum Oxygen Decarburization (VOD) vessels in the electric stainless steelmaking. There were few methods to treat EAF stainless steelmaking dust even though a lot of technologies for the

ferro-steel dust treatment were developed^[1-3]. The direct recycling of EAF stainless steelmaking dust is a remediation option that aims at recovering the metallic elements present in the dust directly to the steel bath of EAF in the steelmaking process. The dust is mixed with carbon as reducing agent, dolomite as flux, and lignosulphonate as binder and then formed into pellets that are subsequently fed to the EAF. Under the conditions that prevail in the EAF, the reducing agent is expected to reduce the metal oxides in the dust. The operation above is inexpensive to apply. Main costs involved are the purchase of the reducing agent, the binder and pelletization. Carbon, dolomite and

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lignosulphonate are cheap and easily available.

A number of research steps were completed prior to this study. The characteristics of the flue dust generated from EAF stainless steelmaking were investigated^[4]. The isothermal^[5] and non-isothermal^[6,7] kinetics models of the reduction were established using a thermo-gravimetric furnace (TGF) in the laboratory-scale experiments. The results showed that iron and nickel in the dust could be reduced and recovered well by reducing agent carbon. But it was difficult to fully reduce chromium only by carbon. Some of chromium got into the smelting slag, and aluminum or calcium-silicon was added in the end of the smelting to improve the recovery of chromium by reducing more of chromium from the slag. On the other hand, the pre-reduction for the pellets hinders metal recoveries from the dust^[8,9]. This study focuses on the thermodynamic calculation on the steelmaking slag of the direct recycling process.

2 EXPERIMENTAL

2.1 Experimental materials

The dust was taken from a stockpile located in the open air. As it was exposed to the atmosphere, the dust contained a large amount of moisture which caused particles to agglomerate over time. As a result, the range of particle sizes in the dust samples was in a very wide diameter from less than

38 μm to approximately 5 cm. Elemental analysis of dust samples was performed using X-ray Fluorescence (XRF) for Al, Ca, Cr, Fe, K, Mg, Mn, Na, P, Si, Ti and Inductively Coupled Plasma (ICP) for Ni, Pb and Zn. The compositions of the samples are given in Table 1. Since the dust was formed in air at high temperature, most of the elements within it were oxidized. X-ray Diffraction (XRD) observations indicated that the main phases present in the dust were Fe_3O_4 , Fe_2O_3 and CrO. The study by N. D. Souza *et al* on the same dust confirmed this result^[4]. The main phases of the dust are listed in Table 2.

The dust and dolomite whose composition is given in Table 3 were screened to below 0.45 mm in order to be suitable for pelletization. Pellets were made with 5% mass fraction of dolomite and suitable lignosulphonate (whose composition and properties are shown in Table 4) used as a binder and 15% mass fraction of fine activated carbon as a reducing agent after all the fines were thoroughly mixed. A disc pelletizer was used to agglomerate the mixture. The pellets produced were screened to be larger than 10 mm in diameter and then dried in air at room temperature for 4 days. The SEM observation for the central section of the pellets is given in Fig. 1, showing that the dust and carbon are mixed well.

Table 1 Composition of EAF dusts

No.	w/%													
	Al	Ca	Cr	Fe	K	Mg	Mn	Na	Ni	P	Pb	Si	Ti	Zn
1	0.43	6.02	11.29	39.38	0.08	2.01	2.80	0.24	2.82	0.02	0.07	2.71	0.15	0.24
2	0.46	5.83	10.19	37.14	0.12	1.85	2.61	0.20	3.52	0.02	0.13	2.67	0.14	0.48
3	0.35	6.53	10.33	40.57	0.26	2.10	2.95	0.07	5.42	0.02	0.16	2.55	0.12	1.06
Avg.	0.41	6.13	10.60	39.12	0.15	5.96	8.36	0.17	3.92	0.02	0.12	2.64	0.14	0.59

Table 2 Main phases of EAF dust

w/%									
SiO_2	Al_2O_3	CaO	CrO	Fe_2O_3	MnO_2	NiO	PbO	ZnO	MgO
5.45	0.66	9.14	13.51	58.00	4.67	6.70	0.16	0.93	3.48

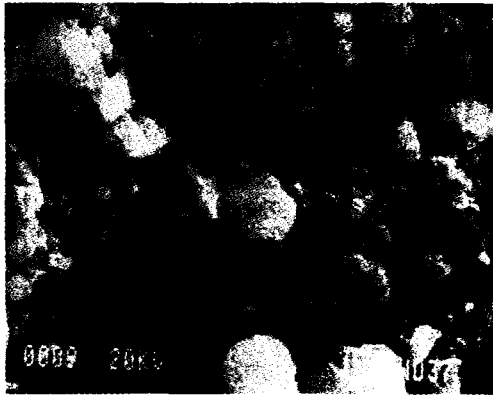


Fig. 1 SEM observation of the pellet

Table 3 Composition of dolomite w/%

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O
4.27	0.32	2.64	6.99	0.52	36.57	33.46	0.26

2.2 Experimental approach

The experimental smelting was conducted in a 23 kg capacity induction furnace. Heating process was started by melting 2.3 to 13.6 kg of pure iron. Alumina crucibles were used to hold the liquid metal. This iron bath was used to simulate the metal bath of the EAF. Once the iron melted at about

1580 °C, pellets were fed to the furnace in batches of approximately 0.5 kg each. After having added all the pellets, a period of time was allowed for reactions in the bath to reach completion. When visual observation indicated that no more reactions occurred within the steel bath, aluminum or calcium-silicon was added at 1550 °C to further reduce the metal oxides in the slag. Throughout the experiment, the slag and steel were stirred using an iron rod. Temperature was measured periodically using an R-type thermocouple. The process lasted between 1.0 h and 1.5 h. The experimental parameters, mass ratios of pellets to start iron (m_1/m_2) and metal reducing agent to pellets (m_3/m_1), were controlled as shown in Table 5. The furnace was then turned off and the steel and slag were allowed to freeze in the crucible. Once it cooled down to room temperature, the crucible was broken to recover and weigh the ingot and slag. The compositions of the ingot and slag were analyzed using Optic Emission Spectroscopy (OES) and X-ray Fluorescence. The analysis results are given in Table 6.

Table 4 Chemical composition and properties of lignosulphonate w/%

Lignosol	Reducing sugar	S	Ca	Na	N	pH	Ash	Moisture	Gravity/(kg · m ⁻³)
80.0	7.0	6.6	5.0	0.2	0.1	4.5	20.0	5.0	16

Table 5 Experimental smelting parameters of direct recycling

No.	1	2	3	4	5	6	7	8
m_1/m_2	2.01	1.96	2.78	0.31	0.20	0.20	0.20	0.06
m_3/m_1	0	0.10	0.04	0.32	0.07	0.10	0.10	0.09

Table 6 Composition of ingot and slag w/%

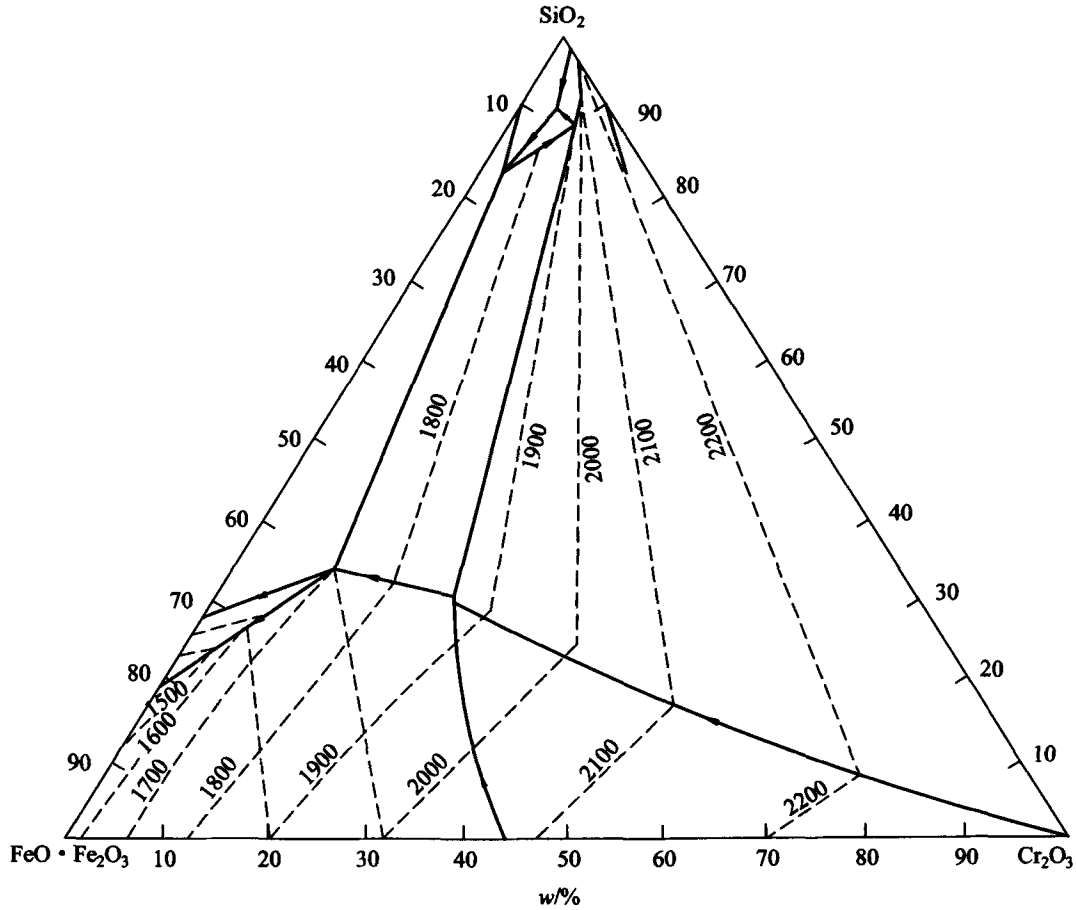
	SiO ₂	17.50	12.65	16.11	20.97	9.29	20.98	11.87	11.96
In slag	Cr ₂ O ₃	19.06	4.57	18.95	6.25	2.42	1.93	0.77	2.71
	MgO	12.49	10.24	12.37	4.99	10.92	8.50	5.04	3.47
	FeO	6.87	1.35	3.17	3.91	1.84	4.32	0.97	6.22
	Cr	3.80	6.09	3.92	1.14	1.22	1.29	1.25	0.31
In steel	Fe	90.84	86.64	90.69	87.93	97.54	96.99	97.09	99.11

3 THERMODYNAMIC CALCULATION

3.1 Basic species of slag

There are two types of slag theories to ascertain the basic species of melted slag at high temperature, one is Ionic Theory and

the other is Molecular Theory. Molecular Theory indicates that all substances in slag exist in the form of molecules and Ionic Theory points out that the substances in slag exist in ionic form. But the fact is that substances in slag could exist in two forms


 Fig. 2 Phase diagram of FeO-Cr₂O₃-MgO-SiO₂ slag

according to Coexistence Theory^[10]. In this consideration, there are MgSiO₃, Mg₂SiO₄ and Fe₂SiO₄ in the slag according to MgO-SiO₂ and FeO-SiO₂ phase diagrams and HSC Chemistry^[11]. FeCr₂O₄ is formed in the slag based on XRD and FeO-Fe₂O₃-SiO₂-Cr₂O₃ phase diagram (see Fig. 2). The basic species of the slag of direct recycling of stainless steelmaking dust is Fe²⁺, Cr³⁺, Mg²⁺, O²⁻ simple ions and SiO₂, Fe₂SiO₄, FeCr₂O₄, MgSiO₃, Mg₂SiO₄ molecules.

3.2 Calculation model

Let $b_1 = \sum x(\text{FeO})$, $b_2 = \sum x(\text{Cr}_2\text{O}_3)$, $b_3 = \sum x(\text{MgO})$, $b_4 = \sum x(\text{SiO}_2)$, $x_1 = x(\text{FeO})$, $x_2 = x(\text{Cr}_2\text{O}_3)$, $x_3 = x(\text{MgO})$, $x_4 = x(\text{SiO}_2)$, $x_5 = x(\text{FeCr}_2\text{O}_4)$, $x_6 = x(\text{MgSiO}_3)$, $x_7 = x(\text{Fe}_2\text{SiO}_4)$, $x_8 = x(\text{Mg}_2\text{SiO}_4)$, $C_1 = C(\text{FeO})$, $C_2 = C(\text{Cr}_2\text{O}_3)$, $C_3 = C(\text{MgO})$, $C_4 = C(\text{SiO}_2)$, $C_5 = C(\text{FeCr}_2\text{O}_4)$, $C_6 =$

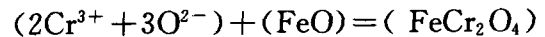
$C(\text{MgSiO}_3)$, $C_7 = C(\text{Fe}_2\text{SiO}_4)$, $C_8 = C(\text{Mg}_2\text{SiO}_4)$, where $\sum x$ stands for summation of molar fraction, x for molar fraction and C for active concentration. The thermodynamic calculation was undertaken at 1550 °C as follows.

3.2.1 Chemical equilibrium



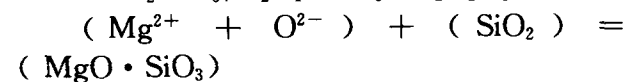
At 1550 °C, $\Delta G^0 = 26940 \text{ J/mol}$, $k_1 = 0.1691$,

$$k_1 = C_7 / C_1^2 C_4 \text{ or } C_7 = k_1 C_1^2 C_4 \quad (1)$$



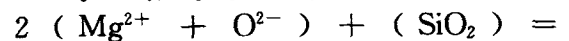
At 1550 °C, $\Delta G^0 = -1025 \text{ J/mol}$, $k_2 = 1.07$,

$$k_2 = C_5 / C_2 C_1 \text{ or } C_5 = k_2 C_2 C_1 \quad (2)$$



At 1550 °C, $\Delta G^0 = -29736 \text{ J/mol}$, $k_3 = 7.11$,

$$k_3 = C_6 / C_3 C_4 \text{ or } C_6 = k_3 C_3 C_4 \quad (3)$$



(2MgO · SiO₂)

At 1 550 °C, $\Delta G^0 = -60\,565$ J/mol, $k_4 = 54.37$,

$$k_4 = C_8/C_3^2 C_4 \text{ or } C_8 = k_4 C_3^2 C_4 \quad (4)$$

3. 2. 2 Mass measurement

$$C_1 + C_2 + C_3 + C_4 + k_2 C_2 C_1 + k_3 C_3 C_4 + k_1 C_1^2 C_4 + k_4 C_3^2 C_4 = 1 \quad (5)$$

$$b_1 = x_1 + 2x_7 = \sum x(0.5C_1 + 2k_1 C_1^2 C_4) \quad (6)$$

$$\sum x = b_1 / (0.5C_1 + 2k_1 C_1^2 C_4) \quad (7)$$

$$b_2 = x_2 + x_5 = \sum x(0.5C_2 + k_2 C_2 C_1) \quad (8)$$

$$b_3 = x_3 + x_6 + 2x_8 = \sum x(0.5C_3 + k_3 C_3 C_4 + 2k_4 C_3^2 C_4) \quad (9)$$

$$b_4 = x_4 + x_8 + x_7 + x_8 = \sum x(C_4 + k_3 C_3 C_4 + k_1 C_1^2 C_4 + k_4 C_3^2 C_4) \quad (10)$$

3. 2. 3 Calculation model

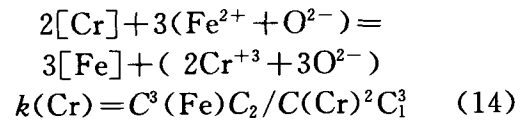
Make Equation (7) into (8), (9) and (10), then we get

$$b_1(0.5 + k_2 C_1)C_2 = b_2(0.5 + 2k_1 C_1 C_4)C_1 \quad (11)$$

$$b_1(0.5 + k_3 C_4 + 2k_4 C_3 C_4)C_3 = b_3(0.5 + 2k_1 C_1 C_4)C_1 \quad (12)$$

$$b_1(1 + k_3 C_3 + k_1 C_1^2 + k_4 C_3^2)C_4 = b_4(0.5 + 2k_1 C_1 C_4)C_1 \quad (13)$$

Active concentrations of substances in FeO-Cr₂O₃-MgO-SiO₂ slag can be obtained from the resolution of simultaneous Equations (5), (11), (12) and (13). The chromium distribution between slag and steel is dependent on the following reactions.



The distribution coefficient of chromium between slag and steel can be expressed as

$$L(\text{Cr}) = w(\text{Cr}_2\text{O}_3) / w(\text{Cr}) = 152 \sum x(0.5 + k_2 C_1)C_2 / w(\text{Cr}) \quad (15)$$

3. 2. 4 Calculation results

The thermodynamic calculation was undertaken according to model above and a computer program was developed for the calculation. The calculation results are given in Table 7.

Table 7 Thermodynamics calculation results of direct recycling slag

No.	C(FeO)	C(Cr ₂ O ₃)	C(MgO)	C(SiO ₂)	C(2FeO · SiO ₂)	C(FeCr ₂ O ₄)	C(MgO · SiO ₂)	C(2MgO · SiO ₂)	k(Cr)	L(Cr)
1	0.186 9	0.373 4	0.152 8	0.063 1	0.000 3	0.074 7	0.068 6	0.080 1	3.959 1	0.030 6
2	0.088 2	0.254 1	0.157 8	0.136 8	0.000 2	0.024 0	0.153 6	0.185 3	9.990 0	0.006 0
3	0.109 0	0.454 1	0.152 3	0.069 2	0.000 1	0.052 9	0.075 0	0.087 3	22.84 5	0.017 7
4	0.172 2	0.210 1	0.041 0	0.387 4	0.001 9	0.038 7	0.113 1	0.035 5	31.62 5	0.084 0
5	0.252 6	0.223 6	0.225 3	0.317 5	0.003 4	0.060 4	0.000 0	0.876 6	9.325 0	0.048 2
6	0.240 7	0.080 7	0.115 9	0.844 7	0.008 3	0.020 8	0.000 0	0.617 1	3.476 6	0.073 7
7	0.116 7	0.079 8	0.116 1	1.000 1	0.002 3	0.001 0	0.000 0	0.732 9	32.139 0	0.031 7
8	0.425 7	0.113 2	0.109 5	0.574 3	0.017 6	0.051 6	0.000 0	0.374 4	15.268 0	0.716 7

4 DISCUSSION

The main composition of EAF dust is iron and chromium oxides. Aluminum or calcium-silicon is used to reduce the metal oxides from slag in the experiment. The thermodynamic calculation model for FeO-Cr₂O₃-MgO-SiO₂ slag in this study is suitable for practical condition based on the thermo-

chemistry theory. But it is found that the reaction constant $k(\text{Cr})$ in Equation (14) and distribution coefficient $L(\text{Cr})$ of chromium between slag and steel are fluctuant (see Table 7), showing that the experimental conditions of direct recycling smelting affect the reaction equilibrium. The important parameters of smelting are the mass ratios of pellets to start iron and metal reducing agent

to pellets according to the results of the experiments and calculations. The effects of the mass ratios on the reaction equilibrium are given in Fig. 3 and Fig. 4.

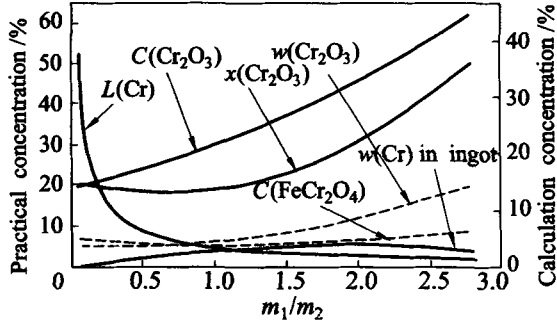


Fig. 3 Effect of mass ratio of pellets to start iron on reduction

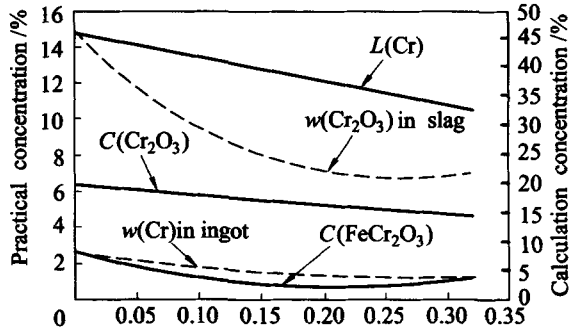


Fig. 4 Effect of mass ratio of metal reducing agent to pellets on reduction

Figure 3 shows the effect of the mass ratio of pellets to start iron on the characteristics of chromium in the reduction smelting. It can be seen from Fig. 3 that $L(\text{Cr})$ drops down with the increase of the mass ratio of pellets to start iron. In order to achieve high chromium recovery, it is necessary to control the ratio below 0.20. And it can also be seen from Fig. 3 that the active concentrations of chromium in the steel and slag increase with the increase of pellets added. The chromium distribution between slag and steel decreases with the increase of the ratio. These maybe result from the fact that chromium first exists in the slag and only when its concentration in the slag gets high enough could it begin to be reduced and get into steel under the experimental condition.

Figure 4 gives regression results of the calculation of experimental data about the

effect of amount of metal reducing agent on the chromium reducing properties. It shows that the chromium concentration in the slag decreases remarkably with the increase of the amount of metal reducing agent. This tendency slows down after the mass ratio of metal reducing agent to pellets reaches 0.18. In order to achieve high chromium recovery, it is necessary to control the ratio over 0.18. But on the other hand, the effects of the increase of metal reducing agent on the concentration of chromium in the steel and the concentration of FeCr_2O in the slag are small. The reduction process is complex because chromium oxides are reduced by carbon and metal reducing agent one after another. The reduction goes step by step and there may be Cr^{2+} existing in the slag^[12,13] and the reduction process of chromium is controlled by kinetic conditions and very difficult to fully complete^[14,15].

5 CONCLUSIONS

1) The active concentrations of substances in $\text{FeO-Cr}_2\text{O}_3\text{-MgO-SiO}_2$ slag of direct recycling of stainless steelmaking dust are calculated according to the thermodynamic model and the chromium apparent equilibrium constant and distribution between slag and steel are fluctuant, which shows that they are affected by the smelting parameters.

2) The mass ratio of pellets to the steel in the EAF for the direct recycling practice should be controlled below 0.20 in order to get satisfactory chromium recovery.

3) The mass ratio of metal reducing agent to pellets in the terminal period of EAF steelmaking for the recycling of the dust should be over 0.18 to ensure enough chromium recovery.

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