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Energy-saving research on the preheating of manganese ore in the rotary kiln of the hot charging smelting process

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ABSTRACT

Through thermodynamic calculation and analysis of the preheating process of the manganese ore raw materials in the rotary kiln, and through phasic analysis of cold and hot ore materials with X-ray diffraction, the results of manganese ore preheating and pre-reducing processes are obtained in a qualitative and pre-quantitative manner, and it also has been discovered that, in the rotary kiln, the multiple oxides of manganese could be decomposed or reduced in advance at a relatively low temperature(30℃ lower than the normal furnace atmosphere), which may result in a 39% saving of electricity in the smelting of one tone of high-carbon manganese in the submerged–arc furnace, and in a monthly increase of 17% in the production of manganese-rich slag. This is good enough to show that hot charging ore material is an ore dressing technology with obvious energy-saving result.

KEYWORDS

Hot charging material; Rotary kiln; Manganese ore; Manganese-rich slag.

INTRODUCTION

Cold charging of smelting materials has been the major method adopted in the manganese alloy smelting process up to this day. That is means raw materials including manganese ore and lime are directly added to the submerged-arc furnace for smelting. There have been some theoretic formulations[1] for the technology of hot charging that is only to charge manganese-silicon alloys as the deoxidizer at a liquid state, and the ore raw materials are still directly melted in the submerged-arc furnace. Some experiments have also been carried out by some manufacturers with many problems unsolved. For instance, in the present technology of direct material charging, when the manganese ore, containing a lot of high oxides and combined water, enters the furnace without preheating, intensive chemical decomposition reactions will occur upon its reaching the high-temperature zone, which might lead to seething of slag and iron water or even explosion[2-3]; this, in turn, will generate a low furnace operability, thus greatly threatening safe operation and production. However, if the manganese ore were preheated, the above-mentioned problems could be avoided so as to achieve safe operation and low consumption of power in the smelting processes[4]. Because the preheating temperature could be as high as 800-900℃ plus[5], this technology is difficult to some extent.

In view of this, hot charging smelting technology of preheating ore materials in the rotary kiln was, for the first time, developed and adopted in the smelting of manganese alloy by Jiaocheng County Yiwang Ferroalloy Plant of Shanxi Province, China. Before the manganese ore enters the submerged-arc furnace, the ore was reduced and roasted in advance in the rotary kiln, which was followed by hot material dosing and hot charging smelting processes[6]. Coal dust and coke-oven gas could be used as heat resources of the rotary kiln.

This paper is a research on the preheating functions of the rotary kiln in the hot charging process. Through thermodynamic calculation, pre-reducing temperature of the ore materials in the rotary kiln is obtained, and influences of the burning atmosphere in the kiln on the manganese ore reduction and its advantages are studied in a quantitative manner. It has also been discovered that preheating of the cold ore can help lower the initial reduction temperature of high valent manganese, and almost all the ore materials have been reduced to MnO of low valent before entering the submerged-arc furnace, which will reduce energy consumption in the furnace, shorten smelting time[7], and get high quality manganese ferroalloy.

MANGANESE ORE RAW MATERIALS AND CHEMICAL COMPOSITION OF COAL GAS

The manganese ore used in Yiwang is relatively abundant in calcium and silicon. For the contents of its chemical elements, see TABLE 1.

TABLE 1 : Chemical composition of manganese ore raw materials(wt%)

Element or Phase	Mn	Fe	SiO2	CaO	Al2O3	MgO	Crystal water	Other impurities
Contents	42	4	4.4	4	1.36	3.04	20	<1

About 20% or so weight loss will occur due to the volatilization of the crystal water and burning losses of other volatilized gases.

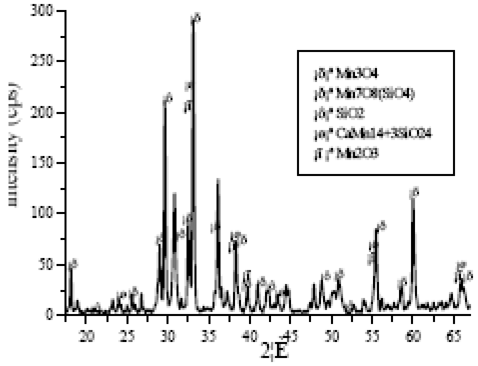
The phasic composition of the ore materials, after the XRD, is shown in TABLE 2 and 3. XRD chart is shown in Figure 1 and 2.

TABLE 2 : XRD result of original manganese ore (wt%)

Phase	Mn2O3	Mn3O4	Mn7O8(SiO4)	CaMn14+3SiO24	SiO2
Original ore	11	15.5	16.5	29.3	27.7

TABLE 3 : XRD result of preheated manganese ore (wt%)

	MnO2	Mn2O3	Mn3O4	MnO	CaMn2O4	Notes
Preheated ore	34.2	9.3	23.9	5.2	27.4	950 ℃
Amount increased	+34.2	-1.7	+8.4	+5.2		



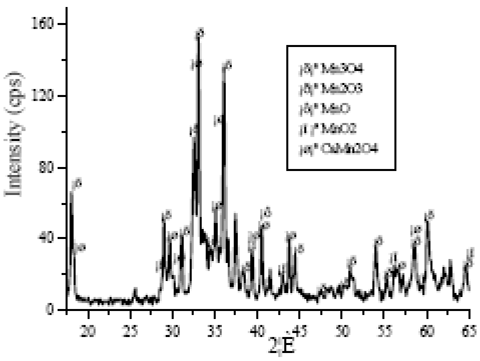


Figure 1 : XRD chart of raw Fig.2 XRD result of preheated carbonic acid manganese ore carbonic acid manganese ore

The gas used in the rotary kiln under this research is the coal gas supplied by a local coal and coke plant, the combustible gas contents of which are show in TABLE 4.

TABLE 4 : Chemical composition of coal gas (vol%)

Composition of coal gas	CH4	H2	CO	O2	CO2	N2
Volume	25.84	63.41	5.83	0.2	2.3	2.39

According to thermodynamic data from the combustion reactions, specially in the range of preheating temperature of manganese ore, CH_4 could be fully combusted with sufficient oxygen supply and proper temperature[8].

The combustion reaction of H_2 is similar to that of CO, with a large amount of heat release and stronger affinity with oxygen than with CO at a temperature higher than 810°C[9]. And H_2 promotes also carbon burning[10], thus there is the resulting in a full combustion in the high temperature zone of the rotary kiln.

CALCULATION OF PARTIAL PRESSURE OF INDIVIDUAL GAS PHASE AT HIGH TEMPERATURES

From TABLE 4, we know that the gases in the rotary kiln include, among others, CH_4, H_2, CO, CO_2, and O_2 etc. From the components of the combusting materials, the following main chemical reaction processes and their Gibbs free energy parameters could be obtained[11]:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

$$\Delta G^0_{T(1)} = 128.039T\ln T + 19.18\times10^{-3}T^2 - 863.844T - 7.624\times10^5 \text{ (J)} \tag{1}$$

$$2H_2 + O_2 = 2H_2O$$

$$\Delta G^0_{T(2)} = -492876 + 108.78T \text{ (J)} \tag{2}$$

If all the gases are assumed at an ideal state, the equilibrium constants of the above two equation, based on partial pressure, are:

$$K_{(1)} = \frac{P^2_{H_2O}P_{CO_2}}{P^2_{O_2}P_{CH_4}} \tag{3}$$

$$K_{(2)} = \frac{P^2_{H_2O}P_0}{P_{O_2}P^2_{H_2}} \tag{4}$$

In which, P_i with some subscripts stands for gas' partial pressure, and P_0 represents standard atmospheric pressure (100KPa).

Only three elements of C, H and O are contained in the above gas system, and they are in a balanced state. The overall amount of individual element remains unchanged and is not related to its components. The total amount of elements in all phases should be a constant. Thus, their relations of mole numbers are as follows:

$$n_C = n_{CH_4} + n_{CO_2} = N_{CH_4} + N_{CO_2} \tag{5}$$

$$n_H = 4n_{CH_4} + 2n_{H_2} + 2n_{H_2O} = 4N_{CH_4} + 2N_{H_2} + 2N_{H_2O} \tag{6}$$

$$n_O = 2n_{CO_2} + 2n'_{O_2} + n_{H_2O} = 2N_{CO_2} + 2N_{O_2} + N_{H_2O} \tag{7}$$

In which, n_i represents the mole number of a particular element, n represents an analyzed value, and N is the balanced component under the calculated temperature. In Equation (7), n'_{O_2} is the oxygen supplied by air blast machine in the combusting process.

Analyzed gas values in TABLE 4 represent volume percentages and the corresponding mole numbers. In addition, according to empirical value, natural air in the rotary kiln is supplied at a ration of 1:8 between coal gas and air[12], which, in combination with data in TABLE 4, could lead to the following equations：

$$n_C = 0.031266,\quad n_H = 0.255754,\quad n_O = 0.378888。$$

According to $P_i = \frac{n_i}{\Sigma n}P$, equations (5),(6),(7)could, based on partial pressure, also be expressed as follows：

$$n_C = P_{CH_4} + P_{CO_2} = 0.031266 \quad \textbf{(8)}$$

$$n_H = 4P_{CH_4} + 2P_{H_2} + 2P_{H_2O} = 0.255754 \quad \textbf{(9)}$$

$$n_O = 2P_{CO_2} + 2P_{O_2} + P_{H_2O} = 0.378888 \quad \textbf{(10)}$$

The rotary kiln outlet operates under a slight vacuum pressure (0.99 atmosphere pressure), so the total atmospheric pressure within the kiln could be regarded as lower than one atmosphere pressure:

$$P_{CH_4} + P_{H_2} + P_{O_2} + P_{CO_2} + P_{H_2O} + P_{N_2} + \sum P' = 0.99 \times 100\text{KPa}$$

In the above equation, ∑P’ stands for some neglected gases.

The partial pressure of nitrogen contents in the kiln air is 78% ×(8/9)=0.69333 atmosphere pressure, and the gases of N_2、CO(with little contents and to be neglected in later calculations) in coal gas is (2.39+5.83)%×(1/9)=0.009 atmosphere pressure, both of which totals 0.702466 atmosphere pressure. Therefore, the partial pressure of the five main gases totals 0.99-0.702466=0.287534 atmosphere pressure, i.e.:

$$P_{CH_4} + P_{H_2} + P_{O_2} + P_{CO_2} + P_{H_2O} = 0.287534 \times 100\text{KPa} \quad \textbf{(11)}$$

From the above six equations of (3),(4),(8),(9),(10),(11), six unknown partial pressure numbers could be obtained(including inert nitrogen that does not take part in reaction).

According to relationship between the equilibrium constants and free energy parameters, when in a balances state, it takes place that $\Delta G = -RT \ln K$, and, $K = \text{anti}\ln \frac{\Delta G}{-RT}$.

When T=1173K(900°C), $K_1=4.29\times10^{30}$, $K_2=1.21\times10^{16}$.

We cold get the partial pressures at 900°C by solving the above six equations, as shown in TABLE 5.

TABLE 5 : Partial pressures of each gas at 900℃(100KPa)

Gas phase	P_{H_2O}	P_{CO2}	P_{O2}	P_{CH_4}	P_{H_2}
Partial pressure	0.0593	0.0311	0.1286	1.3×10-4	0.0683

DECOMPOSITION OF MANGANESE OXIDES IN ROTARY KILN (900℃)

Manganese ore, when heated, will first be decomposed into MnO_2, a high valent oxide, then be gradually reduced at high temperatures in the order of high valence to low valence[13-14].

For the balance of $MnO_2 \leftrightarrow Mn_2O_3$ and $Mn_2O_3 \leftrightarrow Mn_3O_4$, the relations of oxygen partial pressure and temperature are as follows[15] :

$$4MnO_2 = 2Mn_2O_3 + O_2 \ \ 527°\text{C above}$$

$$\log P_{O_2} = -\frac{8277.7}{T} + 11.2045 \quad \textbf{(12)}$$

$$6Mn_2O_3 = 4Mn_3O_4 + O_2 \ \ 900°\text{C above}$$

$$\log P_{O_2} = -\frac{11380.8}{T} + 13.9 - 1.339\log T - 0.656\times10^{-3}T + 1.113\times10^{5}T^{-2} \quad \textbf{(13)}$$

Based on the calculating results from TABLE 5, when the oxygen partial pressure in the rotary kiln is P_{O2}=0.1286×100KP, the balanced temperature of $4MnO_2=2Mn_2O_3+O_2$ is determined to be 684K（411°C） per equation (12), and the balanced temperature of $6Mn_20_3=4Mn_3O_4+O_2$ is determined to be 1133K（860°C） per equation (13). This shows that 411°C is the decomposing temperature of MnO_2, and 860°C is the decomposing temperature of Mn_2O_3. The interval of 411－860°C is a stable existing range for Mn_2O_3, and the corresponding temperature range in the open system (atmospheric environment) is 424－889°C. This result indicates that the decomposing temperature in the rotary kiln is 13－29℃ lower than in atmospheric environment. Therefore, the atmosphere in the kiln is favorable for the reduction and decomposition of manganese ore. XRD results in Tab 3 also prove that many manganese multi oxides are reduced.

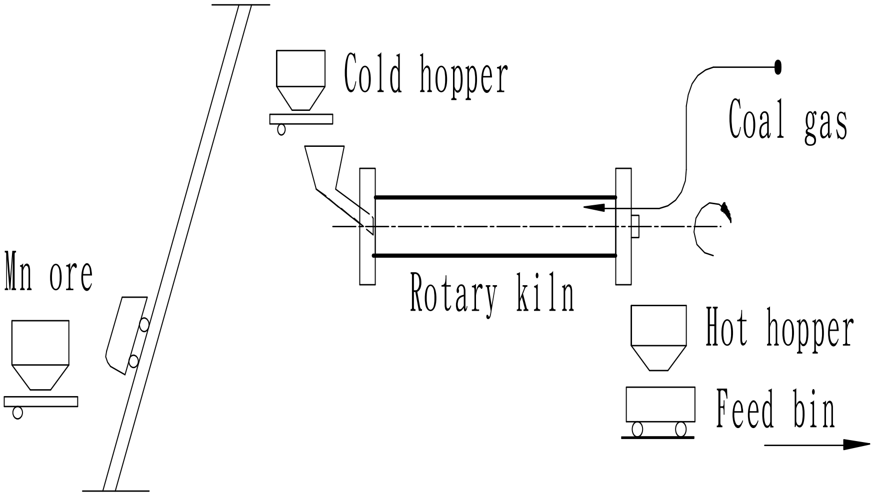


Figure 3 : Rotary kiln processes sketch map

The actual technological process of rotary kiln heating manganese ore we use is as displayed in Figure 3. The equipment of a rotary kiln and its major technological parameters are: the kiln length is 45m and its inner diameter is 1.8m. The working speed is 2.3 turns per minute. The designed production capacity for the kiln is 5 tons per hour. That working processes are the following: the manganese ore is lifted by the lifting truck and then enters the cold hopper at the left of the rotary kiln. After the gas heating session inside the kiln, heated ore leaves the kiln through the right opening to the hot hopper, and is added to the feed bin after weighting. Then it is sent to the arc furnace for actual use. The temperature at entrance in the kiln is approximately 300℃, the temperature at exit is approximately 700℃.

By the roasting in the rotary kiln, the manganese ore takes place prereduction, at the same time, it has lost some volatilizable impurity such as crystal water etc, and has had a effective mineral separation for the following smelt. As a result, it has not just shortened the smelting time in the furnace, but also improved the furnace practice and increased the output. According to the comparison with random statistics for both old and new technical processes, the energy-saving effectiveness is shown in TABLE 6.

TABLE 6 : A comparison of indexes in producing rich-Mn slag and high-carbon ferromanganese

	Output (ton/month)		Electricity consumption (kW/ton)	
	Rich-Mn slag	**high carbon ferromanganese**	**Rich-Mn slag**	**high carbon ferromanganese**
Old technology	1338	231	1140	1933
New technology	1569	753	700	1223
Increase (%)	+17%	+225%	-39%	-36%

***note: the monthly output indicates actual output of the furnace at that time.**

CONCLUSION

To heat the manganese ore in the rotary kiln, by adopting the hot charging smelting process, results in the decomposition and reduction of manganese multiple oxides at a relatively low temperature（about 411－860℃）in the kiln, and the decomposition temperature range in the kiln atmosphere is 13－29℃ lower than in the open system (with a variation in temperature due to different coal gas composition). The 39% of electricity energy could be saved per ton in producing high-carbon ferromanganese in the submerged–arc furnace, and the 17% of manganese-rich slag output is increased per month.

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