

INFLUENCE OF ADDITIVES ON SLAG-IRON SEPARATION DURING DIRECT REDUCTION OF COAL-BASE HIGH-IRON-CONTENT RED MUD^①

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ABSTRACT The influence of additives on slag-iron separation when high-iron-content red mud was directly reduced by coal was researched. The results showed that a relatively satisfactory index can be gained by the following conditions: the amount of oxygen-type additive is 3%, reducing time is 120 min and the reducing temperature is 1473 K.

Key words red mud additives direct reduction

1 INTRODUCTION

In the light of the characteristics of the gibbsite bauxite in Guangxi Province, which has low aluminum content and high iron content (with main chemical composition of 27.50% Al_2O_3 , 42.99% Fe_2O_3 and 6.89% SiO_2), the goal of the program of "Aluminum earlier and iron later" put forward by CSUT has been successfully achieved, resulting in comprehensively retrieving the valuable elements and mitigating the environmental pollution.

"Iron later" means directly reduce the red mud which is one of the products of Bayer Processing. This kind of red mud contains much more iron than other kinds and as a result, it's called high-iron-content red mud. However, when it's used for direct reduction, the iron grade is relatively low. In addition, iron oxide is inlaid in the gangue mineral and they wrap each other too. Moreover, the size of the milled mineral is limited and monomial separation can't be realized. So, there exist some difficulties during the direct reduction and the concrete condition is

that it's relatively hard to separate slag from iron. Therefore, it's necessary to search for a suitable additive to solve this problem.

2 EXPERIMENTAL

2.1 Material

The chemical composition of the red mud was mainly 54.60% Fe_2O_3 , 15.08% Al_2O_3 , 8.90% SiO_2 and 1.85% Na_2O . The reductive used was bituminous coal which was screened out by experiments^[1] and it's main composition was 68.5% fixed carbon, 3.5% volatile matter and 28.0% ash. The chemical composition of the ash was mainly 52.34% SiO_2 , 26.67% Al_2O_3 , 9.66% TFe (total iron). Four sorts of additives, compound salt, magnesium salt, calcium salt and sodium salt, were used in the experiments. Hereafter, these additives are denoted with 01, 02, 03 and 04 respectively, and the experiment with no additives is represented by 00 for comparing easier.

2.2 Method

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The coal, red mud and additive were mixed and agglomerated into the lumps with the size of dia. 12 mm \times 12 mm under the pressure of 1.96 MPa. After the lumps were dried at the temperature of 378 K, they were put into a tube furnace to be reduced in the reducing atmosphere. The reduced product was then removed, cooled in water, finely ground and magnetically separated. TFe, MFe (metallic iron), Al_2O_3 , SiO_2 , Na, η_{Me} (metallization degree) and R (reduction degree) were used as the main basis for judging the experiments.

3 EXPERIMENTAL RESULT AND DISCUSSION

3.1 Preliminary Research on Additives Catalyzing Reduction

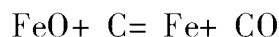
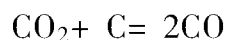
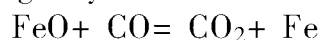
It can be learned from the experimental result (Fig. 1) that the relatively suitable amount of additives 01, 02, 03 or 04 is 3%, 4%, 4% or 1.5% respectively.

According to the optimum amount of the additives determined by experiments, the experiments of direct reduction of red mud lumps and magnetic separation have been carried out and the results are listed in Table 1.

It can be seen from Table 1 that all additives can promote the slag-iron separation, but with the change of additives their effects are also variable.

All additives can cut down the activation

energy of reducing reaction and catalyze the reducing reaction, which are considered as the reason of being able to promote the slag-iron separation. When iron oxide is directly reduced by coal, its reaction process is carried out under the following way^[2]:



Based on the oxide's reducing kinetics, the kinetics model of the coal-base direct reduction of red mud may be described using the contracting unreacted nucleus model as follows. At the initial stage the reaction is controlled by the crystal-chemical reaction, and there exists such a velocity equation as

$$1 - (1 - R)^{1/3} = Kt / (r_0 \rho) \quad (1)$$

At the later stage, the reaction is controlled by inner diffusion and the velocity equation is

Table 1 The influence of additives sort on the slag-iron separation (at 1423 K in 100 min)

additive	concentrate index / %					
	TFe	MFe	Al_2O_3	SiO_2	Na	η_{Me}
00	67.51	40.17	11.16	10.97	0.68	59.5
01	86.31	77.68	4.61	4.06	0.20	90.0
02	74.63	52.24	9.31	8.99	0.51	70.0
03	77.74	66.08	7.34	7.16	0.45	85.0
04	81.18	72.66	6.21	6.00	0.35	89.5

Fig. 1 The relation between R , metallization rate (η_{Me}) and the concentration of additives

(a) —01; (b) —04; (c) —03; (d) —02; $t = 100 \text{ min}$; 1 — R ; 2 — η_{Me}

$$1 - \frac{2}{3}R - (1 - R)^{2/3} = \frac{2MD_e\Delta c}{\alpha\rho_0^2} \cdot t \quad (2)$$

When the inner diffusion velocity is equal to the crystal chemicochemical reaction velocity, the reaction is controlled by these two factors and the velocity equation is

$$\frac{K}{6}[3 - 2R - 3(1 - R)^{2/3}] + \frac{D_e}{r_0}[1 - (1 - R)^{1/3}] = \frac{KD_eC_0}{r_0^2\rho} \cdot t \quad (3)$$

where

K —the reaction velocity constant conveyed by gravity change;

t —time, s;

R —reduction degree, %;

r_0 —the initial radius of iron pellets, m;

ρ —the density of iron oxide, kg/m³;

M —the molecular weight of iron oxide;

D_e —the constant of diffusion velocity;

Δc —the difference between reducing gas density and balance density, mol/m³;

C_0 —the density of reducing gas, mol/m³;

α —the mol ratio between gas reductive and oxide during the reducing reaction

On a certain condition, ρ , α , r_0 , Δc , D_e , M , C_0 are constants and equation (1), (2) can be simplified as

$$1 - (1 - R)^{1/3} = K' t \quad (4)$$

$$3 - 2R - 3(1 - R)^{2/3} = D_e' t \quad (5)$$

The red mud, coal and different additives were mixed and agglomerated into pellets. These pellets were reduced in different time at different temperatures and the results are shown in Fig. 2.

The solid line zones close by the left and right ordinates in Fig. 2 denote the reactions occurred in these zones are respectively controlled by the crystallochemical reaction or inner diffusion. The dotted line zones denote the reactions occurred in these zones are synthetically controlled by crystallochemical reaction and inner diffusion.

K' and D_e' can be worked out from Fig. 2 and they are listed in Table 2.

Fig. 3 can be gained from Table 2 and the following equation^[4]:

$$E = - R \frac{d(\ln K)}{d(1/T)} \quad (6)$$

where

E —activation energy, J/mol;

R —constant of ideal gas, 8.314 J/mol•K;

K —the constant of reaction velocity;

T —absolute temperature, K

The apparent activation energy at different

Fig. 2 The relation between $[1 - (1 - R)^{1/3}]$, $[3 - 2R - 3(1 - R)^{2/3}]$ and t
1—01; 2—04; 3—03; 4—02; 5—00

**Table 2 The influence of additives
on K' and D_e' ($\times 10^7$)**

temp. / K constant		additives				
		00	01	02	03	04
1 173	K'	120	613	153	220	400
	D_e'	5.88	188	11.8	32.4	58.8
1 273	K'	453	1360	533	613	900
	D_e'	647	847	118	145	218
1 423	K'	560	2500	720	940	1720
	D_e'	443	1340	560	882	1210

Table 3 The apparent activation energy

Stage	the apparent activation energy/($\text{J}\cdot\text{mol}^{-1}$)				
	00	01	02	03	04
1*	109 121	83 140	103 925	98 729	88 336
2**	257 734	128 036	230 298	177 088	166 280

* stage 1 —the stage controlled by crystallochemical reaction; ** stage 2 —the stage controlled by inner diffusion

arranged in descending order of E_{00} , E_{02} , E_{03} , E_{04} , E_{01} , (i. e. $E_{00} > E_{02} > E_{03} > E_{04} > E_{01}$). And the reason for the formation of this order is explained below.

The contents of Al_2O_3 and SiO_2 in red mud are relatively high and the exact values are 15.08% and 8.90%, respectively. The coal ash is also mainly composed of Al_2O_3 (52.34%) and SiO_2 (26.67%); and the FeO is easy to react with Al_2O_3 or SiO_2 during the reducing process resulting in the formation of complex compounds, such as $2\text{FeO} \cdot \text{SiO}_2$, $\text{FeO} \cdot \text{Al}_2\text{O}_3$, $2\text{FeO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ etc. When these compounds are formed, the activity coefficient of FeO is dropped and the activation energy of the reaction is raised, so it becomes more difficult for the reaction to go on.

When strong basic additives are used during the reducing process, FeO can be displaced by these additives from the complex compounds and again becomes free, so the activity coefficient of FeO is raised, the activation energy is dropped and the reducing velocity is increased. At the same time, different additives have different basic capacity B (i. e. $B_{01} > B_{04} > B_{03} > B_{02} > B_{00}$) and the ability (A) that different additives displace FeO from the complex compounds is different (i. e. $A_{01} > A_{02} > A_{03} > A_{04} > A_{00}$), so the results listed in Table 3 were obtained.

It's obvious that the apparent activation energy order is also $E_{00} > E_{02} > E_{03} > E_{04} > E_{01}$ when the reaction stays at the synthetical control stage. Furthermore, the time that the reaction stays at the synthetical control stage is very short and most time is still respectively budgeted by crystallochemical reaction and inner diffusion. So, when additives are used during the reducing process, the activation energy of the reducing reaction can be effectively dropped, the reducing

**Fig. 3 The relation between
 $\ln K'$, $\ln D_e'$ and $[(1/T) \times 10^4]$**
1—01; 2—04; 3—03; 4—02; 5—00

reaction stages when different additives are used can be gained from Fig. 3 and they are listed in Table 3.

From Table 3 the following conclusion can be made: No matter what controls the reaction velocity, the apparent activation energy(E) is

reaction is catalyzed, reduction degree and metallization degree are raised, the growth of the iron crystals is promoted (Fig. 4) and all these are of course profitable to slag-iron separation during the magnetic separation.

3. 2 *Further Optimization of the Reducing Condition and Further Raise of the Slag-Iron Index*

3. 2. 1 Effect of the Additive Amounts

It can be learned from paragraph 3. 1 of the paper that the optimal additive is 01 and the optimal amount of this additive is preliminarily defined as 3%. In order to further determine the amount of additive 01, a group of experiments (1 423 K, 100 min) has been carried out and the results are shown in Fig. 5.

It can be seen from Fig. 5 that the optimal amount of additive 01 gained from paragraph 3. 1 is correct. And the reason of using an optimal additive amount lies in the fact that, when the amount of additives is not adequate, the reducing reaction cannot be fully catalyzed; when the additive amount exceeds the optimal amount, the superfluous part then becomes a kind of impurity and forms the slag phase during the reducing process. The newly formed iron crystals are

wrapped in the newly formed slag phase and this is, of course, harmful to the slag-iron separation during the magnetic separation.

3. 2. 2 The Effect of Reducing Time

The red mud pellets, in which 3% additive 01 is used, is reduced in different time at the temperature of 1 423 K. and the results are shown in Fig. 6.

It can be learned from Fig. 6 that the reduction degree and the metallization degree do not change, on the whole, when the reducing time is over 100 min. But along with the time being prolonged, the content of Al_2O_3 , SiO_2 and Na in magnetically processed concentrate drop continuously. The reason is what expounded below: The growth of the iron crystals formed during the reducing reaction needs a relatively long period of time. Though the reduction degree and metallization degree do not change on the whole after the reducing reaction has been conducted for 100 min, the iron crystals are continuously growing and getting coarser (Fig. 7). Therefore, it's beneficial to the slag-iron separation during the magnetic separation.

It can be seen from Fig. 7 that when the reducing reaction is conducted at a temperature of 1 423 K, the iron crystals formed in 180 min are

Fig. 4 SEM photographs($\times 1\,000$) of the reduced products
(1 423 K, 100 min)
(a) —no Additive be used; (b) —Additive 01 is used

Fig. 5 The influence of the concentration of additive 01 on the content of Al_2O_3 , SiO_2 and Na in the concentrate

1 — SiO_2 ; 2 — Al_2O_3 ; 3 — Na

Fig. 6 The influence of reduction time on the slag-iron separation

1 — R ; 2 — η_{Me} ; 3 — Al_2O_3 ; 4 — SiO_2 ; 5 — Na

much bigger than those formed in 100 min (Fig. 4 (b)).

3.2.3 The Effect of the Reducing Temperature

The red mud, coal and additive 01 were mixed and agglomerated into pellets. The pellets were then directly reduced in 120 min at the temperature of 1473 K and the SEM photograph of the reduction products is shown in Fig. 8.

When the temperature is raised, the energy needed by the reducing reaction and the growth

of iron crystals can be more greatly satisfied, so the iron crystals can get an enough growth in a short while. Comparing Fig. 7 with Fig. 8, it can be seen that the iron crystals formed in 120 min at the temperature of 1473 K have the coarser size than those formed in 180 min at the temperature of 1423 K, so it's more beneficial to the slag-iron separation during the magnetic separation and the improvement of the concentrate index. The concentrate index got from this experiment is listed as: 95.50% η_{Me} , 1.71% Al_2O_3 ,

1.58% SiO₂, 0.11% Na, 94.12% rate of recovery.

4 CONCLUSIONS

(1) The coal-base direct reduction of high-iron-content red mud can be efficiently catalyzed by additives, so the slag-iron separation can be promoted. At the same time, different additives have different effects.

(2) The amount of additives, reducing temperature and reducing time have also great effect on the slag-iron separation.

(3) When additive 01 is used and the red mud pellets are reduced in 120 minutes at the temperature of 1 473 K, the concentrate can get the following index: 91.79% TFe, 95.50% η_{Me} , 1.71% Al₂O₃, 1.58% SiO₂, 0.11% Na, 94.12% rate of recovery.

**Fig. 7 SEM photograph(× 1 000)
of the reduction products**
(1 423 K, 180 min)

**Fig. 8 SEM photograph(× 1 000)
of the reduction products**
(1 473 K, 120 min)

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