

Research on Sticking Prevention During Reduction
in a Mixed Fluidized Bed⁽¹⁾

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ABSTRACT

Sticking is a typical problem for iron ore reduction in fluidized bed. An experimental research was carried out to explore the mechanism of this problem. Two different kinds of sticking were found during the test. One of them was due to the high viscosity of iron ore during reduction. The other was an aftereffect of iron appearance in whisker form. Methods to prevent sticking were discussed and validated using a mixed fluidized bed of iron ore and coal char.

KEY WORDS: fluidized bed, sticking, coal.

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The main advantage of fluidized bed reduction is its ability to use fine iron ore directly. That is favorable for environment protection and cost reducing. One of the problems, which counteracts its development, is the sticking phenomenon. Sticking is very easy to appear during the reduction and interrupts the fluidized state^{1,2,3}. The main purpose of this paper is to research into the causes of sticking and to find a method for prevention from it.

1 Investigation on sticking phenomenon

Figure 1 shows the main equipment for investigation

The reactor is a fluidized bed with a diameter of 25 mm and a height of 1000 mm. It can be operated in two different ways. The first one is discontinuous mode and the second one is continuous mode.

The samples can be charged continuously through the reduction gas or direct in the reactor before the test.

Offgas is cleaned using a dust catcher. The collected dust is injected back into the reactor through the reduction gas.

The reduction temperature is measured using a thermocouple in the center of the fluidized bed.

The fluidized operation is watched through a manometer. It gives an obvious reaction, if the fluidized bed is broken down.

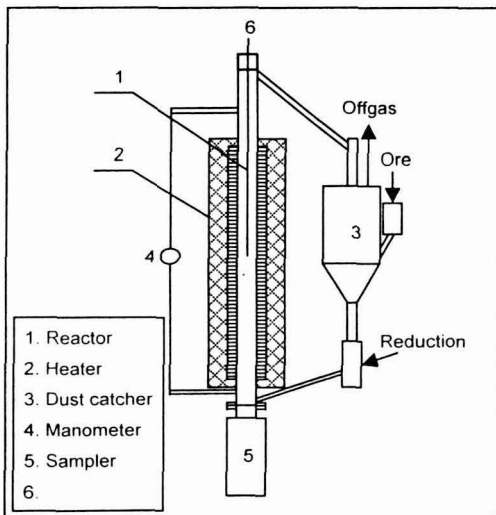


Figure 1 Fluidized bed reactor

The sample size of iron ore was 0.1 to 0.15 mm. Table one gives the composition of the iron ore.

Table I Composition of Mount-Wright iron ore /%

T_{Fe}	FeO	C	S	P	CaO	MgO	SiO ₂	Al ₂ O ₃	TiO ₂
63.0	3.09	0.068	0.007	0.012	0.16	0.04	3.46	0.25	0.17

Two kinds of reduction gases were used. Gas 1 was a mixture of CO (50%) and N₂ (50%). Gas 2 was a mixture of CO (75%) and H₂ (25%).

The tests for research on sticking phenomena used discontinuous mode and homogeneous bed of iron ore.

Figure 1 shows a group of test results. In this group, gas 1 with a flow velocity (V) of 45 cm.s⁻¹ was used for reduction. T is reduction temperature in °C and R is reduction degree in %.

In figure 1, a critical temperature can be found. Below this temperature, there was simply no sticking phenomenon and above this temperature, sticking appears with a certain reduction degree. This sticking reduction degree is marked as R_s and this sticking temperature is marked as T_s . This rule was also found in tests using gas 2.

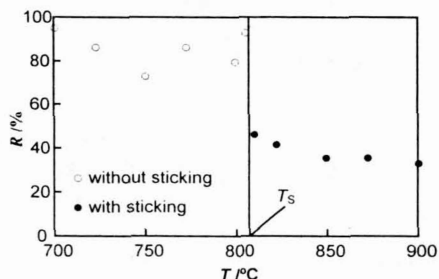


Figure 1 Influence of

R_s was independent of gas composition and gas flow velocity. Figure 2 shows R_s in relationship with reduction temperature using different gases and gas flow velocities.

T_s is approximately a constant with different gas compositions but rises with higher

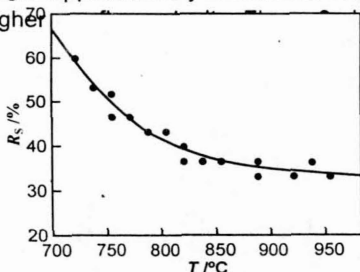


Figure 2 Relationship between R_s and

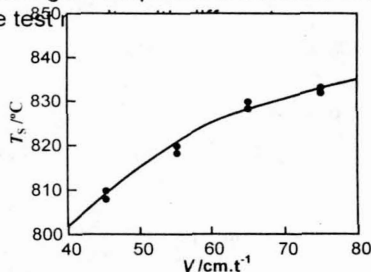


Figure 3 Influence of gas velocity on

The results of offgas analysis have shown an interesting phenomenon, which is useful to open out the mechanism of sticking. This phenomenon is shown in figure 4. Where, t is the time recorded since the beginning of the reduction and C is the content of CO_2 in offgas. During the reduction, two peak values of CO_2 content have appeared. The reduction degree as the second peak began to appear is marked as R_P . R_P is relational to reduction temperature. Figure 5 shows the relationship.

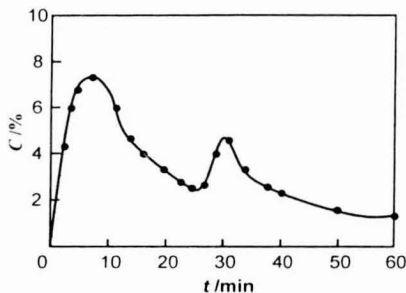


Figure 4 CO_2 content in

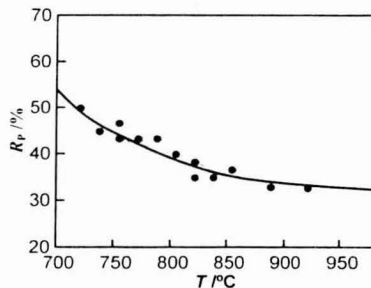


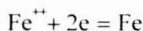
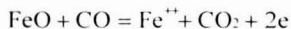
Figure 5 Relationship between R_P and

2 Mechanism of sticking

A common point for all tests with sticking is that the breaking down of the fluidization presented after the appearance of the second peak of CO_2 content. The differences between R_S and R_P are not so big and become smaller at higher temperature. That is shown in figure 6.

In this case, the hoist of reduction velocity is the only causation for the hoist of CO_2 content. The first peak is a typical representation of the self-catalysis behavior. The question is only about the second peak.

The values of R_P have shown that the second peak appeared during the reduction of FeO . This process can be divided in two steps:



The equilibrium constant for the second step is:

$$K = \frac{a_{\text{Fe}}}{a_{\text{Fe}^{++}} a_{e^2}}$$

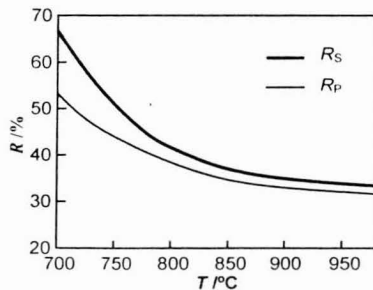


Figure 6 Relationship between R_S and

At the beginning of FeO reduction, there is no metallic iron as the center for crystallization. The second step cannot begin with normal content of Fe^{++} . The real content of Fe^{++} is much larger than normal state. High Fe^{++} content quickens the reverse reaction of the first step. That makes a low value region of CO_2 content before the second peak.

After the appearance of metallic iron, the content of Fe^{++} reduces suddenly to normal level and the low content of Fe^{++} accelerates the first step at once. That is the reason of the second peak. At lower temperature, the appearance of metallic iron needs a higher content of overmuch Fe^{++} and that causes a falling tendency with the rising temperature of the R_p curve.

According to figure 6, the fluidization will be broken down after the appearance of metallic iron. The appearance of metallic iron is a precondition for sticking. That is the first conclusion.

Two different forms of sticking have been found under different conditions:

1. Type 1

In the tests using gas 2, the samples were incompact also after the breaking down of the fluidization. Through the observation using an electron microscope, it can be seen that the surface of the samples was slick. Hydrogen in the reduction gas is the reason of the slick surface⁴⁾. That is to say, the sticking structure was weak and destroyed during the discharge.

A test was done in following way:

First step: Reduce the iron ore at a temperature bellow T_S (800 °C) to a reduction degree above R_S (about 65%).

Second step: Use N_2 instead of reduction gas and keep the fluidization.

Third step: Heat the reactor to a temperature above T_S (900 °C).

No sticking has happened during above test. This result suggested that only newly reduced iron is the causation of sticking.

Newly reduced iron is fresh. The crystallization process of fresh iron is still not fully finished. There are a lot of disfigurements at its surface. Therefore, the surface energy of fresh iron is much higher than that of normal iron. This energy increases the tendency to reduce its surface. That tendency is a kind of viscosity. According to this, the sticking tendency is relational to the mass of fresh iron. Suppose the newly reduced iron can keep its fresh state in duration D , the time of metallic iron appearance is t_0 , the fresh iron mass can be calculated as follows:

$$M = \int_0^t f(t) dt = F(t) - F(t_0) \quad \text{when } t < t_0 + D$$

$$M = \int_{t-D}^t f(t) dt = F(t) - F(t-D) \quad \text{when } t \geq t_0 + D$$

Where, $f(t)$ is the velocity of iron forming and $F(t)$ is the integral of $f(t)$. It can be seen that the mass of fresh iron is mainly depend to the velocity $f(t)$. The fresh iron mass reaches its maximal value at t_0+D . The sticking must happen during t_0 and t_0+D , if it happens. After that, there is no sticking danger.

$f(t)$ with gas 2 is much higher than that with gas 1. Therefore, sticking in this form has been most found during the reduction using gas 2.

At lower temperature, iron can keep its fresh state for a longer time (D is larger) and the viscosity of fresh iron is also lower (more fresh iron is needed for sticking). Therefore, the difference between R_S and R_P is larger at lower temperature than that at higher temperature.

2. Type 2

In the tests using gas 1, conglomerations have been always found also in the samples without breaking down of the fluidization. In the samples with breaking down of the fluidization, the scales of the conglomerations were different with different gas velocities. The grain number of the conglomerations increased with the rising of gas velocity from some ones to hundreds. At higher temperature, the scale was also larger and solidier.

Under electron microscope, whisker structure can be always seen. After the conglomerations were destroyed, more developed whisker growth at the joint surface between the grains can be observed. It is clear that the whiskers have combined the grains together.

As shown in figure 6, this type of sticking happened also after the appearance of metallic iron. Before the sticking, a small part of the grains has been reduced more deeply, for example the grains with smaller size. Metallic iron has formed at the surface in whisker form⁵⁾. The other grains are still in the state with overmuch Fe ions.

Collision happens often in a fluidized bed. If the collision happens between two or more grains with different reduction depths, the whiskers at the surfaces of the grains with deeper reduction degree are just the crystallization centers for the overmuch Fe ions in the other grains. The crystallization process happens suddenly and binds the grains together. In this case, the reduction velocity rises and the second peak forms.

The growth of the conglomerations goes continuously until metallic iron appears at all grains. As the conglomerations grow up in a scale, the fluidization of which cannot be supported by the gas, the fluidization is broken down.

Higher gas velocity can support the fluidization of greater grains. Therefore, the size of conglomerations from tests with higher gas velocities was also greater. According to this, using higher gas velocity is an effective method against breaking down of the fluidization caused by sticking type 2.

3 Prevention from sticking

It can be seen that the contact or collision between iron ore grains is the precondition for sticking with different mechanisms. To reduce the occasion of the contact should be one of the best methods to prevent sticking. Using mixed beds of iron ore and other different materials is a tryout¹⁾ of that. The mixed fluidized bed of iron ore and coal is perhaps the most practical one, because it uses coal as the main fuel. That can free fluidized bed reduction from the limitation of natural gas in addition. A series of validate experiments were carried out according to following industrial process:

1. Mixed charge of iron ore and coal is used in fluidized bed
2. A part of coal is combusted with air to supply the heat.
3. The other part of coal is in the form of coal char after the reduction.

Table II Analysis of Datong coal.

Industrial analysis						Element analysis				Ash melting points		
M_{ad} %	A_d %	V_{daf} %	FC_{ad} %	$Q_{gr,ad}$ J.mol ⁻¹	$S_{1,d}$ %	C_{daf} %	H_{daf} %	N_{daf} %	O_{da} r %	T_1 °C	T_2 °C	T_3 °C
0.80	15.8 9	30.2 5	58.2	27 096	0.9 0	82.4	4.93	1.16	10. 4	1130	1370	1430

Table III Main parameters of tests

Code	r_c	P_{CO}	Composition of gas /%		
			CO	H ₂	N ₂
0	-	0	32	14	54
1	0	0.25	32.65	11.70	55.65
2	0.2	0.30	32.11	13.15	54.74
4	0.4	0.35	31.60	14.54	53.86
5	0.6	0.40	31.09	15.91	53.00

Table III gives the conditions of tests. The compositions of gases and the quantities of coal char were calculated according to different overmuch ratios of carbon.

In table III, r_c is overmuch ratio of carbon for reduction and P_{CO} is the proportion of coal char to iron ore in charge. The gas compositions of tests 1 to 5 are similar. They will be replaced by an approximate composition, namely the composition of test 0.

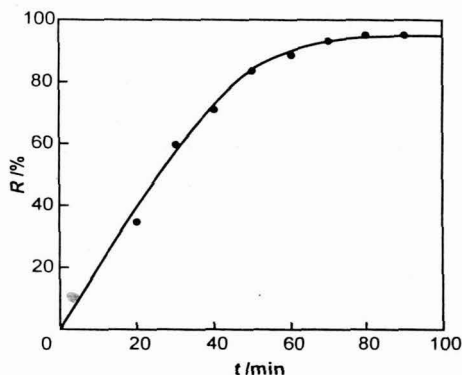


Figure 7 Reduction degrees at different time

All of the tests were carried out in continuous mode with a gas velocity of 0.9 m.s^{-1} . The maximal reduction temperature was $1000 \text{ }^\circ\text{C}$. There is melting risk of iron ore or coal ash at higher temperature.

A series of tests was carried out at $830 \text{ }^\circ\text{C}$ and with different reduction durations. P of these tests was 0.25. The main aim of that was to get suitable reduction duration for other tests. Figure 7 shows the results.

If no sticking happened, the reduction duration for all other tests was 90 min. Otherwise the test was stopped at once, when sticking happened. The main results are shown in table 4. The effect of the mixed coal char is represented very clear in this table.

Table IV Main results of validate experiments

Code	800		850		900		950		1000	
	Stickin g	R /%	Stickin g	R /%	Stickin g	R /%	Stickin g	R /%	Stickin g	R /%
0	No	81.8 6	Yes	43.2 5						
1	No	89.6 7	No	92.2 3	No	91.6 5	No	93.7 8	No	94.3 5
2	No	90.4 4	No	91.2 8	No	92.7 4	No	93.4 5	No	93.8 9
3	No	92.6 3	No	93.6 6	No	94.5 0	No	95.0 0	No	95.6 6
4	No	93.8 6	No	95.0 0	No	95.4 8	No	95.2 6	No	95.7 5
5	No	93.9 0	No	94.3 1	No	94.5 4	No	95.6 7	No	96.8 8

4 Conclusion

1. Sticking occurs after the appearance of metallic iron.
2. There are different types of sticking.
3. The first type of sticking is caused by the viscosity of fresh iron. It happens often by reduction with hydrogen.
4. The second type of sticking is caused by whisker growth of iron. It happens often by reduction with CO.
5. Using mixed fluidized bed of iron ore and coal is an effective method to prevent sticking.
6. The reduction velocity rises with the increasing of temperature and the coal char quantity in the mixed fluidized bed.

Acknowledgments

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