1. Introduction

With the rapid consumption of iron ore around the world, the iron ore deposits have been exhibited an increasingly complex mineralogical composition. It is predicted that the identified premium grade iron ore with low phosphorus content under 0.05 wt% will be depleted within 30 years at the current rate of mining.1,2) Especially in China, as the biggest iron ore import country, it is urgent to exploit the domestic iron ores like the rich high phosphorus oolitic hematite resource, while it is difficult to make use of it due to the high phosphorus content. Therefore, promoting an efficient way of dephosphorization and then fully utilize the high phosphorus oolitic iron ore could be a possible way to alleviate the shortage of iron ore resources both in China and around the world.

As the apatite and chamosite phases in the high phosphorous oolitic iron ore are so intimately intermixed, it is impractical to grind it to a fine enough size to separate the iron oxides from the phosphorus containing phase directly. So it needs some other methods to deal with this kind of ore. In recent years, the main dephosphorization process for high phosphorus iron ores includes: (1) the hydrometallurgy method, such as the reverse flotation process,3,4) the bioleaching process,5–8) the acid leaching process 9,10) and the alkaline leaching process;11) (2) the thermometallurgy method combined with physical separation, such as the coal-based direct reduction assisted with grinding and magnetic separation process,12,13) which is beneficial for the DRI recovery but confronted with the problem of separating the ferrous phase from the phosphorus containing gangue, and the degree of sintering of the reduced phases was a critical parameter in the grinding and magnetic separation treatment. When the reduction temperature is above 1 473 K, the apatite will be reduced to elemental P which can be smelt into metal iron. But lowering the reduction temperature will hinder the reduction rate and the sintering of DRI phase. So this contradiction is the major defect of process (2).

E. Matinde14,15) and W. Yu16) have widely studied the dephosphorization effect of pre-reduction, mechanical crushing and screening method. W. Yu further investigated the function of Ca(OH)2 and Na 2CO3 as additives on coal-based reduction and the phase evolution. This method can result in the low recovery of iron oxide while the iron loss with acid leaching method in this study is under 0.6 wt%.17) M. J. Fisher-White18) has studied the effects of a heat treatment with sodium hydroxide followed by leaching with water and a caustic leach on the removal of phosphorus from goethitic iron ores, and he found that phosphorus associated with the goethite in high-phosphorus iron ores can be removed to 0.075% P (0.15 wt% in raw ore) using a heat treatment at 573 K–623 K for 1 h with 10 wt% NaOH, followed by a water leach. But the high levels of sodium or other elements in the additives may be detrimental in a blast furnace feed.15,19)

J. T. Yu17) and M. J. Fisher-White20) have studied the dephosphorization effect on the goethitic iron ore and the oolitic hematite iron ore respectively by sulphuric acid leaching method. With suitable treatment, the phosphorus can be removed with little dissolution of iron and lower acid consumption.

A process with acid leaching followed by hydrogen-based fluidized reduction and melt separation is presented for recovering DRI (direct reduced iron) from high-phosphorus oolitic hematite in this study, and the aim of this study is to provide theoretical and technical basis for economical and rational use of high phosphorus oolitic iron ores. The reducibility of the ore can be improved by acid leaching, which is caused by the formation of voids in the ore particles after acid leaching and enhancing the internal gas diffusion. The phosphorus content in the DRI is still relative high even though there is no carbon in DRI, and it can be decreased to 0.087 wt% (raw ore 1.2 wt%) with the optimum condition in this study. It is proved that P exists in the DRI recovered from melt separation in the form of P2O5 inclusions or Fe xP as solid solutions, while not in the form of Ca3(PO4)2 inclusions. Finally, a combined flowsheet for the treatment of high phosphorus oolitic iron ore is designed in this study.

KEY WORDS: dephosphorization; acid leaching; DRI; fluidized bed; melt separation.
As most of the pre-dephosphorization processes require pulverous high phosphorus iron ore, which is the well feedstock of the fluidized bed reduction, but the influence of acid leaching on the fluidized reduction behavior of high phosphorous iron ore fines is still not clear. And the transform and transmission mechanism of the phosphorus during melt separation process without carbon is not yet completely clarified. So the combined process of acid leaching, hydrogen-based fluidized reduction and melt separation to highly utilize the high phosphorus oolitic iron ore was investigated in this study.

S. Fukagai has studied the reaction mechanism of the 2CaO·SiO$_2$ phase and the FeO$_x$–CaO–SiO$_2$–P$_2$O$_5$ slag, and he reported the different mass transfer characteristics of phosphorus between 2CaO·SiO$_2$ saturated and not saturated slags and the 2CaO·SiO$_2$ particles. Some researchers think that the P exists in the metal as apatite inclusions, while this view is reconsidered in this study with different experimental results and thermodynamic calculation.

2. Experimental

2.1. Apparatus

The schematic diagrams of the experimental setup are shown in Fig. 1. The samples after acid leaching treatment were feed into the fluidized bed for reduction.

2.2. Specimens

The ore used in this experiment was from Hubei province of China, the lump ore was crushed and screened to 110–149 μm in particle size, the chemical compositions of the raw ore and the ore after acid leaching are listed in Table 1. The data was achieved by the XRF method. The calcium and phosphorus were extremely removed after acid leaching treatment, and that was caused by the dissolution of the apatite into the acid liquor. The apatite or fluorapatite phases are proved to be the main existence form of calcium and phosphorus. They distribute in the oolitic structures of the high phosphorus iron ores as illustrated in Fig. 2. It can be seen clearly that hematite together with chlorite and apatite builds the concentric shell of oolites, the iron oxides and gangue minerals are intimately intergrowth. XRD result of Fig. 3 shows the phase evolution of the iron ore with acid leaching and fluidized reduction treatment. The apatite phase cannot be detected after acid leaching.

2.3. Experimental Procedure

(1) Acid leaching

The dilute sulphuric acid solution of 0.2 mol/L was chosen as the leachant in this experiment, the liquid-solid ratio was 25 to 2 which was 300 ml acid liquor and 24 g iron ore powder. The leaching temperature was 323 K and the rate of agitation was 200 r/min. After 40 min leaching treatment, the samples were cleaned with deionized water for several times until the water became transparent, then put them in the drying oven under 393 K for 12 hours. The dephosphorization reaction in this experiment is:

$$\text{Ca}_3(\text{PO}_4)_2(\text{F,OH,Cl}) \rightarrow 5\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4 + \text{H(}\text{F,OH,Cl)}.$$ 

(2) TG (Thermogravimetric) analysis

The influence of the acid leaching treatment on the reduction kinetics was investigated using LINSEIS STA PT 1600 thermal analysis instrument. Each batch of 20 mg sample was first heated from ambient temperature to a predetermined temperature at 15 K/min in argon gas atmosphere. When it rose to the target temperature, the reducing gas of 30 ml/min H$_2$ and 70 ml/min Ar were feed into the apparatus, and the isothermal reduction started subsequently.

(3) Fluidized bed reduction

Batches of 20 g iron ore powder was isothermally reduced in the fluidized bed with the gas flow of 1 L/min Ar and 2 L/min H$_2$ at 1 073 K. 80 min of normal fluidization
can be achieved for the raw ore, while sticking happened at 11 min of fluidization for the acid leaching ore, so 1.5 wt% of MgO powder as sticking-prevention agent was added into the acid leaching ore samples to sustain 80 min of fluidized reduction. After reduction, the reduced samples were cooled to ambient temperature in Ar atmosphere and prepared for subsequent melt separation treatment.

(4) Melt separation

Batches of 7 g of the reduced sample were put into the alumina crucibles of 10 ml and covered with lid, then placed the crucibles into the muffle furnace at the target temperature under ambient atmosphere for melt separation treatment. Keeping the samples in the furnace for the fixed time and then took them out to cool in the ambient temperature.

2.4. Analysis and Characterization

(1) The metallization ratio is defined as:

\[ M_R = \frac{M_{Fe}}{T_{Fe}} \times 100\% \] ........................... (1)

where \( M_R \), \( M_{Fe} \), \( T_{Fe} \) are the metallization ratio (%), the total metallic iron (wt%) and the total iron (wt%) respectively. The mass fraction of the total iron and the metallic iron in the reduced samples were measured by the chemical analytical method.

(2) The reduction degree is defined as:

\[ \alpha = \frac{w}{w_0} \times 100\% \] .......................... (2)

where \( \alpha \), \( w \), \( w_0 \) are the reduction degree, the actual and the theoretical oxygen weight loss of iron oxides. All the gangue phases cannot be reduced by H2 reduction in this experiment, so the weight loss of the sample during reduction was considered to be equal to the oxygen weight loss in iron oxides. The iron oxides in the high phosphorus iron ore are mainly in the type of Fe2O3 and FeO. Assume that the total weight of the iron ore is “m” g, of which the Fe2O3 weight is “a” g and the FeO weight is “b” g, then the total oxygen weight loss of Fe2O3 and FeO are 3/10 \( a \) g and 2/9 \( b \) g respectively. The total iron in the raw ore is 47.1 wt% with the total ferrous iron of 1.17 wt%, and the total iron in the acid leaching ore is 52.3 wt% with 1.43 wt% of total ferrous iron (The mass fractions of total iron and total ferrous iron were measured by the chemical analytical methods according to the national standard GB/T 6730.5-2007 and GB/T 6730.8-1986 in China). Then in the raw ore:

\[ a = \frac{0.471m - 0.0117m \times 160}{56 \times 2} = 0.566m \]

\[ b = 0.0117m \]

The theoretical total weight loss is: \( w_0 = 3/10a + 2/9b = 0.1994m \).

In the acid leaching ore:

\[ a = \frac{0.523m - 0.0143m \times 160}{56 \times 2} = 0.727m \]

\[ b = 0.0143m \]

The theoretical total weight loss is: \( w_0 = 3/10a + 2/9b = 0.2212m \).

(3) The iron recovery rate is the mass ratio between the
weight of the DRI recovered from melt separation and the total metallic iron weight in the ore before melt separation.

(4) The P, Ca and total iron contents in the DRI and ore were measured by the ICP method with OPTIMA 7000DV. Before ICP analyzing, the samples were firstly dissolved in concentrated hydrochloric acid at 373 K, several drops of hydrofluoric acid were added into the samples to help to dissolve the gangue phases such as silicate minerals especially for the raw ore. Afterwards, the samples were concentrated by evaporation to eliminate the redundant acid, finally diluted the desolved samples to 200 ml preparing for analyzing. With this dissolution treatment there was no residue left and the samples after concentrate can all be dissolved into water. The total oxygen was analyzed with the LECO-TCH600 nitrogen-oxygen analyzer, and the total carbon was measured with the HORIBA-EMIA-820V carbon-sulfur analyzer.

3. Results and Discussion

3.1. Effect of MgO Addition on the Sticking Behavior after Acid Leaching

The raw ore can accomplish 80 min of normal fluidization without sticking in this experiment, but the acid leaching ore sticks after 11 min of fluidized reduction. This phenomenon may cause by the removal of apatite phase as the gangue phases containing Ca, Si, Mg elements are usually against sticking. Moreover, the increase of total iron content as shown in Table 1 will increase the metallic iron concentration on the ore particle surface which may also promote sticking. Then MgO as sticking prevent agent was added into the samples prevent the undesirable sticking. The relationship between the MgO addition amount and the fluidization time, metallization ratio of acid leaching ore is shown in Fig. 4. The fluidization time can be prolonged to much more than 80 min (e.g. 120 min can be achieved) when the MgO addition amount reaches 1.0 wt%. As the metallization ratio can reach to more than 82% with 80 min of reduction and scarcely increase after that, furthermore, in order to uniform the metallization ratio of the reduction samples, 80 min of fluidized reduction time was chosen as the uniform reduction time in this study, and the reduction was manually stopped when the fluidization had sustained for 80 min without sticking.

3.2. Effect of Acid Leaching on Reduction Kinetics

Except for the influence of acid leaching on the sticking trend of high phosphorus iron ore, the reduction rate and reduction extent can be improved by acid leaching treatment. To further study this phenomenon, both the raw ore and the acid leaching ore were subjected to isothermal reduction TG analysis (section 2.3 (2)). The reduction curves are plotted in Fig. 5.

The model function integral method was introduced to analyze the reduction degree data. The integral kinetic model function is defined as follows:

\[ G(\alpha) = \int_{0}^{t} \frac{d\alpha}{f(\alpha)} \]

The kinetic model function under isothermal conditions is:

\[ \frac{d\alpha}{dt} = kf(\alpha) \], that is \[ \frac{d\alpha}{f(\alpha)} = kd(t) \]

So Eq. (3) can be changed as:

\[ G(\alpha) = \int kd(t) = kt \]

In above equations, \( G(\alpha) \) stands for different reduction kinetics mechanism function. The general used kinetics mechanism functions are listed in Table 2, where \( F_p \) is shape factor of solid particle and for infinite flat \( F_p=1 \), for cylinder \( F_p=2 \), for sphere or cubic \( F_p=3 \). For instance, to substitute the experimental reduction degree data for “\( \alpha \)” in the interface reaction mechanism function \( G(\alpha)=kt=1- \)
$(1 - \alpha)^{1/2}$, and then plot the relationship between the calculated values of $1 - (1 - \alpha)^{1/2}$ and reduction time $t$ with symbol points as shown in Fig. 6. Analyzing work with different kinetics mechanism functions in Table 2 was carried out as the steps described above, and the linearity of those symbol points in the reduction time interval of 0–500 s was also compared. The kinetics analyzing with this method was mainly used to model the early reduction period before reaching the reduction speed turning point. So the time range for kinetics analyzing was chosen from 0 s to 500 s, because after 500 s the reduction has gradually approached the maximum extent as shown in Fig. 5.

<table>
<thead>
<tr>
<th>$G(\alpha)$</th>
<th>Shape factor/$F\alpha$</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 - (1 - \alpha)$</td>
<td>1</td>
<td>Interface reaction</td>
</tr>
<tr>
<td>$1 - (1 - \alpha)^{2/3}$</td>
<td>2</td>
<td>Interface reaction</td>
</tr>
<tr>
<td>$1 - (1 - \alpha)^{1/3}$</td>
<td>3</td>
<td>Interface reaction</td>
</tr>
<tr>
<td>$\alpha + (1 - \alpha) \ln(1 - \alpha)$</td>
<td>2</td>
<td>One dimensional diffusion</td>
</tr>
<tr>
<td>$1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)$</td>
<td>3</td>
<td>Three dimensional diffusion</td>
</tr>
<tr>
<td>$[1 - (2/3) \alpha ] - (1 - \alpha)^{2/3}$</td>
<td>3</td>
<td>Ginstling-Brounshte equation</td>
</tr>
<tr>
<td>$[1 - (1 - \alpha)^2]^3$</td>
<td>3</td>
<td>Jander equation</td>
</tr>
<tr>
<td>$- \ln(1 - \alpha)$</td>
<td>1</td>
<td>First-order equation</td>
</tr>
<tr>
<td>$[- \ln(1 - \alpha)]^{1/2}$</td>
<td>2</td>
<td>Avrami-Erofeiev equation</td>
</tr>
<tr>
<td>$[- \ln(1 - \alpha)]^{1/3}$</td>
<td>3</td>
<td>Avrami-Erofeiev equation</td>
</tr>
</tbody>
</table>

Among those kinetics mechanism functions, the interface reaction mechanism function $G(\alpha)=kt=1 - (1 - \alpha)^{1/2}$ shows the best linearity and it is the most suitable one to model the reduction kinetics. Then fit the experimental symbol points with straight lines as shown in Fig. 6, and the slopes are the corresponding chemical reaction rate constant $k$ under different conditions. As the reduction speed of raw ore at 1073 K has sharply dropped at later stage before 500 s as shown in Fig. 5, the time range for kinetics analyzing of raw ore at 1073 K was chosen from 0 s to 400 s in order to model the reduction behavior better.

As the Arrhenius function describes,

$$k = A \exp \left( - \frac{E}{RT} \right),$$

that is $\ln k = - \frac{E}{RT} + \ln A$ ...... (6)

So the slope and the intercept of linear fitting curves as plotted in Fig. 7 between $\ln k$ and $(1/T) \times 1000$ at different temperatures are the values of $-E/R$ and $\ln A$ respectively. Then the values of the apparent activation energy “$E$” and frequency factor “$A$” can be calculated, the result is listed in Table 3.

In the Arrhenius function, the frequency factor “$A$” stands for the total effective collision frequency of the activated molecules. The frequency factor of acid leaching ore has three times larger than that of raw ore as seen in Table 3, and that effect is given by increasing specific surface area of ore due to leaching.

On the other side, as seen in Table 4, according to the analysis of the relations between the apparent activation energies and mechanisms for the H2-based Fe2O3 reduction

![Fig. 6. Linear fitting curves of $1 - (1 - \alpha)^{1/2}$ and reduction time at different temperatures.](image)

![Fig. 7. Linear fitting curves of $\ln k(T)$ and $(1/T) \times 1000$.](image)
by J. H. Liu, the value of apparent activation energy for the raw ore is 37.77 kJ/mol, so the reaction mechanism for the raw ore is the mixing control of gaseous internal diffusion and interface reaction; the value of apparent activation energy for the acid leaching ore is 47.76 kJ/mol, which indicates that the reaction mechanism for the acid leaching ore is the control of interface reaction. And the “E” value of the raw ore is lower than that of the acid leaching ore, which indicates that the resistance of gaseous internal diffusion is more obvious for the raw ore, that is, the gaseous diffusion condition is improved for the ore powder after acid leaching treatment.

The change of ore’s reduction characteristics after acid leaching treatment can be explained by the microstructure evolvement during acid leaching. As shown in Fig. 8, the surface of the raw ore particle is smooth and dense while lots of voids show up after acid leaching. Referring to the compositional variation shown in Table 1, the content of “Ca”, “P” decreased sharply after acid leaching, so that may attribute to the dissolution of apatite phase in the ore and leave a porous microstructure. The voids can be beneficial for the gas conveying within the ore particles during reduction, which promotes the reduction rate and extent consequently.

H. Q. Tang studied the reduction kinetics of the high phosphorus iron ore after microwave pretreatment, he found that the oolitic unit generated cracks and fissures due to microwave treatment, the particle’s structural change effect (increase of particle’s specific surface area) is similar to that caused by acid leaching in this study. So the gas conveying within the ore particles could also be apparently intensified, and finally achieved 10%–13% increase of metallization ratio by microwave treatment. As shown in Fig. 9, after 80 min of reduction the metallization ratio of the ore with acid leaching treatment is about 13.7% higher than the raw ore.

### 3.3. Reduction and Melting Separation Behavior

Fluidized reduction experiment was carried out before melt separation, the experimental conditions have been described in section 2.3 (3), the metallization ratios with different reduction times are shown in Fig. 9. With the same 80 min of fluidized reduction, the acid leaching ore can obtain 81.9% of metallization ratio, there is about 13% of increase compared to 68.2% of the raw ore.

The samples after reduction were then subjected to melt separation at 1 773 K and 1 823 K with different holding times and basicities. The experimental condition of each sample is listed in Table 5. The cross section morphology of the DRI finally recovered is shown in Fig. 10, which can infer the melt separation effect between the DRI and slag.

Because the metallization ratio of the reduced raw ore is lower than that of the acid leaching ore, the content of FeO in the slag of raw ore is more, which is beneficial for the fluidity of the slag. What’s more, low basicity can deteriorate the fluidity of the melts and the CaO content in the acid leaching ore is so tiny as shown in Table 1. With lower content of FeO and CaO, the slag and DRI separation effect of the acid leaching ore is worse than the raw ore at 1 773 K as shown in Figs. 10(a), 10(b). In the DRI recovered from the melt separation of acid leaching ore at 1 773 K, there are some large slag inclusions as shown in Figs. 10(b)–10(e). When the melt temperature reaches 1 823 K, large slag inclusions can no longer be found with naked eye, thus, higher temperature can promote the separation of slag and DRI. The melting point of pure iron is 1 808 K, while the metallic iron can soften and aggregate when the temperature (like 1 773 K) is near the melting point. So the metallic iron and the slag can also be separated to some extent at high temperatures under the melting point of pure iron.

Too short melt separation time will decrease the separation extent of DRI and slag and lead to slag inclusions (Fig. 10(k)) or even no separation at all (Fig. 10(o)). There was no separated slag obtained in the “No. ø” melt separation treatment as the slag and DRI was still in a mixing state, so
The slag-DRI bulk after melt separation treatment was much bigger than others as seen in Fig. 10(o). This phenomenon may be caused by the higher metallization ratio and lower basicity of sample No. o compared to No. k as explained in the above paragraph. Adding CaO into the ore with definite basicity before melt separation will also promote the DRI and slag separation (comparing b and q, r in Fig. 10).

The iron recovery rates of the samples are shown in Fig. 11. As the slag inclusion weight is also included in the weight of the recovered DRI, the value of iron recovery rates of the acid leaching ore are higher than the raw ore. Similarly, the DRI and slag separation effect of the acid leaching ore at 1 773 K is worse than that of 1 823 K, so the iron recovery rate at 1 773 K is a bit higher than that of 1 823 K.

3.4. Dephosphorization Effects in this Process

Measured by the ICP method, the P content of the iron ore after fluidized reduction is shown in Fig. 12. It can be seen that the reduction treatment scarcely makes difference on the P content of those two kinds of ores. The dephosphorization effect by melt separation treatment and in whole process is indicated with P removal rate as listed in Table 6. It can be seen that the total P removal ratio in the whole process with acid leaching and melt separation can reach to about 94%, and the P removal ratio of the acid leaching ore is about two times of that of the raw ore only via the melt separation.

The P content in the DRI after melt separation is shown in Fig. 13. The increase of temperature promotes the dephosphorization effect in the melt separation process of raw ore and acid leaching ore, of which the P content is decreased to around 0.2 wt% in the recovered DRI from melt separation of acid leaching ore at 1 823 K. Adding CaO to the ore

---

Table 5. Experimental conditions of the melt separation treatment.

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Ore type</th>
<th>Basicity</th>
<th>Melt separation time (min)</th>
<th>Melt separation temperature (K)</th>
<th>Reduction time (min)</th>
<th>Metallization ratio</th>
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<tbody>
<tr>
<td>a</td>
<td>R</td>
<td></td>
<td></td>
<td>1 773</td>
<td>80</td>
<td>68.2</td>
</tr>
<tr>
<td>b</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td>80</td>
<td>81.9</td>
</tr>
<tr>
<td>c</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>75.7</td>
</tr>
<tr>
<td>d</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>77.3</td>
</tr>
<tr>
<td>e</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>74</td>
</tr>
<tr>
<td>f</td>
<td>R</td>
<td></td>
<td>15</td>
<td>1 773</td>
<td>80</td>
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</tr>
<tr>
<td>g</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td>80</td>
<td>81.9</td>
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<tr>
<td>h</td>
<td>A</td>
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<td>10</td>
<td>74</td>
</tr>
<tr>
<td>k</td>
<td>R</td>
<td></td>
<td>5</td>
<td>1 823</td>
<td>80</td>
<td>68.2</td>
</tr>
<tr>
<td>l</td>
<td>R</td>
<td></td>
<td>5</td>
<td></td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>R</td>
<td>1.0</td>
<td>15</td>
<td></td>
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</tr>
<tr>
<td>n</td>
<td>R</td>
<td>2.0</td>
<td>15</td>
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</tr>
<tr>
<td>o</td>
<td>A</td>
<td>Original</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>A</td>
<td>Basicity</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>q</td>
<td>A</td>
<td>1.0</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r</td>
<td>A</td>
<td>2.0</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R: Raw ore; A: Acid leaching ore; Basicity: \((m_{CaO}/m_{SiO_2})\)%

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Fig. 10. Cross section pictures of DRI recovered from melt separation.

Fig. 11. The iron recovery rate of different samples.
sample with basicity of 1.5% before melt separation, the P content in the DRI decreases a step further. So adding CaO into the ore sample is definitely beneficial for the dephosphorization during melt separation. Comparing Figs. 12 and 13, it can be found that the P content in the DRI obtained by metal/slag separation of reduced raw ore without adding CaO is higher than that in the raw ore. It indicates that under this experimental condition P has concentrated in the metallic iron to some extent compared to the slag, detailed P migration behaviors is discussed in latter paragraphs of this section.

P content in the recovered DRI after melt separation at 1823 K with different CaO dosage is shown in Fig. 14. The dephosphorization effect increases obviously with the increase of basicity for the raw ore, and as the relatively low P content in the acid leaching ore, the promotion on the dephosphorization effect with increasing basicity is limited. The P content has been decreased to 0.087 wt% at the optimum condition.

To explore the mechanism of P migration among the slag phase and the DRI phase, melt separation experiments with different melt times and temperatures were carried out, and the contents of Fe, P, Ca, O and C elements were paid full

<table>
<thead>
<tr>
<th>Table 6. Main components in the DRI with different melt separation conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Elements Iron P removal ratio/ %</td>
</tr>
<tr>
<td>time/min</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>1853 K Raw ore</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>Raw ore</td>
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<tr>
<td>30</td>
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<tr>
<td>60</td>
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<tr>
<td>Acid leaching ore</td>
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<td>60</td>
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<tr>
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</tbody>
</table>
Before doing the thermodynamic calculations, one thing should be clear: Theoretically, the activities of P\textsubscript{2}O\textsubscript{5} or Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} phases in the actual homogeneous molten slag are much lower than 1. But during the melt separation process, the iron and gangue phases firstly become softening and agglomerate into small units before melting into liquid state. And the special oolitic structure of the high phosphorous iron ore contributes to the great contact area between the gangue phase and iron phase, so on a micro level, the activity values of P\textsubscript{2}O\textsubscript{5} or Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} phases can be considered close to that in standard state. Thus, the thermodynamic calculations with the data from HSC Chemistry\textsuperscript{®} 5.1 software in Fig. 15 are proper to be used to explain the experimental phenomena during gas-based reduction and metal/slag separation processes in this study.

Using the thermodynamic data under equilibrium condition in Fig. 15 as reference, the reactions among the ore phases at actual situation can be analyzed as: according to the values of Gibbs free energy (delta G) and equilibrium constant (K), conclusions can be drawn as: the P element in apatite phase can be reduced to Fe\textsubscript{2}P, P\textsubscript{2} vapor or PO vapor by carbon above 1 129 K, 1 471 K and 1 771 K respectively as shown in Fig. 15, while very hard to be reduced by H\textsubscript{2} in the temperature range of 300 K–1 900 K\textsuperscript{2,16,19} as the values of delta G are all above zero and the values of K are so tiny (below 6.28\times10\textsuperscript{–5} even the temperature reaches 1 873 K). So it can be inferred that it is easy for the P to mix in the metallic phase and cause the high P content during melt separation or DRI aggregation process at high temperatures when there is carbon in the ore, but in this study the reducing agent is H\textsubscript{2} and there is no carbon in the raw ore, so the apatite phase remains stable in the iron ore reduced by hydrogen in this experiment (Fig. 3).

If the P content exists in DRI in the form of apatite inclusions like Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}, the mass ratio between Ca and P should be around 120/62. But in this study, the P content is much higher than that of the Ca content in the DRI as listed in Table 6, and there is no Ca, Si or Al detected in the P contained inclusions as shown in element mappings of Fig. 16. This provides evidence that P does not exist in the DRI in the form of apatite inclusions, and the O content in the P contained inclusions as shown in Fig. 16 may prove that part of P exists in the DRI in the form of PO\textsubscript{x}.

As shown in Fig. 17, indicated by the thermodynamic calculation under equilibrium condition with HSC Chemistry\textsuperscript{®} 5.1 software, the values of delta G are all below zero and the values of K are very high. Theoretically, those two reactions are very easy to happen and generate Fe\textsubscript{2}P or Fe\textsubscript{3}P phases. It can be inferred that the P content may also exists in the form of solid solutions in DRI.

3.5. Discussion and Flowsheet Design

The flowsheet to efficiently treat high phosphorous oolitic iron ore is designed as described in Fig. 18. Firstly, the P content can be efficient removed by the acid leaching dephosphorization unit, and without pelleting or sintering.

![Image](image_url)
process the acid leaching ore after drying can be directly utilized in the fluidized bed reduction process, the reducing gas can get from natural gas pyrolysis and some sticking prevention agent can be added into the fluidized bed to avoid the defluidization. Then the DRI or HBI product produced by the fluidized reduction unit can be used in the EAF (electric arc furnace) melt separation unit or other steelmaking processes.

4. Conclusions

The feasibility of the combined acid-leaching fluidized-reduction and melt-separation process was studied in this study. The influence of acid leaching on the reducing characteristics of high phosphorus iron ore as well as the transform and transmission mechanism of the phosphorus during melt separation process without carbon were also investigated.

The acid leaching treatment can deteriorate the sticking problem during fluidized reduction of ore powders as the cutting down of apatite phase, but it is beneficial for the increase of reduction rate and extent by the formation of voids in the ore particles.

Higher temperature and basicity can both improve the slag and metallic iron separation efficiency and help to shorten the melt separation time. Proper dosage of CaO is surely can help to remove P in the metallic iron. P does not exist in the metallic iron in the form of Ca$_3$(PO$_4$)$_2$, as there was too low Ca content detected in the metallic iron and no Ca detected in the P contained inclusions.

P content in the metallic iron cannot be expectedly removed by the elimination of carbon in DRI as it can exists in the metallic iron in the form P$_2$O$_5$, and Fe may also reduce P$_2$O$_5$ to Fe$_3$P at high temperatures.

The flowsheet of the proposed process to treat high phosphorus oolitic iron ores is designed, but the P in the metallic iron is still a bit high for steelmaking. A lot of works are needed to further increase the reduction extent of the iron ore and clarify the transform and transfer mechanisms of P during melt separation.

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REFERENCES

2) H. Han, D. Duan, P. Yuan and S. Chen: Ironmaking Steelmaking, 42 (2015), 1.
7) T. M. Bhatti and W. Yawar: Hydrometallurgy, 103 (2010), 54.