Preparation of Ti-rich Feedstock by Hydrochloric Acid Leaching of High Titanium Blast Furnace Slag

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**Keywords:** High ti-bearing blast furnace slag, Titanium dioxide, Ti-rich feedstock.

**Abstract.** Ti-rich feedstock was prepared by acidic decomposition of air-cooled high-Ti blast furnace slag. Ti-rich feedstock with over 45% TiO\(_2\) can be obtained at the condition of hydrochloric acid concentration = 7 mol/L, mass ratio of acid and slag = 1.7:1, decomposition temperature at 90 \(^\circ\)C and reactive time = 7 h.

Panzhihua is a well-known capital city of vanadium and titanium and its proved titanium storage accounts for 90.54% in China and 35.17% in the world, with a potential economic value of 8000 billion dollars. However, the current steel production process only utilizes 20% (mass fraction) of titanium in vanadium titano-magnetite. The TiO\(_2\) in iron concentrate, after processing in the blast furnace, generally is passed to blast furnace slag and finally discarded together with slag \(^1\). The Panzhihua Iron and Steel Co. (short for Pangang) blast furnace slag contains up to 20% - 23% of TiO\(_2\) (mass fraction). On this basis, with an annual production of 4 million tons of iron, the annual production of blast furnace slag is 3.2 million tons, which is estimated to be about 0.9 million tons of TiO\(_2\) or an economic loss up to 5 billion RMB. PanGang has discharged an accumulation of 50 million tons of Ti-bearing blast furnace slag. Besides a small part used as building materials, the majority has been stacked in two slag fields. The current comprehensive utilization rate is below 15%, which indicates severe resource waste and potential risks of environmental pollution. Thus, comprehensive and efficient use of Ti-bearing PanGang blast furnace slag is of significant economic values and social benefits\(^1\).

The titanium iron ores used in blast furnaces outside of China generally only contain 3% -4% (mass fraction) of TiO\(_2\), and the resulting blast furnace slag contains less than 10% of TiO\(_2\), which does not need special treatment. Researchers from Germany, US and Japan have studied Ti extraction from PanGang blast furnace slag, but nearly all pointed out the severe difficulty and have not given any efficient solution \(^2\). To solve the problem of comprehensively utilizing high-Ti blast furnace slag, Chinese researchers have conducted numerous studies in recent years and preliminarily identified some techniques, including compound method, application phase separation method, high-temperature carbonization & low-temperature chlorination, selective separation of valuable components, and TiCl\(_4\) preparation from Ti-containing blast furnace slag \(^3\)\(^-\)\(^7\). These methods have respective advantages, but are restricted by some limitations. So far, none of these methods can be industrialized.

PanGang high-Ti blast furnace slag is divided into water-cooled slag and air-cooled slag, which are cooled down by water and by air after outputted from the blast furnace, respectively. Compared with water-cooled slag, the air-cooled high-Ti blast furnace slag is featured by high crystal orderness, stable physiochemical properties, and acid insolubility of TiO\(_2\) at normal temperature \(^8\). According to these properties, HCl decomposition can be conducted to remove the soluble impurities from the slag and to prepare Ti-rich feedstock. However, there is no report in this field.

**Experimental**

**Materials and Instruments**

In this study, air-cooled high-Ti blast furnace slag was collected from the Baguanhe Slag Field of PanGang. After drying, high-energy ball milling and screening, the particle sizes of slag were 0-160
meshes. The chemical composition is listed in Table 1. The HCl, ammonia and NaOH (all analytically pure) were bought from Chengdu Kelong Chemical Ltd. Co.

<table>
<thead>
<tr>
<th></th>
<th>TiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>ΣFe</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20.24</td>
<td>20.16</td>
<td>8.13</td>
<td>14.13</td>
<td>23.55</td>
<td>8.48</td>
<td>5.31</td>
</tr>
</tbody>
</table>

The major instruments used here included an SX2-1700 °C chamber-type resistance furnace (Tianjin Taisite Instruments Ltd. Co.), an SYP- glass thermostat waterbath tank (Nanjing Sangli Eleotronic Equipment Factory), and a 202-thermostatic drying oven (Beijing Yongguangming Medical Instruments Company).

**Experimental Methods**

**Preparation of Ti-rich Feedstock.** Ti-rich feedstock slag was prepared as follows: the 100 - 600 mesh blast furnace slag was heated in a water bath to a certain temperature, and decomposed by a certain concentration of HCl under stirring for a certain period, followed by cooling, filtering and washing.

**Analytical Methods[9]**

Mass fraction of TiO₂ in the Ti-rich feedstock was determined by a ferric ammonium sulfate volumetric method (GB/T 4102.1—1983). Mass fraction of total iron was measured by a dichromate titration method (GB/T 4102.2—1983). Mass fraction of Al₂O₃ was detected by ethylene diamine tetraacetic acid (EDTA) volumetric method (GB/T 4102.8—1983). Mass fractions of Mg and Ca were measured by EDTA volumetric method (GB/T 4102.12—1983).

**Results and Discussion**

**Acidic Decomposition of Ti-rich Slag**

**Effects of Reaction Temperature on TiO₂ Mass Fraction in Acidic Decomposition Slag.** The effects of reaction temperature on acidic decomposition are illustrated in Fig. 1, under the condition of 30 g of blast furnace slag (100-160 mesh), HCl concentration = 7 mol/L, and reaction time = 6 h.

Clearly, the mass fraction of TiO₂ in the acidic decomposition slag increases with the rise of reaction temperature, and stabilizes at 70 °C. Considering that temperature rise would increase the costs, we think the optimal acidic decomposition temperature should be controlled around 70 °C.

![Figure 1. Effect of reaction temperature on dosage of TiO₂](image1)

![Figure 2. Effect of concentration of HCl on rate of TiO₂ of slag.](image2)

**Effects of HCl Concentration on TiO₂ Mass Fraction in Acidic Decomposition Slag.** The effects of HCl concentration on TiO₂ mass fraction in acidic decomposition slag are showed in Fig. 2, under the conditions of reaction temperature = 90 °C, reaction time = 6 h, and acid-slag ratio = 1.7: 1. Clearly, the TiO₂ mass fraction in the acidic decomposition slag is the highest at HCl concentration of 7 mol/L, and beyond that concentration, a part of TiO₂ entered the liquid phase,
leading to the decline of TiO$_2$ mass fraction in the final slag. Thus, the optimal HCl concentration should be lower than 7 mol/L.

**Effects of Reaction Time On TiO$_2$ Mass Fraction in Acidic Decomposition Slag.** The effects of reaction time on TiO$_2$ mass fractions in acidic decomposition slag are illustrated in Fig. 3, under the conditions of reaction temperature at 90 °C, HCl concentration = 7 mol/L, and acid to slag ratio = 1.7: 1. Clearly, with the prolonging of reaction time, the TiO$_2$ mass fraction in the acidic decomposition slag increases, and maximizes to 46.65% after 6 h. After that, a part of TiO$_2$ was dissolved with further prolonging of time, which led to a reduction in the mass fraction of TiO$_2$. Thus, the optimal reaction time should be controlled around 6 h.

![Figure 3. Effect of reaction time to rate of TiO$_2$ of slag.](image)

![Figure 4. Effect of ratio of HCl and slag to rate of TiO$_2$ of slag.](image)

**Effects of Acid-slag Ratio on TiO$_2$ Mass Fraction in Acidic Decomposition Slag.** The effects of acid-slag ratio on TiO$_2$ mass fractions in acidic decomposition slag are illustrated in Fig. 4, under the conditions of reaction temperature at 90 °C, reaction time = 6 h, and HCl concentration = 7 mol/L. Clearly, at the acid-slag ratio of 1.7:1, the TiO$_2$ mass fraction in the acidic decomposition slag maximizes to 46.5%. After that, the TiO$_2$ mass fraction slightly declines, because the TiOCl$_2$ resulting from the reaction between HCl and Ti was dissolved in the solution, while the hydrolysis from TiOCl$_2$ to TiO$_2$ was hard, leading to a reduction of TiO$_2$ mass fraction in the slags.

**Orthogonal Test of Acidic Decomposition Process**

To determine the influence factors and optimal process conditions of acidic decomposition, we selected four factors according to the single-factor test results and conducted orthogonal tests: HCl concentration, temperature, acid-slag ratio, and reaction time. The levels and results of test factors are listed in Tables 2 and 3.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>A HCl/(mol·L$^{-1}$)</th>
<th>B Temperature / °C</th>
<th>C Acid-slag ratio</th>
<th>D Reaction time /h</th>
<th>w(TiO$_2$)/%</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>90</td>
<td>1.6:1</td>
<td>5</td>
<td>43.14</td>
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<tr>
<td>2</td>
<td>6</td>
<td>80</td>
<td>1.7:1</td>
<td>6</td>
<td>42.12</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>70</td>
<td>1.8:1</td>
<td>7</td>
<td>41.05</td>
</tr>
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<td>4</td>
<td>7</td>
<td>90</td>
<td>1.7:1</td>
<td>7</td>
<td>46.22</td>
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<tr>
<td>5</td>
<td>7</td>
<td>80</td>
<td>1.8:1</td>
<td>5</td>
<td>45.01</td>
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<tr>
<td>6</td>
<td>7</td>
<td>70</td>
<td>1.6:1</td>
<td>6</td>
<td>43.63</td>
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<tr>
<td>7</td>
<td>8</td>
<td>90</td>
<td>1.8:1</td>
<td>6</td>
<td>43.50</td>
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<tr>
<td>8</td>
<td>8</td>
<td>80</td>
<td>1.6:1</td>
<td>7</td>
<td>42.10</td>
</tr>
<tr>
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<td>8</td>
<td>70</td>
<td>1.7:1</td>
<td>5</td>
<td>41.87</td>
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Table 2. Factors and results of orthogonal tests.

<table>
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<tr>
<th>Factor</th>
<th>K$_1$</th>
<th>K$_2$</th>
<th>K$_3$</th>
<th>k$_1$</th>
<th>k$_2$</th>
<th>k$_3$</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>126.31</td>
<td>134.86</td>
<td>127.47</td>
<td>42.10</td>
<td>44.95</td>
<td>42.49</td>
<td>2.46</td>
</tr>
<tr>
<td>B</td>
<td>126.55</td>
<td>129.23</td>
<td>132.86</td>
<td>42.18</td>
<td>43.08</td>
<td>44.29</td>
<td>2.11</td>
</tr>
<tr>
<td>C</td>
<td>128.87</td>
<td>130.21</td>
<td>129.56</td>
<td>42.96</td>
<td>43.40</td>
<td>43.19</td>
<td>0.44</td>
</tr>
<tr>
<td>D</td>
<td>130.02</td>
<td>129.25</td>
<td>129.37</td>
<td>43.34</td>
<td>43.08</td>
<td>43.12</td>
<td>0.26</td>
</tr>
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Table 3. Results of different factors.

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According to Tables 2 and 3, the optimal reaction condition is: HCl concentration = 7 mol/L, reaction temperature = 90 °C, acid-slag ratio = 1.7:1, and reaction time = 7 h. Under this condition, the TiO₂ mass fraction in the Ti-rich slag is 46.22%. Among the four influence factors, the effects on the TiO₂ mass fractions rank as follows: HCl concentration (A) > reaction temperature (B) > acid-slag ratio (C) > reaction time (D).

**Conclusions**

1) Through hydrochloric acid decomposition of air-cooled Ti-containing blast furnace slag, we separated Ti and Si from the majority of soluble impurities to obtain Ti-rich slag, which contained ≥45% w(TiO₂) and could be used into Ti production. The optimal process condition is: HCl concentration = 7 mol/L, reaction temperature = 90 °C, acid-slag ratio = 1.7:1, and reaction time = 7 h.

2) This process is simple and easy-to-use and thus contributes to appropriate development and utilization of Ti-containing blast furnace slag that has been largely piled in Panzhihua Iron and Steel Co..

**References**


