Separation of silica from pyrite cinder via reverse cationic flotation

Wang Quanliang$^{1,2}$ and Feng Qiming$^1$

$^1$School of Minerals Processing and Bioengineering, Central South University, Changsha, China
$^2$Hunan Research Institute of Nonferrous Metals, Changsha, China

ABSTRACT

This paper describes effective reagent combinations for removal of quartz by reverse cationic flotation from pyrite cinders. This work is based on a hypothesis that a further development in reverse cationic flotation of iron ores implies. A more detailed consideration of the nature of the pyrite cinders. The results indicate that the pyrite cinder is man-made porous ore. Starch was used as a depressant, and laurylamine as the cationic collector. Optimum pH is 8.0~8.5 and optimum mean particle size is around 5um. Flotation of pyrite cinders in both bench and pilot scales is effective and producing of concentrates with SiO$_2$ content below 0.8% and Fe contents up to 68% was obtained from pyrite cinders with SiO$_2$ content 3.9%.

Key words: Pyrite cinders; Porous; Reverse cationic flotation; Flotation reagents

INTRODUCTION

Annually, a large amount of sulfuric acid is produced in china. Pyrite is commonly used as the raw material[1]. The process involves the roasting of pyrite concentrates to generate sulfur dioxide gas followed by its catalytic oxidation to sulfur trioxide gas prior to the eventual conversion of the latter to sulfuric acid. The roasting process also yields solid wastes known as pyrite cinders, which are composed mainly of iron oxides[2]. Theoretically, around 67% of pyrite in the feed is converted into hematite (Fe$_2$O$_3$) during the roasting process. Therefore, large quantities of pyrite cinders as solid wastes are produced as a by-product of industrial sulfuric acid manufacturing operations. The pyrite cinder contains hazardous heavy metals and acids which are potential environmental risks for disposal[3]. Nowadays, only a small amount of pyrite cinders is recycled as building materials, the rest is dumped as solid wastes, not only occupying much land, but also causing a great waste of iron resources. It also poses a serious threat to the environment, public health and safety due to the release of acids and toxic substances[4].

Although pyrite cinder is industrial waste, it is also a kind of potential resource as it contains Fe$_2$O$_3$, Fe$_3$O$_4$, SiO$_2$, CaO, S etc. During the past decade, considerable researches were devoted to the comprehensive utilization of pyrite cinder. At present, several areas for potential use of pyrite cinder are reported, including recycling of the contained metals[5-9], using as brick-making materials[10-11], preparing iron-based pigments like iron oxide red and iron black [12-15].

Hematite and magnetite floatability are always lower than that of quartz under the same physic-chemical conditions. The reverse cationic flotation is one of the main processes used by the iron ore industry. In this process, Laurylamine is the main collector for quartz, and starch is the depressor for the iron minerals. The aim of this work is at the searching of efficient reagent regimes in reverse cationic flotation to lower SiO$_2$ content towards 0.8% in concentrates used for the production of direct-reduced iron.
EXPERIMENTAL SECTION

2.1 Raw materials
The pyrite cinder used in this test was taken from Yunfu, Guangdong Province, China. This sample was characterized by chemical analysis, X-ray diffraction (XRD, using Rigaku D/max 2500PC), laboratorial size analysis, and scanning electronic microscopy (SEM, using CAMSCAN CS44FE).

Soluble starch used as iron mineral depressant was bought from Sinopharm Chemical Reagent Co. Ltd in Shanghai. The weight average molar mass is 200,000–400,000 g/mol which is measured by the manufacturer. The reagent solutions were prepared fresh before using by dispersing a known weight in cold water and then dissolving it with hot water. A commercial laurylamine from Chemical Engineering and Technology Corporation of Shanghai was used as quartz collector. Sodium hydroxide was used as pH conditioner. A commercial Sodium butyl xanthate was used as pyrite collector.

2.2 Bench scale flotation
A 1.0 kg pyrite cinder sample was milled using a laboratory scale stainless steel stirred mill. The milled slurry was transferred to a 3.0L laboratory XFG cell. The air flow rate was kept at 0.1Nm3/h monitored with a flowmeter and impeller speed which was set at 1200 rpm. The concentrates, rougher and scavenger productions were weighed and chemical analyses separately after filtration and drying, and the recovery was calculated.

2.3 Pilot plant scale flotation
A 2.5 t/h pyrite cinder sample were milled using industrial scale steel stirred mill and the milled slurry was transferred to BF-1.2 XFG cell for flotation (Fig. 1). During the plant test, samples were taken from all pulp flows. The method used was total flow interception, in order to establish the mass and metallurgical balances. The next increment was taken only after the operation was stabilized again.

3.1 Sample characterization
The chemical composition of the pyrite cinder is given in Table 1. The mineralogical composition of the samples was identified by X-ray diffraction (Fig. 2). The raw pyrite cinder is mainly composed of hematite, magnetite, and quartz etc. The surface morphology of the samples was examined by scanning electron microscopy (Fig. 3). As shown in table 1, Fig. 2 and 3, the raw pyrite cinder is porous, and composed of hematite, magnetite, and quartz etc. The particle size analysis and iron monomer dissociation rate results of pyrite cinder are shown in Tables 2. It could be concluded that the iron monomer dissociation rate is weak and the relationship of intergrowth is complex.

<table>
<thead>
<tr>
<th>Components</th>
<th>TFe</th>
<th>S</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>CaO</th>
<th>MgO</th>
<th>Mn</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite cinder</td>
<td>62.01</td>
<td>0.23</td>
<td>3.98</td>
<td>0.24</td>
<td>0.31</td>
<td>0.10</td>
<td>0.07</td>
<td>0.10</td>
<td>0.09</td>
<td>0.008</td>
<td>2.57</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particle size interval (um)</th>
<th>+147</th>
<th>-147+104</th>
<th>-104+74</th>
<th>-74+37</th>
<th>&lt;37</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>1.50</td>
<td>3.12</td>
<td>21.28</td>
<td>37.87</td>
<td>36.23</td>
</tr>
<tr>
<td>Iron monomer dissociation rate</td>
<td>57.5</td>
<td>79.4</td>
<td>83.5</td>
<td>89.4</td>
<td>91.5</td>
</tr>
</tbody>
</table>

Fig.1 Diagram of (a) raw pyrite cinder and (b) industrial scale steel stirred mill and (c) BF-1.2 XFG cell

RESULTS AND DISCUSSION

3.1 Sample characterization
The chemical composition of the pyrite cinder is given in Table 1. The mineralogical composition of the samples was identified by X-ray diffraction (Fig. 2). The raw pyrite cinder is mainly composed of hematite, magnetite, and quartz etc. The surface morphology of the samples was examined by scanning electron microscopy (Fig. 3). As shown in Table 1, Fig. 2 and 3, the raw pyrite cinder is porous, and composed of hematite, magnetite, and quartz etc. The particle size analysis and iron monomer dissociation rate results of pyrite cinder are shown in Tables 2. It could be concluded that the iron monomer dissociation rate is weak and the relationship of intergrowth is complex.
3.2 Bench-scale tests

Bench scale flotation tests with pyrite cinder were systematically conducted. Firstly, the roughing-circuit aiming to find the appropriate size of grinding product and dosage of reagents were tested. The flotation separation flowchart is shown in Fig. 4, and the results of separation are shown in Fig. 5. As shown in Fig. 5(a), the optimum mean particle size is about 5μm, and more or less than this mean particle size can cause the decrease of grade of concentrates. As shown in Fig. 5(b), the optimum pH is 8.2. As shown in Fig. 5c, and 5d, the optimum dosage of starch and laurylamine is 800, and 200 g/t, respectively.
The open-circuit flotation separation of pyrite cinder was studied at pH 6.4~6.7 and 8.0~8.5, respectively. The flow sheet of open-circuit separation of pyrite cinder is shown in Fig.6, and the results are shown in Table 3. The results showed that the separation of silica from pyrite cinder by reverse flotation is possible and good selectivity can be achieved at about pH 8.2.

**Table 3 Results of reverse flotation of actual pyrite cinder ore (wt%)**

<table>
<thead>
<tr>
<th>Production</th>
<th>Yield</th>
<th>Grade</th>
<th>Recovery</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TFe</td>
<td>SiO2</td>
<td>S</td>
</tr>
<tr>
<td>Iron concentrate</td>
<td>66.18</td>
<td>68.14</td>
<td>0.72</td>
<td>0.06</td>
</tr>
<tr>
<td>Scavenging froth</td>
<td>12.03</td>
<td>56.92</td>
<td>6.36</td>
<td>0.16</td>
</tr>
<tr>
<td>Roughing froth</td>
<td>21.79</td>
<td>45.81</td>
<td>12.28</td>
<td>0.77</td>
</tr>
<tr>
<td>Feed ores</td>
<td>100.00</td>
<td>61.92</td>
<td>3.91</td>
<td>0.23</td>
</tr>
</tbody>
</table>

(a) Effect of mean particle size with addition 850g/t of starch and 180 g/t of laurylamine at pH 8.0~8.5.

(b) Effect of pH with addition 850g/t of starch and 180 g/t of laurylamine. Mean particle size 5.5 um.

(c) Effect of dosage of starch with addition 180 g/t of laurylamine at pH 6.3~6.8. Mean particle size 5.3 um.

(d) Effect of dosage of laurylamine with addition 800g/t of starch at pH 6.4~6.7. Mean particle size 5.8 um.
3.3 Pilot plant tests
Pilot plant tests were carried out using the same samples used for the bench tests. To meet quality of concentrates, a rougher-scavenger1-scavenger2 circuit was adopted (Fig. 7), in which the scavenger 1 feed is the rougher flotation tailing and the scavenger 2 feed is the scavenger 1 flotation tailing. The results of mass metallurgical balances for the pilot plant are showed in Fig. 8. The pilot plant test yielded a concentrate with Fe recovery 71.99% and the concentrate grade of Fe 68.35% at pH 8.0~8.5.

Fig. 7 Pilot flotation plant flow sheet of flotation separation form pyrite cinder

Fig. 6 Flow sheet of flotation from Pyrite cinder
CONCLUSION

(1) Pyrite cinder studied in this work is a kind of man-made porous ore with 62.01% Fe, 3.98% SiO$_2$ and 0.23% S. The iron monomer dissociation rate is weak and the relationship of intergrowth is complex.

(2) The cationic flotation of quartz from pyrite cinder proved to be feasible in both bench and pilot scales tests. The best reagents are laurylamine as the quartz collector, and soluble starch as hematite and magnetite the depressant, at pH 8.0~8.5.

(3) The pilot plant tests yielded a concentrate with Fe recovery 71.99%, and the concentrate grade of Fe, SiO$_2$ and S is 68.35%, 0.75% and 0.07%, respectively, which indicates that the product is suitable to feed the production of direct-reduced iron.

Acknowledgments

The author would like to thank Yunfu Pyrite Mine Corporation, Guangdong Province, China for their support of this research.

REFERENCES