Alkalic Leaching and Stabilization of Arsenic from Pyrite Cinders

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Abstract:

Introduction:
Pyrite cinder is one of the important secondary resources, but typically contains a certain amount of arsenic, which is harmful to metallurgical process. It usually hopes to remove the arsenic prior to recycle the valuable element in the pyrite cinders.

Methods & Materials:
In this study, the arsenic in the cinders was selectively removed using the alkalic leaching method so as to reduce the loss of ferric and other valuable elements.

Results & Discussion:
The content of arsenic in pyrite cinders was reduced to 0.08% through the investigation of the factors, including particle size, alkaline concentration, temperature, solid-liquid ratio (S/L) and leaching time. Then, the ferric precipitation method was used to remove the arsenic in the leaching solution. More than 99% of the arsenic can be removed by controlling the pH and the ratio of ferric and arsenic (Fe/As) in ambient temperature, and the arsenic concentration in the solution was reduced to less than 0.5mg/L.

Conclusion:
It was found that the precipitated arsenic was mainly amorphous based on the analysis of sediment.

Keywords: Arsenic, Pyrite cinders, Alkaline leaching, Precipitation, Ferric sulfate, Solid-Liquid Ratio.

1. INTRODUCTION

Pyrite cinders are the waste residues generated during the process of producing sulfuric acid from pyrite, and 0.7-1.0t pyrite cinders will be generated in order to obtain 1.0t sulfuric acid. In China, more than 30% sulfuric acid is produced from pyrites, and at least 10 million tons of pyrite cinders are produced through the roasting of pyrite [1]. However, only 30% pyrite cinders are recycled as the building materials such as cement, brick and roof tiles, while most of the remaining cinders are dumped as waste residues [2, 3]. This is not only occupying a large number of lands, but also may cause serious environmental pollution to the soil, water and air around the storage ground, which may endanger the public health and safety [4].

With the continuous utilization of mineral resources, recycling of the valuable metals from pyrite cinders has received more and more attention, which is also beneficial to the environmental protection. The main component of the cinders is hematite (Fe₂O₃), and generally contains 20-60% ferric [5], in which the high iron slag has a greater value of recycling. The iron oxide concentrate can be extracted through beneficiation, pelletization and other processes, and used...
as raw material for blast furnace [6, 7]. In addition, the pyrite cinders can also be used to prepare iron-based pigments, iron oxide and so on [5, 8], or direct reduction of the cinders to obtain metals [9]. The cinders also contain a small amount of Cu, Zn, Pb, Au, Ag and other valuable metals, which are important for recycling [10, 11]. Therefore, the recycling of nonferrous metals in the cinders, especially gold and silver, is also an important research direction [12 - 14].

Pyrite usually contains a certain amount of arsenic, and most of the arsenic will get into the furnace gas in the process of roasting, then into the acid sludge, waste water and sulfuric acid through gas washing. However, there will still be a small amount of arsenic in the cinders [15]. The arsenic in the cinders is not only an important cause of environmental pollution, but also hinders the reuse of cinders as an important secondary resource [16]. Arsenic into molten iron in the smelting process greatly decreases steel’s thermoplastic property and induces the steel crack easily in the stress processing [17]. Therefore, it should be removed before the reuse of cinders. The arsenic usually exists in the form of arsenate or arsenious oxide, and is mainly removed by acid leaching [18, 19]. There will be substantial amount of iron, copper and zinc into the leaching solution due to the poor selectivity of acid leaching, which will bring great difficulties to the following processing of solution treatment and increase the production cost. In view of the requirements of environmental protection and the simplification of the subsequent treatment process, this paper used the alkaline leaching method to selectively remove arsenic in the pyrite cinders, and arsenic in the leaching solution was treated harmlessly by ferric slat precipitation.

2. MATERIALS AND EXPERIMENTAL

2.1. Materials

The pyrite cinders used in this study were taken from one sulfuric acid plant in China. The main chemical compositions of the cinders were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, optima 8000) and Atomic Absorption Spectroscopy (AAS, WFX-130A), as the results are shown in Table (1). The sample was examined by X-ray diffraction (XRD, X’Pert PRO MPD) as shown in Fig. (1). According to the analysis results, the main component of the cinders is Fe$_2$O$_3$, Fe$_3$O$_4$ and SiO$_2$. The content of total ferric is 59.39%, in which hematite (Fe$_2$O$_3$) is 72.9% and magnetite (Fe$_3$O$_4$) is 17.3%. In addition, the zinc content is 1.51% and gold is 1.4g/t. Therefore, the pyrite cinder has a great recycling value. However, it is not conducive to reuse the cinders due to 0.45% arsenic content. The arsenic needs to be removed before recycling the cinder.

Table 1. Chemical composition of the pyrite cinders.

<table>
<thead>
<tr>
<th>Component</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Fe</th>
<th>As</th>
<th>Au(g/t)</th>
<th>Ag(g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>0.79</td>
<td>1.51</td>
<td>0.92</td>
<td>59.39</td>
<td>0.45</td>
<td>1.40</td>
<td>4.92</td>
</tr>
</tbody>
</table>

![Fig. (1). XRD pattern of the pyrite cinders.](image-url)
2.2. Experiment

A certain amount of cinders with fine grinding and alkaline solution was put into a 250mL erlenmeyer flask, which was heated in a water bath pot. When the bath temperature went up to the specified temperature, the time was set as zero. After leaching and filtration, the residue was dried and determined by XRD, ICP-OES, AAS and SEM-EDS (JSM-7001F+INCA-MAX). The composition in the solution was analyzed by ICP-OES and AAS.

The leaching solution and washing solution were collected after each experiment. A specific amount of mixed liquid was taken in an Erlenmeyer flask and hydrogen peroxide was added. The solution pH was adjusted using sulfuric acid at room temperature (25 °C). Then, the ferric sulfate was added and stirred to dissolve. After the precipitation, the pulp was filtrated. The content of arsenic in the filtrate was measured by ICP-OES, and the leaching residue was analyzed by XRD and SEM-EDS.

3. RESULTS AND DISCUSSION

The surface morphology of the pyrite cinders was observed by a scanning electron microscope, as shown in Fig. (2). The two electronic results of area 1 show the content of arsenic to be 0.83%, which may exist in the form of ferric arsenate or arsenic oxide. The arsenic oxide can react with alkaline in the leaching solution. In addition, the zinc and lead can also be leached into the solution. However, the results of the analysis show that the solution almost contained no lead, and the lead content in the leaching residue changed slightly.

![Fig. (2). SEM-EDS results of the pyrite cinders.](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>O K</td>
<td>28.43</td>
</tr>
<tr>
<td>Al K</td>
<td>0.52</td>
</tr>
<tr>
<td>Si K</td>
<td>0.87</td>
</tr>
<tr>
<td>Fe K</td>
<td>69.35</td>
</tr>
<tr>
<td>As L</td>
<td>0.83</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
</tr>
</tbody>
</table>

3.1. The Arsenic Leaching from Pyrite Cinders

3.1.1. Effect of the Particle size on the Leaching of Arsenic

The pyrite cinders were finely ground to the size 0.074mm. The content of As and Zn in the leaching residue is
shown in Fig. (3) under the conditions of 80°C, S/L=1:5, 1mol/L NaOH, 3 hours of leaching time. Fig. (3) indicates that the particle size influenced the leaching of As and Zn. The arsenic content in the residue decreased with the decrease in fine quality of the mineral. When the particles size was less than 96%, the arsenic decreased rapidly with the decreasing size. While the size under 0.074mm accounted for more than 96%, the As content changed slightly with further grinding. With regard to Zn content, the change in Zn was not obvious. This indicates that most of the zinc was exposed to leaching solution. Therefore, the size under 0.074mm accounted for 96% of the optimum fineness.

Fig. (3). Effect of the particle size on the arsenic content in leaching residue.(80°C,3h,1mol/LNaOH,S/L=1:5)

3.1.2. Effect of the Temperature on the Leaching of Arsenic

Temperature showed an significant influence on the leaching efficiency, so the effect of temperature between 25-90°C was studied under the conditions of S/L=1:5, 1mol/L NaOH, 3 hours of leaching time, as shown in Fig. (4). The results show that the content of arsenic in leaching residue decreased rapidly with the increase in temperature. Especially when the temperature was less than 80°C, the arsenic content changed from 0.25% at 25°C to 0.12% at 80°C. While it was more than 80°C, the arsenic content reduced slightly, which basically maintained at 0.12% at 90°C. In addition, the zinc content in the residue decreased with the increase in temperature at temperature more than 80°C. Therefore, it is beneficial to reduce the zinc loss at temperature below 80°C.

Fig. (4). Effect of temperature on the arsenic content in leaching residue. (3h 1mol/LNaOH S/L=1:5)

3.1.3. Effect of the Alkaline Concentration on the Leaching of Arsenic

The concentration of NaOH solution is an important factor affecting the leaching behavior of arsenic in the cinders.
Fig. (5) shows the changes in arsenic and zinc contents in the residue with the increase in the sodium hydroxide concentration. As observed, the arsenic content decreased gradually with the increase in the alkaline concentration. The arsenic content decreased to 0.08% when the NaOH concentration increased to 2.0mol/L. As the alkaline concentration further increased, the arsenic content changed indistinctly. However, the zinc content decreased gradually with the increase in the NaOH concentration, from 1.46% at 0.5mol/L to 1.3% at 3.0mol/L.

![Graph showing changes in arsenic and zinc contents](image)

**Fig. (5).** Effect of alkaline concentration on the arsenic content in leaching residue. (3h, 80°C, S/L=1:5)

### 3.1.4. Effect of S/L on the Leaching of Arsenic

Fig. (6) shows the effect of the solid-liquid ratio (S/L) on the arsenic and zinc contents in the leaching residue. The arsenic content decreased from 0.17% to 0.11% as the S/L increased from 1:1 to 1:5. However, the effect of S/L on zinc content was not obvious, therefore, the increase of the S/L ratio is beneficial to the arsenic leaching.

![Graph showing effect of S/L](image)

**Fig. (6).** Effect of S/L on the arsenic content in leaching residue. (3h, 80°C, 1mol/L NaOH)

### 3.1.5. Effect of Reaction time on the Leaching of Arsenic

Fig. (7) shows changes in the arsenic and zinc concentrations in the solution with time. At the beginning of the reaction, the leaching rate of arsenic increased rapidly, and the concentration reached to 570mg/L. As the reaction time extended to 4h, the arsenic concentration only increased to 595mg/L. However, the Zn concentration increased gradually with time, which even accelerated the trend after 2h. Therefore, the leaching time should be strictly controlled to reduce the zinc loss.

![Graph showing reaction time effect](image)

**Fig. (7).** Effect of Reaction time on the Leaching of Arsenic.
In summary, alkaline concentration and temperature have an important effect on the leaching efficiency of arsenic. Most of the arsenic in pyrite cinders can be alkalic leached under the conditions of 80°C, with 96% fineness, 2mol/L NaOH, S:L=1:5 and 3h reaction time. The residues still contained about 0.08% arsenic after the verification test, which is possibly in the form of iron arsenate or being wrapped.

3.2. The Arsenic Precipitation in the Leaching Solution

The precipitation method is widely used for the removal of arsenic in solution, in which ferric salt precipitation is one of the most common techniques [20]. Many researches show that several factors including arsenic concentration, pH and the molar ratio of iron to arsenic (Fe/As) affect the removal of arsenic [21 - 23]. Fe(OH)$_2$ and Fe(OH)$_3$ are produced by the hydrolysis of ferric salt in water, which can not only react with arsenic to produce precipitation, but also adsorb the arsenic in the solution [24, 25]. Because the toxicity and mobility of As (III) are much higher than that of As (V), the As (III) is usually oxidized to As (V) before arsenic precipitation [26]. In this study, the As (III) was firstly oxidized to As (V) using hydrogen peroxide at room temperature (25°C), then the arsenic was removed from the leaching solution by ferric sulfate.

3.2.1. Effect of pH on the Arsenic Removal Efficiency

The effect of pH value within the range of 1-12 on the arsenic removal is shown in Fig. (8). The results show that no precipitation was produced with the pH below 1.5; the removal rate of arsenic was about 64% at pH=2.1. When the pH
reached to 4.6, the arsenic removal was more than 99% and the arsenic concentration was observed to be less than 5mg/L. Because the ferric arsenate was found to equilibrate with two-line ferrihydrite as the pH>7 [27]:

$$FeA_3O_4 \cdot (2 + x)H_2O + 2OH^- \rightarrow FeOOH \cdot (2 + x)H_2O + HAsO_4^{2-}(aq)$$  \hspace{1cm} (1)

The arsenic precipitation rate begins to decline when the pH is more than 8, which was only 91% at pH=9.6. Therefore, the pH plays an important role in arsenic precipitation from the leaching solution by ferric sulfate, and the optimal pH for arsenic removal is between the range of 4-8.

### 3.2.2. Effect of Fe/As on the Arsenic Removal Efficiency

Fig. (9) shows the removal rate of arsenic in solution with the increase of the Fe/As. The results indicate that the removal rate increased with the increase of the Fe/As. Only 95% arsenic was removed at Fe/As=1, which illustrates that the ferric sulfate did not equivalently react with the arsenic. When Fe/As reached to 1.2, the removal rate of arsenic in the leaching solution was over 99%.

![Fig. (9). Effect of Fe/As on the arsenic removal efficiency (pH=6-8).](image)

More than 99% arsenic in the leaching solution can be removed by controlling the pH and Fe/As at room temperature. The surface morphological images of precipitations at Fe/As=0.8, 1, and 2 are shown in Fig. (10). It has been found that the precipitation mainly exists in the amorphous form agglomerated by superfine particles, whose stability is less than the crystalline ferric arsenate [28, 29]. The XRD result of arsenic precipitation proved this result as shown in Fig. (11). Min X. et al. pointed out that it can obtain ferric arsenate with higher crystallinity when the pH value was between 2-4, but the arsenic precipitation rate was only 84.6% at pH=4 [30]. In this study, the removal rate at
pH=3 was about 97%. Therefore, if the pH was less than 4, the arsenic in leaching was possibly not removed thoroughly, which also increased the acid consumption.

Fig. (11). XRD result of arsenic precipitation.

CONCLUSION

The alkalic leaching method was used to selectively remove the arsenic in the pyrite cinders, and the arsenic in the leaching solution was treated harmlessly by ferric slat precipitation. The arsenic in pyrite cinders can be removed through alkalic leaching under the conditions of 80°C, with 96% particle size, 2mol/L NaOH, S:L=1:5 and 3h of the reaction time, and the arsenic in the leaching residue was reduced to 0.08%. The arsenic in leaching solution was precipitated using ferric sulfate. More than 99% arsenic was removed at pH=4-8 and Fe/As>1.2, and the concentration in the solution reduced to less than 5mg/L. The precipitated arsenic may exist in the form of amorphous ferric arsenate under the precipitation conditions of pH=6-8 and Fe/As < 2.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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REFERENCES


[http://dx.doi.org/10.1016/0043-1354(94)E0089-O]

[http://dx.doi.org/10.1007/s11663-007-9081-y]

[http://dx.doi.org/10.1021/je900151s]

[http://dx.doi.org/10.1016/0304-386X(89)90028-5]

[http://dx.doi.org/10.1016/S1003-6326(15)63728-1]