Study on Arsenic Removal by Scorodite

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Abstract: During heavy metal smelting and ore mining, there is a large amount of arsenic in flue gas and waste acid, forming acid sewage. If it is discharged into the natural environment directly, a large amount of arsenic will be placed in the natural environment, causing arsenic pollution and harms to the health of animals, plants and human beings. This article explores the waste acid of copper smelting solution as research object. For the solution, the scorodite - a kind of solidarsenic bearing is low residue of arsenic, easy to store and more stable-prepare by the environment with Ultrasonication. For the solution, in order to achieve discharge standards, we use the Lime - iron - washing precipitation method and sulfidation to the arsenic, after that we use the TCLP experiments to check the toxic leaching rate.

1. Introduction

In the Fe (III) - As (V) - H2O system, a series of amorphous iron arsenate salts of different sizes, different crystalline forms and crystallinity and high crystallinity can be prepared by changing the different conditions of the external system [1]. Amorphous iron arsenate can be produced during the coprecipitation process of waste tailings, acid mine drainage and arsenic iron. Iron arsenate is not suitable for storing arsenic slag because of its poor stability, leaching toxicity and solubility [2]. It is necessary to convert arsenic and iron into stable stingray crystals.

The process of formation of scorodite: 4H3AsO4•2FeAsO4•2H2O+8H2O=4FeAsO4•2H2O+2H2SO4. The transformation process of scorodite is the removal of crystalline water, which is making the rate of Fe:As:H2O is 1:1:2 [3]. In this paper, we study the effects of initial pH value, different temperature, different arsenic and iron ratio, different ultrasonic power, and so on.

2. Methods

1) The alkaline arsenic solution with a concentration of 15.6 g/L is prepared from crude sodium arsenate solution. Adjusting the PH of arsenic solution by dropping sulfuric acid. Adding the solution to the top of the beaker which has a special lid, and the circle in the middle of the lid can penetrate the ultrasound, At the same time, a thermometer and a flowmeter can also be inserted into the solution through the circles of the lid. The stirring speed is about 180±20 when the solution is heated and stirred.

2) According to the theoretical value of arsenic-iron ratio, a certain amount of ferric sulfate is taken and put into a beaker, and a proper amount of distilled water is added to prepare ferric sulfate solution. Adding NaOH to regulate pH of ferric sulfate solution so that we can control pH at 2±0.1. Then, Pouring the ferric sulfate solution into the flowmeter.
3) The sodium arsenate solution is heated to a certain temperature and stirred. The ferric sulfate solution is dripped into the solution at a certain speed while stirring. In order to maintain pH value of 2, at set intervals a few solutions are taken to check PH.

4) After dropping the mixture of arsenic and iron, the solution is kept at a constant temperature and pH value. After heating for a certain time, it is removed and filtered to form a sandy solid, which is the scorodite.

5) After reaction, the content of arsenic and iron in solid volatile scorodite and solution was analyzed.

3. Results

3.1 Effect of different temperatures on the synthesis of scorodite

When forming the scorodite, in the chemical reaction, the temperature has great influence on the chemical reaction. In 1988, the first synthesis of the scorodite was made by using the hydrothermal method with Fe(NO₃)₃ and As (V) at 160°C[4]. In 1995, in the case of 90°C in the Fe (III) - As (V) H₂O system, the saturation was controlled step by step, and the high crystallinity of the scorodite was prepared. It is found that a good crystalline scorodite can be prepared at high temperature[5]. The experimental temperature is set at room temperature (20 °C), 40 °C, 60 °C, 80 °C, 87 °C. The pH value of the arsenic solution is within 2, the pH value of the iron solution is within the range of 2, the molar ratio of Fe / As is 2:1, the heating temperature of the solution is 20-87°C, and the stirring speed is 200/min, balancing time is 5h.

Table 3.1 Effect of reaction temperature on the removal rate of arsenic in molten pool

| Temperature °C | Filter pH | Arsenic content g/L | Removal rate % |
|---------------|----------|---------------------|---------------|
| 20            | 2.11     | 2885.3              | 88.37         |
| 40            | 2.08     | 3343.9              | 81.83         |
| 60            | 2.06     | 2798.1              | 84.91         |
| 80            | 1.97     | 949.0               | 98.92         |
| 87            | 1.97     | 672.7               | 97.12         |

It can be seen from the table 3.1 that with the increasing of the reaction temperature, the pH value in the filtrate have a slight decrease, but the amplitude is not large, and the pH value falls when the initial value from 2.12 to 1.97. When the temperature is 23°C - 60°C in the mixed solution, the arsenic content in the solution is up to 2000mg / L and above. At this time, the removal rate of arsenic in the solution is about 80%, which is far from enough to meet the national emission standard. When the temperature is 23°C, the iron solution is dripped into the arsenic solution. Before the stirring, the red compound is gathered in the clarified arsenic solution. After agitation, the color of the solution is becomes to the dark red, and the color becomes deeper with the addition of the iron solution. With the further increasing of temperature, red brown opaque compound, uniform distribution of arsenic and iron will appear in the solution. When the temperature is 60°C, some colloidal solids will be found in the solution, and the precipitation color is dark red. When the temperature is 80°C, the solid colloid precipitation in the arsenic solution is less, the color of the solution is slightly dark green, and white precipitation is in solution, when the temperature is 87°C, the edge of solution is sand shape precipitate, and the upper layer is clarified solution. After mixing the solution, removing 100ml solution and remove the filter residue for three times after filtration. It can be seen from the table that when
temperature is room temperature, the amount of slag is less but more viscous. With the growth of the temperature, the amount of slag is increased obviously. When the temperature is 87°C, the slag amount is up to 30.2g, which is about 2 times than the room temperature. The degree of crystallization is better than the crystallization at room temperature.

3.2 Effect of different iron and arsenic ratio on the synthesis of scorodite

When the ferric sulfate solution is dripped into the sodium arsenate solution, whether it is the formation of the scorodite precursor or the formation of the FeAs•2H₂O precipitation of the better crystalline scorodite[6], the theoretical of Fe:As is 1:1. We prepared the arsenic iron solution in the actual production experiment to obtain the better crystal of the scorodite, and when Fe:As > 1:1, it is better for experimental results. In this chapter, Fe:As is controlled by 1, 2, and 4, the pH value of the arsenic solution is controlled within 2, the pH value of the iron solution is within the range of 2, the heating temperature of the solution is 87°C, and the stirring speed is about 200/min. Balance time 5h.

Table 3.2 Effect of different arsenic iron ratio on the removal rate of arsenic in molten pool

| Fe:As(mol) | pH  | Arsenic content g/L | Removal ratio % |
|------------|-----|---------------------|-----------------|
| 1          | 2.02| 1247.7              | 88.21           |
| 2          | 1.98| 652.7               | 93.52           |
| 4          | 2.01| 4427.2              | 67.50           |

This chapter mainly investigates the effect of iron and arsenic ratio on the synthesis of scorodite.

From table 3.2, it can be seen that as the ratio of the arsenic and iron ratio becomes larger, the equilibrium pH value is more stable and the difference between the size value is less than 0.1, but the difference of arsenic removal effect is larger. When the ratio of arsenic and iron is 1, the effect can reach 88.21%, and with the extraction of arsenic iron ratio is increasing, the effect of arsenic removal also improved significantly, which is reaching to the maximum value of 93.52%, but when we continue to increasing the arsenic iron ratio in the solution, the removal of arsenic has not increased, even fall as cliff, the result is, when the ratio is 4, the removal of arsenic is only 67.50%, and no clear precipitation generated, the production is the gel precipitation and the color is red brown, and the morphology is similar to the Fe(OH)₃ precipitation. It is presumed that the excess ferric sulfate solution and the arsenic solution are hydrolyzed to produce Fe(OH)₃ under the action of ultrasonic wave.

Fig 3.2 SEM diagram of different arsenic iron ratio for synthetic scorodite

Scanning electron microscopy shows that there was no significant difference in morphology when the ratio of iron to arsenic was 1 and 2. Relatively speaking, when the ratio of iron to arsenic was 1, the crystalline state was obviously greater than that of iron to arsenic was 2, and there was no significant difference in other parts.
3.3 Effect of different ultrasonic power on the synthesis of Scorodite

In the literature [7-9], the effect of ultrasonic can supplement or strengthen the nucleation energy needed in the crystallization process, reduce the annual and tension of the solution, and promote the formation of the nucleation. The ultrasonic wave can effectively improve the nucleation rate, reduce the growth rate of crystals, and change the steady state of saturated solutions.

In this chapter, we controlled the Fe:As is 2, the pH value of the arsenic solution and iron solution is within 2, the heating temperature is 87°C and the stirring speed is 200/min. The dropping time is 8h, the balance time is 5h, and the ultrasonic frequency is set to 0W, 400W, 800W, 1200W and 1600W.

Table 3.3 Effect of different ultrasonic power on arsenic removal rate in molten pool

| Power/W | pH   | arsenic content g/L | Removal ratio % | Slag amount g/L |
|---------|------|---------------------|----------------|----------------|
| 400     | 1.98 | 652.7               | 93.52          | 29.4           |
| 800     | 2.02 | 2174.2              | 84.87          | 35.2           |
| 1200    | 2.01 | 2397.4              | 83.97          | 24.5           |
| 1600    | 2.04 | 4710.8              | 66.30          | 14.2           |

Fig 3.3 Effect of different ultrasonic power on arsenic removal rate in molten pool

In this section, the effect of different ultrasonic power on the synthesis of scorodite is investigated. It is shown in table 3.3 that the change of power will not cause a greater change in the pH value of the solution. When the power is 800W, the pH value will appear a larger value, then decline, and the overall trend of the pH value shows a decline. With the power increasing, the dearsening effect decreased obviously. When the power value increased from 400W to 1200W, the dearsening effect decreased by 9.53%. With the further increase of ultrasonic power, the dearsening effect was obviously weakened and the drop value was 17.67%. From this, we can know that the effect of dearsening is obviously weakened with the increasing of power.

3.4 Effect of different balance time on the synthesis of scorodite

Table 3.4 Effect of balance time on the removal rate of arsenic in molten pool

| Balance time/h | pH   | arsenic content g/L | Removal ratio % | Slag amount g/L |
|----------------|------|---------------------|----------------|----------------|
| 0              | 1.98 | 4744.2              | 65.81          | 14.2           |
| 2              | 2.02 | 1928.2              | 66.78          | 25.2           |
| 4              | 2.01 | 1730.7              | 88.08          | 25.3           |
| 6              | 2.01 | 1691.0              | 88.43          | 25.4           |
| 8              | 2.02 | 1344.6              | 90.74          | 26.5           |

Fig 3.4.1 Effect of balance time on the removal rate of arsenic in molten pool

In this section, the effect of different equilibrium time on the synthesis of scorodite is investigated. In the process of the synthesis of scorodite, the iron sulfate solution is added to the arsenic solution at 30ml / L speed. The arsenite mixed solution needs a certain balance time to make the crystal grow. This chapter is finished in the solution respectively, when the balance time is 0h, 2h, 4h, 6h and 8h were mixed for five time periods, the solution was evenly stirred and 50ml was removed for use.

It can be seen from the diagram that when the balance time is 0, that is, the solution is finished, the content of arsenic in the solution can reach to 4744.2mg/L, with the balance time increasing in two
hours, the arsenic content in the solution from 2816mg/L up to 1928.2mg / L. During the flow and collision in the solution, the rate of the crystal growth is larger. With the increasing of the equilibrium time, the dearsenizing speed tends to be stable. After balancing 6h, the removal of arsenic is only 3.96%, and the lifting range is small. At this time, the crystal growth area of the solution is stable, and the effect of ultrasonic mechanical effect is not significant. With the increasing of the balance time, the effect is obvious less and less.

There is a certain relationship between the crystal surface shape and the equilibration time. In the process of balanced crystallization, ultrasound produces a series of effects in the solution. In the process of synthesis, the thermal effect plays a positive role. After balancing 2h, 86.78% of the arsenic solution has formed the scorodite. However, the thermal effect will produce heat in the process of bubble cavitation or vibration, which can melt part of the scorodite solution, and reduce the rate of crystallization. The mechanical effect is evident in scanning electron microscopy (SEM). When some crystals are melted, burr edges are formed under the action of mechanical effect. In the process of ultrasonic crystallization, the ultrasonic effect not only accelerates the nucleus formation, but also improves the crystallization rate. At the same time, it also demonstrates the destruction of crystallization. Excessive thermal effect, cavitation effect and mechanical effect will destroy some formed crystals.

4. TCLP experiment
In this paper, a series of arsenic-containing solids were synthesized by adding catalysis of ultrasonic which is on the basis of common synthesized scorodite. According to the toxic leaching method of TCLP, the arsenic concentration of these solids was detected to determine whether the synthesized scorodite conformed to the standard of general solid waste storage.

4.1 Test method:
1) Extractant: Add 5.7 ml glacial acetic acid to 500 ml reagent water, add 64.3 ml, 1 mol/L NaOH, dilute to 1L. The pH value of the solution should be 4.93±0.05
2) Drying samples: Take part of the scorodite sample and weigh it after drying. When the two
constant weight error is less than 1%, it can be used as a sample for leaching toxicity experiments.

3) Scorodite l-5g was weighed and placed in 2L extraction bottle. According to the water content measured by the sample, the extractant was added according to the liquid-solid ratio of 20:1 (L/kg). After the cover is tightened, it is placed in the overturning oscillator. The speed is adjusted to 30

4) Measure the content of arsenic iron in the solution.

In the process of experiment, because the equipment is small and the slag is limited, this section only inspects several kinds of smelly scorodite produced under different external conditions, and carries on the toxic leaching according to the TCLP leaching toxicity method, inspects its leaching situation under the fixed condition. During the inspection process, we focused on the odorite crystal with a large gap between the XRD pattern and the standard map.

4.2 Different initial pH values

| pH | 1   | 2   | 3   | 4   | 5   |
|----|-----|-----|-----|-----|-----|
| mg/L | 7.9 | 6.6 | 9.4 | 11.3| 15.2|

5. Conclusion

In this chapter, we investigating the influence of various factors on the scorodite, and the optimum conditions for the formation of the scorodite under the action of ultrasound are determined, and the toxicity analysis experiment of some samples is carried out to prove the safety of the generated scorodite.

(1) The initial pH value of the arsenic iron solution plays a huge role in the formation stage of the arsenite crystal. With the increasing of the pH value of the solution, the content of the arsenic in the solution increases gradually after the reaction, and the content of the slag is also increased. When the value of the pH is 2, the main product ion is the crystal of the scorodite. At this time the crystallization rate is over which is over 90%. With the increasing of pH value, the crystallization effect of the scorodite is worse. When pH>5, the crystallization effect of the solution is poor, the pH value of the solution is 1-4, and the crystallinity is higher. But it still needs to be dealt with further. With the increasing of temperature, the pH value of solution will decrease slightly. When the mixed solution temperature is 23-60°C, the arsenic content in the solution is always high, up to 2000mg/L and above. At this time the removal rate of arsenic in the solution is about 80%. When the temperature is higher than 60°C, there is a better crystallization of the stone. When the temperature is 80°C, the solid colloid precipitation in the arsenic solution is less, the color of the solution is a white precipitate with a slightly dark green color. When the temperature is 87°C, it is stratified and distinct in the beaker after the balance. The edge is a solid sand precipitate, and the upper layer is a clarified solution.

(2) In the crystallization process of the scorodite The ratio of Fe:As is 1:1. In the process of actual production and test, Fe:As > 1:1 can obtain better experimental results. When Fe:As is 1:1, the removal rate of arsenic is 88.21%. When Fe:As is 2:1, the removal rate of arsenic is 93.52%. When Fe:As is 4:1, the arsenic removal effect is only 67.50%, and no precipitate is formed.

(3) The equilibrium time is 0h, that is, when the solution is finished, the content of arsenic in the solution can reach 4744.2mg/L, the balance time increases two hours, the arsenic content in the solution is 2816mg/L, 1928.2mg/L, indicating that in the balanced 2h, ultrasound promotes arsenic solution in solution. During the flow and collision of molten iron solution in liquid and solution, the growth rate of crystal is larger. With the increase of balance time, the removal rate of arsenic tends to be stable. In the 6h after equilibrium time, the removal of arsenic is only 3.96%, and the lifting range is small. At this point, the crystal growth region in the solution is stable, and the effect of ultrasonic mechanical effect is not significant.
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