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To cite this article: Lifa Sun *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **218** 012142

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# Research progress of arsenic removal from wastewater

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**Abstract.** The wastewater discharged from metallurgical and chemical industries often contains toxic heavy metal element arsenic. If the wastewater discharged directly without treatment, it will cause serious damage to the environment. In this review, different treatment processes of arsenic-containing wastewater with different concentrations are compared and summarized. Hence, the future development of arsenic removal process is prospected.

## 1. Introduction

Along with the development of metallurgical and chemical industries and the exploitation of poor ores, arsenic has been accompanied by the development of major elements. Arsenic in sewage mainly comes from ore mining, fossil fuel combustion, smelting of non-ferrous metals, preparation of arsenic-containing drugs, volcanic eruption, arsenic-solidified residues and the use of pesticides. Arsenic and all arsenic compounds are highly toxic protoplasts. Many countries in the world are seriously affected by arsenic pollution. Arbitrary discharge of arsenic-containing non-wastewater will cause serious harm to human's health and environmental balance. Arsenic can hinder the normal metabolism of cells and cause cell death. Chronic arsenic poisoning can lead to skin keratinization even canceration. Therefore, it is important to control the content of arsenic to protect the water environment and ensure the safety of drinking water. The harmless treatment of arsenic-containing wastewater has become a focus of global concern. This paper summarizes the harmless treatment methods of arsenic-containing wastewater with different concentrations and arsenic residue. Besides, it looks forward to the focus and the development direction of removing arsenic in the future.

## 2. High arsenic wastewater treatment process

The high arsenic wastewater is mainly arsenic-containing waste acid produced by smelting copper and other non-ferrous metals. The waste acid mainly comes from circulating cooling water, acidic heavy metal wastewater and domestic wastewater. There are lots of sewage and its composition is complex. What's more, high arsenic wastewater contains arsenic, copper, lead, zinc, cadmium, bismuth and other harmful metal ions. So, it needs to be further treated and discharged up to the standard. For high concentration arsenic-containing wastewater, chemical precipitation is the main method to reduce arsenic concentration in wastewater by forming solid arsenic compounds. To protect the environment, it is important for us to remove arsenic from waste acid from non-ferrous metals smelting and realize discharge of waste acid up to the standard and recycling of water. This paper mainly introduces several methods of removing arsenic from high concentration waste acid.



### 2.1. Arsenic removal by lime and iron salt method

Lime-ferric salt method uses arsenate and arsenite to form stable precipitation with calcium ion which is insoluble in water. Trivalent iron ion has the properties of adsorption and precipitation after hydrolysis removing arsenic from water. The Lime-iron salt process is simple and inexpensive. It is a common high arsenic waste acid treatment method<sup>[1,2]</sup> in modern smelting industry. Scholars have done a lot of research on the arsenic removal effect and the mechanism of arsenic removal. On the basis of the two stage arsenic removal, a neutralization<sup>[3]</sup> precipitation calcium arsenic three stages lime iron salt method is proposed. After treatment, the arsenic content in the water was 0.28mg/L, which met the discharge standard. And the first stage slag can be used as cement additive, and the second stage slag can be used to produce calcium arsenate, which reduces the amount of slag. Yalong Liao et al.<sup>[4]</sup> removal through two-stage iron salt arsenic, hydrogen peroxide oxidation of low-valent iron and arsenic in raw material liquor, arsenic content can be reduced to 0.014mg/L, far below the national standard emission standards, but this process costs high, complex process. Guoming Jiang<sup>[5]</sup> made use of the oxidation and flocculation effect of potassium ferrate. The ratio of iron to arsenic was 3:1, the pH value was 6, and the temperature was 30%. The concentration of arsenic was less than 0.01 mg/L after treating arsenic-containing waste acid in 30 minutes. Xiaoliang Li et al.<sup>[6]</sup> found that with the increase of pH value, the content of arsenic in calcium sulfate and the content of arsenic fixation also increased. Under high acid condition or high Fe/As ratio, the mass fraction of arsenic also increased.

### 2.2. Arsenic removal by sulfurization

The solubility product constants of heavy metal sulfides are very small. The sulfide precipitation method for treating heavy metal ion wastewater has the advantages of simple process, less investment, good effect, high removal rate and wide pH range. But the arsenic sulfide residue cannot be effectively used at present, and can only be piled up for a long time, which will cause waste of resources and environmental pollution. Hao Xie<sup>[7]</sup> can convert more than 99% of sulfur into  $\text{AsS}^{3-}$ , by controlling the ratio of arsenic to sulfur, pH value and so on. Under the condition of strong acid, 99.9% arsenic can be removed by direct injection of hydrogen sulfide<sup>[8]</sup> into the waste liquid. The reaction product is arsenic sulfide. Peidong Wang<sup>[9]</sup> used arsenic removal in two steps to treat arsenic waste water. The arsenic in the waste acid was firstly fixed in the form of arsenic sulfide by sodium sulfide, and then the sulfide wastewater was further treated by coagulation sedimentation of lime-ferrous sulfate. After two treatments, the concentration of arsenic is less than 0.5mg/L, and the removal rate of arsenic can reach 99.7%. White Manganese and other people through sulfidation treatment (sodium sulfide and arsenic ratio is 2.25:1). The arsenic removal rate reached 95.39%. Feng Gao et al.<sup>[10]</sup> control sulphuric acid content in sulfuric acid concentration, sodium sulfide content and reaction time. The removal rate of arsenic in leaching solution reached 99.3%.

### 2.3. Remove arsenic by scorodite

Scorodite is a good carrier for arsenic. Its arsenic content is as high as 32%. Compared with other carriers, it has the advantages of high arsenic content, low iron requirement, crystal structure and low arsenic leaching. Kuanling Wang found that high temperature and low pH were favorable for the transformation of iron arsenate into scorodite. Increasing the ratio of  $\text{Fe}^{3+}$  to  $\text{As}^{5+}$  increased the stability of precipitation. The arsenic content of arsenic-containing solid leaching solution was less than 5 mg/L, which could be stored directly. When Zhihong Liu prepared scorodite by different methods, the improved atmospheric pressure method had the best effect, the crystallinity was 84.56%, the particle size was 28.2 micron, the surface area was 3.72  $\text{m}^2/\text{g}$  by BET method, and the ratio of iron to arsenic was 1.05. The stability was atmospheric pressure method < hydrothermal method < improved atmospheric pressure method. The arsenic concentration was 1.14mg/L after 10 days of leaching. High crystallinity, exposed crystal surface and smooth surface of the scorodite prepared by improved atmospheric pressure method (Figure 1). Kitamura et al. on the basis of improving the atmospheric pressure method and adding the role of ultrasonic field, prepared a particle size of more than 10 microns of scorodite, the crystallization effect is better.

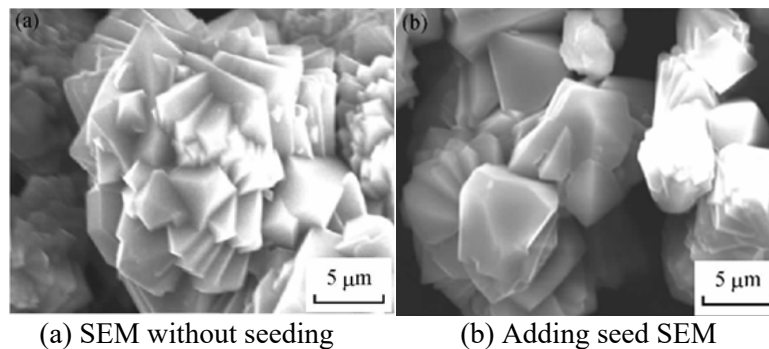


Figure 1. SEM images of IPAS

### 3. Low arsenic wastewater treatment process

#### 3.1. Arsenic removal by adsorption

Adsorption method is simple, mature and has large capacity, but it is only suitable for treating arsenic-containing wastewater with low concentration. There are many kinds of adsorbents available, and the common adsorbents can be divided into two categories. The first category is metal and its alloys, such as manganese oxides, activated alumina and iron compounds; the second category is activated carbon, red mud, coconut shell and other carbon-like materials, the larger the surface area of the adsorbent, the stronger the adsorption effect. At the same time, the pH value of sewage, flow rate, temperature and so on will also affect the adsorption effect, and the adsorption of  $\text{As}^{5+}$  is better than that of  $\text{As}^{3+}$ . Activated carbon prepared by Yan Wang loaded with iron as adsorbent has the best effect on the removal of  $\text{As}^{3+}$  in water. Zhong Sun Natural Mordenite is broken, with 10% sulfuric acid, aluminum sulfate solution of 0.5mol / L and 0.25mol / L copper sulfate soaked in 10h, can make the waste acid and arsenic content decreased from 1.94mg / L to 0.04mg/L. HCO, a rare earth material, has a good absorption effect on arsenic. It can remove arsenic from sewage at a concentration of 2 mg/L and control it below 0.01 mg/L under natural conditions. It is easy to operate and saves cost.

#### 3.2. Arsenic removal by ion exchange

Ion exchange can be divided into two types: inorganic ion exchange and organic ion exchange. Inorganic ion exchangers such as titanium dioxide. Organic ion exchangers such as ion exchange resins. The main characteristic of ion exchange resin is that it contains many exchangeable groups which can be ionized in water. The wastewater can be adsorbed in the reactor by ion exchange with chlorine through a reactor vessel containing anionic exchange resin. So as to achieve the effect of arsenic removal. Different exchangers have different effects on arsenic. When the initial mass concentration of  $\text{As}^{5+}$  is 1 mol/L, the removal rate of arsenic can reach 99.2%. Juetian Hu et al. developed chelate exchange resin column for arsenic removal. The pH value is between 4.6 and 5.5, which can remove 99.99% of arsenic from sewage. Mingtao Wang et al. found that the effect of treating  $\text{As}^{3+}$  and  $\text{As}^{5+}$  by MIEX-DOC was comparable, but only low concentration arsenic wastewater could be treated, which could meet the demand of drinking water.

#### 3.3. Removal of arsenic by membrane separation

Membrane is a kind of material with selective separation function, which mainly includes microfiltration membrane, nanofiltration membrane, ultrafiltration membrane and reverse osmosis membrane. In the experiment, it was found that the nanofiltration membrane was almost completely removed  $\text{As}^{5+}$  in the solution, but the removal rate of  $\text{As}^{3+}$  was slightly lower, only 5%. And with the increase of pH value, the removal effect of As by the membrane was better. Nanofiltration membrane has a good effect on inorganic and organic matters in sewage. So nanofiltration technology has a broad application prospects in the future of sewage treatment and drinking water purification.

### 3.4. Other arsenic removal methods

In addition to the above methods, there are also some other methods for arsenic removal, such as photocatalytic oxidation of arsenic removal method, catalytic reaction can be carried out quickly, the catalyst can also be used permanently. But the effect of catalytic oxidation of  $\text{As}^{3+}$  is not ideal. Emmett et al. used ultraviolet irradiation to oxidize  $\text{As}^{3+}$  and  $\text{Fe}^{3+}$  to absorb and oxidize  $\text{As}^{5+}$ . The activated sludge process achieved good results. Activated sludge arsenic removal process is suitable for the treatment of low concentration arsenic-containing wastewater in sewage treatment plants. There are few reports.

### 4. Solidification of arsenic waste residue

Arsenic-containing slag includes slag from smelting and acid removal. Its main components are arsenic sulfide slag and calcium arsenate slag. Because of their different compositions, their treatment methods are also different. In the treatment of arsenic residue at home and abroad, a certain amount of reagent is added to the waste acid. Arsenite and arsenate with stable properties can be produced by chemical reaction, or valuable metal can be recovered by pyrometallurgical roasting and wet leaching.

The leaching solution of industrial arsenic sulfide residue has strong acidity, pH value is 0.78, acidity is 62.55 mg/L. Hazardous wastes with corrosiveness. The treatment methods of sulfide slag can be divided into two categories: fire roasting and fire wet leaching. Pyrometallurgical roasting can be divided into oxidation roasting, reduction roasting and vacuum roasting. Roasting process is a traditional arsenic extraction process. It can recover arsenic trioxide directly. The process is short and the cost is low, but the arsenic recovery rate is low, and it is easy to cause two pollution. Hot water leaching method, hot metal leaching method, copper sulfate replacement method and alkali leaching method are the main methods. Hot water leaching method, hot metal leaching method, copper sulfate replacement method and alkali leaching method are the main methods. Compared with fire treatment, wet process does not produce dust. Low energy consumption and less pollution, but the process is complex and the operation is relatively difficult. In the process of copper smelting, the treatment of arsenic sulfide residue is mostly stacked or buried. After stabilization treatment, the solid waste landfill standard can be achieved. Most of the solidification use sludge, cement, metal salt, fly ash and yellow sand as curing materials. Xiao Yu added 9 times fly ash, 4 times cement, 20% ferric oxide, 10% sodium phosphate into arsenic sulfide residue, and the concentration of arsenic leaching solution was 1.12 mg/L, which met the landfill standard for hazardous waste.

### 5. Conclusion and prospect

In the process of removing arsenic from copper contaminated acid, the most commonly method is sulfuration and lime iron salt method. Mature technology and low cost can effectively deal with high arsenic wastewater in which disadvantage is the large amount of slag. In the future, we need to solve the problem of harmless treatment and recycling of slag. Some scholars have done more researches on arsenic slag disposal. The removal of fluoride and chloride and the control of the two pollution will become the focus of scientific research. Adsorption and microbiological treatment are effective for the treatment of low concentration arsenic containing wastewater. Ion exchange and membrane separation technology failed to industrialize due to immature technology and supporting facilities. In the development of arsenic removal by waste acid, enterprises should focus on the following points.

(1) Recovery and utilization of valuable metals: roasting and leaching are the two most important ways to recover arsenic sulfide residue. Arsenic sulfide can be recovered by oxidizing calcination and condensing arsenic trioxide. But the recovery rate is low and the quality of products is poor. Hydrometallurgical leaching can recover valuable chemicals such as sodium arsenate and arsenic trioxide with high operating cost and large investment. Copper contaminated acid also contains a certain amount of lead, zinc, nickel, cobalt, selenium, tellurium and other metals. How to effectively realize the secondary recovery of valuable metals in the process of arsenic removal and improve economic efficiency are also thinking directions of enterprise profits.

(2) Removal of fluoride and chloride ions and control of secondary pollution: under acidic conditions, fluoride and chloride ions have a strong corrosiveness. It will damage the pipeline, equipment, metal materials and ceramics, glass materials. Evaporation and condensation, defluorination chlorine<sup>[11]</sup> is the most common method to remove fluorine. During the storage of high arsenic slag in the yard, under the action of rain water immersion and wind erosion, soluble arsenic salts and heavy metal ions will be dissolved, and part of them will enter the lake under the action of rain water. Some of them infiltrate underground under the action of gravity, migrate and diffuse in soil and aquifer, and form secondary pollution of water source and soil. The effective solidification of arsenic slag and the control of arsenic salt dissolution will be an effective way to control the pollution.

With the development of society, people have paid more attention to environmental protection. In the future, the trend of arsenic removal technology should be developed in multiple arsenic removal methods. The reagents with low price, stable property and obvious effect of arsenic removal, as well as the solidification and pollution-free treatment of arsenic residue will be developed. Hence, the development of nanofiltration membrane which can separate many kinds of ions is a very promising area.

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