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Research of acid mine wastewater treatment technology

Li Bicai[a*], He Liansheng[b], Meng Rui[b] and Song Juanjuan[a]

[a]*College of Chemical and Environmental Engineering, Hunan City University, China*
[b]*Chinese Research Academy of Environmental Sciences, China*

ABSTRACT

In many countries and areas, acid mine drainage leads to serious environmental pollution. The article analyses the source and mechanism of the acidic mining waste water. Some commonly used treatment technologies and principle of mine acid waste water treatment were analyzed. And the characteristics of several treatment methods are discussed in this paper. At present, of the acidic mining waste water treatment methods and main method of sulfide precipitation floatation, method of displacement, extraction method, combined processing and biochemical electrode method, etc.

Key words: acid mine wastewater; formation mechanism; treatment principle; processing

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INTRODUCTION

1 The source and mechanism of the acidic mining waste water

The exploitation of the quarries includes two process: mining and mineral processing. Mining process is the first word processes of mineral resources industry, including mining process in open pit mining technique and mine mining process. Mining waste water treatment process, according to management process, is divided into two kinds: mining industrial wastewater and acidic mining waste water. The mining industry wastewater mainly comes from component cooling water, such as the mine air compressor cooling water, etc. The mining industry wastewater is with no harm to the environment, and after cooling it can be recycled for production. Acidic mining waste water is rock dust water, and its major pollutant is suspended solids, after precipitation it can be recycled. And acidic mining waste water has the following characteristics[1] : (1) contains several metallic ions, pH value in more than 2 ~ 6; (2) the waste water amount is large, the time is long; (3)the drainage is scattered, and water quality and water amount of point spread dramatically.

Acidic mining waste water is the main management object of mining waste water. Its formation mechanism[2] is shown as below, mining waste water is usually for oxygen (the oxygen in air), water and Sulphide (MeS) produces chemical reaction generated, microbial may also play a role:

$$2MeS_2 + 2H_2O + 7O_2 \rightarrow 2MeSO_4 + 2H_2SO_4$$
$$4MeSO_4 + 2H_2SO_4 + 5O_2 \rightarrow 2Me_2(SO_4)_3 + 2H_2O \quad (1)$$
$$Me_2(SO_4)_3 + 6H_2O \rightarrow 2Me(OH)_3 + 3H_2SO_4$$

2 Acidic mining waste water treatment

At present, the acidic mining waste water treatment methods are mainly neutralizational process, vulcanization method, replacement and method, precipitation floatation method, extraction electrode, biochemical technology and joint treatment method, etc.

2.1 Neutralizational process1. The treatment theory of neutralizational process

Acidic mining waste water is a type of sulfuric acid, general pH value for waste water 2 ~ 6[2], so low sulfuric acid content of obviously not recycling value, so and processing method is acidic mining waste water treatment of the main method. The basic principle is to input neutralizer into acid wastewater, to make heavy metal ions and hydroxyl ions react, generate precipitation of hydroxide dissolution difficulty in water, and, finally, make water to purify wastewater meets emission standard. When we use the method to deal with wastewater, we should know the best pH value of all sorts of heavy metal form hydrogen chloride precipitation and the heavy metal concentration in the solution after dispose. pH value of completely precipitation of different kinds of heavy metal is an obvious difference, accordingly we can execute and recovery of all kinds of metal. But for amphoteric metal like zinc, lead, chromium, tin, aluminum and so on, a very high pH can form complex and make the precipitation happened to dissolve phenomenon. For example, when the pH value is nine, Zn^{2+} is in almost all the precipitation. But when pH value is more than 11, it produces soluble Zn $(OH)_4^{2+}$ complexation ion or zinc root ion $(ZnO_2)^{2}$-. Therefore, optimal pH value must be strictly controlled and maintained.

2. Technological process of neutralizational process

And precipitation processing method is to use a precipitation reaction and crystal kind of cyclic response. The former is simple neutralization process, the latter is to add fine crystal seeds (return sludge) to the system to promote the forming of good precipitating crystallization. The processing flow is as shown in figure 1 below.

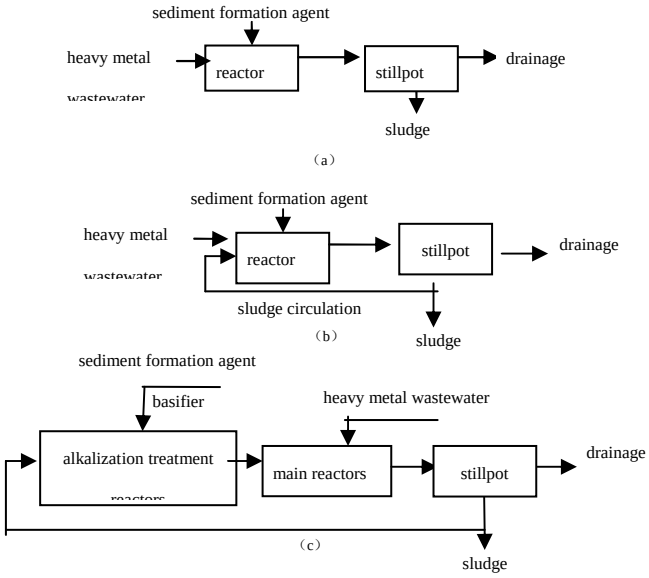

Figure 1: Technological process of neutralizational process

(a) is to introduce heavy metal sewage into reactive tank, input precipitant, stir the mixture to react, add the necessary flocculant to form a larger flocculation, then introduce heavy metal sewage into sedimentation tank to do solid-liquid separation. Because of its failing to provide crystal seeds. The sediment of this treatment is often microcrystalline n/med tuberculosis, the sludge sedimentation speed is slow, and high moisture content.

(b) is the seed circulation treatment method, its characteristic is not only to input precipitant, but also to return a moderate amount of precipitation sludge, and then mix and stir, after the concentration in settling pond, part of concentrated returned to reaction tank. Precipitation sludge produced by the method, is large grains, fast precipitation, low moisture content and good water effect.

(c) is Alkalization treatment the seed cyclic response method. That is to set a sediment alkalization treatment slot before the reaction tank, timing dose alkaline elixir in sediment alkalization treatment slot to react，and the generated mud is a kind of alkalization agent, it responses to heavy metal sewage in reactive tank, and then do solid-liquid separation in setting pond, return part of the sludge precipitation enrichment to alkalize treatment response slot。

Neutralizer used in industry is limestone, lime, caustic alkali, soda, industrial dust and the ferrous oxide, etc. Because the lime has the advantages of wide source and simple operation, it becomes common neutralizer. Compared with that of lime, the sludge of neutralization of limestone is small size, small space occupation, low moisture content, easy to dehydration, and it also can produce high concentrations of sludge, but the speed of

neutralization reaction is not faster. Although soda and caustic soda response quickly and effectively, the price is high, generally not be adopted.

According to different neutralizers used, neutralization process can be divided into the method of milk of lime neutralization and two steps of neutralization[3][9]. The method of milk of lime neutralization only uses the lime milk, according to the need to process acid sewage, can adopt step or more steps process.

2.2 Sulphide precipitation process

2.2.1. The treatment theory of Sulphide precipitation process

Sulphide precipitation refers to join Sulphide precipitation agent make heavy metal ion in waste water generate Sulphide precipitation and remove it of[6].Metal Sulphide solubility is usually lower than hydrogen peroxide several orders of magnitude, so if the occasion of Sulphide is cheap and available, it is a good choice to input Sulphide in wastewater to move the Sulphide precipitation formed of metal ions in sewage.

Compared to neutralization process, the advantages of Sulphide precipitation are: heavy metal Sulphide's solubility lower than its hydrogen chloride, and PH value in 7~ 9, so the treated wastewater generally does not need to neutralize. The defect of Sulphide precipitation is: small Sulphide deposit article, easy to form colloid; Sulphide precipitation agent it, if in the water it generates hydrogen Sulphide acid residues in gas, produces the secondary pollution. In order to prevent secondary pollution problems, research out of the improved Sulphide precipitation, namely to input Sulphide ions and another heavy metal ions (the heavy metal Sulphides ion average concentration is higher than the heavy metal pollutants need to get rid of the balance). Because the heavy metal Sulphide added is more likely to dissolve than the heavy metal Sulphides, so the original heavy metal ion is faster separate from than the heavy metal ion added, and at the same time solve the problem of harmful gas hydrogen Sulphide generation and Sulphide ion residues.

In order to not generate hydrogen Sulphide gas, method of SulpHex is to use iron Sulphide precipitate metal. Need to add pulpous precipitation agent, in PH value for 8 ~ 9. Japanese electronics companies use iron Sulphide to remove heavy metals, mix sewage with molysite, add alkali and to oxidize in the air, produce ferrite and remove contaminant through sediment the filter or magnetic fields. In the PH value of 6.5 ~ 7.5, the method of iron Sulphide precipitation can effectively remove arsenic in water. However, if Sulphide deposits sludge is not sealed underwater or excluded oxidizing condition, it is possible for it to generate sulfuric acid again, make PH lower, dissolve heavy metal and produce environmental problems again. If metal Sulphide can be sold, Sulphide precipitation has economic benefit. As to the tailings, in the future the Sulphide weathering and oxidation can lead to sulfuric acid formation and metal dissolution, cause environmental pollution. Therefore, the Sulphide precipitation should undertake integrated consideration.

2.2.2 .Technological process of Sulphide precipitation process

For instance, a copper mine sewage mainly come from mining field, quality listed in schedule.

Table 1: Quality of untreated sewage (mg/L)

item	Fe	Zn	Cu	SO_4^{2-}
concentration	720	23	50	2148.5

Note: the pH value of 2.6.

The quality of sewage reveals the concentration of Fe, Zn, Cu, SO_4^{2-} is higher, Sulphide precipitation process is a better method to treat wastewater and the process is shown in figure 2.

First of all, add lime adjust pH of 4.0 to precipitate Fe^{3+}, because Fe^{3+} in sewage is the optimal, it is no need to set oxidation process to transform Fe^{2+} to Fe^{3+};Then, put solution into sewage to make copper precipitate in the form of CuS; copper slag is high grade and can be recycled. At last, add lime to improve pH value to make overflow acidity of copper precipitation decline to reach emissions standards[4].The water quality index of treated sewage reveals sewage treatment is successful, and quality of treated sewage is shown in table 2.

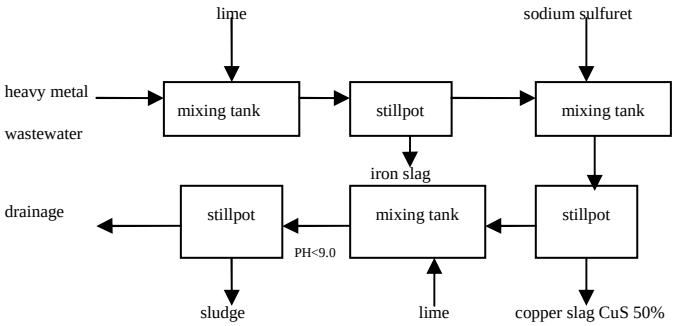

Figure 2: Technological process of Sulphide precipitation process

Table 2: Quality of treated sewage （mg/L）

item	Fe	Zn	Cu	SO_4^{2-}
concentration	6.00	trace	trace	809.3

Note: the pH value of 6.5.

2.3 Method of displacement

In aqueous solution electronegative metal can replace electropositive metal so to achieve the purpose of separating from the water, this is the replacement method[9]. Since iron is more electronegative than copper, to use scrap iron replace copper can get higher grade spongy copper. But replacement method can't make sewage acidity down, it must combine with neutralization[8], to achieve the purpose of discharge or reuse sewage. If a copper mine sewage mainly come from miningfield, quality listed in schedule.

$$Fe + Cu^{2+} \rightarrow Cu + Fe^{2+} \quad (2)$$

Table 3: Quality of untreated sewage （mg/L）

item	Fe	Zn	Cu	As	Cd	Pb
concentration	806	46	173	0.07	0.75	0.24

Note: the pH value of 2.5

The quality of sewage reveals the concentration of Cu is higher, should be recycled. Scrap iron replacement and neutralization process is a better method to treat wastewater and the process is shown in figure 3.

In order to improve the effect of iron sedimentation and reduce acidity, after using iron replace copper, adopt the method of second consecutive neutralization and join the flocculant to improve the heavy iron efficiency and reduce sewage acidity. Copper content of sponge cope from sewage treatment is 20% ~ 30%, it can be used as raw materials, and water can be directly discharged. After replacement and neutralization process, quality of sewage reaches the national emission standard. Specific quality of effluent water is shown in table 3.

Table 4: Quality of treated sewage（mg/L）

item	Fe	Zn	Cu	As	Cd	Pb
concentration	11.0	<0.08	<0.08	<0.03	0.00007	<0.02

Note: the pH value of 8.2.

2.4 Precipitation floatation method

Precipitation floatation method[7] is to translate metal ions into hydrogen peroxide or Sulphide precipitation, then utilize the method of flotation sediment to one by one to recover valuable metals, that is add flotation reagent to firstly inhibit some metal and select another kind of metal, and then reactivate and select other valuable metals. The advantages of this method is the high efficiency, wide adaptability, using the less land and less output mud slag, so it becomes common method of sewage treatment.

Acid wastewater comes from mining field, its quality listed in schedule.

Table 5: Quality of untreated sewage （mg/L）

item	Fe	Zn	Cu	Pb	SO_4^{2-}
concentration	3312	3.0	223	0.09	8341

Note: the pH value of 2.0.

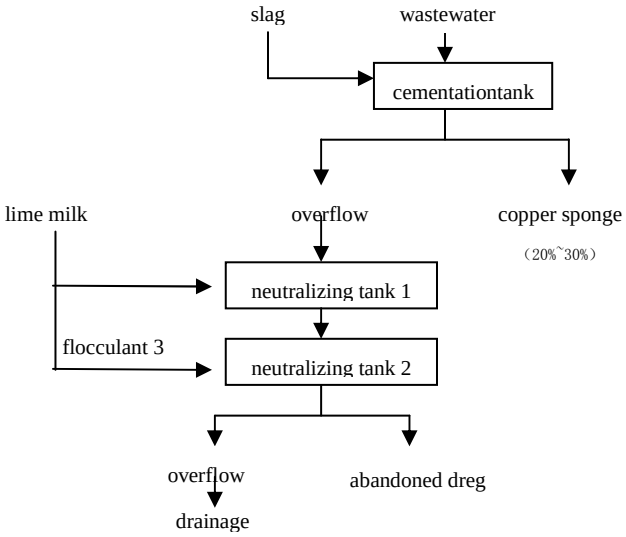

Figure 3: Technological process of iron replacement method

The quality of sewage reveals the concentration of Fe、SO42-and Cu is higher, should be recycled Precipitation floatation method is a better method to treat wastewater and the process is shown in figure 4.

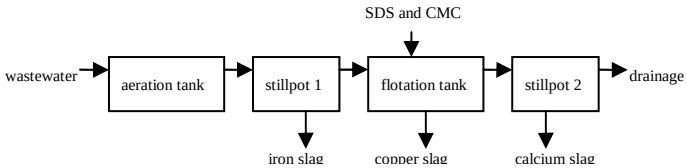

Figure 4: Technological process of precipitation floatation method

Firstly, utilize air aeration to translate Fe^{2+} into Fe^{3+}. Then, control pH value to precipitate Fe^{3+} as iron slag (ferric hydroxide). But at high pH, the other ion is consequent precipitation. In order to get copper preferentially, join SDS and CMC to select to get contains more than 50% of the copper slag, then precipitate and separate copper slag with CaSO499%.The process conditions is PH value of 3.4 ~ 4.0 at one section ; pH value of about 8.0 at second section. After Precipitation floatation process, quality of sewage reaches the national emission standard. Quality of water is shown in table 5.

Table 6: Quality of treated sewage（mg/L）

item	Fe	Zn	Cu	Pb	SO42-
concentration	0.13	trace	0.03	0.03	3154

Note: the pH value of 8.0.

2.5 Extraction electrolytic method

Extraction electrolytic method is to use the principle of distribution law, with a kind of organic solvent which can not dissolve with water and dissolve with some pollutants, to separate and remove pollutants. The advantages of this method are simple device, simple operation, high heavy metal content in the extractant, after reextraction getting metal by electrolysis. The defect is the requirement of the metal content is high, or else the treatment efficiency is low and the cost is high.

Acid wastewater comes from mining field, its quality listed in schedule.

Table 7: Quality of untreated sewage （mg/L）

item	Fe	Zn	Cu	Pb	As	Cd
concentration	26858	133	6294	0.97	33	7

Note: the pH value of 1.5.

The quality of sewage reveals the concentration of Fe and Cu is higher, pH value is low. Extraction electrolytic method is a better method to treat wastewater. And the process is shown in figure 5.

After extraction, reextraction and the electrolytic process, the concentration of secondary electrolytic copper in water is 99.90%, and can be recycled. Add ammonia water into raffinate phase to get iron slag which can be used as the iron oxide red of coating after burning. The pH value of iron filtrate is low, the addition of lime for two times is to improve the pH value, make sewage meets emission standard.

After Extraction electrolytic method, quality of sewage reaches the national emission standard. Quality of water is shown in table 8.

Table 8: Quality of treated sewage （mg/L）

item	Fe	Zn	Cu	Pb	As	Cd
concentration	trace	0.47	0.02	trace	trace	0.08

Note: the pH value of 8.5.

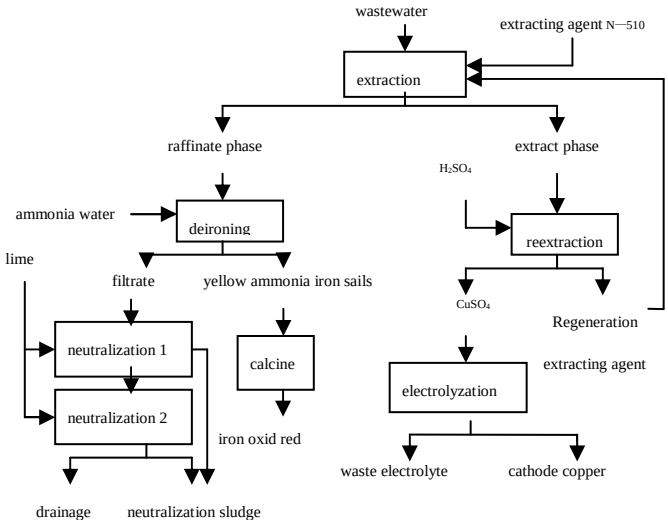

Figure 5: Technological process of extraction electrolytic method

2.6 Biochemical method

The nature of the bacteria is divided into two kinds, one kind is heterotrophic bacteria absorbing their activities need energy and the component cells carbon sources from organic material. Another kind is self-sustaining bacterial, absorbing their activities need energy from oxidating inorganic compounds and the component cells carbon sources from CO2 in the air. The relationship between self-sustaining bacterial and heavy metal is varied, and it can be used to deal with the acidic mining waste water. The main mechanism [10] : oxidation, the existence of bacteria oxidating heavy metal, such as oxygen iron bacteria etc; adsorption and concentration ,,the existence of bacteria adsorbing the heavy metal to surface or of the bacteria and algae.

At present, the best-studied bacteria are iron oxygen bacteria and sulphate reducting bacteria, iron oxygen bacteria is extensively applied in practice. Iron oxygen bacteria is a kind of bacteria good at acid, halogen ions will impede the growth, therefore, wastewater must be sulfuric acid, in addition, PH value, water temperature, the kinds and concentration of heavy metal , the change of water load and so on also have a greater influence. Sulfate reducting bacteria grows slowly[11], reduzate of SO_4^{2-} (H2S、HS-、S2-、metallic disulfide, etc) inhibits and poisons biochemical reaction to flora.

2.7 Other methods

At present, home and abroad have positive development in new processing technology such as artificial wetland method[13],Liquid membrane method[14],ion exchange chromatography[9][15], reverse osmosis method[16] and electrodialysis method. Artificial wetland method covers a big area, treatment effect influenced greatly by environment, and residual H2S of treated sewage will release from the soil. Exchange resin of Ion exchange method needs frequent replacement, so the operating cost is high. The problem of film polluted by calcium sulfate and iron precipitates is easily happen in reverse osmosis method.

2.8 Combined process

Joint treatment method is two or more kinds of sewage treatment method combining together. For acidic mining waste water with complicated composition, it is not good to use one method of sulfide precipitation floatation,

method of displacement, extraction method, combined processing and biochemical eletrode method, etc, it needs to combine several methods together.

CONCLUSION

The composition of acid wastewater is diverse and complex. Even in numerous methods, neutralization process is technique-matured and the most widely used. Precipitation floatation method although have the following advantages：fast at solid-liquid separation, small area cover, high-quality of treated water, small row mud, low water content of sludge, it has secondary pollution, in the practical application, precipitation floatation method is the second choice. Sulfide precipitation in acidic environments has the following advantages: steady reaction, less sludge, easy dehydration, high grade precipitation metal which is helpful for the precious metal recycling. But pH value is hard to control and the cost is high, the water quality of emission is hard to reach national standards, it is easy to generate H_2S and cause secondary pollution[21]. Wastewater quality and quantity of extraction electrode processing is limited, power consumption and cost of treatment is higher. Replacement method is to the iron filings as replacement agent, and the subsequent processing is complex. Biochemical method i is a new technology in recent years, it has the following advantages: low treatment cost and free of secondary pollution, but it depends on the fond of microorganism of acid-resisting and heavy metal tolerance,, and vulnerable to the environment, so applicable range was limited. Therefore, it is important to choose and determine the corresponding treatment methods for different nature of the acidic mining waste water, if necessary, should combine two or more methods for technical integration, solve the problem of acidic mining waste water pollution, also reached the purpose of treating waste with waste, fully reclaim valuable resources.

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