

# Biogeochemical Cycle of Acid Mine Drainage from Pyrite Mines and Its Environmental Impact

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**Abstract:** Acid wastewater from pyrite mines is a serious environmental pollutant, whose formation and evolution is a complex microbial ecology and biogeochemical cycle process. This paper reviews the research progress on the microbial classification and distribution, microbial diversity and abundance, biogeochemical cycle process of acid wastewater, etc., reveals the key role of microorganisms in the formation mechanism, environmental impact and utilization and treatment of acid wastewater, and provides theoretical basis and technical support for the monitoring, assessment and management of acid wastewater. The sustainable and ecological study of acid wastewater, etc., hoping to provide more scientific evidence and innovative ideas for the sustainable management and utilization of acid wastewater.

**Keywords:** Mine environment, acid wastewater, pollution prevention, iron mine.

## 1. Introduction

Pyrite ( $\text{FeS}_2$ ) is a sulfur-bearing metal mineral that is widely distributed around the world and is the main host mineral of many important metals (such as copper, nickel, cobalt, zinc, etc.). During the mining and processing of pyrite, oxidation reactions occur due to exposure to air and water, producing acid wastewater and waste slag, which cause serious environmental pollution[1-3]. Acid mine drainage (AMD) refers to wastewater with a pH lower than 4 and high concentrations of sulfates and heavy metals, which is one of the main sources of mine pollution[4]. The formation and flow of acid wastewater cause the quality of the surrounding water, soil, vegetation and atmosphere to decline[5], affect the structure and function of the ecosystem, and even endanger human health[6].

The production and evolution of acid wastewater is a complex biogeochemical process, involving the oxidation-reduction transformation of various sulfides, accompanied by the release and utilization of energy[7]. In this process, microorganisms play a key role, by using different valence states of sulfides as electron donors or acceptors, to achieve the oxidation-reduction transformation of sulfur, and also affect the cycling of other elements (such as iron, carbon, nitrogen, etc.). The sulfur cycle involved by microorganisms is not only the main driving force of acid wastewater, but also the main means of treatment, because microorganisms can use organic or inorganic substances in acid wastewater as energy or carbon sources, for biometallurgy, bioenergy, bioremediation and bioproducts, etc. utilization and treatment.

Microorganisms in acid wastewater have the characteristics of diversity, adaptability and functionality, and their community structure and metabolic activity are affected by various environmental factors, such as pH, temperature, oxygen, metal ions, organic matter, microbial interactions, etc. Therefore, a deep understanding of the microbial ecology and biogeochemical cycle of acid wastewater is of great theoretical and practical significance for revealing the formation mechanism, assessing the environmental impact, and optimizing the utilization and treatment of acid wastewater.

## 2. Acid Wastewater Cycle Process

Microorganisms in acid wastewater are the main participants of the biogeochemical cycle of acid mine drainage from pyrite mines. They use different valence states of sulfides as electron donors or acceptors to achieve the oxidation-reduction transformation of sulfur, and also affect the cycling of other elements (such as iron, carbon, nitrogen, etc.). Microorganisms in acid wastewater have the characteristics of diversity, adaptability and functionality, and their community structure and metabolic activity are affected by various environmental factors, such as pH, temperature, oxygen, metal ions, organic matter, microbial interactions, etc.

### 2.1. Classification and distribution of microorganisms

Microorganisms in acid wastewater mainly include three major categories: bacteria, archaea and fungi, among which bacteria and archaea dominate, and fungi are relatively rare. According to the energy source of microorganisms, microorganisms in acid wastewater can be divided into two categories: autotrophic and heterotrophic. Autotrophic microorganisms can use inorganic substances (such as sulfides, sulfates, ammonia, carbon monoxide, etc.) as energy sources, and convert inorganic carbon (such as carbon dioxide) into organic carbon through chemical synthesis or photosynthesis. Heterotrophic microorganisms need to use organic substances (such as sugars, fats, proteins, etc.) as energy and carbon sources, and decompose organic carbon into carbon dioxide and other substances through respiration or fermentation. Autotrophic microorganisms account for a higher proportion in acid wastewater, because organic substances in acid wastewater are often scarce, while inorganic substances are relatively abundant.

### 2.2. Diversity and abundance of microorganisms

Microorganisms in acid mine drainage have high diversity, which means the number and proportion of different kinds of microorganisms. The microbial diversity in acid mine drainage is influenced by various factors, such as the source,

composition, temperature, pH, redox potential, metal concentration of acid mine drainage, etc. Generally speaking, the microbial diversity in acid mine drainage increases with the increase of pH, and decreases with the increase of temperature and metal concentration. This is because the increase of pH alleviates the stress of acid mine drainage on microorganisms, while the increase of temperature and metal concentration enhances the stress of acid mine drainage on microorganisms. The planktonic microbial community has the highest diversity, the biofilm microbial community has the lowest diversity, and the attached microbial community has the intermediate diversity. This is because the planktonic microbial community is affected by the flow and diffusion of acid mine drainage, and is easy to mix with other microorganisms, while the biofilm microbial community is

affected by the interaction among microorganisms, and tends to form a stable structure, and the attached microbial community is between the two.

### 3. Biogeochemical Cycles of Acid Mine Drainage

The biogeochemical cycles of acid mine drainage from pyrite mines mainly include the following processes: (1) oxidation of pyrite; (2) reduction of sulfate; (3) oxidation of sulfide; (4) disproportionation of sulfur. These processes involve the transformation of sulfur between different states and forms, and also affect the cycles of other elements (such as iron, carbon, nitrogen, etc.) (Figure 1).

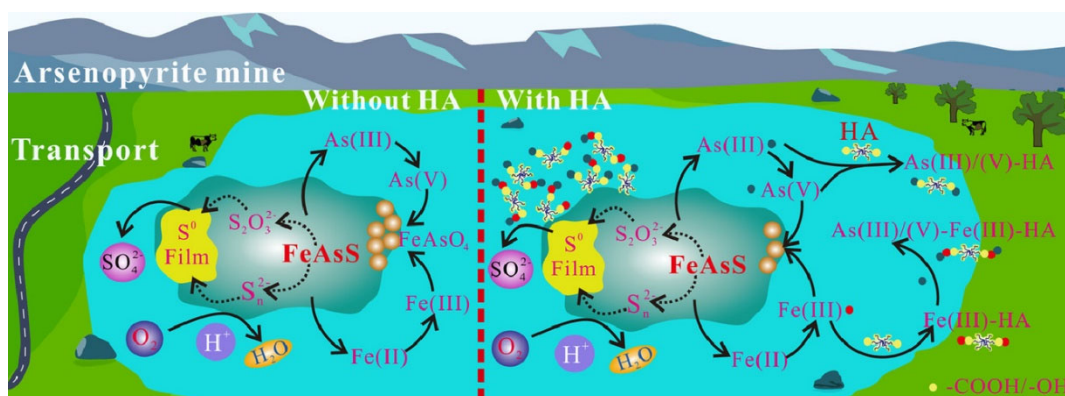


Figure 1. Weathering behavior of arsenopyrite in water medium without/with humic acid[5]

#### 3.1. Oxidation of pyrite

The oxidation of pyrite is the initial and key step of the biogeochemical cycles of acid mine drainage from pyrite mines, which leads to the formation of acid mine drainage and the release of heavy metals[8]. The oxidation of pyrite can be divided into two types: chemical oxidation and biological oxidation. The former is mainly participated by oxygen and water, and the latter is mainly catalyzed by pyrite-oxidizing bacteria (such as *Acidithiobacillus ferrooxidans*) and sulfur-oxidizing bacteria (such as *Acidithiobacillus thiooxidans*).

The oxidation of pyrite produces a large amount of sulfate, iron ions and acidic substances, which lower the pH of acid mine drainage, and also release a certain amount of elemental sulfur and hydrogen sulfide and other sulfur compounds. The oxidation rate of pyrite is influenced by many factors, such as temperature, pH, oxygen, metal ions, organic matter, microorganisms, mineral surfaces, etc. Generally speaking, the increase of temperature and metal concentration, the decrease of pH, the increase of oxygen, the presence of organic matter, the action of microorganisms, and the activity of mineral surfaces all promote the oxidation rate of pyrite[9].

#### 3.2. Reduction of sulfate

The reduction of sulfate is one of the important processes of the biogeochemical cycles of acid mine drainage from pyrite mines, which can alleviate the acidity of acid mine drainage, and also produce some beneficial or harmful substances. The reduction of sulfate is mainly catalyzed by sulfate-reducing bacteria (SRB), which can use sulfate as an electron acceptor, and organic matter or inorganic matter (such as  $H_2$ ,  $CO$ ,  $NH_4^+$ , etc.) as an electron donor, to achieve the reduction of sulfate[10].

The reduction of sulfate produces hydrogen sulfide,

bicarbonate, hydroxylamine and other substances, among which hydrogen sulfide is a toxic and odorous gas, but it can also form insoluble sulfide precipitates with heavy metal ions, thus reducing the concentration of heavy metals; bicarbonate is a weak acidic substance, which can neutralize the acidic substances in acid mine drainage, thus increasing the pH of acid mine drainage; hydroxylamine is a strong reducing agent, which can participate in some redox reactions, thus affecting the cycles of other elements. The reduction rate of sulfate is influenced by many factors, such as temperature, pH, oxygen, sulfate, organic matter, microorganisms, minerals, etc. Generally speaking, the increase of temperature and organic matter, the decrease of pH, the decrease of oxygen, the increase of sulfate, the action of microorganisms, and the presence of minerals all promote the reduction rate of sulfate.

#### 3.3. Oxidation of sulfide

The oxidation of sulfide is one of the important processes of the biogeochemical cycles of acid mine drainage from pyrite mines, which can produce some beneficial or harmful substances, and also affect the cycles of other elements[11]. The oxidation of sulfide can be divided into two types: chemical oxidation and biological oxidation. The former is mainly participated by oxygen and water, and the latter is mainly catalyzed by sulfur-oxidizing bacteria (such as *Acidithiobacillus thiooxidans*) and sulfur-oxygen-reducing bacteria (such as *Thiobacillus denitrificans*).

The oxidation of sulfide produces sulfate, nitrogen gas and acidic substances, among which sulfate can be used as an electron acceptor by sulfate-reducing bacteria, thus promoting the degradation of organic matter and carbon cycle; nitrogen gas is an inert gas, which can alleviate the disorder of nitrogen cycle and eutrophication problem; acidic

substances can lower the pH of acid mine drainage, but can also be neutralized by bicarbonate and other substances. The oxidation rate of sulfide is influenced by many factors, such as temperature, pH, oxygen, sulfide, nitrate, organic matter, microorganisms, minerals, etc. Generally speaking, the increase of temperature and sulfide, the decrease of pH, the increase of oxygen and nitrate, the presence of organic matter, the action of microorganisms, and the presence of minerals all promote the oxidation rate of sulfide.

### **3.4. Disproportionation of sulfur**

The disproportionation of sulfur is one of the important processes of the biogeochemical cycles of acid mine drainage from pyrite mines, which can produce some beneficial or harmful substances, and also affect the cycles of other elements[12]. The disproportionation of sulfur is mainly catalyzed by sulfur-disproportionating bacteria (such as *Desulfocapsa thiozymogenes*), which can use elemental sulfur as an electron acceptor and donor, and decompose elemental sulfur into hydrogen sulfide and sulfate.

The disproportionation of sulfur produces hydrogen sulfide and sulfate, among which hydrogen sulfide can form insoluble sulfide precipitates with heavy metal ions, thus reducing the concentration of heavy metals; sulfate can be used as an electron acceptor by sulfate-reducing bacteria, thus promoting the degradation of organic matter and carbon cycle. The disproportionation rate of sulfur is influenced by many factors, such as temperature, pH, oxygen, elemental sulfur, organic matter, microorganisms, minerals, etc. Generally speaking, the increase of temperature and organic matter, the decrease of pH, the decrease of oxygen, the increase of elemental sulfur, the action of microorganisms, and the presence of minerals all promote the disproportionation rate of sulfur.

## **4. Impact of Biogeochemical Cycles on The Environment**

The biogeochemical cycles of acid mine drainage from pyrite mines refer to the oxidation, reduction and other reactions of pyrite in the mine waste under the participation of microorganisms, which produce different valence states of sulfur compounds and iron compounds, and thus affect the cycles and balance of sulfur, iron, carbon, nitrogen and other elements in the environment.

### **4.1. Impact on water environment**

The main impact of the biogeochemical cycles of acid mine drainage from pyrite mines on the water environment is the acidification and enrichment of heavy metals in the water[13]. The oxidation of pyrite is the main cause of acid mine drainage formation. Pyrite is chemically oxidized to sulfate and iron hydroxide under the action of air and water, and then further oxidized to sulfuric acid and iron oxide by acidophilic bacteria and iron-oxidizing bacteria, releasing a large amount of H<sup>+</sup>, lowering the pH of the water. The pH of acid mine drainage is generally between 2 and 4, or even lower than 1. The H<sup>+</sup> in acid mine drainage also dissolves heavy metals in minerals, such as copper, zinc, cadmium, lead, mercury, etc., making them exist in the water in free or complexed forms, causing heavy metal pollution in the water. Heavy metals have toxic effects on aquatic organisms and human health, such as affecting the growth, reproduction, metabolism, etc. of organisms, or causing bioaccumulation and

biomagnification of organisms, or causing damage to human organs such as nervous system, liver, kidney, etc. Acid mine drainage also affects the cycles of other elements in the water, such as inhibiting nitrification, promoting denitrification, increasing the content of ammonia nitrogen and nitrite in the water, or dissolving phosphate in the water, increasing the content of phosphorus in the water, thus affecting the balance and eutrophication degree of nitrogen and phosphorus in the water.

### **4.2. Impact on soil environment**

The main impact of the biogeochemical cycles of acid mine drainage from pyrite mines on the soil environment is the acidification and accumulation of heavy metals in the soil. Acid mine drainage reacts with soil through surface runoff or underground infiltration, lowering the pH of the soil, reducing the buffering capacity of the soil, and reducing the fertility of the soil. The heavy metals in acid mine drainage also enter the soil with the water flow, or accumulate in the soil by precipitation or adsorption, causing heavy metal pollution in the soil. Heavy metals have toxic effects on soil organisms and plants, such as affecting the activity, diversity and function of soil microorganisms, or affecting the growth, photosynthesis, root absorption, etc. of plants, or entering the food chain through plants, endangering human health[14].

### **4.3. Impact on biological environment**

The main impact of the biogeochemical cycles of acid mine drainage from pyrite mines on the biological environment is the reduction of biodiversity and the increase of biological toxicity. The low pH and high heavy metal content in acid mine drainage pose serious threats to the survival and reproduction of aquatic and soil organisms, resulting in a significant reduction of biodiversity. The sulfides and sulfates in acid mine drainage are also utilized by some microorganisms, producing some toxic and harmful metabolites, such as hydrogen sulfide, dimethyl sulfide, sulfur dioxide, etc., causing toxic effects on organisms. Acid mine drainage also affects the physiological functions of organisms, such as inhibiting enzyme activity, destroying cell membrane integrity, interfering with signal transduction and gene expression, etc.

### **4.4. Impact on climate environment**

The main impact of the biogeochemical cycles of acid mine drainage from pyrite mines on the climate environment is the emission of greenhouse gases and the formation of aerosols. The sulfides and sulfates in acid mine drainage produce some greenhouse gases, such as carbon dioxide, methane, nitrous oxide, etc., under the action of microorganisms, increasing the concentration of greenhouse gases in the atmosphere, and aggravating the trend of global warming[15]. The sulfides and sulfates in acid mine drainage also oxidize to sulfate aerosols in the atmosphere, affecting the radiation balance of the atmosphere, changing the properties and distribution of clouds and precipitation, and having adverse effects on the stability and predictability of the climate.

## **5. Remediation of Acid Mine Drainage**

### **5.1. Reasons and objectives of remediation**

The reasons for the remediation of acid mine drainage from pyrite mines are to reduce the harm of acid mine drainage to the environment, restore the function and ecological balance

of the environment, and improve the quality and sustainability of the environment. The objectives of the remediation of acid mine drainage from pyrite mines are to lower the pH of acid mine drainage, remove or stabilize the heavy metals and

harmful substances in acid mine drainage, achieve the harmless, reduction and resource utilization of acid mine drainage, and meet the national or local emission standards or water quality standards (Figure 2).

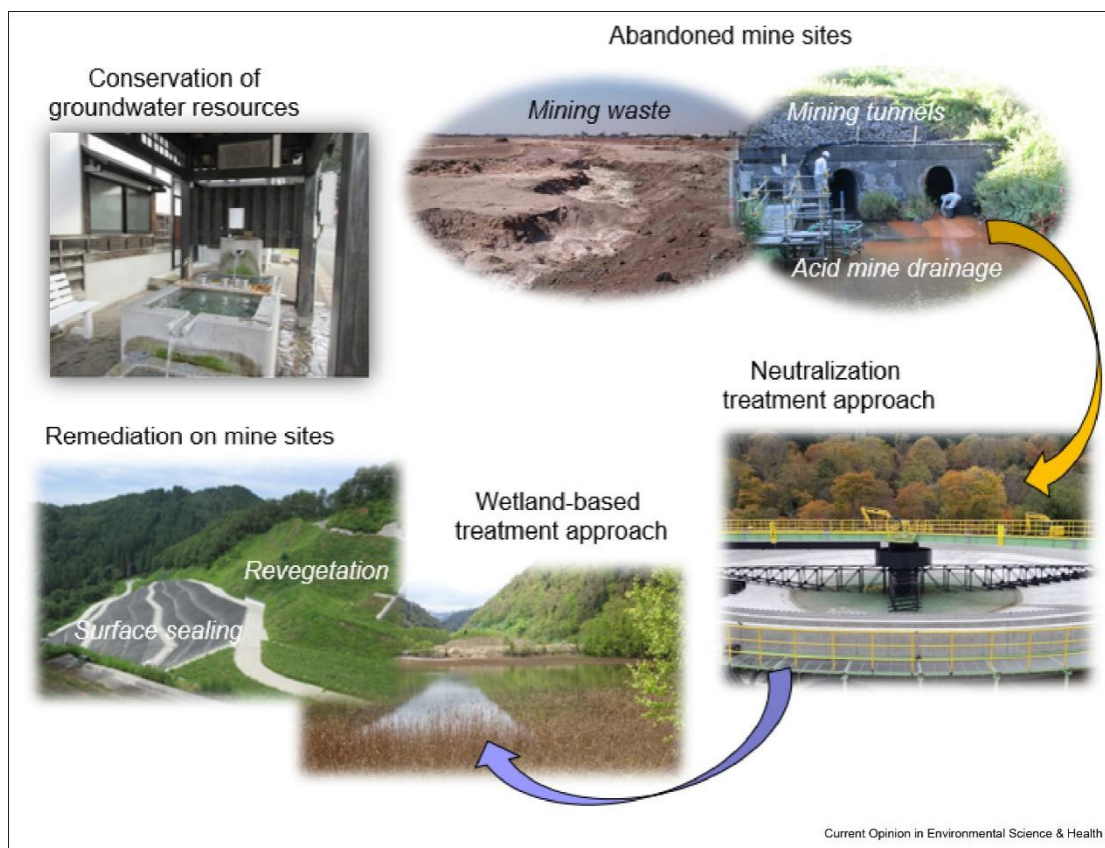


Figure 2. Remediation and wetland-based treatment approaches for the protection of groundwater resources[16].

## 5.2. Principles and methods of remediation

The principles of the remediation of acid mine drainage from pyrite mines are source control, comprehensive remediation, recycling and ecological restoration, that is, to reduce the production of acid mine drainage at the source, use a variety of technologies and means for comprehensive remediation, achieve the recycling and resource utilization of acid mine drainage, and carry out ecological restoration and environmental monitoring at the same time, to ensure the effectiveness and efficiency of remediation. The methods of the remediation of acid mine drainage from pyrite mines mainly include physical, chemical, biological and engineering methods.

## 5.3. Effects and evaluation of remediation

The effects and evaluation of the remediation of acid mine drainage from pyrite mines refer to the monitoring, analysis and evaluation of the process and results of remediation, to judge whether the remediation meets the expected objectives and standards, and whether the remediation has economic, social and environmental benefits and impacts. The methods of the effects and evaluation of remediation mainly include water quality analysis, environmental monitoring, cost-benefit analysis, risk assessment, etc.

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