Flocculation of mineral processing wastewater with Polyacrylamide

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Abstract. A lot of waste water and tailings were produced during mineral processing. Polyacrylamide, as an organic polymer flocculant, was widely used in the flocculation treatment of mineral processing wastewater and tailings. In this paper, the types of polyacrylamide commonly used in flocculation of wastewater generated from the beneficiation of metal ore, oil sand and phosphate ore were summarized.

1. Introduction
There were many harmful substances in mineral processing wastewater, such as heavy metal ions, various organic and inorganic flotation reagents used in ore flotation, including highly toxic cyanide and cyano chromide. The wastewater also contained a variety of insoluble coarse and fine suspended particles[1]. Mineral processing wastewater often contained sulfate, chloride or hydroxide such as sodium, magnesium and calcium. The acid in mineral processing wastewater was mainly formed by mixing sulfur-bearing minerals with water by air oxidation. The pollutants in mineral processing wastewater mainly included suspended solids, acid and alkali, heavy metals and arsenic, fluorine, beneficiation reagents, chemical oxygen consumption substances and other pollutants, such as oil, phenol, ammonium, phosphine. The harm of heavy metals such as copper, lead, zinc, chromium, mercury and arsenic and their compounds was well known.

Water-soluble polyacrylamide (PAM) has been widely used as a flocculant in this field[2]. Mineral processing wastewater was required to be purified to meet the environmental standards before discharge or recycling. Mineral processing wastewater often contained a large amount of fine suspended particles, which was difficult to settle naturally under the action of gravity. In this case, PAM was used to improve the speed of solid-liquid separation, so that the particles settled quickly and the supernatant became clear. It was obviously that the selection of appropriate PAM products played a very important role in the effective solid-liquid separation to reduce the operation cost.

2. Type of Polyacrylamide

2.1. Anionic PAM
Anionic PAM was a kind of water-soluble polymer which was prepared by anionic monomer and acrylamide monomer, or obtained by hydrolysis of PAM. There were both amide group and anion group with negative charge on the long chain of the polymer, such as maleic anhydride, acrylic acid and its sodium salt. It was mainly used for scale inhibition, sedimentation and clarification treatment of industrial wastewater, such as copper mine tailings, metallurgical wastewater, coal washing wastewater, oil sands tailings, steel plant wastewater and electroplating plant wastewater.
2.2. **Cationic PAM**

Cationic polyacrylamide (CPAM) was a kind of macromolecular compound which was polymerized by cationic monomer and acrylamide monomer in different proportion. There were both amide group and positive charge cationic group in the long chain of CPAM, such as dimethyldiallylammonium chloride (DADMAC), and acryloyloxyethyl trimethylammonium chloride (DAC). It had the functions of turbidity removal, decolorization, adsorption and adhesion. It was suitable for the dehydration of municipal sewage, municipal sludge, papermaking sludge and other industrial sludge, and the flocculation performance of acid fracturing fluid wastewater and oil production wastewater was also excellent.

2.3. **Amphoteric PAM**

Amphoteric PAM was a kind of macromolecular compound containing both positive and negative charge groups in the chain of PAM. It can be used in the pollution system of anion and cation coexistence, wide range of pH value and good salt resistance. It was widely used for decolorization of dye wastewater, sludge dehydrating agent and metal ion chelating agent.

2.4. **Nonionic PAM**

Nonionic PAM was an anionic polyacrylamide with hydrolysis degree of less than 5%. Due to the existence of a certain number of polar groups in its molecular chain, it can be a bridge among the suspended solid particles in water to combine the particles or agglomerate the particles to form large flocs by neutralization. Its flocculation effect reflected in clarification and purification, sedimentation promotion, filtration promotion, thickening and others. It was widely used in nickel ore dressing, coal washing wastewater, papermaking wastewater, sludge thickening and dewatering.

3. **Applications**

3.1. **Metal mine wastewater disposal**

In mineral processing, PAM was mainly used as a flocculant and filter aid. It was used in dewatering before grinding, concentrate dewatering, tailings dewatering, tailings filling, and middling dewatering.

3.1.1. **Gold and silver beneficiation.**

The content of gold in the ore was very low. In order to extract gold, it was necessary to crush and grind the ore and preconcentrate or separate gold from the ore by mineral processing. Flotation and gravity separation were widely used in gold processing. Gravity separation played an important role in gulch-gold production. Flotation method was widely used in rock gold mine[3]. No matter gravity separation or flotation, the ore must be ground very fine. In this way, in the process of sedimentation, concentration and dehydration of fine gold ore, the problem of slow sedimentation due to fine particles occurred. The settling rate of concentrate can be accelerated and the dewatering efficiency can be improved with adding a few PAM flocculant. PAM was also needed for gold extraction. Cyanidation was the main method for extracting gold from ore or concentrate. The process of gold extraction by cyanidation included cyanide leaching, washing and filtration of leaching pulp, extraction of gold from cyanide solution or cyanide pulp and smelting of finished products. One of the important process was the washing and filtration of leaching pulp. A large amount of gold mud was formed in the process of cyanidation and dissolution. The impurities inside needed to be settled in a short time. At this time, the sedimentation rate was greatly improved with the addition of PAM. The flocculant needed in this process was generally nonionic PAM.

High concentrations of heavy metals and metalloids including As, Cd, Co, Cu, Hg, Mn, Ni, U, and Zn existed in the gold mine tailings, which was significant potential ecological and human health risk associated with metal and metalloid exposure from contaminated soils around gold mine tailings dumps[4]. Anionic polyacrylamide was commonly used for gold mine tailings flocculation.
3.1.2. Potash ore wastewater.
A large number of potash mine tailings was produced by ore flotation, which were characterized by high insoluble matter and low grade[5]. Nonionic PAM was used in combination with other chemicals for flocculation and dewatering of this solid potash ore tailings. The results showed that the recovery rate of mother solution was relatively high when Nonionic PAM was used alone; the flocculation sedimentation rate was fast when sodium pyrophosphate and Nonionic PAM were used together; the flocculation products obtained by using sodium dodecyl sulfate solution and Nonionic PAM had good filtration performance and fast sedimentation rate[6].

3.1.3. Kyanite mine wastewater.
Kyanite was a mineral containing high alumina with the molecular formula $\text{Al}_2[\text{SiO}_4]\text{O}$. In the treatment of beneficiation wastewater from flotation of Kyanite with oleate, the turbidity of wastewater was high, and the pH of backwater should be controlled at about 7.5. Aluminum sulfate combined with nonionic PAM can be used to treat the backwater to greatly reduce the turbidity, and iron salt was not suitable as a coagulant[7-8].

3.1.4. Bauxite wastewater.
In the treatment of bauxite ore dressing tailings, the content of fine particles in tailings was high. Sodium carbonate was used as adjusting agent in beneficiation. The pulp was alkaline and the surface of particles was negative[9]. In the process of treatment, pH can be adjusted to neutral, and then anionic PAM can be used for flocculation. When flocculated with cationic PAM, the absolute value of the surface potential of the particles decreased, and the electrostatic adsorption between cations and tailings was the main way to produce loose flocs; when flocculated with anionic PAM, there was no charge neutralization between anionic groups and tailings particles, and hydrogen bond adsorption occurred between the polar groups on the molecular chain and the kaolin surface in the tailings to form porcelain flocs. Therefore, the effect of anionic PAM was better. When inorganic coagulant and anionic PAM were used together, the pH was not required to be adjusted[10].

3.1.5. Molybdenum mine wastewater.
In molybdenum ore dressing, sodium silicate was usually added as a mud dispersant and inhibitor, and lime was used as a pH regulator, which made it difficult for molybdenum ore tailings to settle naturally and pH of tailings was alkaline. When aluminum sulfate or ferrous sulfate was used alone, the sedimentation rate was slow, but the flocculation sedimentation rate was improved significantly when anionic PAM and lime cream were used together[11-12].

3.1.6. Nickel containing wastewater.
Advances in technology such as the electronics and metal planting industries have increased the demand for Ni, and some industrial wastewater contain large amounts of Ni, leading to environmental pollution as excessive intake of heavy metals was harmful to humans and as wastewater lead to environmental pollution[13]. For the low concentration nickel containing wastewater, Polyphosphate ferric sulfate (PFPS) was a good flocculant. In the process of treatment, pH was adjusted to neutral by buffer solution, PFPS was subsequently added, and PAM was then added and stirred for a few time to obtain high nickel removal rate[14].

3.1.7. Lead-zinc mine wastewater.
High alkali flotation was used in lead-zinc ore beneficiation and flotation. The wastewater contained a lot of suspended particles, residual reagents and some heavy metal ions with high pH value. The wastewater mainly included concentrate overflow and tailings overflow. When Polyaluminum chloride (PAC) and alum were combined used, the flocculation behavior was good only when the wastewater was in neutral condition, and when Polyferric sulfate (PFS) was used in alkaline condition, good flocculation effect can be achieved. In the process of treatment, pH should be adjusted to the
optimal value (neutral), PFPS was then added with stirring for a certain time, and PAM was finally added. After coagulation, organic matter in the wastewater had been absorbed by activated carbon, and the generated backwater was recycled for mineral processing and reuse[15-16].

3.1.8. Copper and copper nickel ore dressing wastewater.
The main pollutants in copper nickel ore dressing wastewater were suspended solids, chroma, turbidity, and various heavy metals[17]. Cationic PAM with molecular weight of about 8 million and cationic degree of 25% was commonly selected for flocculation and sedimentation treatment in solid-liquid separation of copper leaching pulp from low-grade copper bearing waste residue. Anionic PAM with molecular weight of 18 million and hydrolysis degree of about 30% was usually used for copper mine tailings flocculation[18].

3.1.9. Tungsten ore dressing wastewater.
The main pollutants in waste water of tungsten ore dressing included suspended solids, turbidity, cadmium, etc. The wastewater flocculated with PAC, activated silicic acid (AS) and PAM all had good removal rate of cadmium; for turbidity removal, performance with PAM was the best, follow by PAC, and AS was beyond satisfied, but PAM flocculation might increase the amount of sludge[19-20].

3.1.10. Iron mine tailings.
The pH of iron mine tailings was generally alkaline, and it was usually flocculated with anionic PAM, sometimes combined with inorganic coagulant. PAM that commonly used in iron ore treatment was an anionic one with hydrolysis degree of 25% - 35% and feed concentration of 0.2%-0.5%[21-22].

3.2. Application of oil sand tailings treatment
Oil sand tailings were a mixture of fine clay, sand, water and residual asphalt produced in the process of extracting asphalt from oil sands. The tailings were pumped into the tailings ponds and the solids were settled from the water. When the tailings were transported to the tailings ponds, the large particles of sand settled to the bottom, and the water rose up. The intermediate layer was mature fine tailings (MFT), which was composed of fine clay particles suspended in water with particle size of 10μm-80μm. some of these particles settled down, but most of them were still in suspension. According to historical experience, it took decades for MFT to settle sufficiently, so as to meet the reclamation conditions. Therefore, more and more oil sand tailings ponds were needed. Tailings wastewater treatment had become a very critical issue[23-24].

![Figure 1. The flow chart of oil sand tailings flocculation.](image-url)
Polyacrylamide as a flocculant had been widely used in the treatment of oil sand tailings [25]. The common flow chart was shown in Figure 1. The tailings were discharged into two thickeners and feed wells via two outlet pipes after separated in the gravity distributor. At the feed well, the tailings were diluted with the supernatant recovery water from the thickeners, and then mixed with the prepared flocculant solution. The function of flocculant was to gather solid and promote the sedimentation of fine particles in the thickener. In each thickener, the flocculated solid settled to the bottom of the tank. The slowly rotating rake pushed the flocculated tailings into the bottom central sediment discharge column. Each thickener had a separate tailing pipeline, and the sediment was transported to the tailings ponds by centrifugal pump.

For the flocculation of oil sand tailings, anionic PAM with molecular weight of about 10 million and hydrolysis degree of about 30% was generally used combined with polydadmac bead polymer. Bench scale experiments has been carried out to testify that the underflow concentration after flocculation reached more than 50%, and the overflow solids was less than 0.5% with only about 300g/ton PAM.

3.3. Slime water treatment

3.3.1. Composition of slime water.
After the raw coal was classified, deslimed, cleaned and dehydrated, a large number of fine particles (less than 0.5mm) remained in the water to form slime water. The function of slime water treatment process in coal preparation plant was to recover slime through solid-liquid separation and realize closed-circuit circulation of washing water. The composition of slime was very complex, mainly including coal and various minerals. Due to the strong hydrophobicity of coal, the particles were easy to agglomerate and settle, so the coal in the suspended solids circulating with water was not the main factor for many difficult settling slime water, but the mineral composition of slime water, including clay, oxides and hydroxides, sulfate minerals, sulfides and other minerals.

![Figure 2. The coagulation and flocculation mechanism graph of main slime water.](image)

3.3.2. Characteristics of slime water.
The main characteristics of slime water were as follows: high concentration, high content of fine particles, high ash content, many negative charges on the surface of particles. These particles kept stable dispersion in the water due to the repulsion of the homoelectric charge. The pH of slime water was generally neutral and alkaline, and weak acid slime water was produced only in some high sulfur coal preparation plants.
3.3.3. Flocculation and sedimentation of slime water.

There were two processes during the flocculation and sedimentation of slime water, coagulation and flocculation[26-27]. The coagulation of slime water referred to the addition of electrolytes to the slime water. The electrolytes generated ions to neutralize the negative charge on the surface of the particles in the water, which made the colloidal particles destabilize, and then the particles combined and became larger due to Van Der Waals force. The flocculation of slime water was that the amide group (-CONH) in the high molecular flocculant PAM was compatible with many substances and forms hydrogen bond by adsorption. The high molecular weight PAM acted as a bridge with the adsorbed particles to form large flocs through bridging connection, which accelerated the settlement of particles to clarify the slime water. The flocculation mechanism of PAM was mainly in wrapping sedimentation under the condition of high concentration of slime water. The coagulation and flocculation mechanism of main slime water was shown in Figure 2. Anionic PAM with molecular weight of 8-12 million and hydrolysis degree of about 30% was commonly used in slime water flocculation. The particles in the slime water were mainly negative charged, so it was difficult to bridge the high electrical fine particles to form flocs due to the repulsion force; there was no electric neutralization effect on the coal particles with weak electrical property, only bridging adsorption occurred. Therefore, it was common that PAM combined with inorganic coagulant was applied in this field.

3.4. Phosphate treatment

The disseminated particle size of phosphate rock ore was very fine, and the useful minerals were closely associated with gangue minerals. The grinding fineness requirement for the dissociation of phosphate mineral monomer in flotation was -0.075mm, and the content of that was more than 90%[28]. Therefore, the particle size of flotation concentrate was fine, and the content of -10μm particle size was generally up to 40%. The suspension system formed by fine particles was extremely stable. After natural sedimentation, there was still no recognizable clarification interface, and the upper liquid was turbid. In the process of concentration, the solid content of overflow was relatively high with large loss rate of phosphorus concentrate.

The particles in phosphate slurry were generally negatively charged. The electrostatic repulsion between the particles in the slurry made the solution stable and hardly to settle. Both inorganic electrolyte and organic polymer flocculant can improve the sedimentation performance of phosphate concentrate. When inorganic electrolyte was added, the electric double layer was compressed and diffused by electric neutralization, which made the fine suspended particles agglomerate and settle, the overflow clarity was higher, and the sedimentation rate of the agglomerate was slow; With adding organic polymer flocculant, the fine suspended particles were connected to form flocs and settle through the bridging effect of active groups, the overflow clarity was a little bad, and the settling rate of flocs was fast[29]. It was obviously that the sedimentation rate of phosphate concentrate was accelerated and the solid content in overflow was reduced with both inorganic coagulant and organic polymer flocculant are combined used in the process of concentration of phosphate concentrate.

4. Conclusion

With the rapid development of mining industry, the wastewater produced in the mining process increased day by day and the composition became more and more complex. Polyacrylamide was widely used in various mineral process and the treatment of mineral processing wastewater. However, the mineral processing technology and tailings pollutants varied in different plants due to the different diagenetic structure and associated minerals in different mines. In order to play a better role of flocculation, PAM, as a flocculant, should be screened reasonably according to the on-site conditions in different plants.

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