Study on Coagulation Settlement Test of Mineral Processing Wastewater from a Tungsten-Molybdenum Mine

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Abstract. In view of the problem that the turbidity and suspended solids produced by the mineral processing wastewater containing ultrafine mineral particles and residual mineral processing agents in a tungsten-molybdenum concentrator have a high impact on its direct reuse, the exploratory and field test of coagulation and sedimentation reagents is carried out. The BK-A coagulant has better sedimentation performance. The experimental results show that the optimum reaction conditions of BK-A coagulant are: sedimentation pH 9-10, BK-A dosage 20-25 mL/L, PAM dosage 6 mL/L. The turbidity and suspended solids of the treated tailings pond wastewater can basically meet the water quality index of clean water, and the silicate in the tailings pond wastewater can be stably reduced to about 100 mg/L.

1. Introduction

The total amount of mineral processing wastewater discharged by metal mine concentrators accounts for about 1/10 of the total amount of industrial wastewater in China. Due to the addition of a large number of mineral processing agents, these agents remain in the waste water discharged from the plant, which contains suspended solids, metal ions, organic and inorganic agents and other substances, direct discharge will cause serious pollution to the land, water bodies within the basin, pressure on the ecological environment. With the increasingly strict environmental protection requirements, how to effectively treat and reuse the mineral processing wastewater is a major problem that has long been urgent to solve in metal mines, and also a technical problem that must be considered in the process of mineral processing. A molybdenum company is mainly tungsten-molybdenum ore, and the wastewater generated in the process of dressing can not be directly reused because it contains impurities such as suspended particles and ore dressing chemicals, which is currently put into tailings storage. In order to improve the water recycling efficiency and relieve the pressure of shrinking tailing pond volume, we commissioned our company to carry out a series of coagulation sedimentation treatment experiments on the tailing pond wastewater. The purpose is to reduce the suspended substance content and turbidity in the wastewater, so as to create conditions for the recycling of the mineral processing wastewater for mineral processing production. This article through to the tailings waste water for laboratory and site coagulation precipitation test and research, determine the optimum coagulant, kind and amount of flocculant, determines the optimum reagent system, basic can realize tailings to replace or partly replace new water and mineral processing wastewater to a certain extent, alleviate the pressure of the tailings storage, improve the factory waste water cycle utilization.
2. Wastewater quality

The mineral processing wastewater quality provided by the plant is shown in the following table:

| Date  | appearance | pH  | Total Hardness (mg/L) | SS  | COD | Silicate (mg/L) |
|-------|------------|-----|-----------------------|-----|-----|-----------------|
| 9.14  | clear      | 11.75 | 1060                 | 273 | 235 | 572             |
| 9.26  | clear      | 11.68 | 1200                 | 107 | 183 | 601             |
| 10.9  | clear      | 11.88 | 1400                 | 126 | 253 | 466             |
| 10.17 | clear      | 12.01 | 60                   | 187 | 200 | 493             |
| 10.26 | clear      | 12.13 | 480                  | 230 | 223 | 464             |
| 11.7  | turbid     | 11.98 | 660                  | 250 | 162 | 470             |
| 11.17 | clear      | 11.82 | 1120                 | 252 | 190 | 457             |
| 11.25 | muddy      | 11.95 | 76                   | 207 | 182 | 596             |

As can be seen from the above table, the characteristics of tungsten mineral processing wastewater quality are: pH is alkaline, suspended matter and turbidity fluctuates greatly, COD exceeds the standard, contains a certain amount of silicates, the water quality fluctuates greatly, it is recommended to treat to a certain level after back for mineral processing process.

3. Preliminary screening test of coagulant in laboratory

3.1. Preliminary screening test of coagulant

Firstly, the primary test of coagulant was carried out in the laboratory. The waste water was obtained from the tungsten and molybdenum waste water from the mineral processing plant. The test results are shown in the figure below:

![Figure 1. Raw water, plus PAC, plus FeCl₃, plus CaO (from left to right)](image)

As can be seen from the above figure that conventional coagulants have certain coagulation effect on suspended substances in mineral processing wastewater, but it is not ideal to directly use a single coagulant for sedimentation, and there are always fine particles in the supernatant that cannot settle.
3.2. Exploration test of compound flocculant

In order to achieve better coagulation and sedimentation result, a flocculant compounding exploration test was carried out in the laboratory. The flocculant compounding experiment was conducted by using the compounding agent to conduct coagulation test. The size of floc and settlement time were observed. A more effective flocculation-coagulant formula, named BK-A, was selected through exploration and research. The test results are shown in the figure below:

![Figure 2. BK-A condition test of flocculation reaction](image)

3.3. Laboratory exploration test results

The preliminary exploration test results show that due to the complex water quality of tungsten and molybdenum mineral processing wastewater in the company, the suspended particles are small, and the effect of conventional coagulant is not so good. After adopting the compound BK-A coagulant, the settling time was shortened obviously, the floc was large and dense, and the supernatant was clear.

4. Field test study

4.1. The experiment purpose

Aiming at the actual tungsten and molybdenum mineral processing wastewater produced in the field, the optimization test of coagulation and sedimentation process was carried out to determine the best technological parameters and pharmaceutical system, so as to improve the wastewater treatment effect and reduce the waste water treatment cost.

4.2. The experimental chemicals

Experimental chemicals: compound coagulants BK-A and PAM were used according to the initial screening conditions:

- Bk-A solution: concentration of 1~3%;
- PAM solution: concentration 0.1%.

4.3. The experiment of water quality

In the field test, the raw water is DDP mineral processing wastewater (tailings pond backwater). At room temperature ~20°C, the water sample is not specially treated. See the following table for water quality:
Table 2. Analysis data of mineral processing wastewater quality of DDP tailings pond

| Sample name                  | pH     | Turbidity (NTU) | SS (mg/L) | Total Hardness (mg/L) | Silicate (mg/L) | COD (mg/L) |
|------------------------------|--------|-----------------|-----------|-----------------------|----------------|------------|
| DDP wastewater               | 10.16  | 336             | 440       | 230                   | 277            | 61         |
| DDP tailings pond wastewater | 11.06  | 266.49          | 428.22    | 460.82                | 691.22         | 190.90     |

5. Discussion on the results of field test

5.1 pH Test on coagulation and sedimentation of tailings pond wastewater
BK-A has a wide range of pH. Different pH conditions will affect the settling process of flocs after the final addition of PAM. The Tailings Pond Wastewater 1L is taken and BK-A solution 30mL is added. After 10 minutes of stirring reaction, the pH of the mixed solution is adjusted to 10, 9, 8, 7, 6 respectively. Then the quantitatively prepared PAM solution is added, and the precipitation time is 5 minutes. Sample analysis, analysis data source provided by the plant, the results are shown in Table 3.

Table 3. pH on coagulation sedimentation test results

| S/N | BK-A Dosage (mL) | pH     | Turbidity (NTU) | SS (mg/L) | COD (mg/L) | Total hardness (mg/L) | Silicate (mg/L) | Sludge (mL) |
|-----|------------------|--------|-----------------|-----------|------------|-----------------------|----------------|-------------|
| 1   | 0 (Raw water)    | 10.16  | 336             | 440       | 61         | 230                   | 277            | 0           |
| 2   | 30               | 9.86   | 9               | 45        | 86         | 280                   | 132            | ~200        |
| 3   | 30               | 9.03   | 4               | 34        | 81         | 370                   | 125            | ~210        |
| 4   | 30               | 8.35   | 5               | 34        | 83         | 270                   | 141            | ~200        |
| 5   | 30               | 7.23   | 3               | 32        | 67         | 440                   | 155            | ~210        |
| 6   | 30               | 6.07   | 15              | 46        | 58         | 496                   | 179            | ~300        |

Experimental Static Settlement Process phenomena:
1#: The raw water of tailings reservoir is not treated.
2#: The formation of large alum, flocs, fast settling speed, less than 5 minutes to complete the basic settlement, the upper clear liquid with a small amount of bulk flocs difficult to settle, the overall settlement effect is best;
3#: The formation of large alum, flocs, fast settling speed, less than 5 minutes to complete the basic settlement, the upper clear liquid with a small amount of bulk flocs difficult to settle, the overall settlement effect is best;
4#: The formation of alum is larger, flocs are more, fine flocs in supernatant increase, and settlement is basically completed in about 5 minutes. The overall settlement effect is better.
5#: Alum particles are fine, flocs are small, and it is difficult to settle. The coagulation effect is better after adding 5 mm LPAM solution.
6#: The formation of alum particles is small and the settling speed is slow. After 5 minutes, it still does not completely settle down. After adding 5 mm LPAM solution, the formation of alum is still unsatisfactory and difficult to settle.

The experimental results show that when the settling pH is adjusted to 9-10, the settling effect is best, the supernatant is clear and transparent, and the floe settling effect is good. At the same time, the silicate can also be reduced to about 120 mg/L at the same time.
5.2. BK-A dosage test on coagulation and sedimentation of tailings reservoir wastewater

Too much coagulant will produce too much slag and consume more PAM agent, which will increase the burden for subsequent treatment, and too little will lead to poor sedimentation. DDP Tailings Pond Wastewater 1L was taken and BK-A solution of 40, 35, 30, 25, 20, 15 and 10mL were added in turn. After 10 minutes of stirring reaction, the pH of the mixed solution was adjusted to 9 respectively, and then the PAM solution was added to the quantitative preparation. After 5 minutes of static sedimentation, sampling analysis was carried out. The results are shown in Table 4.

| S/N | BK-A Dosage (mL) | pH  | Turbidity (NTU) | SS (mg/L) | COD (mg/L) | Total Hardness (mg/L) | Sicilale (mg/L) | Sludge (mL) |
|-----|------------------|-----|----------------|-----------|------------|----------------------|----------------|------------|
| 1   | 0 (Raw water)    | 10.16 | 336           | 440       | 61         | 230                  | 277            | 0          |
| 2   | 40               | 9.03  | 2             | 31        | 65         | 340                  | 108            | ~350       |
| 3   | 35               | 9.07  | 3             | 31        | 63         | 320                  | 122            | ~300       |
| 4   | 30               | 9.05  | 6             | 34        | 64         | 280                  | 105            | ~210       |
| 5   | 25               | 9.04  | 5             | 34        | 62         | 300                  | 154            | ~210       |
| 6   | 20               | 9.07  | 5             | 34        | 58         | 366                  | 92             | ~200       |
| 7   | 15               | 9.10  | 4             | 32        | 66         | 410                  | 92             | ~200       |
| 8   | 10               | 9.08  | 2             | 31        | 65         | 340                  | 108            | ~180       |

Comparison conclusion of experimental static settlement process:

The amount of slag in sedimentation experiments of 4#, 5#, 6#, 7# and 8# are not different from each other, however, when the amount of BK-A is less than 25mL, the floc in the supernatant gradually increases and the floc volume decreases. When the dosage of BK-A was 30mL and 25mL, the floc of adding 5mL PAM was formed and settled rapidly. When the amount of BK-A was more than 30mL, the amount of small flocs in the supernatant was basically the same as that in 4# and 5#, and the amount of slag increased.

Test results: in the pretreatment of 1L DDP tailing pond wastewater, the optimal amount of BK-A is 20–25mL. In practice, the amount of BK-A should be adjusted according to the fluctuation of water quality. When the turbidity and suspended solids of tailing pond wastewater change, the amount of BK-A can be appropriately adjusted according to the floc settlement. The concentration of silicate in wastewater can be reduced to about 100mg/L.

In summary, when the settlement pH is around 9–10, it is more appropriate to pretreat 1L DDP tailing pond wastewater with BK-A 20–25mL coagulant with BK-A mass fraction of 3%. The effect of treated water sample is shown in the figure below.
5.3. *pH Test of BK-A on coagulation of tailings pond wastewater*

Test results are shown in the following table:

| S/N | Coagulation pH | BK-A Dosage (mL) | sedimentation pH | PAM Dosage (mL) | Turbidity (NTU) | COD (mg/L) | Total Hardness (mg/L) | Silicate (mg/L) | Sludge (mL) |
|-----|----------------|------------------|------------------|----------------|----------------|------------|------------------------|----------------|-------------|
| 1   | 11.78          | 0                | -                | -              | 63.5           | 128        | 249                    | 810            | -           |
| 2   | 11.78          | 20               | 9.06             | 6              | 1.65           | 103        | 176                    | 182            | ~150        |
| 3   | 11.04          | 20               | 9.07             | 6              | 1.96           | 157        | 157                    | 130            | ~150        |
| 4   | 10.27          | 20               | 9.21             | 6              | 7.38           | 115        | 255                    | 182            | ~150        |
| 5   | 9.01           | 20               | 9.01             | 6              | 2.16           | 115        | 184                    | 174            | ~150        |

According to the observation and analysis of the experimental phenomena, during the coagulation reaction, the particle size and formation rate of alum formed by the reaction basically have little...
difference under the four conditions of pH about 12, 11 and 9, while the rate of alum formed under the condition of pH 10 is slightly slow, and the flocculation sedimentation process has little difference at last. According to the analysis of experimental results, after 5min of sedimentation, the amount of sedimentation mud is about 150ml, and the turbidity of supernatant is about 1-8, which is not much different from that of clear water.

In summary, coagulation reaction pH has little effect on the sedimentation effect of DDP tailings pond wastewater.

5.4. PAM dosage test on coagulation and sedimentation of tailings reservoir wastewater

Testing process: 1 L of DDP tailings pond wastewater was taken and 20 mL BK-A solution was added. After 10 minutes of stirring reaction, the pH of the solution was adjusted to 9-10. Then 10, 8, 6, 4 and 2 ml PAM solution was added to flocculate and settle for 5 minutes. Sampling analysis was made. The results are shown in the table below.

| S/N | BK-A Dosage (mL) | pH   | PAM Dosage (mL) | Turbidity (NTU) | COD (mg/L) | Total Hardness (mg/L) | Sicilicate (mg/L) | Sludge (mL) |
|-----|-----------------|------|-----------------|-----------------|------------|-----------------------|-----------------|-------------|
| 1   | 0               | 11.78| 0               | 63.5            | 128        | 50                    | 814             | ~0          |
| 2   | 20              | 9.29 | 10              | 1.39            | 130        | --                    | --              | ~150        |
| 3   | 20              | 9.29 | 8               | 3.66            | 128        | --                    | --              | ~150        |
| 4   | 20              | 9.29 | 6               | 2.54            | 122        | --                    | --              | ~150        |
| 5   | 20              | 9.29 | 4               | 5.63            | 135        | --                    | --              | ~150        |
| 6   | 20              | 9.29 | 2               | 4.44            | 140        | --                    | --              | ~150        |

In the figure, the addition amount of PAM from left to right is 2ml, 4ml, 6ml, 8ml and 10ml successively. According to the observation and analysis of the experimental phenomena, when the dosage is 6~10mL in the flocculation process, the alum flocculates formed in the flocculation process are good and the alum flower particles gathered are large, which has a good settlement.

However, when the dosage of PAM is reduced to 2-4ml, the alum flowers formed in the flocculation process are in fine strips, which are difficult to gather together to form the alum flowers with larger particles, and the sedimentation rate slows down.

According to the analysis of the experimental results, when PAM adds 6-10ml, the settlement is basically completed in 5min, and the volume of sludge volume remains unchanged. When PAM adds
2-4ml, the settlement time increases, and the final turbidity of supernatant is about 1-6, not much different from that of clear water.

In conclusion, for this batch of DDP water samples, the dosage of PAM is about 6 ml.

6. Conclusion
(1) Coagulation test results show that the using coagulation sedimentation technology to treat wastewater from DDP tailings pond, the sedimentation pH is 9-10, the dosage of BK-A coagulant is about 20-25 mL/L, and the turbidity and suspended solids of the treated tailings pond wastewater can basically meet the water quality index.

(2) by adopting the optimized coagulant settling agent system, the silicate ions in tailings pond wastewater can be reduced to about 100mg/L stably.

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