Research of reagent treatment methods for mine waters from sulfates

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Abstract. The most important environmental challenge for the mining industry is the efficient treatment of mine wastewater. The solution to this problem is complicated by the large volumes of this wastewater, which requires significant material and economic costs. Analysis of the wastewater drainage mine composition "Limestone" shows that it is contaminated with impurities, in quantities that significantly exceed the admissible concentration limit for wastewater discharged into water bodies fish of sulfates, salts (dry residue) and calcium. So, the sulfates concentration exceeds admissible concentration limit by about 9–10 times, salinity - by 1.5–1.6 times, and calcium – by almost 2 times. There is also a several-fold excess in suspended solids, in petroleum products, iron, copper and magnesium, and other ingredients. However, the main pollution of mine wastewater needs to be cleaned is sulfates, the total salinity and calcium concentration will accordingly decrease after the water treatment process. Sulphates are the most difficult to remove pollution, because they are in dissolved form and have a high concentration. Therefore, the proposed research work is devoted to the development of effective methods for treating mine water in a given mine from sulfates in the first place.

1. Introduction

Significant environmental damage to water bodies is caused by insufficiently treated wastewater from mining enterprises. Therefore, the development of effective and economical wastewater treatment methods for mines is an important and urgent task. The difficulty in solving this problem lies in large volumes of wastewater data and their composition.

So, for example, the water discharge of the Limestone mine (Norilsk) is about 540 m³ / h or about 13000 m³ / day, and the Sibaysky mine (Bashkir copper and sulfur plant) [1] is 19200 m³ / day. Wastewater from mining enterprises is polluted in mainly suspended substances, various salts, heavy metals, have high salinity, etc. If the removal of suspended solids does not have any difficulties, then the deep wastewater treatment from heavy metal ions and sulfates is a rather difficult task. Table 1 shows the chemical analysis data for the wastewater of these mines.

Sulfates concentration at Limestone mine exceeds the maximum allowable discharge of substance into water body for their release into fishery pond by almost 9–10 times, dry residue is 1.43–1.63 times, the concentration of Ca²⁺ is 1.72–1.96 times, there are excess concentrations of some metals in individual samples (for copper, iron, lead, as well as polyphosphates) can be seen from table 1. Maximum allowable discharge of substance into water body excess in the wastewater of the Sibay mine in all these indicators and in others is many times greater.
It was found that it is most difficult to effectively clean mine wastewater from heavy metal ions and sulfates. However, it should be noted that a new highly efficient and economical technology was developed for the deep purification of wastewater from heavy metal ions by single-stage filtration at NSUACE (Sibstrin) [2], which novelty is confirmed by 3 patents for inventions. The essence of the developed technology is heavy metal ions conversion into their sulfide form, followed by retention on filters with a granular charge. The type of granular loading is not significant. Due to the fact that solubility of heavy metal sulfides formed is trapped in upper layers of granular charge, and dissolved sulfides react with flakes of iron hydroxide. Moreover, these flakes fill lower layers of the granular charge along with the wash water at the end of filter wash before it ends. Moreover, residual concentration of heavy metal ions in the treated wastewater after the filter does not exceed maximum allowable discharge of substance into water body for its release into water bodies even for fishery purposes. So, for example, residual concentration of iron in purified water is 0.072 mg / L (with maximum allowable discharge of substance into water body = 0.1 mg / L), zinc – 0.003 mg / L instead of 0.01 mg / L (see table 1), copper 0.001 mg / L, which corresponds to a maximum concentration limit of 0.001 mg / L, etc. [2].

Therefore, sulfates are the main pollution that is difficult to remove from mine wastewater. The article is devoted to the study of an effective method development for treating wastewater from sulfates. It should be noted that during mine water purification from sulphates to maximum allowable discharge of substance into water body = 100 mg / L, residual salt content of water will accordingly
decrease to a concentration of less than 1000 mg / L, i.e. below maximum allowable discharge of substance into water body for fishery reservoirs, i.e. at the same time, a decrease in admissible concentration limit is achieved by two indicators at once.

There are many different methods for treating wastewater from sulfates, which are reviewed in numerous publications (reagent, electrochemical, galvanic coagulation, ion exchange, membrane, etc. [3–11], each of which has a number of advantages and disadvantages. However, one of the simplest to implement and hardware design is the reagent method. We will study the effectiveness one in this article.

The most widely used reagents for the deposition of sulfates, along with lime and aluminum oxychloride or aluminum oxosulfate are barium compounds: BaCO₃, BaS, Ba(OH)₂ or BaCl₂ [8, 11–13]. So, a method for purifying wastewater from phosphates and sulfates is proposed in NSUACE (Sibstrin), which consists in acidifying wastewater with hydrochloric acid to pH = 4, subsequent introduction of barium chloride in amount of 130–640 mg / L and activated sludge in amount of 100–300 mg / L at a sulfate concentration of 150–350 mg / L [14]. In this case, residual concentration of sulfates is 100 mg / L. However, concentration of sulfates in the mine water of Limestone mine is on average about 900–1000 mg / L, and that of the Sibaysky mine is 1200–10000 mg / L. Therefore, it was necessary to check the effectiveness of sulfates removal by barium salts at their higher concentrations, and also to establish the dependence of their residual concentrations on the dose of barium salts.

2. Materials and Methods
The experiments were carried out in the laboratory of the Water supply and Water Treatment Department of NSUACE (Sibstrin) on real mine water delivered from Limestone mine (Norilsk).

Sulfates concentration in the source and treated wastewater was determined using a NASGE DR 3900 spectrophotometer according to a standard method using a set of reagents for determining sulfates LCK 153, operating in the concentration range 40–150 mg / L. Wastewater sample was diluted with distilled water the required number of times. As a sulfate precipitating reagent, barium chloride was used with more than 150 mg / L in a sulfate concentration.

Required dose of barium chloride (in the form of BaCl₂·2H₂O) was introduced into the treated wastewater acidified with 3.5% hydrochloric acid to pH = 4.0 or pH = 5.0. pH value of the treated wastewater was monitored using NITRON pH meter. A portion of barium chloride was weighed on an analytical balance with an accuracy of 0.001 g. After that, the mixture was stirred for 20 min to dissolve the barium chloride and form insoluble barium sulfate on “ECROS 6500” mixing device.

Then, the treated wastewater with a suspension of barium sulfate was settled in a glass cylinder for at least 1.5–2 hours, from its top a clarified water sample was taken, and then filtered through a paper filter (blue ribbon). After that, the concentration of sulfates was determined in this filtered sample.

Sulfates concentration was determined on a spectrophotometer after LCR 153 set of reagent introduction into wastewater, mixing them and holding the tube for 2 minutes. Doses of barium chloride ranged from 330 to 3000 mg / L. Previously, sulfates concentration in the source mine water was found, which was 1050 mg / L.

3. Results
The results of experiments on finding the dependence of sulfates residual concentration in purified mine water on the dose of barium sulfate (at pH = 4) are presented in table 2.

Residual sulfate concentration is 53.4 mg / L at a dose of barite of 3000 mg / L, which is significantly less than the required 100 mg / L, as can be seen from the table 2. Thus, it is possible to reduce the required dose of barium chloride to approximately 2600–2650 mg / L.

Additionally, experiments were carried out on cleaning mine water from sulfates at higher pH values (pH = 5.5). Also, the process of purification from sulfates continues, but the dose of barium chloride increases slightly.
Table 2. Experiments results of the barium chloride dose dependence on the sulfates residual concentration.

| Dose of barium chloride, mg / L | 0   | 330 | 900 | 2000 | 3000 |
|---------------------------------|-----|-----|-----|------|------|
| Sulfates concentration in purified mine water, mg / L | 1050 | 800 | 540 | 185  | 53.4 |
| Purification effect, %         | 0   | 23.81 | 48.57 | 82.38 | 94.91 |

For clarity, the results of these experiments are graphically presented in Figure 1 and Figure 2.

It should be noted that a suspension of barium sulfate suspension very slowly and poorly despite the high effect of purification from sulfates. It takes almost a day to completely precipitate this suspension. Therefore, to intensify its deposition, a coagulant aluminum oxychloride with a dose of 30 mg / L and powdered activated carbon were used. However, a significant improvement in the deposition process and an increase in the effect of purification from sulfates were not observed. In addition, a suspension of barium sulfate is so finely dispersed that it passes even through dense paper filters along with the filtrate.

![Figure 1. Dependence of sulfates residual concentration in the treated mine water on the dose of barium chloride.](image)

Experiments to select the brand and dose of flocculant were conducted to intensify the deposition of barium sulfate. Good results were obtained using the anionic flocculant Magnoflock 52–57 at a dose of about 6 g / m³. Moreover, the flocculation effect was higher with fractional dosing (4 g / m³ and 2 g / m³). The deposition process almost ended in 20–30 minutes. The volume of sediment after 1 hour of sedimentation was about 2%.

After such treatment, the treated wastewater met maximum allowable discharge of substance into water body requirements for fishery reservoirs in all respects except chlorides. Chloride concentration in the treated water was significantly higher than the permissible value due to the high doses of barium chloride.

Therefore, it is proposed to use its hydroxide instead of barium chloride to eliminate this drawback. Its use is also quite effective, but does not increase the concentration of chlorides in purified water [15]. We should also note, it should be noted the high cost of barium salts, which creates certain obstacles to their use at high mine wastewater costs. Therefore, additional research is required to find effective, but cheaper reagents.
4. Conclusion
1. The studies of real water from Limestone mine confirmed the effectiveness of barium-containing reagents (barium chloride) even with a high sulfate content in original mine water. Moreover, these reagents can reduce the concentration of sulfates to admissible concentration limit for release into the fishery reservoir, i.e. reduce the concentration of sulfates by more than 10 times.

2. The dependence of barium chloride doses on sulfates residual concentrations in purified mine water has been experimentally established.

3. A flocculant was found that accelerates the flocculation and sedimentation process of the fine-dispersed suspension of barium sulfate formed as much as possible, which reduced the settling time to 20–30 minutes and allowed reducing volume of settling structures many times.

4. It is proposed to use barium hydroxide instead of its chloride to remove sulfates in order to exclude the excess of chloride concentration in treated mine water above admissible concentration limit.

5. Therefore, it is necessary to continue research on the selection of a sufficiently effective, but cheaper reagent for cleaning mine water from sulfates, because barium salts have a high cost.

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