



Barium Use for Sulphates Removal at Various pH Values

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Abstract

Sulphates occur in waters mainly as a simple anion $(SO)_4^{2-}$. In waters with high sulphate concentration also ion associate anions with some cation occurrence is possible. Together with bicarbonates and chlorides they form a major part of anions in natural waters. In common groundwaters and surface waters sulphate content ranges in tens to hundreds of milligrams/liter. Particularly rich in sulphates are some mineral waters.

The article describes options of desulphurisation of real mine water. After the stage of aluminium compound using in previous research we examined using of barium compounds, namely $BaCO_3$ and $Ba(OH)_2$. After application of these compounds on an artificial model solution we focused on the real mine water from a flooded mine Smolník. The tests were conducted at various values pH, at 12, 8, 4.5 with pre-treated real water and at pH 3.9 with untreated real water. From the results it can be concluded that there was high efficiency of desulphurisation at all levels of pH. In terms of the selection of a particular compound barium hydroxide $Ba(OH)_2$ was confirmed as the best.

Keywords: mine water, precipitation, sulphate removal, barium compounds

Introduction

Sulphate is a common constituent of many natural waters and wastewaters, which is present as a dissolved compound in seas and oceans or as insoluble salt (e.g., gypsum-layers). Industrial wastewaters are responsible for most anthropogenic emissions of sulphate into the environment. Domestic sewage typically contains between 20 and 500 mg.l⁻¹ sulphate while certain industrial effluents may contain several thousands of milligrams per liter [1]. According to Slovak legislation – Government Regulation No. 269/2010, the limit concentration of sulphates in surface and drinking water is 250 mg.l⁻¹.

The main source of sulphate in the laboratory wastewaters is the use of sulphuric acid in many routine chemical analyses. Sulphur compounds are also present in wastewaters used in the research activities, such as those from the pulp and paper industry, the food processing industry and the photographic sector, among others. The damage caused by sulphate emissions is not direct, since sulphate is a chemically inert, non-volatile, and non-toxic compound. However, high sulphate concentrations can unbalance the natural sulphur cycle. The accumulation of sulphate-rich sediments in lakes, rivers and sea may cause the release of toxic sulphides that can provoke damages to the environment [2].

A number of methods are currently used to promote the removal of dissolved sulphate. They include reversed osmosis, electro dialysis, or nanofiltration, which are expensive, can be poisoned by impurities, and require a post-treatment of the brine. Ion exchange,

biological treatment – by sulphate-reducing bacteria capable of reducing sulphates to sulphides by dissimilatory bioenergetic metabolism [3] and chemical precipitation are also systems used for sulphate-rich effluents treatment. Chemical precipitation is a widely used, proven technology for the removal of metals and other inorganic compounds, suspended solids, fats, oils, greases, and some other organic substances (including organophosphates) from wastewater. Previous investigators have reported successful reduction of soluble sulphate from water by formation of calcium aluminate and sulphotoaluminates, and from pure and waste sulphuric acid/lime suspension by formation of calcium sulphate. Chemical precipitation through the addition of barium or calcium salts is an alternative, mainly if applied to the treatment of wastewaters that contain high sulphate concentrations [2].

Treatment by barium salts

Chemical treatment of mine water using lime or limestone will remove sulphates from 1500 to 2000 mg.l⁻¹ depending on the solubility of gypsum. Gypsum solubility depends on the composition and ionic strength of the solution. Baryte ($BaSO_4$) is a highly water insoluble salt, this makes it a suitable phase to remove SO_4^{2-} from mine water. Chemical treatment of mine water using Ba salts has proved to be capable of removing sulphates to less than 250 mg.l⁻¹ [4].

The barium salts commonly used for sulphate removal by precipitation include $Ba(OH)_2$ and $BaCO_3$, after the following reactions:

Tab. 1 Decreasing of selected metals after pH increasing and post filtration

Tab. 1 Zmniejszenie zawartości metali po zwiększeniu pH i po filtracji

Water Smolnik	Fe	Cu	Mn	Zn	Al	As
	mg.l ⁻¹	mg.l ⁻¹	mg.l ⁻¹	mg.l ⁻¹	mg.l ⁻¹	µg.l ⁻¹
untreated	302.0	1.7	22.8	8.5	56.4	7.8
after filtration	0.06	0.04	0.20	<0.02	<0.04	<5

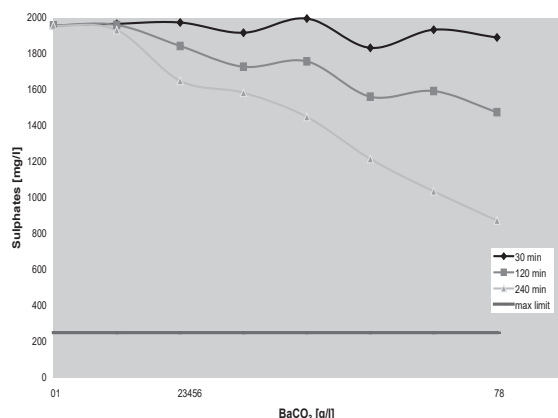
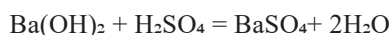
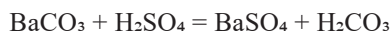


Fig. 1 Sulphates reducing by BaCO₃ (pH=11.7)

Rys. 1 Redukcja siarczanów za pomocą BaCO₃ (pH=11.7)



Barium hydroxide is highly effective in removing dissolved sulphate over the entire pH range. Barium carbonate is less effective under neutral to strongly alkaline conditions and under very acidic conditions; sulphate removal by barium carbonate is strongly reduced. This sulphate treatment process can also be modified to include the removal of dissolved metals from acid mine drainage (AMD) [5].

All processes can remove sulphate from solution from very high levels to within regulatory standards. In the case of Ba(OH)₂ acidic solutions can be treated directly, although in practice some lime treatment is required for very acidic solutions to prevent metal hydroxide precipitation on the surface of the barium salt. The process additionally removes transition metals, Mg, NH₃ and, to a limited extent, Na. Thus the overall TDS (total dissolved solids) is lowered as well as the concentration of deleterious elements. The Ba(OH)₂ causes significant CaSO₄ precipitation improving sulphate removal by up to 30%, but increasing the volume of sludge requiring disposal [6].

Material and methods

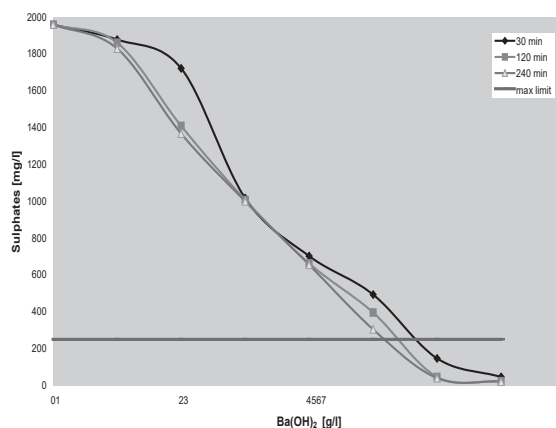


Fig. 2 Sulphates reducing by Ba(OH)₂ (pH=11.7)

Rys. 2 Redukcja siarczanów za pomocą Ba(OH)₂ (pH=11.7)

In this experiments we focussed on real mine water obtained from Pech shaft in Smolnik. BaCO₃ and Ba(OH)₂ were used as precipitants and Ca(OH)₂ was used for pre-treatment of mine water in the first step of experiments. The input values of mine water were: pH = 3.7 and SO₄²⁻ = 2391 mg.l⁻¹.

In the second step only Ba(OH)₂ and real mine water were used. The input values of mine water were: pH = 3.9 and SO₄²⁻ = 2305 mg.l⁻¹.

Sulphate analysis was performed on Ion Chromatograph DIONEX 5000, pH was measured by pH meter MeterLab PHM 210 and solutions were stirred by magnetic heating stirrer Heidolph MR-hei standard. The concentration of metals in water was measured by AAS.

Experimental

Tests of sulphate content reduction with real mine drainage Smolnik-Pech (pre-treated)

After series of desulphurisation tests with model solutions in year 2014, we started laboratory tests using the real mine drainage from the abandoned mine Smolnik, from the Pech shaft. Only two precipitating agents, i.e. BaCO₃ and Ba(OH)₂, were used for these tests. It was established in the previous experiments that significantly stronger effect is achieved

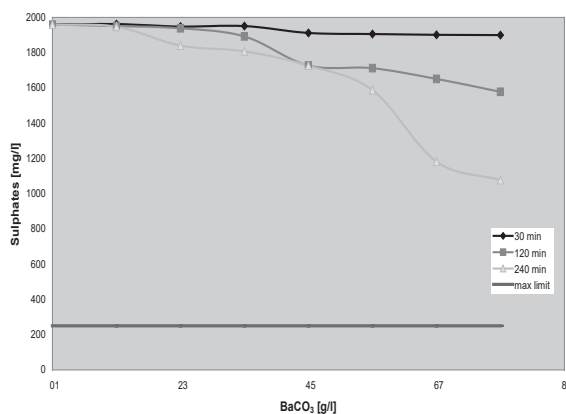


Fig. 3 Sulphates reducing by BaCO_3 (pH=8.0)

Rys. 3 Redukcja siarczanów za pomocą BaCO_3 (pH=8.0)

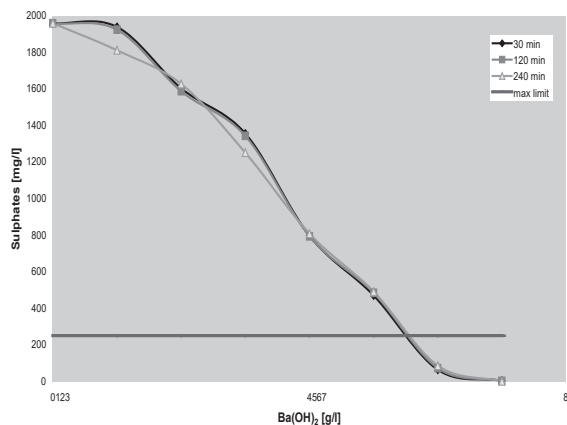


Fig. 4 Sulphates reducing by Ba(OH)_2 (pH=8.0)

Rys. 4 Redukcja siarczanów za pomocą Ba(OH)_2 (pH=8.0)

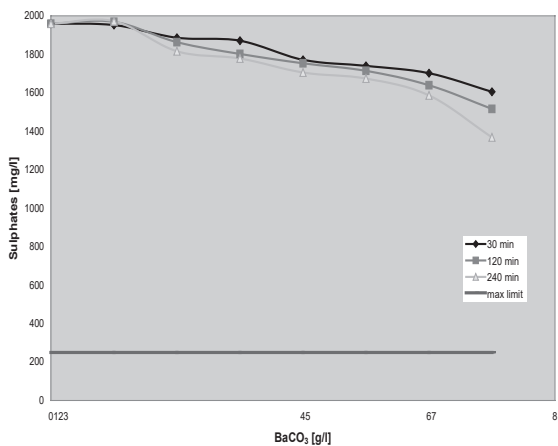


Fig. 5 Sulphates reducing by BaCO_3 (pH=4.5)

Rys. 5 Redukcja siarczanów za pomocą BaCO_3 (pH=4.5)

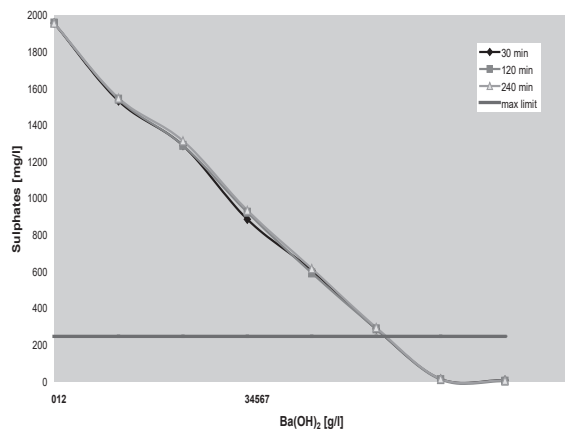


Fig. 6 Sulphates reducing by Ba(OH)_2 (pH=4.5)

Rys. 6 Redukcja siarczanów za pomocą Ba(OH)_2 (pH=4.5)

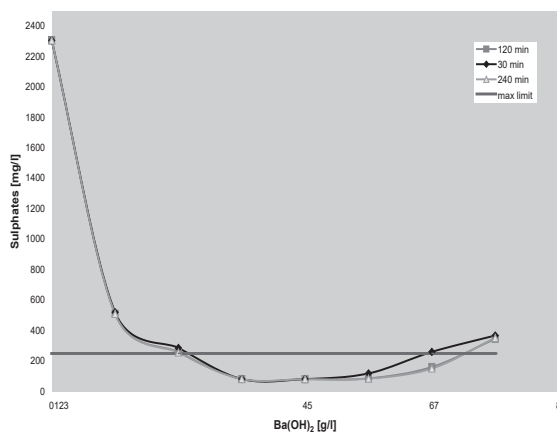


Fig. 7 Sulphates reducing by Ba(OH)_2 (pH=3.9 untreated water)

Rys. 7 Redukcja siarczanów za pomocą Ba(OH)_2 (pH=3.9 woda bez dodatków)

when barium hydroxide is used comparing to barium carbonate [7].

The first phase was focused on adjustment of pH value from the original value 3.7 to 12 in order to get better precipitation of metals in drainage. The value of sulphates was 2391 mg.l⁻¹. After reaching the planned pH value the sample was filtered, and the trapped sludge contained a majority of precipitated metals and a part of sulphates was also removed [8]. Reduction of selected metals is given in Table 1. Sulphates dropped from 2391 mg.l⁻¹ to 1959.5 mg.l⁻¹ and pH value stabilized at 11.7.

Tests of sulphate content reduction with real mine drainage Smolník-Pech (untreated)

Tests at pH= 3.9

The last step of these experiments was desulphurisation of untreated water from old mine Smolník. Experiments were carried out without Ca(OH)₂ using. We have worked with raw water, pH was 3.9 and initial SO₄²⁻ concentration 2305 mg.l⁻¹. On the basis of the previous experiments results with pre-treated water, we tested only Ba(OH)₂. The conditions were same as in previous tests, stirring time, sampling after 30, 120 and 240 minutes, Ba(OH)₂ dosing from 1 up to 7 g per litre. Values of sulphates are shown in Figure 7.

Discussion

The first part deals with the experiments with the mine water, pre-treated by Ca(OH)₂ to pH levels 4.5, 8 and 11.7. Figures 1, 3 and 5 show effects of BaCO₃ on sulphates decrease. It is evident on first view that maximum permissible concentration – 250 mg SO₄²⁻ per liter have not been achieved after chemical precipitation, not even with maximum dose (7 g per liter). Sulphates concentration from the original value 2390 mg.l⁻¹ dropped only to 800 mg.l⁻¹. The pH values ranged between 5.5–8.9. We can also observe considerable differences with the change of stirring time. A different situation occurs by using of Ba(OH)₂. Figures 2, 4 and

6 show that concentration of sulphates at all pH values got under maximum limit, they were below 10 mg.l⁻¹. The pH values ranged from 11 to 12, because Ba(OH)₂ increases pH value much more than BaCO₃. Stirring time in this case was less significant, only small differences between 30 and 240 minutes were showed. Dosing 6 g of Ba(OH)₂ and stirring time 30 minutes have been proven as optimal.

The second part of the experiments was without Ca(OH)₂ using. We have been working with untreated - raw water. The conditions were the same as in previous tests, both the precipitant concentration and the stirring time. Figure 7 shows an excellent effect of Ba(OH)₂ on sulphates elimination. Although sulphates did not drop below 10 mg.l⁻¹, as in the first part of experiments, they were low enough, under the permitted concentration. The values ranged around 80 mg.l⁻¹. The best results have been achieved at pH values 11.5–12 and Ba(OH)₂ dosing 3–5 g.l⁻¹. With increasing of precipitant dose the pH value decreased, the effect of desulphurisation either.

Conclusions

Seeing that Ba(OH)₂ significantly increases the pH value and causes precipitation of metals similar to Ca(OH)₂, the Ca(OH)₂ use for pre-treatment is not necessary. From our results (Figure 7) are also evident following facts: stirring time 30 minutes is sufficient and optimal precipitant dose (Ba(OH)₂) is 3–5 g.l⁻¹. This could be reasoned by the fact that in this dose range are the highest pH values, from 9.5 to 11.9. By adding of higher doses of precipitant the pH value decreases and desulphurisation effect too. Finally, an important fact that the use of lime pre-treatment is not necessary causes a significant reduction in the cost of sulphates removal.

Acknowledgement

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Wykorzystanie baru do usuwania siarczanów przy różnym pH

Siarczany występują w wodach głównie jako anion $(SO_4)^{2-}$. W wodach o wysokim stężeniu siarczanów możliwe jest również występowanie anionowych wiązań jonowych z pewną liczbą kationów. Wraz z wodorowęglanami i chlorkami stanowią one znaczną część anionów w wodach. W wodach gruntowych i wodach powierzchniowych zawartość siarczanów wynosi od dziesiątek do setek miligramów na litr. Szczególnie bogate w siarczany są niektóre wody mineralne.

W artykule przedstawiono opcje odsiarczania wody kopalnianej. Zbadano możliwości wykorzystania związków baru, mianowicie $BaCO_3$ i $Ba(OH)_2$. Przeprowadzono badania na próbkach wzorcowych i próbkach rzeczywistych - wodzie kopalnianej z zatopionej kopalni Smolnik. Testy prowadzono przy różnych wartościach pH = 12; 8; 4,5 za pomocą wody o pH naturalnym i przy pH 3,9. Na podstawie wyników można stwierdzić, że na wszystkich poziomach pH uzyskano wysoką skuteczność odsiarczania. Najlepsze wyniki uzyskano dla wodorotlenek baru $Ba(OH)_2$.

Słowa kluczowe: woda kopalniana, osad, usuwanie siarczanów, związki baru