

# Effective Ways of Desulphurization of Acid Mine Drainage

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## Abstract

The article describes other options of desulphurisation of real mine water. After the stage using of aluminium compounds we examined using of barium compounds, namely  $\text{BaCO}_3$  and  $\text{Ba(OH)}_2$ . 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, 7.5 and 4.5. From the results it can be concluded that there was high efficiency of desulphurization at all levels of pH. In terms of the selection of a particular compound was confirmed as the best that has been applied barium hydroxide –  $\text{Ba(OH)}_2$ .

Keywords: AMD, desulphurisation, precipitation, barium, neutralisation

## 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  $\text{mg.l}^{-1}$  sulphate while certain industrial effluents may contain several thousands of milligrams per liter. 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 [1].

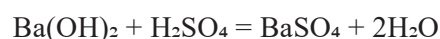
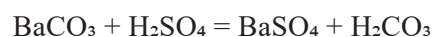
A number of methods are currently used to promote the removal of dissolved sulphate. They include reversed osmosis, electro dialysis, or nanofiltration, which are expensive, can be poisoned by impurities, and require a post-treatment of the brine. Ion exchange, biological treatment – by sulphate-reducing bacteria capable of reducing sulphates to sulphides by dissimilatory bioenergetic metabolism [2] 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 sulphoaluminates, 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 [1].

## Barium salts treatment

Chemical treatment of mine water using lime or limestone will remove sulphates from 1500 to 2000 ppm depending on the solubility of gypsum. Gypsum solubility depends on the composition and ionic strength of the solution. Baryte ( $\text{BaSO}_4$ ) is a highly water insoluble salt, this makes it a suitable phase to remove  $\text{SO}_4^{2-}$  from mine water. The Ba salts commonly used for sulphates removal are  $\text{BaCO}_3$ ,  $\text{Ba(OH)}_2$  and  $\text{BaS}$ . Chemical treatment of mine water using Ba salts has proved to be capable of removing sulphates to less than 250 ppm [3].

Baryte ( $\text{BaSO}_4$ ) is highly insoluble making it an excellent candidate as removal phase for sulphate treatment. The Barium salts commonly used for sulphate removal by precipitation include  $\text{Ba(OH)}_2$ ,  $\text{BaCO}_3$  and  $\text{BaS}$  after following reactions:



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

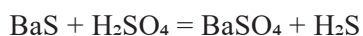
Tab. 1. Zmniejszenie ilości wybranych metali po wzroście pH po filtracji

Water Smolník	Fe	Cu	Mn	Zn	Al	As
	mg.l <sup>-1</sup>	mg.l <sup>-1</sup>	mg.l <sup>-1</sup>	mg.l <sup>-1</sup>	mg.l <sup>-1</sup>	µg.l <sup>-1</sup>
untreated	302	1.66	22.8	8.5	56.4	7.8
after filtration	0.06	0.04	0.2	<0.02	<0.04	<5



Fig. 1a, 1b, 1c. pH adjustment of mine water

Rys. 1a, 1b, 1c Poprawa pH wody kopalnianej



Both barium hydroxide and barium sulphide are 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 AMD water [4].

All three processes can remove sulphate from solution from very high levels to within regulatory standards. In the case of BaS and Ba(OH)<sub>2</sub> 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, NH<sub>3</sub> 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)<sub>2</sub> causes significant CaSO<sub>4</sub> precipitation improving sulphate removal by up to 30%, but increasing the volume of sludge requiring disposal. A major benefit of the process is that valuable by-products are created, the sale of which can

be used to offset treatment costs. In the BaCO<sub>3</sub> and BaS processes sulphur, metals and Ba-salts can be commercially produced while NaHS is produced in the Ba(OH)<sub>2</sub> process [5].

#### Material and methods

A synthetic solution, similar to AMD from shaft Pech from beginning of 20th century, when sulphate values were in range 4000–5000 mg.l<sup>-1</sup> (old mine Smolník in Slovakia) was used as feed water. Solution was prepared with distilled water, FeSO<sub>4</sub>, CuSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. Solution contained cca 4200 mg SO<sub>4</sub><sup>2-</sup>.l<sup>-1</sup>, (real value in the year 2009 was only 2320 mg SO<sub>4</sub><sup>2-</sup>.l<sup>-1</sup>) [6], 450 mg Fe.l<sup>-1</sup>, 1.56 mg Cu.l<sup>-1</sup> and pH was 3.91. Lime was used for pH changing, to value 11.7 for better precipitation metals from solution. Pre-treated solution containing about 2400 mg SO<sub>4</sub><sup>2-</sup>.l<sup>-1</sup> after “lime treatment” was used in this study. Cu values decreased from 132 mg.l<sup>-1</sup> to 0.07 mg.l<sup>-1</sup> and Fe from 450 mg.l<sup>-1</sup> to 0.05 mg.l<sup>-1</sup> [7] (measured by method AAS – Varian). For this experiment distilled water, Ca(OH)<sub>2</sub>, BaCO<sub>3</sub>, Ba(OH)<sub>2</sub> and BaCl were used. 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. It was first step of experiments.

Tab. 2. Desulphurisation by BaCO<sub>3</sub> pH= 11.71 (Sulphates [mg.l<sup>-1</sup>] A – pretreatment by Ca(OH)<sub>2</sub>)Tab. 2. Odsiarczanie za pomocą BaCO<sub>3</sub> pH= 11.71

BaCO <sub>3</sub>	0 [g.l <sup>-1</sup> ]	A	1 [g.l <sup>-1</sup> ]	2 [g.l <sup>-1</sup> ]	3 [g.l <sup>-1</sup> ]	4 [g.l <sup>-1</sup> ]	5 [g.l <sup>-1</sup> ]	6 [g.l <sup>-1</sup> ]	7 [g.l <sup>-1</sup> ]
30 min	2391	1959	1968	1975	1918	1997	1834	1935	1892
2 hours	2391	1959	1961	1844	1729	1759	1562	1594	1476
4 hours	2391	1959	1933	1651	1584	1450	1216	1036	873

Tab. 3. Desulphurisation by Ba(OH)<sub>2</sub> pH= 11.71 (Sulphates [mg.l<sup>-1</sup>] A – pretreatment by Ca(OH)<sub>2</sub>)Tab. 3. Odsiarczanie za pomocą Ba(OH)<sub>2</sub> pH= 11.71

Ba(OH) <sub>2</sub>	0 [g.l <sup>-1</sup> ]	A	1 [g.l <sup>-1</sup> ]	2 [g.l <sup>-1</sup> ]	3 [g.l <sup>-1</sup> ]	4 [g.l <sup>-1</sup> ]	5 [g.l <sup>-1</sup> ]	6 [g.l <sup>-1</sup> ]	7 [g.l <sup>-1</sup> ]
30 min	2391	1959	1878	1722	1017	702	493	<b>146</b>	<b>46</b>
2 hours	2391	1959	1861	1409	1007	662	395	<b>46</b>	<b>22</b>
4 hours	2391	1959	1829	1367	1000	655	304	<b>39</b>	<b>20</b>

Tab. 4. Desulphurisation by BaCO<sub>3</sub> pH= 8.01 (Sulphates [mg.l<sup>-1</sup>] A – pretreatment by Ca(OH)<sub>2</sub>)Tab. 4. Odsiarczanie za pomocą BaCO<sub>3</sub> pH= 8.01

BaCO <sub>3</sub>	0 [g.l <sup>-1</sup> ]	A	1 [g.l <sup>-1</sup> ]	2 [g.l <sup>-1</sup> ]	3 [g.l <sup>-1</sup> ]	4 [g.l <sup>-1</sup> ]	5 [g.l <sup>-1</sup> ]	6 [g.l <sup>-1</sup> ]	7 [g.l <sup>-1</sup> ]
30 min	2391	1959	1962	1948	1951	1912	1906	1901	1900
2 hours	2391	1959	1951	1938	1892	1727	1712	1651	1578
4 hours	2391	1959	1947	1840	1808	1726	1588	1182	1077

The second and finally step was experiments with real mine water from Smolník shaft.

### Tests of reduction of sulphate content with real mine drainage Smolník-Pech

After series of desulphurisation tests with the model solution, we started laboratory tests, using the real mine drainage from the abandoned mine Smolník, from the Pech shaft. Only two precipitating agents, i.e. BaCO<sub>3</sub> and Ba(OH)<sub>2</sub>, were used for these tests [8]. It was established in the previous tests that significantly stronger effect is achieved when barium hydroxide is used comparing to barium carbonate. The first phase was focused on adjustment of pH value from the original value of 3.72 to 11.9 in order to get better precipitation of metals in drainage. The value of sulphates was 2391 mg.l<sup>-1</sup>. After reaching the planned value the sample was filtered, and the trapped sludge contained a majority of precipitated metals and a part of sulphates. Reduction of selected metals is given in Table 1. Sulphates dropped from 2391.3 mg.l<sup>-1</sup> to 1959.5 mg.l<sup>-1</sup> and pH value stabilised at 11.71. Figure 1 (a, b, c) shows colour changing during pH adjustment of samples.

## Results and discussion

### Tests at pH = 11.71

In the first series BaCO<sub>3</sub> was used, and on the basis of knowledge obtained from testing with the model water the mutual interaction periods, i.e. mixing periods, were prolonged and the samples were taken after 30, 120, and 240 minutes. Dosage of precipitating agent was the same, i.e. 0,1,2,3.....7 g.l<sup>-1</sup>. Values of sulphates are shown in Table 2.

Tests with Ba(OH)<sub>2</sub> at the same conditions, values of sulphates are shown in Table 3.

### Tests at pH = 8.01

In the second phase was pH value adjusted and stabilised at 8.01 by adding about 0.8 g Ca(OH)<sub>2</sub> per liter of mine water. BaCO<sub>3</sub> was used and mixing periods were prolonged and the samples were taken after 30, 120, and 240 minutes. Dosage of precipitating agent was the same, i.e. 0,1,2,3.....7 g.l<sup>-1</sup>. Values of sulphates are shown in Tab. 4 and Tab. 5. The conditions were same as in the first tests at pH = 11.71.

### Tests at pH = 4.5

In the third phase was pH value adjusted and stabilised at 4.5 by adding 0.1g Ca(OH)<sub>2</sub> per liter

Tab. 5. Desulphurisation by Ba(OH)<sub>2</sub> pH= 8.01 (Sulphates [mg.l<sup>-1</sup>] A – pretreatment by Ca(OH)<sub>2</sub>)Tab. 5. Odsiarczanie za pomocą Ba(OH)<sub>2</sub> pH= 8.01

Ba(OH) <sub>2</sub>	0 [g.l <sup>-1</sup> ]	A	1 [g.l <sup>-1</sup> ]	2 [g.l <sup>-1</sup> ]	3 [g.l <sup>-1</sup> ]	4 [g.l <sup>-1</sup> ]	5 [g.l <sup>-1</sup> ]	6[g.l <sup>-1</sup> ]	7 [g.l <sup>-1</sup> ]
30 min	2391	1959	1939	1603	1356	796	470	<b>63</b>	<b>3.8</b>
2 hours	2391	1959	1924	1587	1343	793	484	<b>72</b>	<b>2.2</b>
4 hours	2391	1959	1811	1627	1251	808	491	<b>86</b>	<b>0.09</b>

Tab. 6. Desulphurisation by BaCO<sub>3</sub> pH= 4.5 (Sulphates [mg.l<sup>-1</sup>] A – pretreatment by Ca(OH)<sub>2</sub>)Tab. 6. Odsiarczanie za pomocą BaCO<sub>3</sub> pH= 4.5

BaCO <sub>3</sub>	0 [g.l <sup>-1</sup> ]	A	1 [g.l <sup>-1</sup> ]	2 [g.l <sup>-1</sup> ]	3 [g.l <sup>-1</sup> ]	4 [g.l <sup>-1</sup> ]	5 [g.l <sup>-1</sup> ]	6[g.l <sup>-1</sup> ]	7 [g.l <sup>-1</sup> ]
30 min	2391	1959	1952	1886	1871	1771	1740	1702	1605
2 hours	2391	1959	1969	1863	1802	1753	1714	1639	1516
4 hours	2391	1959	1972	1816	1778	1705	1674	1586	1368

Tab. 7. Desulphurisation by Ba(OH)<sub>2</sub> pH= 4.5 (Sulphates [mg.l<sup>-1</sup>] A – pretreatment by Ca(OH)<sub>2</sub>)Tab. 7. Odsiarczanie za pomocą Ba(OH)<sub>2</sub> pH= 4.5

Ba(OH) <sub>2</sub>	0 [g.l <sup>-1</sup> ]	A	1 [g.l <sup>-1</sup> ]	2 [g.l <sup>-1</sup> ]	3 [g.l <sup>-1</sup> ]	4 [g.l <sup>-1</sup> ]	5 [g.l <sup>-1</sup> ]	6[g.l <sup>-1</sup> ]	7 [g.l <sup>-1</sup> ]
30 min	2391	1959	1534	1291	889	610	291	<b>17.5</b>	<b>11.3</b>
2 hours	2391	1959	1544	1292	927	596	291	<b>13.3</b>	<b>5.4</b>
4 hours	2391	1959	1550	1317	938	620	298	<b>17.9</b>	<b>9.9</b>

of mine water. BaCO<sub>3</sub> was used and mixing periods were prolonged and the samples were taken after 30, 120, and 240 minutes. Dosage of precipitating agent was the same, i.e. 0,1,2,3.....7 g.l<sup>-1</sup>. Values of sulphates are shown in Tab. 6 and Tab 7. The conditions were same as in the first tests at pH = 11.71.

### Conclusion

Looking at the all pH values, under which were experiments conducted, it can be stated as follows: In contrast to tests with synthetic solutions that were made before, fundamental difference is the absolute inappropriateness of BaCO<sub>3</sub> use, throughout the whole pH values extent, prolonged periods of stirring the sample, even when using higher doses of the agent. This is also evident from Tables 2, 4 and 6. The situation was quite different

by Ba(OH)<sub>2</sub> using. It can be used substantially in the whole range of pH values. Expected value 250 mg sulphates per liter was achieved in all 3 testing values of pH, and even at the shortest time of samples mixing at adding 6 or 7 grams of agent (Tables 3, 5 and 7). Economically, it is clear that the required levels of sulphates may be obtained using 6 g Ba(OH)<sub>2</sub> and 30 minutes of stirring time. Higher doses of the agent and lengthening of the mixing time are in fact unnecessary and uneconomic.

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### *Efektywne sposoby usuwania siarki podczas drenażu kwaśnych wód*

Artykuł opisuje inne opcje odsiarczania wody kopalnianej. Po etapie zastosowania związków glinu zbadano zastosowanie związków baru, konkretnie  $\text{BaCO}_3$  oraz  $\text{Ba(OH)}_2$ . Po zastosowaniu tych związków na sztucznym modelu roztworu skoncentrowano się na prawdziwej wodzie kopalnianej z zalanej kopalni Smolnik. Testy zostały przeprowadzone przy różnych wartościach pH, 12, 7.5 oraz 4.5. Na podstawie wyników można stwierdzić wysoką skuteczność odsiarczania na każdym poziomie pH. W kontekście wyboru konkretnego związku potwierdzono, że na najlepszym wyborem jest wodorotlenek baru  $\text{Ba(OH)}_2$ .

Słowa kluczowe: AMD, odsiarczanie, strącanie, bar, neutralizacja