



# Treatment of AMD from Old Smolník Mine by Aluminium and Barium Compounds

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## Abstract

The formation and treatment of acid mine drainage is the biggest environmental problem relating to mining and processing activities in the worldwide. Various methods are used for the sulphates and heavy metals removal from acid mine drainage, but any of them is universal. The main aim of the paper is the interpretation of chemical methods for the metals and sulphates removal from acid mine drainage sample. The chemical method is based on the sulphates precipitation by polyaluminium chloride and calcium hydrate and barium. In Slovakia, there are some localities with existing AMD generation conditions. The most critical values were observed in the abandoned deposit Smolník. [1] For this study acid mine drainage from the abandoned and flooded deposit of Smolník located in Slovak Republic was sampled.

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

## Introduction

Introduction The abandoned mining area Smolník in Slovakia belongs to the old environmental loads because of acid mine drainage (AMD) production.[2]The source of acid mine drainage (AMD) is the residues of mining activity (e.g. flooded adits and shafts, heaps and sludge lagoons) mainly after the mining of deposits with the content of sulphide minerals. AMD contains sulphate acid, metals in the soluble form and its pH can be very low [3]. In Slovak Republic there are some localities with existing AMD generation conditions. Deposits Smolník is the typical example. The stratiform deposit of Smolník belongs to the historical best-known and richest Cu-Fe ore deposits in Slovakia. In 1990 the mining activity at the locality was stopped. The mine was flooded till 1994. In 1994 the ecological collapse occurred, which caused the fish-kill and the global negative influence on the environment. The mine-system represents geochemical partly-opened system where rain and surface water drain into [4]. The continuance of AMD generation at the locality of Smolník is not possible to stop and there is no chance of situation self-improvement. It is necessary to respect this situation, monitor the quality of these waters and develop the methods of their treatment. Various methods are used for redevelopment of AMD in the world, but any of them is universal. Their application depends on geochemical, technical, natural, financial, and other factors. The traditional methods of AMD treatment represent the chemical methods, mainly the lime or limestone neutralization. The disadvantage of this method is the creation of great deal of non-utilizable sludge. For the AMD neutralization can used other chemical reagent such as sodium aluminate in combination with calcium hydrate [5].

## Mine water desulphatation by sodium aluminate (ALR-F) from locality Smolník

The first part of the experiments was focused on the treatment of AMD with sodium aluminate with the trade name ALR-F.

The concentration of sulphate ions in tested water, calculated as an average out of three measured values was 2984 mg/l and pH 3.34. The precipitation runs quantitatively at pH above 12.4. To achieve such a pH, it is necessary to add 5–5.6 g of Ca(OH)<sub>2</sub> to the litre of treated water.

To precipitate the ions of SO<sub>4</sub><sup>2-</sup>, a reagent ALR-F was used. It is concentrated solution of sodium aluminate, with 17 % active aluminium content.

Precipitation of SO<sub>4</sub><sup>2-</sup> ions in the presence of Ca(OH)<sub>2</sub> and ALR-F reagent

## Methodical process of precipitation:

1. Ca(OH)<sub>2</sub> - 15 minutes of mixing at 200 r.p.m.
2. ALR-F - 30 minutes of mixing at 200 r.p.m.
3. Filtration of suspension.
4. Determining of sulphate concentration and pH value.

## Material and methods

### Acid mine drainage

For this study acid mine drainage from the abandoned and flooded deposit of Smolník located in Slovak Republic from the shaft Pech was sampled. Water characterisation is reported in Table 1.

### Chemical reagent

Sodium aluminate (ALR-F) is product of firm Chemax from Žiar nad Hronom in Slovakia. 1 liter of solution ALR-F contains:

Tab. 1. Characterisation of the AMD sample from the shaft Pech (deposit of Smolník Slovakia)

Tab. 1. Charakterystyka próbek AMD z szybu Pech (złożę Smolník, Słowacja)

Indicator	pH	Eh	RL	SO <sub>4</sub> <sup>2-</sup>	Fe	Mn	Mg	Ca	Cu	Zn	Al	As
		mV					[mg/l]					
<b>Value</b>	3.7	499	4 184.0	2 937.8	306.7	25.9	299.8	119.0	5.3	9.3	76.7	0.021

Tab. 2. Elimination of SO<sub>4</sub><sup>2-</sup> by combination of calcium hydrate (ALR-F) with sodium aluminateTab. 2. Usuwanie SO<sub>4</sub><sup>2-</sup> wodorotlenkiem wapnia (ALR-F) z glinianem sodu

Ca(OH) <sub>2</sub> [g.l <sup>-1</sup> ]	ALR-F [ml.l <sup>-1</sup> ]	pH	SO <sub>4</sub> <sup>2-</sup> [mg.l <sup>-1</sup> ]	Effect desulph. [%]
5.2	3.2	12.56	118.28	96.03
5.2	3.4	12.56	199.6	93.31
5.2	3.6	12.56	49.92	98.32
5.2	3.8	12.56	45.28	98.48
5.4	3.2	12.56	64.4	97.84
5.4	3.4	12.56	123.28	95.87
5.4	3.6	12.55	65.0	97.82
5.4	3.8	12.55	49.64	98.33
5.6	3.2	12.58	114.4	96.17
5.6	3.4	12.58	42.96	98.56
5.6	3.6	12.58	0.48	99.98
5.6	3.8	12.58	0.97	99.97

Tab. 3. Decreasing of selected metals after increasing pH and post filtration

Tab. 3. Zmniejszenie zawartości wybranych metali po zwiększeniu pH i 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

Tab. 4. Desulphatation by Ba(OH)<sub>2</sub> pH= 11.71 [Sulphates (mg.l<sup>-1</sup>); A – pretreatment by Ca(OH)<sub>2</sub>]Tab. 4. Odsiarczanie za pomocą Ba(OH)<sub>2</sub>, pH = 11,71 [Siarczany (mg/l<sup>-1</sup>); A – wstępna obróbka za pomocą Ca(OH)<sub>2</sub>]

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. 5. Desulphatation 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 [siarczany (mg/l<sup>-1</sup>); A - wstępna obróbka za pomocą Ca(OH)<sub>2</sub>]

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. Desulphatation by Ba(OH)<sub>2</sub> pH= 4.5 [Sulphates (mg.l<sup>-1</sup>); A – pretreatment by Ca(OH)<sub>2</sub>]Tab. 6. Odsiarczanie za pomocą Ba(OH)<sub>2</sub>, pH = 4,5 [siarczany (mg/l<sup>-1</sup>); A - wstępna obróbka za pomocą Ca(OH)<sub>2</sub>]

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>



Fig. 1. pH adjustment

Rys. 1. Regulacja pH

$\text{Na}_2\text{O}_c$	g/l	302.2	20.57%
$\text{Na}_2\text{O}_k$	g/l	292.9	19.94%
$\text{Al}_2\text{O}_3$	g/l	279.0	18.99%

In ppm also amounts contains  $\text{Fe}_2\text{O}_3$ ,  $\text{SO}_4^{2-}$ , Cl-,  $\text{Cr}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ , As, Cd, Pb etc. Density is 1469 g/l.

### Results and discussion

The results of chemical neutralization by sodium aluminate in combination with calcium hydrate are demonstrated in Table 2. It shows that optimal amount of mentioned chemical reagent was 5.6 g/l  $\text{Ca}(\text{OH})_2$  and 3.6 ml/l ALR-F. Optimal pH value is 12.58.

### Tests of reduction of sulphate content with barium

After series of desulphurisation tests using sodium aluminate (ALR-F), we started laboratory tests, using barium. At the beginning of the barium compounds experiments we worked with three compounds:  $\text{Ba}(\text{CO}_3)_2$ ,  $\text{Ba}(\text{SO}_4)_2$  and  $\text{Ba}(\text{OH})_2$ , but on the basis of the first results we focused on the most efficient, for  $\text{Ba}(\text{OH})_2$ . 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 3. Sulphates dropped from 2391.32 mg.l<sup>-1</sup> to 1959.5 mg.l<sup>-1</sup> and pH value stabilised at 11.71. Figure 1 shows colour changing during pH adjustment of samples.

### Tests at pH = 11.71

In the first series  $\text{Ba}(\text{OH})_2$  was used and samples were taken after 30, 120, and 240 minutes. Dosage of precipitating agent was 0,1,2,3...7g.l<sup>-1</sup>. Values of sulphates are shown in Tab. 4.

### Tests at pH = 8.01

In the second phase was pH value adjusted and stabilised at 8.01 by adding 0.8 g  $\text{Ca}(\text{OH})_2$  per liter of mine water.  $\text{BaCO}_3$  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...7g.l<sup>-1</sup>. Values of sulphates are shown in Tab. 5. The conditions were same as in the first tests at pH = 11.71.

### Tests at pH = 4.5

In the third phase pH value was adjusted and stabilised at 4.5 by adding 0.1g  $\text{Ca}(\text{OH})_2$  per liter of mine water.  $\text{BaCO}_3$  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...7g.l<sup>-1</sup>. Values of sulphates are shown in Table 6. The conditions were same as in the first tests at pH = 11.71.

From results in Tables 4, 5 and 6 is clear that barium hydroxide is effective and the desulphurized water complies with the standards applicable to SR. This applies to all pH values, about 4–12. The optimal dose of reagent is 6–7 g/l. We have changed the time of interaction from 30 to 240 minutes, and the shortest time – 30 minutes is enough.

### Conclusions

Two chemical desulphurization methods have been verified in this paper, using sodium aluminate in combination with calcium hydroxide and, on the other hand, with barium hydroxide. It should be said that both methods are effective and the water after desulphurization meets the maximum permissible concentration of sulphates in surface waters according to the valid laws in the SR.

In the case of sodium aluminate desulfurization (ALR-F), very high efficiency was achieved when the sulphate values were reduced to below 1 mg.l<sup>-1</sup>. A disadvantage of this method is the need to adjust the pH value to a rather high value about 12.5, which also requires the use of another agent – calcium hydroxide.

On the other hand, when using barium hydroxide, we have also achieved a decrease in sulphates below 1 mg.l<sup>-1</sup>, but the big advantage is the fact that pH adjustment is not necessary, the desulphurisation effect is

excellent at all pH values. The need for calcium hydroxide is minimal to none. It follows that this method is more advantageous and certainly significantly easier.

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#### *Oczyszczanie AMD (kwaśnych odcieków z kopalń) z kopalni Old Smolník przez związki glinu i baru*

*Powstawanie i oczyszczanie kwaśnego drenażu kopalnianego jest największym problemem środowiskowym związanym z wydobywaniem i przetwarzaniem kopalnin na całym świecie. Do usuwania siarczanów i metali ciężkich z odwadniania kopalń stosuje się różne metody, ale każda z nich jest uniwersalna. Głównym celem artykułu jest analiza chemicznych metod usuwania metali i siarczanów z próbki drenażu kwaśnego. Metoda chemiczna oparta jest na wytrącaniu siarczanów przez chlorek glinu i wodorotlenek wapnia i baru. Na Słowacji jest kilka miejscowości z istniejącymi warunkami powstawania kwaśnego drenażu kopalnianego (AMD). Najwyższe wartości zaobserwowano w opuszczonym złożu Smolník. [1] Do badania wybrano próbkę kwaśnego odcieku z opuszczonego i zatopionego złoża Smolník w Republice Słowackiej.*

*Słowa kluczowe: woda kopalniana, strącanie, usuwanie siarczanów, związki baru, AMD*