

## Reduction of Sulphates from Mining Waters and Old Mining Loads

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*This article deals with the comparison of different methods of AMD desulphurisation. In experiments, the following chemical methods were used – precipitation using Ca (OH)<sub>2</sub> and Al ions, sorption using different types of zeolites, activated charcoal, their various combinations, inorganic composite sorbent and ion-exchangers. Test results were graphically compared*

**Key words:** acid mining waters, chemical precipitation, desulphurisation, sorption, slovakite, ion-changers, ettringite

### Introduction

Heavy industry and the impact of mining, although it is in decline, significantly contribute to deterioration of quality of surface waters. In addition to the influence of technological water from existing plants, a huge amount of mining waters contaminated by secondary activities is generated. (Vidlář, Schejbal, 2000)

The rainfall water in underground areas, in the old mine tunnels reacts chemically and gradually brings oodles of harmful substances that pollute surface waters. These are mainly heavy metals, sulphates, chlorides, phosphates, and other substances.

In terms of the quality of surface waters one of the worst areas in Slovakia is the creek of Smolník, classified into the worst – the fifth grade as a very highly polluted stream. The aim of the research in this article is to focus on the possibilities of reducing the concentrations of these substances under the limits set by the EU directives from mining waters of the former mine of Smolník. (Špaldon, 2007)

### Genetic Type of Mining Water in Smolník

The prominence of the chemical composition of waters from the mines of Smolník, that has been famous for centuries, placed these waters to the most famous ones in Slovakia in the middle ages already. They were classified among other world-famous Slovak mineral (and “strange”) waters (Piešťany, Trenčianske Teplice, Bardejov and others) and Smolník was mentioned together with them. Mineral underground waters are the ones that differ from ordinary groundwater by their composition, quantity of dissolved salts, gases or temperature. (Ilavský, 1968)

From this point of view mineral waters can be divided into the following types:

- mineral,
- thermal,
- mineralized waters.

Each of these water types has its hydro-geological, geochemical or hydrochemical or even balneological criteria. While the dates of mineral and thermal waters are commonly used terms the term mineralized waters behaves in a different way. Even this type of water represents water from the Smolník deposit.

Mineralized waters are those that have an adverse effect physiological on the human organism, while the effect of mineral waters, by contrast, is beneficial. Therefore, mineral waters can be divided into two groups:

- naturally circulating waters in geological structures (like regular waters) which are enriched in the greater rate of some substances. These waters have anomalous, but not too high chemistry mineralization.
- Waters which acquire special mineralization in contact with mineral surroundings. These waters reach very high mineralization, and this includes the waters of the Smolník deposit. In some states, these waters are classified as industrial mineral waters being of practical significance and from which salt and chemical elements may be extracted. In addition to salts, also the following metals may be gained from them: J, Br, B, U, Li, Be, Rb, Cs, and others. Slovakia was known in the past by using of waters with increased content of copper just in two locations – at the deposit of Smolník and also in the location of Špania dolina – Piesky. (Hinie, 1963)

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Chemistry of water goes hand in hand with the mineralogical and petrographic character of the environment and according to the conditions of chemistry formation those waters are classified as petrogenic. In the light of this classification the waters of the Smolník deposit belong here as well. Its origin is natural water almost exclusively vadose – surface. A vast majority of mineral waters has vadose origins. Vadose water is getting into the ground during the environment and under the terms of what he has created in them for your circulation is shaping its chemical composition. Water chemistry is in close correlation with the mineralogical-petrographic nature environment and under the terms of the creation of Chemistry are those waters classified as petrogenic. Within the meaning of this classification also includes water of the smolník deposit. (Jaško, 2007)

### Quality of Mining Water

The quality parameters of flowing mining water have been systematically monitored. The values often fluctuate, often significantly. They depend on rainfall quantity, rainfall intensity, time delays in mining areas, spot (depth), etc. Countless floods and fires, in particular, in the presence of Fe and Cu in the mines, caused their huge increase in the mining waters. The fire in the mine by spontaneous combustion of pyrite caused increase in concentration of Cu to 150 g.l<sup>-1</sup> in 1896-97, the influence of the fire caused increase of concentration of Cu in the 1910 even to 180 g.l<sup>-1</sup>! In 1923, 57.6 tonnes of copper flew into the surface water. (Jaško, 2007) Table 1 shows the quantities of elements during the period of the last 18 years. (Šlesárová, 2007)

Tab. 1. Trend of mining water quality from Smolník in the period from 1986 to 2006.

year	RL [mg.l <sup>-1</sup> ]	SO <sub>4</sub> <sup>2-</sup> [mg.l <sup>-1</sup> ]	Fe [mg.l <sup>-1</sup> ]	Cu [mg.l <sup>-1</sup> ]	Mn [mg.l <sup>-1</sup> ]	pH	Zn [mg.l <sup>-1</sup> ]	Mg [mg.l <sup>-1</sup> ]	Al [mg.l <sup>-1</sup> ]
1986	6470.1	6004.6	72.0	37.2	43.3	2.6	28.2	*	*
1987	8158.0	4634.5	51.2	39.4	65.8	2.8	31.0	*	*
1991	3470.0	1155.8	7.0	11.1	12.3	3.5	6.2	*	*
1992	3588.9	1233.3	19.9	10.7	13.5	2.9	5.8	*	*
1993	3660.8	1481.7	61.3	5.3	12.8	2.6	4.5	*	*
1994 <sup>1</sup>	3787.5	1350.0	57.8	7.2	11.3	2.6	4.9	*	*
1994 <sup>2</sup>	7000.0	4000.0	155.0	11.8	11.0	2.7	17.0	*	*
1994 <sup>3</sup>	17766.7	9512.7	914.7	51.3	104.7	3.1	77.7	*	*
1995	8363.2	5825.2	772.4	7.4	136.2	3.2	21.0	764.8	174.8
1997	5569.0	4133.0	421.4	3.9	37.2	3.4	19.2	526.0	149.0
2000	7050.0	4170.0	137.6	4.3	41.3	3.8	*	465.0	137.6
2001	5595.0	3461.0	556.0	2.8	37.9	3.6	*	361.5	109.5
2002	5765.5	2296.7	620.0	1.7	38.4	3.9	*	381.0	94.3
2003	5160.5	2680.7	501.0	1.5	33.4	3.6	*	332.7	83.6
2004	4499.0	2723.6	425.9	1.5	27.9	3.6	*	292.5	71.8
2005	4260.3	2324.6	415.8	1.5	23.6	3.5	*	287.6	68.2
2006	4198.8	2415.6	410.1	1.5	24.4	3.6	*	281.3	61.3

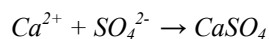
<sup>1</sup> period before ending of flooding, <sup>2</sup> ending of flooding, <sup>3</sup> after flooding, \* unmeasured

Table No. 1 clearly shows a gradual increase, culmination and finally drop of the values in almost all indicators. These changes are, of course, due to the flood and its completion. After nearly four years of exposure of mining waters in the ground environment, there was a strong concentration of all components of high mineralization and went beyond all permissible concentrations (it exceeds even now)

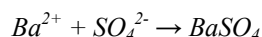
### Chemical Methods of Desulphurisation

From the practical point of view, most frequently used is the technology of the chemical precipitation of sulphates. The process of precipitation must be controlled so that the purified water is not too loaded with ions of the precipitating reagent. The practice uses cations of selected metals that – together with sulphates - form less soluble compounds that are ecologically acceptable.

The easiest way is precipitation using lime or lime milk



Sulphates precipitation to barium sulphate belongs to well known technologies of precipitation:



This method is more efficient compared to precipitation using lime, but significantly more expensive and higher levels of barium in water bring toxicological hazard. (Strnadova, Raclavský, 2001) An interesting solution is precipitation of sulphates in the presence of calcium and aluminium ions into a form of so called Candlot salt – ettringite. It is a little soluble and relatively voluminous compound.

Ettringite was described already in 1939 by Jones. It is generally referred to using the chemical formula of  $Ca_6Al_2(SO_4(OH)_4)_3$ , where the ratio of Ca : Al :  $SO_4 = 6 : 2 : 3$ . Formation of ettringite is assumed in aqueous solutions containing  $CaSO_4$ ,  $Ca(OH)_2$ , and compounds of aluminium in the third stage of oxidation. It may be added in form of sulphate, chloride, nitrate or sodium aluminate. This method must maintain a surplus of calcium ions, because not only ettringite is formed, but also neutralisation, deferrisation, demanganisation and elimination of heavy metals are pursued. (Vidlář, Schejbal, 2000)

### Desulphurisation by Al-ions Precipitation

The concentration of sulphate ions in the testing sample was  $2984 \text{ mg.l}^{-1}$  and pH 3.34. In experiments with the said mining water we had the HACH spectrophotometer, type of DR 2000, and a digital pH meter WTW 330i at our disposal. As it is known that the precipitating reaction takes place at pH above 12.4 in quantitative terms the first task was to identify the optimal dosage of  $Ca(OH)_2$  to adjust the pH to this value. When adjusting the pH with  $Ca(OH)_2$ , partial precipitation of  $SO_4^{2-}$  ions took place.

### $SO_4$ Precipitation only Using $Ca(OH)_2$ ions without $Al^{3+}$ ions

Methodological procedure of precipitation:

1.  $Ca(OH)_2$  – 15 minutes agitation at 200 r.p.m.,
2. filtration of suspension,
3. determination of the content of sulphates and of the pH value.

Tab. 2. Results of Desulphurisation of Mining Water Pech pit by  $Ca(OH)_2$ .

Sample No.	$Ca(OH)_2$ [g.l <sup>-1</sup> ]	pH	$SO_4^{2-}$ [mg.l <sup>-1</sup> ]	Effect des. [%]
1	6	12.59	2400	19.6
2	8	12.60	2362	20.8
3	10	12.61	2385	20.1
Incom. sample	0	3.34	2984	-

As the desired pH value is 12.4 and more, it is evident from Tab. 2 that the sufficient amount of  $Ca(OH)_2$  is 5-6 g.l<sup>-1</sup>. Bigger quantities do not affect the pH values any longer. At the same time, it can be observed that the addition of lime itself does not have a significant impact on reducing the content of sulphates. From the original approx. 2984 mg only 600 g were precipitated having only about 20 percent effectiveness.

### $SO_4^{2-}$ ion Precipitation at Presence of $Ca(OH)_2$ , and Natrium Aluminate (ALR-F)

Methodological procedure of precipitation:

1.  $Ca(OH)_2$  – 15 minutes of mixing at 200 rpm,
2. the ALR-F – 30 minutes of mixing at 200 rpm.
3. filtration of the suspension,
4. the determination of the content of sulphates and pH value.

Experiments were designed to determine the quantities of coagulating agents, their reciprocal relationships with the aim of achieving the greatest possible efficiency of the desulphurisation of mine water. The results of these trials are depicted in table 3.

Tab. 3. Results of mine water desulphurisation from Pech pit at optimal reagents dosing.

Sample No.	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 desul. [%]
1	5.2	3.2	12.56	118.28	96.03
2	5.2	3.4	12.56	199.60	93.31
3	5.2	3.6	12.56	49.92	98.32
4	5.2	3.8	12.56	45.28	98.48
5	5.4	3.2	12.56	64.40	97.84
6	5.4	3.4	12.56	123.28	95.87
7	5.4	3.6	12.55	65.00	97.82
8	5.4	3.8	12.55	49.64	98.33
9	5.6	3.2	12.58	114.40	96.17
10	5.6	3.4	12.58	42.96	98.56
11	5.6	3.6	12.58	0.48	99.98
12	5.6	3.8	12.58	0.97	99.97

The results show optimal effect with the dose of 5.6 g Ca and 3.6 ml ALR-F / 1 litre cleaned water.

### Desulphurisation using Sorbents and Ion Changers

Unlike the static mode, when a sorbent or precipitating reagents are added into the tank with water, where they are slowly blended for a certain optimal time in the dynamic mode, purified water continuously flows through the column in which the bed is made from the sorbent, the ion changer or a mixture containing a sorbent. This method is more demanding on the instrumentation, space and amount of purified water. In laboratory conditions, the simulation of dynamic sorption resembles the classical filtration. The sorptive column contains a glass cylinder, which has a partition in the bottom part on which there is a sorptions bed or the ion changer. The aim of these experiments under the same conditions was, in principle, to verify and to compare selected types of sorbents and ion changers in terms of their effectiveness in the process of desulphurisation and elimination of heavy metals from acid waters, not exploring the optimal flow, sorbent capacity, etc. (Špaldon, 2007).

### Tests with mining water from the Pech pit Smolník mine

Water was stabilized - 5ml HNO<sub>3</sub> (2M). litre<sup>-1</sup>

A-1 non-treated stabilized mining water

A-2 sorbent – active carbon

A-3 ion changer – mixture 50 % Katex – 50 % Anex

A-4 sorbent Zeolit (from Nižný Hrabovec)

A-5 sorbent – mixture 80 % Zeolite – 20 % active carbon

A-6 sorbent – ion changer – 80 % Zeolite – 20 % Katex+Anex

A-7 ion changer Katex – strong acid Ostion

A-8 ion changer alkalic Anex WOB

A-9 sorbent – slovakite (inorganic component sorbent)

Tab. 4. Comparing of desulphurisation affect by individual reagents.

Reag.	Act. carbon	Katex Anex	Zeolit	Zeol-Ac	Zeol-KA	Katex	Anex	Slovak.	Ca Precip.	ALR-F
pH	3.87	3.84	2.59	3.91	2.0	1.1	8.96	3.73	12.6	12.6
SO <sub>4</sub> <sup>2-</sup>	3360	≥0	3200	3310	1900	1830	≥0	1336	2745	≥0
Effect	0 %	≤100 %	4.8 %	1.5 %	43.5 %	45 %	≤100 %	59.3 %	18.2 %	≤100 %

mg/l  $\text{SO}_4^{2-}$

Comparing of desulphatation -sulphates amount after sorption in solution

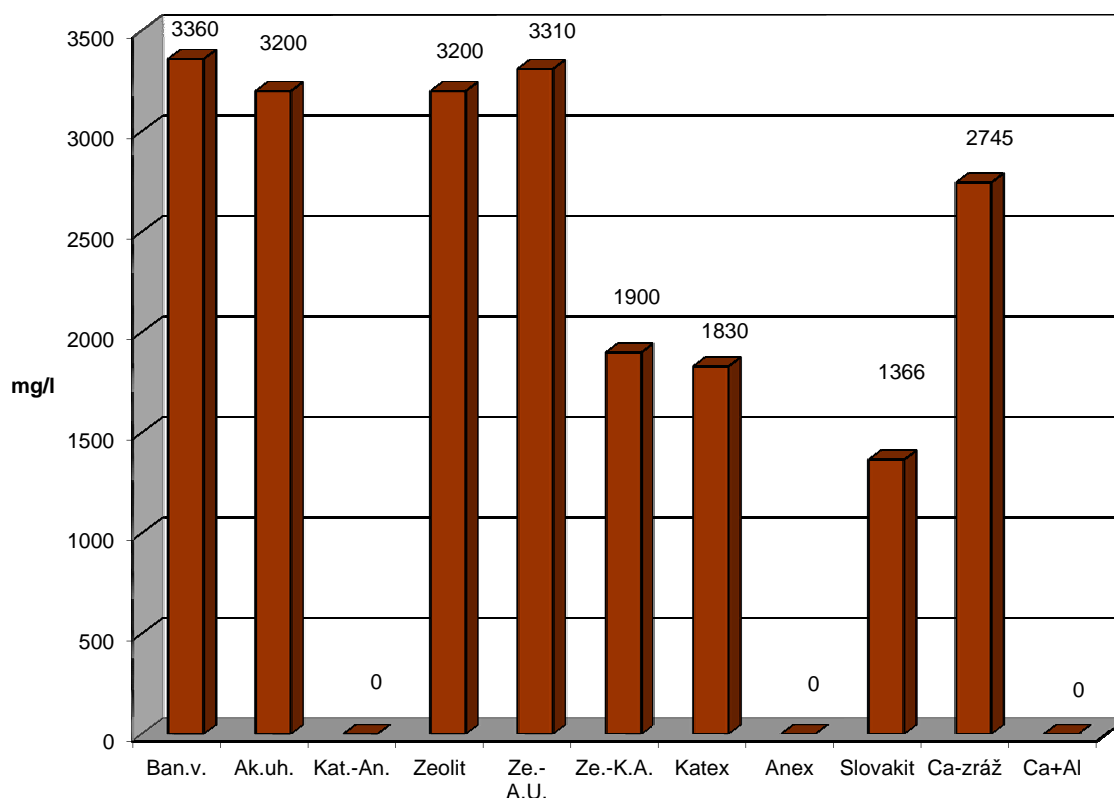


Fig. 1. Graphic presentation of desulphurisation effect by various methods.

### Discussion

On the basis of the results in table 4 we can clearly observe expedience of selected agents. Relatively effective is inorganic sorbent component slovakite. This sorbent was also tested in static mode, where the results were quite inconclusive, only 15 % efficiency was reached. On the other hand, very good results were achieved under dynamic conditions. Elimination of sulphates has reached about 60 %. 100% removal of anions using ion changer Anex was logical. Worse efficiency of activated carbon was expected too. A big surprise was the relatively weak effect of zeolite, only 5 %. A mixture of zeolite with a small amount of ion changer reached the efficiency of 43 %, but only because of the presence of ion changer in the mixture.

### Conclusion

Strict EU limits for outflowing water into the surface flows started to be applied in the new associated countries of the EU. This is the reason why such attention is devoted to this issue, i. e. mining water flowing from the old mine load of Smolník. Here is the possibility to use several methods of purification. Use of ion changers is very effective but, on the other hand, very costly as well. More perspectives are seen in the use of various combinations of physical-chemical methods of neutralization, precipitation of ions or by using Al-sorption by using composite sorbents.

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## References

- Heviánková, S., Vidlář, J.: Study of possibilities of aluminium ions solution from waste-water treatment plant sludge after sulphate mine waters precipitation. In: Proceeding of the Conference on State-of-the-art and Perspectives of Mineral Processing, *VŠB-TU Ostrava*, 10, 2005, 161-166. (in Czech).
- Hinie, O.: Hydrogeology of Czechoslovakia – Mineral waters. Publisher ČSAV Prague, 1963, 265 p. (in Czech).
- Hlavský, J.: Smolník – stratiform deposit of pyrite and chalcopyrite ores. *Report of the Geological Institute of Dionyz Stur, Bratislava*, 1968, 145 p. (in Slovak).
- Jaško, V.: Smolník – comprehensive hydrogeological and hydrochemical assessment of Cu-Fe ores deposit. *Report, Aquipur a.s., Bratislava*, 1998, 125 p. (in Slovak).
- Strnadová, N., Doubek, O., Raclavský, J.: Removal of sulphates from industrial waters. In: Proceedings of the Regional Central - European Conference IUAPPA, *Valuation of influences on Environment, Prague 2000*, 258-262. (in Czech).
- Šlesárová, A.: Simulation of geochemical evolution of acid mine drainage in old mining loads. *PhD. Thesis, Institute of Geotechnics of SAS, Košice 2007*, 104 p. (in Slovak).
- Špaldon, T.: Possibilities of desulphatation of acid mine drainage. *PhD. Thesis, VŠB – Technical University, Ostrava 2007*, 150 p. (in Slovak).
- Vidlář, J., Schejbal, C.: Mine waters with overlimit content of sulphates. In: Proc. of the first International Conference on Minerallurgy and Environmental Technologies, *Herlany 2000*, 103-116. (in Czech).
- Vidlář, J., Schejbal, C., Fečko, P.: Ecologically advantageous method of sulphate mine water cleaning. In: *Transactions of the VŠB - Technical University of Ostrava*, 2002, 1-8.