THE ROLE OF Fe OXYHYDROXIDES IN REMEDIATION OF CONTAMINATED MINE WATERS

Mgr. Ondrej Brachtýr[1]
doc. Mgr. Peter Šottník, PhD.[2]
RNDr. Ľubomír Jurkovič, PhD.[3]
[1, 2] Department of geology of mineral deposits, Comenius University in Bratislava, Faculty of Natural Sciences, Ilkovičova 6, 842 15 Bratislava 4, Slovakia
[3] Department of geochemistry, Comenius University in Bratislava, Faculty of Natural Sciences, Ilkovičova 6, 842 15 Bratislava 4, Slovakia

ABSTRACT

The main goal of our research was to compare the effectiveness of natural and supported attenuation as a remediation method for the removal of potentially toxic elements from mining waters occurring on the sites where sulfide mineralization deposits were present in the past. Samples for this research were taken from sites with abandoned mineral deposits of sulfide ores. These pose a danger to the environment in the form of increased concentrations of some potentially toxic elements (especially: As, Sb, Ni, Hg) in waters flowing out of the abandoned mines. These are the localities in Medzibrod, Poproč, Dúbrava and Pezinok where the main risk is represented by increased concentrations of As and Sb, and the locality in Merník where increased concentrations of Hg and Ni were found. As part of our research, we have successfully proved that natural attenuation is an effective remediation method for mining waters contaminated by potentially toxic elements. We also proved, that supported attenuation (by aeration) significantly increases the amount of precipitates – secondary mineral phases in the form of Fe oxyhydroxides.

Keywords: *mining waters, oxyhydroxides, remediation method, attenuation*

INTRODUCTION

Cleaning of mining waters contaminated by various chemical elements is very demanding, both economically and in terms of time. The source of pollution usually cannot be removed, therefore we can only attempt to reduce its consequences, which can be long-lasting. The remediation of these areas using physico-chemical methods is usually costly and often involves additional environmental risks. Conventional methods of mine water purification include coagulation and flocculation, membrane separation, a few electrochemical methods, chemical extraction, ion exchange and others [1], [2]. Recently, not only natural and synthetic sorbents, but also industrial and agricultural wastes are used to remove contaminants from waters. This can be a cost-effective alternative to commonly used, more expensive methods for removing metals and metalloids from waters [3], [4].

MATERIALS AND METHODS

Samples used in our research are represented by mining waters extracted from abandoned mining areas – Pezinok and Poproč – and naturally emerging secondary mineral phases in the form of Fe oxyhydroxides from localities in Medzibrod, Dúbrava and Merník. Localities in Medzibrod, Dúbrava, Poproč and Pezinok are abandoned mining areas where Sb ore used to be mined and locality Merník is an abandoned Hg mining area.

Main goal of our research was to compare the efficiency of natural attenuation and attenuation supported by aeration. This comparison was carried out on the sample from Pezinok. Sample PK-1 is an uninfluenced sample of mining water. Samples PK-2 and PK-3 were filtered after extraction through filters with pore density of 0,45 µm and 0,2 µm respectively. Sample PK-4 was left to sediment for 5 days (natural attenuation) and then filtered through a filter with pore density of 0,45 µm. Samples PK-5 and PK-6 were aerated using an air pump for 1 day and 5 days respectively, and then filtered through a filter with pore density of 0,45 µm. All samples were stabilized using 1ml of HNO_3 and sent to a laboratory for analysis. Precipitated solids (mainly Fe oxyhydroxides) were left to dry after filtration at 40 °C and then weighed. Sample PK-3 was first filtered through the filter with pore density of 0,45 µm, and then through the 0,2 µm filter. No solid phase was present after the filtration through the 0,2 µm filter.

Samples from other areas of interest were extracted mainly to determine the properties of the emerging solid phases – Fe oxyhydroxides. We chose different mining areas with different geneses to compare qualitative properties of the emerging solids.

RESULTS

Table 1 provides a brief summary of samples from Pezinok locality used for comparison between natural and supported attenuation. All samples were stabilized using 1 ml of HNO_3 and then sent for analysis. Samples PK-4, PK-5 and PK-6 were after sedimentation/aeration filtered through the filter with pore density of 0,45 µm and the collected solids were then dried and weighed.

Table 1: *Summary of samples from Pezinok*

PK-1	unfiltered sample
PK-2	filtered through 0,45 µm filter
PK-3	filtered through 0,2 µm filter
PK-4	5-day sedimentation
PK-5	1-day aeration
PK-6	5-day aeration

Quantitative analysis of samples from Pezinok (table 2) shows, that even the short, 1-day aeration (sample PK-5) helped increase the amount of emerging solid phases by two-fold, compared to the 5-day sedimented sample (PK-4). 5-day aeration (sample PK-6) proved to be the most effective, increasing the amount of emerging Fe oxyhydroxides by almost 3-fold. This is the proof, that the supported attenuation is more effective than natural attenuation.

Table 2: *Quantitative analysis of emerging Fe oxyhydroxides from samples extracted from locality in Pezinok*

Sample	Amount of precipitate [g]	
	5 liters	1 liter
PK-2	0,1111	0,02222
PK-4	0,0919	0,01838
PK-5	0,2102	0,04204
PK-6	0,3286	0,06572

This also corresponds with our other research, which was carried out on the samples of mining waters from the locality in Poproč. Using natural attenuation, we managed to obtain only 0,009 g/l of precipitates. After 3 days of intense aeration, we collected 0,053 g/l of precipitates, which is a proof, that the supported attenuation was almost 6-times more effective than the natural attenuation. Difference in effectiveness between the samples from Pezinok and Poproč may be caused by higher Fe concentrations in the mining waters from the locality in Poproč.

Chemical analysis of samples from Pezinok shown in table 3 also supports the fact, that aeration increased the formation solid phase, because content of Al, Fe and mainly Mn decreased with the level of aeration. These analyses were carried out in the laboratory of Department of Environmental Geosciences, Czech University of Life Sciences, Prague.

Table 3*: Chemical analysis of water samples from the locality in Pezinok*

Sample	Al	As	Ca	Fe	Mn	Sb	Si	Zn
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
PK-1	2,17	1,56	174,01	2,67	0,55	0,41	11,28	0,15
PK-2	0,03	1,07	166,90	0,60	0,49	0,39	9,85	0,02
PK-3	0,03	1,04	166,83	0,39	0,50	0,39	9,92	0,04
PK-4	0,04	0,86	165,84	0,00	0,41	0,39	9,28	0,01
PK-5	0,06	1,02	166,84	0,00	0,37	0,41	9,45	0,00
PK-6	0,05	0,89	145,34	0,00	0,06	0,41	9,32	0,00

Supported attenuation proved to be more effective regarding the quantity of emerging solids. However, considering the removal of potentially toxic elements, supported attenuation was not significantly more effective compared to natural attenuation. All potentially toxic elements seemed to have bound to the Fe oxyhydroxides that precipitated from the mining water even without aeration.

Lower content of potentially toxic elements As, Sb and Zn in samples PK-4, PK-5 and PK-6 also proves, that both, natural and supported attenuation are effective remediation methods for removing potentially toxic elements from mining waters originating from deposits with sulfidic mineralization.

Another important part of our research was the research of properties of Fe oxyhydroxides. Samples for this research were extracted from localities in Medzibrod, Dúbrava and Merník. Chemical analyses of these solid phases were performed by EL spol. s.r.o. and the results are shown in tables 4 and 5.

Table 4: *Chemical analysis of Fe oxyhydroxides from localities in Medzibrod and Dúbrava*

Sample	**Al**	**As**	**Fe**	**Mn**	**Sb**	**Zn**	**Pb**	**Hg**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
M1	553	107484	273677	699	12107	72	24	0,296
D3	537	7399	308013	15823	1925	50	6	0,043

Table 5: *Chemical analysis of Fe oxyhydroxides from locality in Merník*

Sample	**Ni**	**As**	**Sb**	**Hg**	**Cr**	**Fe**
	mg/kg in dry matter					**%** of dry matter
V1	71	46,75	0,84	0,699	199	17,44
V2	358	20,17	1,14	2,214	519	22,81
V3	138	114,82	<LOD	0,775	81	24,73

Interesting about the Fe oxyhydroxides from the locality in Merník is the content of Hg (table 5). It is typical for this locality since it is an abandoned Hg mining area.

Fe oxyhydroxides are main natural sorbents for Sb and can precipitate in the wide range of pH values [5], [6], [7]. These Fe precipitates significantly help to reduce the mobility of dissolved contaminants in water environments [8]. Fillela et al. [9] point out the importance of Fe oxyhydroxides in reducing the mobility of Sb, especially in acidic soils and waters.

Figure 1: *Sample D3 – particle distribution of Fe oxyhydroxides from Dúbrava locality*

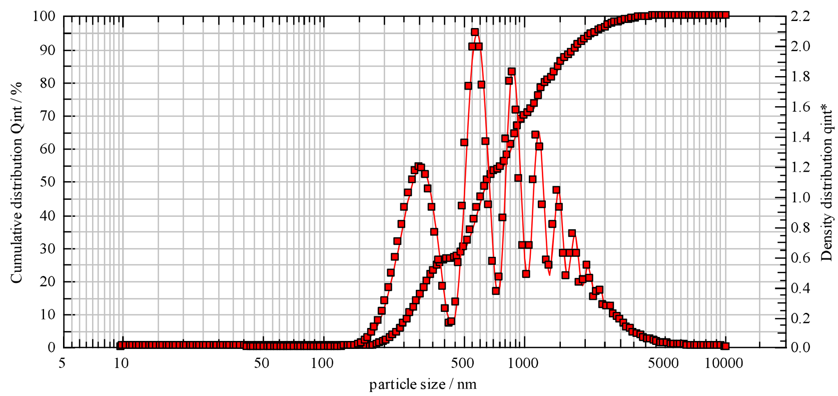
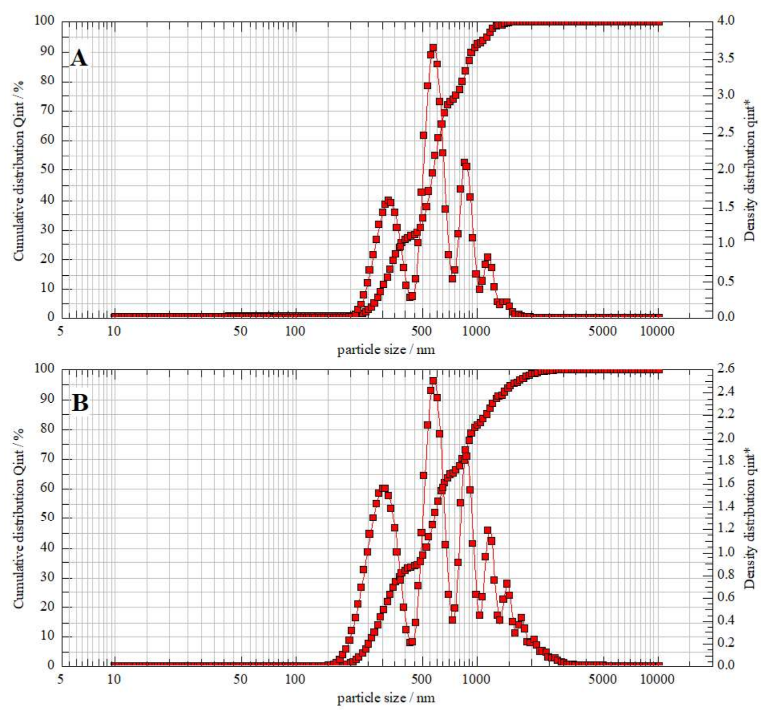


Figure 1 shows size distribution of Fe oxyhydroxide particles expressed by cumulative distribution and density distribution. It can be seen, that all the particles are sized between 150 nm and 4500 nm. Most of the particles have the size of 550 nm.

Figure 2 shows the same kind of particle size analysis on 2 samples from locality in Merník – samples V1 (figure 2 A) and sample V2 (figure 2 B).

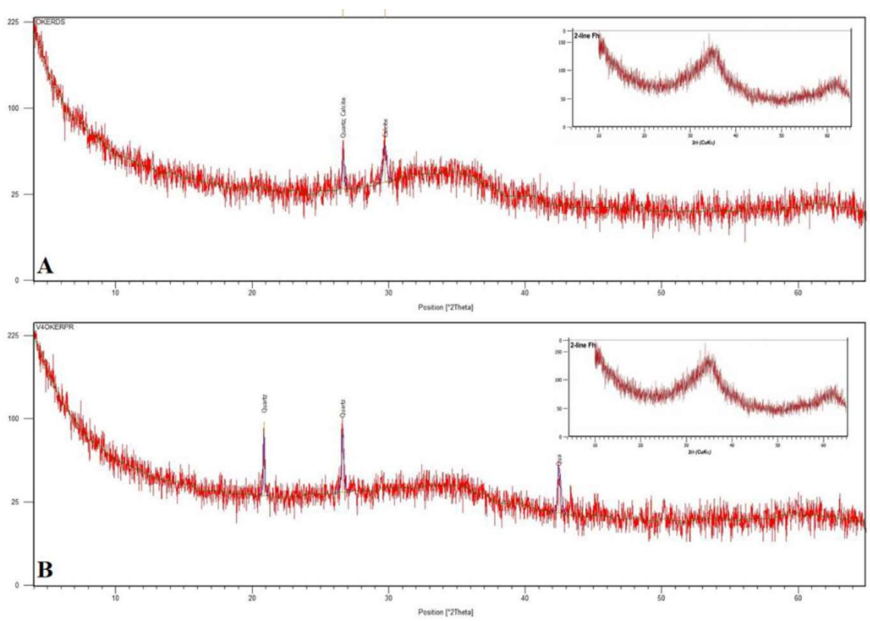
Figure 2: *Sample V1 (A) and V2 (B) – particle size distribution of Fe oxyhydroxides from locality in Merník*



Particle size of the Fe oxyhydroxides varies from 200 nm to 1100 nm in sample V1 (figure 2 A) and from 150 nm to 3000 nm in sample V2 (figure 2 B). Most of the particles in both samples have the size between 550 nm and 600 nm. All particle size distribution analyses were carried out by the Institute of Geotechnics, Slovak Academy of Sciences.

Mineralogical analysis of emerging Fe oxyhydroxides using X-ray diffraction analysis proved, that samples from Dúbrava (figure 3 A) and Merník (figure 3 B) consist mostly of the mineral ferrihydrite. Synthetic 2-line ferrihydrite is shown in the upper right corner of the figure for comparison. XRD analysis was performed by the Earth Science Institute of the Slovak Academy of Sciences.

Figure 3: *XRD analysis of Fe oxyhydroxides from locality in Dúbrava (A) and Merník (B) compared with synthetic 2-line ferrihydrite*



CONCLUSION

In our research, we managed to prove, that supported attenuation (by aeration) is more effective regarding the quantity of emerging solids – secondary mineral phases of Fe oxyhydroxides, compared to natural attenuation. These mineral phases – Fe oxyhydroxides are effective sorbents for the removal of potentially toxic elements (metals and metalloids, especially Sb and As) from mining waters with high contents of Fe. The supported attenuation did not prove to be much more effective than natural attenuation regarding the effectiveness of the removal of potentially toxic elements.

XRD analysis shows, that emerging solids precipitating from mining waters are mostly represented by ferrihydrite. However, these mineral phases are very poorly crystalline, and their mineralogical determination is complicated. The emerging mineral phases are often unstable and tend to transform to more stable goethite [10], [11].

Particle size analysis shows, that most of the particles occurring in the naturally emerging mineral phases of Fe oxyhydroxides have the particle size of 550 nm. Hence the use of filters with pore density of 0,45 µm is sufficient to rid waters of these solid phases and thus reduce the mobility of potentially toxic elements.

ACKNOWLEDGEMENTS

This work was supported by APVV-0344-11, APVV-17-0317, VEGA 1/0597/17 projects and Comenius University Grant no. UK82/2018.

REFERENCES

[1] Ungureanu G., Santos S., Boaventura R., Botelho, C., Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption, Journal of Environmental Management, vol. 151, pp. 326-342, 2015

[2] Li J., Zheng B., He Y., Zhou Y., Chen X., Ruan S., Yang Y., Dai C., Tang L., Antimony contamination, consequences and removal techniques: A review, Ecotoxicology and Environmental Safety, vol. 156, pp. 125-134, 2018:

[3] Sekula P., Hiller E., Šottník P., Jurkovič Ľ., Klimko T., Vozár J., Removal of antimony and arsenic from circum-neutral mine drainage in Poproč, Slovakia: a field treatment system using low-cost iron-based material. Environmental Earth sciences, vol. 77:518/issue 13, 2018

[4] Singh N.B., Nagpal G., Agrawal S., Rachna N, Water purification by using Adsorbents: A Review, Environmental Technology & Innovation, vol. 13, pp. 187-240, 2018

[5] Mitsunobu S., Harada T., Takahashi Y., Comparison of antimony behavior with that of arsenic under various soil redox conditions. Environmental Science & Technology, vol. 40/issue 23, pp. 7270-7276, 2006

[6] Mitsunobu S., Takahashi Y., Terada Y., Sakata M., Antimony (V) Incorporation into Synthetic Ferrihydrite, Goethite and Natural iron oxides. Environmental Science & Technology, vol. 44/issue 10, pp. 31712-3718, 2010

[7] Wilson S.C., Lockwood P.V., Ashley P.M., Tighe M., The chemistry and behavior of antimony in the soil environment with comparisons to arsenic: a critical review. Environmental Pollution, vol. 158/issue 5, pp. 1169-1181, 2010

[8] Lintnerová O., Šoltés S., Šottník P., Environmentálne riziká kyslých banských vôd na opustenom ložisku Smolník. Univerzita Komenského, Bratislava, Slovakia, 157 p., 2010

[9] Filella M., Belzile N., Chen Y., Antimony in the environment: a review focused on natural waters II. Relevant solution chemistry. Earth-Science Reviews, vol. 59, pp. 265–285, 2002

[10] Majzlan J., Lalinská-Voleková B., Chovan M., Jurkovič Ľ., Milovská S., Göttlicher J., The formation, structure, and ageing of As-rich hydrous ferric oxide at the abandoned Sb deposit Pezinok (Slovakia), Geochimica et Cosmochimica Acta, vol. 71/issue 17 pp. 4206-4220, 2007

[11] Bolanz R.M., Bläss U., Ackermann S., Ciobota V., Rösch P., Tarcea N., Popp J., Majzlan J., The Effect of antimonate, arsenate, and phosphate on the transformation of ferrihydrite to goethite, hematite, feroxyhyte, and tripuhyite, Clays and Clay Minerals, vol. 61/issue 1, pp. 11–25, 2013