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Study of Metals Distribution between Water and Sediment in the Smolnik Creek (Slovakia) Contaminated by Acid Mine Drainage

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The Smolnik deposit is one of the historically best-known and richest Cu-Fe ore deposits in the Slovak Republic. The discharging mine waters of pH 3.7-4.1 containing high concentrations of sulphates, Fe, Mn, Cu, Zn and Al have a negative effect, mainly on the Smolnik creek.
The paper deals with the study of metal distribution between water and sediment in the Smolnik creek depending on pH and the metal concentrations. The results of metal concentration decrease in surface water and increase of metal concentration in sediment were compared with the results of our experimental study focused on pH influence on iron, copper, aluminium, zinc and manganese precipitation from raw AMD from mine Smolnik. There was determined that aluminium is precipitated (98.5 %) in the pH range from 4 to 5.5. Precipitation of copper was carried out in accordance with the literature, where copper begins to precipitate at pH > 4 and total precipitation occurs at pH 6 with the efficiency 92.3 %. In spite of iron occurrence in AMD mainly as Fe^{2+}, which precipitates at pH < 8.5, the experimental results confirmed the iron precipitation across studied pH range (4-8) by the progressive oxidation of Fe^{2+} to Fe^{3+} by oxygen from air and its precipitation in the form of $Fe(OH)_3$, which starts at pH 3.5. Zinc is precipitated in the range of pH 5.5 to 7 and 84 % of total Zn was precipitated in this interval.
It was confirmed that increasing of pH of AMD due to its dissolution by surface water induces precipitation of metals and their accumulation in sediment in the determined intervals of pH.

1. Introduction

Acid mine drainage (AMD) is considered as one of the worst environmental problems associated with mining activity. AMD from abandoned mines poses a long-term threat to the environment and directly impacts it by polluting streams, rivers, waterways, drinking and groundwater, disrupting wildlife habitat and destroying the natural landscape. Outflow from mining operations can have negative impacts on the surrounding aquatic environment including heavy loads of suspended solids, decreased pH levels and increased levels of heavy metals.
The abandoned mining area Smolnik in Slovakia belongs now to the old environmental loads because of acid mine drainage (AMD) production. Massive pyrite oxidation and free sulphuric acid production are the major reasons of water acidification and dissolving of heavy metals from metallic ores. This AMD acidifies and contaminates the Smolnik creek water, which transports the pollution into the Hnilec river catchment (Luptakova et al, 2008; Singovszka and Balintova, 2009). Increasing of the pH of water is connected with the metal precipitation in the form of hydroxides.
Metals deposited in contaminated bottom sediments can be released to the water column with changes in different hydrobiological and physico-chemical conditions such as pH, redox potential, salinity

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(Hakansson et al, 1989; Kruopiene, 2007). There are numerous studies on the effect of physico-chemical conditions on the forms of metal occurrence in bottom sediments. Most of them are based on laboratory experiments carried out under specific pH, redox or salinity conditions (Balintová et al., 2009; Calmano et al., 1993).
Mobility and bioavailability of metals in sediments depend also on their chemical form. The objective of the presented study is to analyse the influence of acid mine drainage from the shaft Pech (mine Smolnik) on surface water and sediment quality in the Smolnik creek as well as the influence of pH on metals precipitation from AMD in laboratory conditions and comparison of the results with redistribution of metals in real conditions of water environment of the Smolnik creek.

2. Material and methods

In order to study surface water and sediment quality, two sampling localities along the Smolnik creek were chosen (1 – approx. 200 m under the shaft Pech, 2 – inflow into the Hnilec river). Also the AMD quality from the shaft Pech was monitored (3-shaft Pech). The interaction between AMD and surface water and sediment was studied on the samples water and sediments from the Smolnik creek sampled in 2006 - 2011 (No. 1 and 2).
The chosen physical and chemical parameters were determined by multifunctional equipment METTLER TOLEDO in situ and chemical analyses of water and sediment were determined by AAS method (SpectrAA-30, Varian Australia).

3. Results and discussion

The results of chemical analysis of water samples (samples 1 and 2) from the Smolnik creek as well as AMD from shaft Pech (sample 3) sampled in 2006 - 2011 are presented in Table 1.

Table 1: Contents of selected metals in AMD

No./ year	pH -	Fe [mg/L]	Mn [mg/L]	Al [mg/L]	Cu [µg/L]	Zn [µg/L]	As [µg/L]	Cd [µg/L]	Pb [µg/L]
1/2006	4.98	31.8	2.7	2.03	203	923	1	<0.3	<5
1/2007	5.76	10.8	0.96	0.61	14	187	<1	0.3	<5
1/2008A	4.92	4.93	0.78	4.14	384	338	1	0.7	<5
1/2008B	5.26	16.8	1.32	0.13	50	383	1	1.5	<5
1/2009	5.19	18.8	1.84	4.15	97	379	3	0.7	8
1/2011	5.10	19.8	1.89	1.33	164	655	<1	1.9	<5
2/2006	4.93	17.8	2.22	2.46	207	757	1	<0.3	<5
2/2007	6.17	5.38	0.73	0.12	7	176	<1	0.5	<5
2/2008A	5.34	2.52	0.30	0.32	14	68	<1	<0.3	<5
2/2008B	5.2	1.11	1.21	0.02	42	349	<1	<0.3	<5
2/2009	5.4	10.5	1.3	0.43	31	280	<1	0.5	<5
2/2011	5.16	11.8	1.56	0.35	120	491	<1	1.1	<5
3/2006	3.88	463	36.5	107	3263	12600	18	15	71
3/2007	4.11	433	32.2	79.8	1379	8958	20	27	56
3/2008A	4.01	291	22.5	53.9	1311	6750	50	14.9	59
3/2008B	3.98	392	28.5	69.7	1642	7665	30	21.5	56
3/2009	3.94	351	28.4	67.6	1740	7250	50	14	61
3/2011	3.97	312	25.8	75.3	1700	7996	6	17.8	52
Limits	6-8.5	2	0.3	0.2	20	100	30	5	20

The results were compared to the limit values according to the Regulation of the Government of the Slovak Republic No. 269/2010 Coll. Based on the results in Table 2 we can state that acid mine drainage flowing from the shaft Pech has an adverse effect on the surface water quality in Smolnik creek and causes exceeding of the limit values according to the Regulation of the Government of the Slovak Republic No. 269/2010 Coll. From chemical analysis, given in Table 1, follows, that AMD exceeds each evaluated indicators. After AMD dilution with surface water into the Smolnik creek, the concentrations of Fe, Mn, Al, Cu, Zn are exceeded, too.

Based on laboratory results oriented to the selected metals precipitation from AMD Smolnik (Balintova and Petrilakova, 2011; Petrilakova and Balintova, 2011) and the data from literature, the redistribution of metals Cu, Fe, Mn, Zn and Al between water – sediment in the Smolnik creek was evaluated.
Precipitation of copper begins at pH > 4 and total precipitation occurs at pH 6 (Loska and Wiechula, 2000; Balintova and Kovalikova, 2008). In Figure 1 is presented dependence of immediate Cu concentration in surface water on its concentration in sediment in dependence of the pH. As it is seen in Figure 1, in spite the concentration of Cu in AMD, the decreasing of Cu concentration in surface water with the increasing of pH is connected with its increasing in sediment. This is in accordance with literary data and our results (Loska and Wiechula, 2000; Balintova and Kovalikova, 2008).

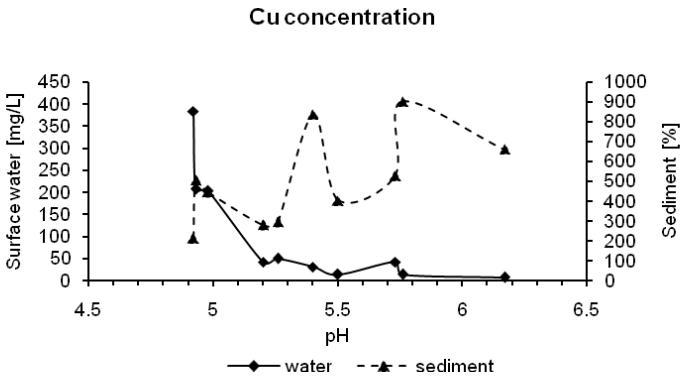

Figure 1: Influence of pH on Cu concentration in water and sediment in the Smolnik creek

It was determined (Balintova and Petrilakova, 2011) that iron is in AMD present mainly as Fe^{2+}, which should be precipitated at pH < 8.5 (Balintova et al., 2009; Xinchao et al., 2005; Gerringa, 1990). The reason of the iron precipitation across the range of studied pH may be progressive oxidation of Fe^{2+} to Fe^{3+} in the presence of oxygen and its precipitation in the form of $Fe(OH)_3$, which starts at pH 3.5 (Balintova and Petrilakova, 2011; Xinchao et al., 2005; Gerringa, 1990). From the study of the dependence of Fe concentration in water and sediment resulted, that Fe concentration in sediment varies in the slightly measure in comparison to its concentration in water (Figure 2).

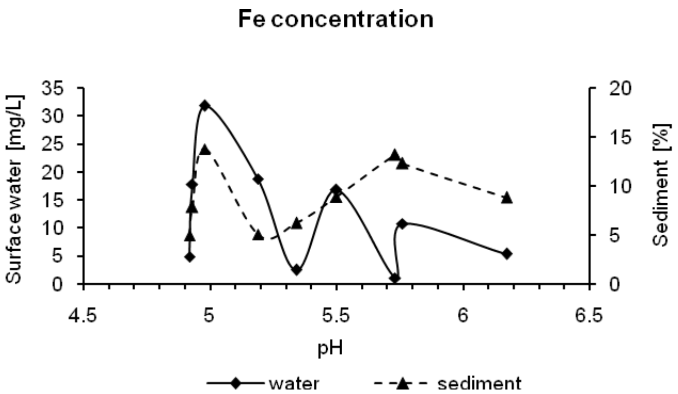

Figure 2: Influence of pH on Fe concentration in water and sediment in the Smolnik creek

The interaction among the metals can influence the reaction rate and oxidation state of the metals in the precipitate. For example, manganese will be simultaneously precipitated with iron (II) in water

solution at pH 8, only if the concentration of iron in the water is much greater than the manganese content (about 4 times more). If the concentration of iron in AMD is less than four times of the manganese content then the manganese can be removed from the solution at pH > 9 (Sheramata and Kuyucak, 1996).
The fact that in the presence of a large excess of iron the manganese is precipitated at pH 8 was not confirmed. At pH 8.2 was precipitated only 15.9 % of total Mn in AMD. Only at pH 11 was precipitated 92.96 % of Mn (Balintova and Petrilakova, 2011).
In the Figure 3 the dependence of the pH on Mn concentration in water and sediment is presented. As it results from Figure 3, the variation of Mn concentration in water has minimal influence on its concentration in sediment. The result is in accordance with literature and our research (Sheremata nad Kuyucak, 1996; Luptakova et al., 2007).

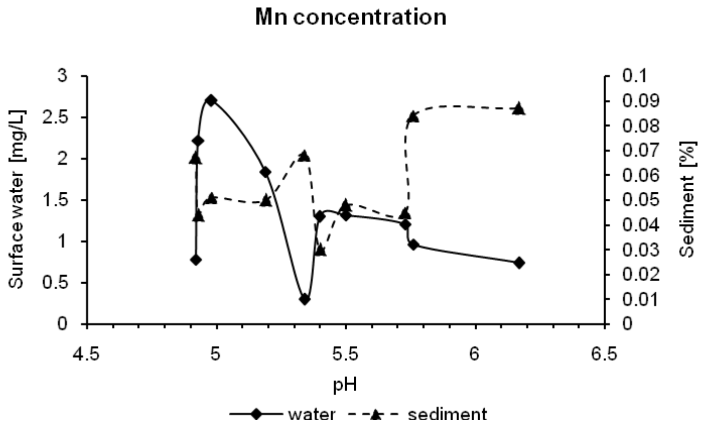

Figure 3: Influence of pH on Mn concentration in water and sediment in the Smolnik creek

According to Balintova et al. (2009), Xinchao et al. (2005) and Gerringa (1990) zinc is precipitated in the range of pH 5.5 to 7. In this interval was precipitated 84 % of total Zn (Balintova and Petrilakova, 2011). This effect was confirmed by rapid decreasing of Zn concentration in water and its simultaneous increasing in sediment at pH 5.76 (Figure 4).

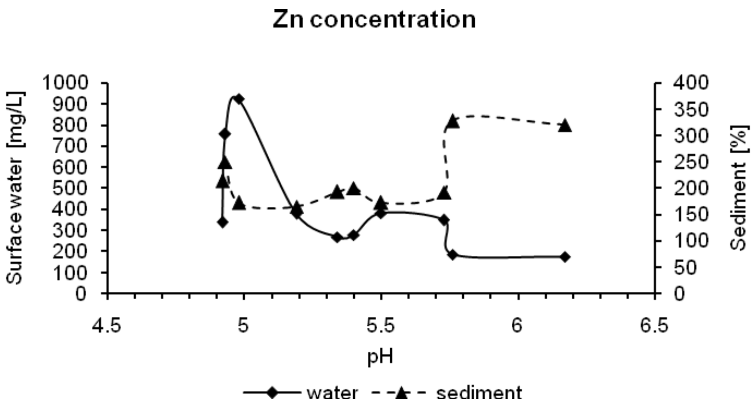

Figure 4: Influence of pH on Zn concentration in water and sediment in the Smolnik creek

Aluminium hydroxide usually precipitates at pH > 5.0 but again dissolves at pH 9.0 (Xinchao et al., 2005; Janke and Diebold, 1983). According to Balintova and Petrilakova (2011) 98.5 % of total aluminium is precipitated from AMD Smolnik in the pH range from 4 to 5.5. The similar tendency can be observed for aluminium, where at the pH> 5.0, the content of Al is decreasing in water and increases in sediment (Figure 5).

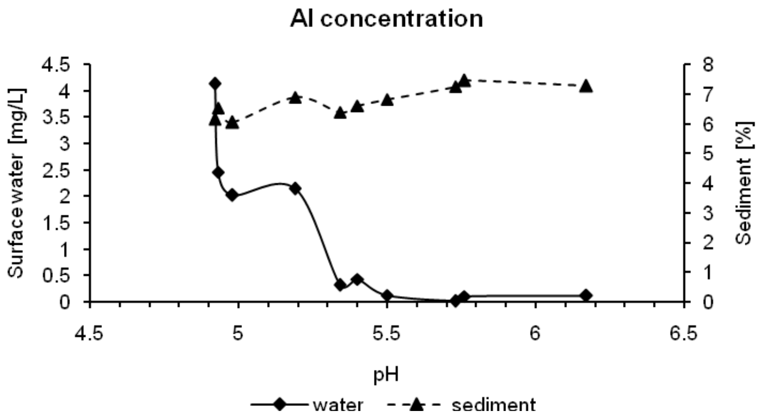

Figure 5: Influence of pH on Al concentration in water and sediment in the Smolnik creek

4. Conclusions

Smolnik deposit belongs to many localities in Slovakia, where the unfavourable influence of acid mine drainage on the surface water can be observed. Acid mine drainage discharged from abandoned mine Smolnik (shaft Pech) contaminates the downstream from the Smolnik mine works to confluence of the stream with the Hnilec river, because of decreasing pH and heavy metal production. This fact was confirmed by exceeding the limited values of followed physical and chemical parameters in water and sediments in Smolnik creek according to Slovak legislation.
The variability of pH also influences the sediment-water partitioning of heavy metals (e.g. Fe, Cu, Zn, Al, Mn) in Smolnik creek polluted by acid mine drainage, that has been confirmed by presented results. Because AMD generation at the Smolnik locality is not possible to stop and there is no chance of self-improvement of this area, it is necessary to accept this situation, monitor the quality of these waters and develop treatment methods.

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