CHEMICAL ENGINEERING TRANSACTIONS

VOL. 52, 2016

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Peng-Yen Liew, Jun-Yow Yong, Jiří Jaromír Klemeš, Hon Loong Lam

ISBN 978-88-95608-42-6; **ISSN** 2283-9216

DOI: 10.3303/CET1652157

Sediment Influenced by Acid Mine Drainage in the Smolnik Creek – Qualitative and Quantitative Characterization

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Water and sediment quality monitoring has one of the highest priorities in environmental protection policy. Heavy metals entering into the river can be from natural or anthropogenic sources. Main anthropogenic sources of heavy metal contamination are mining, disposal of untreated and partially treated effluents contain toxic metals, as well as metal chelates from different industries. In Slovak Republic there are some localities with existing acid mine drainage (AMD) generation conditions. The most critical values were observed in the abandoned deposit Smolnik. Waters from the earth surface penetrated the mine and they are enriched with metals and their pH values decreased.
The paper presents comparison of results of quantitative XRF analysis of sediments from the Smolnik creek sampled in uncontaminated part of creek and in the part influenced by AMD. The characterisation of sediments by statistical analysis are presented, too

1. Introduction

The contamination of aquatic and terrestrial ecosystems with heavy metals and other mining chemicals have been major environmental problems in many mining areas of the world. Industrial wastes, geochemical structure and metals mining form a potential source of metal contaminants in the aquatic environment especially in sediment. Pollution of the natural environment by heavy metals is a universal problem because of their undegradability. When permissible concentration levels are exceeded, most of them have toxic effects on the living organisms. Monitoring sediment quality is one of the highest priorities in environmental protection policies. The main objective is to control and minimise the incidence of pollutant – oriented problems, and to provide water of sufficient quality in order to serve various purposes such as irrigation (Singovszka and Balintova, 2014). In Slovak republic there are some localities with existing AMD generation conditions. The most critical values were observed also in the abandoned deposit Smolnik (Petrilakova and Balintova, 2011). Overflowed mine Smolnik produces AMD with high metal concentrations and low value of the pH (about 3-4) as a result of chemical oxidation of sulphides and other chemical processes. This was the reason for starting a systematic monitoring of geochemical development in acid mine drainage in order to prepare a prognosis in terms of environmental risk and use of these sediment as an atypical source of a wide range of elements (Slesarova et al., 2007). For better knowledge about migration, transformation behaviour and rules of heavy metals in sediment, it is necessary to make an accurate assessment of contamination level and extent at each site.
The distribution of various binding fractions of heavy metals may be influenced by many factors (pH, redox potential, ionic strength, chemical and biological redox reactions, and complexation reactions) (Gunn et al., 1988). Macias-Zamora et al. (1999) showed that the Fe_2O_3 content correlates well with the concentrations of various heavy metals (Ni, V, Cu, Zn, Cr, Cd, Pb, and Mn) in the sediments of the Campeche shelf, Gulf of Mexico and, thus, iron can be used as a normalizing agent. In addition, the oxidizable phase is extremely important in regulating the binding behavior of heavy metals and their bioavailability or toxicity. Unfortunately, the correlations between heavy metals in the sediment matrices have seldom been explored on a quantitative basis (Yu et al., 2001).

Please cite this article as: Singovszka E., Balintova M., Demcak S., 2016, Sediment influenced by acid mine drainage in the smolnik creek – qualitative and quantitative characterization, Chemical Engineering Transactions, 52, 937-942 DOI:10.3303/CET1652157

Paper deals with comparison of results of quantitative XRF analysis of sediments from the Smolnik creek and with the dependencies between increasing and decreasing concentration of heavy metals by correlation matrix.

2. Materials and methods

Sediment sampling sites are located at 48° south latitude and 20° east longitude (Figure 1). Two localities were in the upper part of the Smolnik creek without contamination by acid mine waters from shaft Pech (1 – outside the Smolnik village, 2 - small bridge - crossing to the shaft Pech) and another two sampling localities were located under the shaft (4 - 200 m under the shaft Pech, 5 – inflow into the Hnilec river). The outflow of AMD and sediment from shaft Pech (Smolnik mine) has number 3. Water samples and sediments were collected in 2006 - 2015.

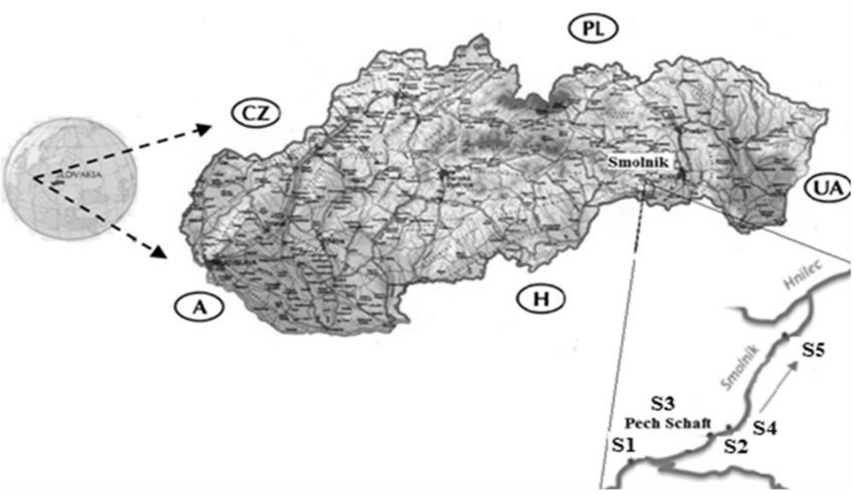

Figure 1: Sediment samplings of Smolnik Creek

The chosen physical and chemical parameters were determined by multifunctional equipment METTLER TOLEDO in situ and chemical analyses of water samples were realized by AAS (SpectrAA-30, Varian), Samples of sediment were taken off from the Smolnik creek at the places showed in Figure 1. The sediment was dried, homogenized and sieved bellow 0.063 mm. Chemical analyses were realized by the XRF and the functional groups were determined using IR method.
The sediment samples were prepared as pressed tablets with diameter of 32 mm by mixing of 5 g of sediment and 1 g of dilution material (M-HWC) and pressed at pressure of 0.1 MPa/m^2. The prepared tablets were studied by X-ray fluorescence spectrometry. The chemical composition of sediments was determined by using SPECTRO iQ II (Ametek, Germany). For infra-red spectroscopy in this study, was used spectrum through 4,000 cm^{-1} to 600 cm^{-1} (Alpha FT-IR Spectrometer, BRUKER OPTICS).
The crystal structure of sediments was identified with diffractometer Bruker D2 Phaser (Bruker AXS, GmbH, Germany) in Bragg-Brentano geometry (configuration Theta-2Theta), using the 1.54060 Å CuKα radiation, Ni Kβ filters and scintillation detector at a voltage of 30 kV and 10 mA current. Scan conditions were identical for all samples, recording times about 5 h, a step size of 0.05° (2Θ) and step time of 15 s. The XRD patterns were processed using the software Diffrac.EVA v. 2.1. The ICDD PDF database (ICDD PDF – 2 Release 2009) was utilized for the phase identification.
Impact of addiction and change the concentrations of heavy metals in sediments were compared by Pearson's correlation matrix at the 0.01 significance level.

3. Result and discussion

The influence of AMD from shaft Pech (sample 3) on the sediment quality in the Smolnik creek is presented in Table 1. The results were compared to the limit values according to the Slovak Act No. 188/2003 Coll. of Laws on the application of treated sludge and bottom sediments to fields. Based on the results in Table 1 we can state that acid mine drainage flowing from the shaft Pech has an adverse effect on the sediment quality in Smolnik creek and causes exceeding of the limit values. From the analyses of sediments quality in the Smolnik creek (Table 1) oriented towards the influence of AMD on sulfate and heavy metals concentration;

and from the comparison of uninfluenced samples by AMD (S1 and S2) and influenced (S4 and S5), it can be stated that the differences are not so evident exceed As, Cd and Pb. The concentrations of As in all samples transcended the standard values 2 – 10 times.

Table 1 Average concentration of heavy metals in sediment from sample sites of Smolnik Creek

		SO_4^{2-}	Ca	Mg	Fe	Mn	Al	Cu	Zn	As	Cd	Pb
		%						mg/kg				
1	Average	0.03	0.29	0.785	4.16	0.09	7.38	132.5	150.60	**44.50**	0.50	43.50
	Min	0.01	0.19	0.68	3.40	0.04	6.32	78.00	113.00	**27.00**	0.50	28.00
	Max	0.07	0.45	0.93	4.92	0.12	8.14	199.00	184.00	**66.00**	0.50	61.00
	St.Dev	0.03	0.08	0.08	0.53	0.03	0.62	44.09	26.01	13.18	0.00	10.99
2	Average	0.39	0.39	0.67	5.05	0.45	6.15	266.23	180.50	**82.30**	4.85	91.35
	Min	0.1	0.14	0.05	0.66	0.04	0.04	6.31	131.00	**56.00**	0.50	0.50
	Max	1.00	1.90	0.81	7.27	4.03	7.32	467.00	273.00	**111.00**	**44.00**	147.00
	St.Dev	0.29	0.53	0.22	1.86	1.26	2.18	131.18	42.52	17.26	13.76	42.97
3	Average	12.05	0.942	0.50	34.36	0.02	2.19	482.40	119.30	**2,137.90**	1.15	679.40
	Min	7.83	0.03	0.50	23.60	0.01	0.46	143.00	45.00	**909.00**	0.50	38.00
	Max	19.08	8.73	1.38	39.70	0.09	4.65	756.00	313.00	**3,617.00**	7.00	**2,731.00**
	St.Dev	3.24	2.74	0.40	5.51	0.03	1.37	201.59	82.13	743.33	2.06	872.19
4	Average	0.81	0.28	0.74	7.95	0.06	6.43	404.10	196.80	**142.20**	0.50	170.90
	Min	0.10	0.19	0.61	3.63	0.04	5.67	113.00	90.00	**46.00**	0.50	52.00
	Max	2.42	0.57	0.89	13.8	0.08	6.91	903.00	328.00	**253.00**	0.50	328.00
	St.Dev	0.70	31.85	0.09	3.64	0.01	0.37	226.45	65.21	73.29	0.00	87.44
5	Average	0.78	0.23	0.67	9.78	0.06	6.23	519.20	240.30	**97.80**	0.50	110.90
	Min	0.09	0.08	0.27	4.42	0.03	2.62	241.00	192.00	**51.00**	0.50	15.00
	Max	4.90	0.32	0.84	31.7	0.09	7.26	836.00	323.00	**146.00**	0.50	176.00
	St.Dev	31.73	0.09	0.18	8.07	0.02	1.31	158.32	49.76	26.66	0.00	44.65
	Limits	**-**	**-**	**-**	**-**	**-**	**-**	**1,000**	**2,500**	**20**	**10**	**750**

The infrared spectrum of sample S3 confirmed presence of schwertmannite which is dominated by a broad, OH-stretching band centred at 3,100 cm^{-1} (Figure 2). Another prominent absorption feature related to H_2O deformation is expressed at 1,634 cm^{-1}. Intense bands at 1,124, and 1,038 cm^{-1} reflect a strong splitting of the $\upsilon_3(SO_4)$ fundamental due to the formation of a bidentate bridging complex between SO_4 and Fe. This complex may result from the replacement of OH groups by SO4 at the mineral surface through ligand exchange or by the formation of linkages within the structure during nucleation and subsequent growth of the crystal. Related features due to the presence of structural SO_4 include bands at 981 and 602 cm^{-1} that can be assigned to υ_1 (SO_4) and υ_4 (SO_4), respectively. Vibrations at 753 and 424 cm^{-1} are attributed to Fe-O stretch; however, assignment of the former is tentative because similar bands in the iron oxyhydroxides usually occur at lower frequencies. A broad absorption shoulder in the 800 to 880 cm^{-1} range is apparent in some specimens and is related to OH deformation (δ (OH)) (Pacakova et al., 2002). This results are in accordance with work where was determined the presence of $Fe_{16}O_{16}(SO_4)_3(OH)_{10}.10H_2O$ by XRD method in sediment from AMD Smolnik. FTIR spectra of all homogenized sediment samples (S2 and S4) showed similar features. IR spectrum (Figure 3) it can be said that the main part of compounds are silicates including quartz (982, 825, 753, 695, 518 cm^{-1}), but hydroxides (3,600 - 3,650 cm^{-1}; 1,652 cm^{-1}) are present, too. The sample S4 has a bigger portion of hydroxides than sample 2. It is influenced by the metal concentration in surface water influenced by AMD.

The XRD patterns of sediments (S2, S3, S4) are shown together in Fig. 4. The spectra of S2 and S4 sediments are almost identical and contain the phases: Q – quartz SiO_2 (PDF 01 – 075 – 8322), M – muscovite 2M1, ferrian K Al1.65 Fe0.35 Mn0.02 (Al0.7 Si3.3 O10) (OH)1.78 F0.22 (PDF 01 – 073 – 9857), and C – clinochlore 1MIIb, ferroan (Mg, Fe)6 (Si, Al)4O10 (OH)8 (PDF 00 – 029 – 0701). The most dominant component is quartz with 6 broad peaks (the strongest line at 26.623° 2Θ). The spectrum of sediment S3 points to a small part of crystalline phase, it contains only three weak peaks of clinochlore and one peak of quartz. According to the literature (Lintnerova, 1996), AMD precipitates from shaft Pech contains minerals such as ferrihydrite, goethite, jarosite or schwertmannite. Fresh precipitates are weakly crystallized, formed crystals are very small (tens to hundreds of nm), which is typical for all studied precipitates. Due to their weak crystallinity, it is hard to identify only by X-ray diffractometry (XRD) (Bigham, 1994), what is evident from XRD pattern of sample S3. Just by a combination of XRD, Mössbauer- and Infrared – spectroscopy a characterization of their structure is possible.

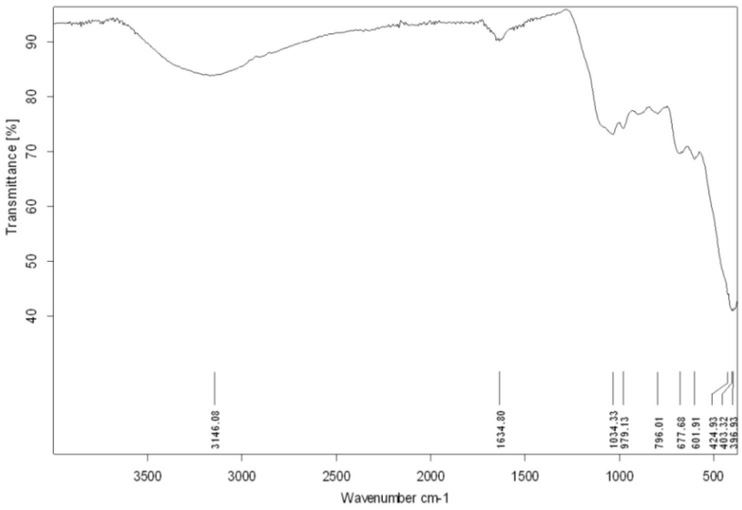

Figure 2: FTIR spectrum of sediment S3

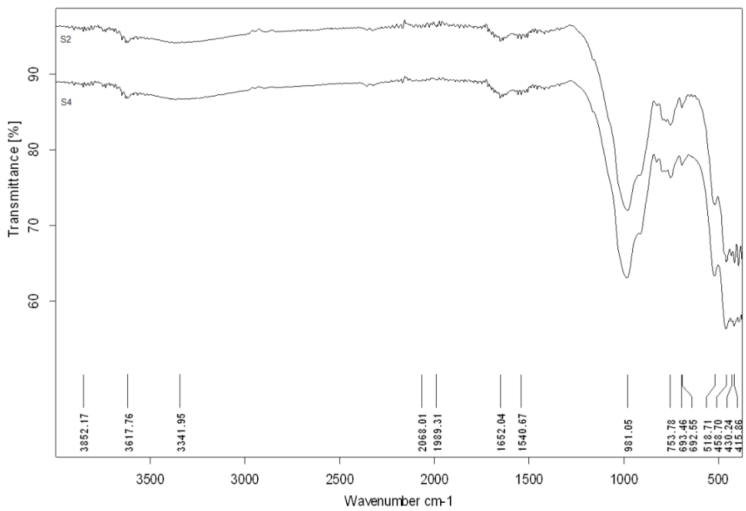

Figure 3: FTIR spectrum of sediments S2 and S4

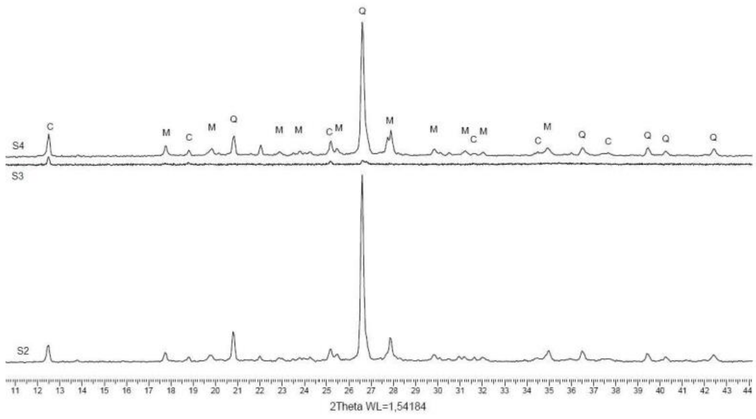

Figure 4: XRD patterns of sediments S2, S3, S4 (Identified compounds: Q – quartz; M – muscovite 2M1, ferrian; C – clinochlore1MIIb, ferroan)

Table 3 shows the correlation matrix of the heavy metals in sediments from the Smolnik creek. The positive correlation coefficient between As and Fe was 0.89, and Cd and Mn was 0.99, which indicates a strong linear correlation at the 0.01 significance level and a common origin of these metals. The correlation curve is Cd = 0.03552 + 10.869xMn. Al exhibited strong negative correlations with both Fe (-0.80) and As (-0.71). Al, Mg, Fe As, Cd and Mn occur in AMD which explains their apparent correlation in the sediments. Zn and Pb are also is contained in sediments, and their correlations with Mg (0.62) and As (0.62) indicate that its occurrence in the sediments was mainly due to contamination by AMD. The lack of significant linear correlation between other heavy metals suggests that concentration in sediments is not depending on their amount.

Table 3: Pearson's corelation matrix of heavy metals in sediments from years 2006-2015

Metal	Ca	Mg	Fe	Mn	Al	Cu	Zn	As	Cd	Pb
Ca	1.00									
Mg	0.39	1.00								
Fe	0.06	-0.49	1.00							
Mn	0.18	-0.37	-0.18	1.00						
Al	-0.25	0.66	-0.80	-0.36	1.00					
Cu	0.00	0.02	0.47	-0.26	-0.22	1.00				
Zn	0.32	0.62	-0.36	-0.08	0.39	0.51	1.00			
As	0.02	-0.37	0.89	-0.10	-0.71	0.38	-0.41	1.00		
Cd	0.16	-0.45	-0.10	0.99	-0.43	-0.24	-0.14	-0.01	1.00	
Pb	-0.07	0.06	0.41	-0.09	-0.21	0.45	-0.05	0.62	-0.07	1.00

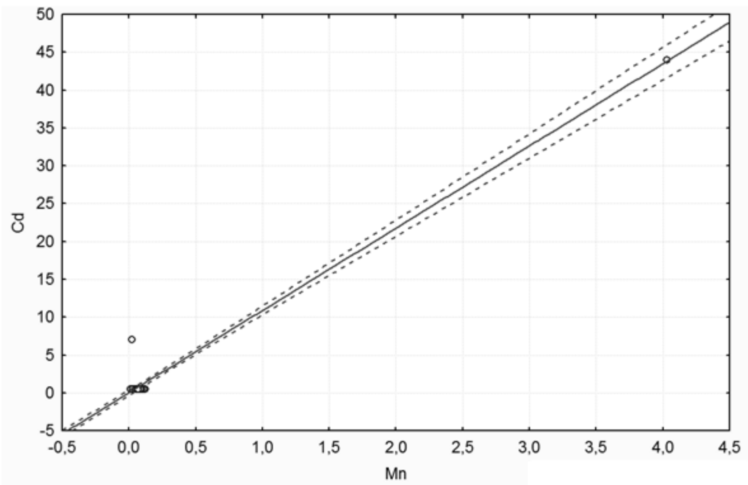

Figure 4: The correlation dependence of Cd and Mn (95% confidence level)

4. Conclusions

The sediment quality influenced by AMD was evaluated using XRF, FTIR and XRD methods. Then was survey the impact of addiction and change the concentrations of heavy metals in sediment. In the sediments were found the inorganic compounds, mainly hydroxides, sulfates mainly in a form schwermannite in sediment influenced only AMD from shaft Smolnik. The sulfates in the sediments from surface water of the Smolnik creek were not confirmed. It can be suggested, that sulfates are changed into the soluble form due to dilution of AMD in surface water. It follows from our experiments that acid mine drainage has bigger impact on the surface water quality than on the sediment quality.

The value of heavy metals concentrations in sediments were compared by Pearson's correlation matrix at the 0.01 significance level. It is evident, that highest positive correlations were between Cd – Mn and As – Fe.

Acknowledgments

This work has been supported by the Slovak Grant Agency for Science (Grant No. 1/0563/15).

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