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Monitoring of the abandoned mine Smolnik (Slovakia) influence on the aquatic environment

S Demcak[1], M Balintova[1] and M Holub[1]

[1] Technical University of Kosice, Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoskolska 4, Kosice, 042 00, Slovak Republic

Abstract. The Slovak Republic has a rich mining history. Despite of the decrease of mine activities in Slovak regions, there are still the abandoned sites that can cause environmental risks due to a generation of the acid mine drainages. These waters contain many toxic pollutants, mainly heavy metals and sulphates, which have negative impact on the environment. The paper deals with a study of the influence of the abandoned mine Smolnik (Slovakia) on the aquatic environment. The chemical analyses of waters reveal negative impact on the Smolnik creek after the contamination by acid mine drainages mainly sulphates and heavy metals as iron, manganese, aluminium, copper, and zinc.

1. Introduction

The mining and processing of the minerals, e.g. copper, iron, gold and nickel, is connected with the formation of different types of waste. These, such as acid mine drainage (AMD), cause long-term degradation of waterways and negatively affects the biodiversity. Furthermore, some of these mining effluents exhibit low pH values and very high concentration of toxic substances, such as heavy metals, sulphates or cyanides, which have serious human health and ecological impacts [1, 2].

Formation of AMD is caused by the oxidation of sulphide containing minerals. During this process water, atmospheric oxygen, micro minerals and aerobic bacteria should be present [3, 4]. As mentioned before AMD are characterized by acidic range of pH value and the high concentrations of heavy metals (Cu, Cd, Zn, Mn, As, Ni, Al, Pb, Cr, Ag, Hg, and Fe) and sulphates. High levels of AMD cause acidification and metal contamination of large areas of land, water and damage the health of wildlife. Importantly, the formation of AMD can remain for hundreds of years, till the deposit is still active (contains sulphide ores) and control is almost impossible from technological and also economical point of view [5, 6]. Results from the above mentioned facts, it is urgent to develop novel approaches for the efficient monitoring and control of AMD production which can minimise its negative impacts.

The territory of Slovakia is bound with the historic mining centres in the Western Europe. Therefore, in Slovakia are many mines sites producing AMD, such as abandoned mines in Smolnik, Poproč, Čučma, Pezinok, landfill of mining waste in Šobov and many others [7]. The processes that cause the production of AMD are an environmental threat in the long term. Therefore, it is necessary to regularly monitor and look for methods of their processing in order to valorise them as potential sources of minerals and chemical compounds for commercial use.

In this study the influence of the abandoned mine Smolnik (Slovakia) on the aquatic environment were investigated. In 2006–2017, surface waters in the Smolnik brook were analysed before and after AMD contamination. The concentrations of sulphates and heavy metals exceeded the limits in the effluent AMD. After mixing AMD and surface water, the limits for Fe, Mn, Al, Cu, and Zn were still exceeded. During 12 years lasting monitoring of Smolnik locality we can observe decreasing trends in the concentrations of contaminants.

2. Material and methods

2.1. History of Smolnik mine

The abandoned mine Smolnik (in the village Smolnicka Huta) is one of the medieval historically most important and richest deposit of pyrite and chalcopyrite ores in Slovakia [8]. In addition to ore mining, the copper was extracted on site by cementation techniques. In 1990 the mining activity was terminated and the mine was flooded. Five years later there was an environmental disaster in which the fish died in the Smolnik creek. Even today, there are negative impacts on the environment. The mine underground complex represents a partially open geochemical system into which rainwater and surface water directly flow. More than 6 million tons of pyrite and chalcopyrite ores are exposed to physico-chemical and biochemical factors that result in the formation of AMD [7, 9, 10].
According to the results of the chemical analysis and the flow rate of AMD (5-30 l/s; depending on the hydrogeological conditions) it can be assumed that approximately 280 t S, 90 t Fe, 22 t Al, 7 t Mn, 2.5 t Zn, 370 kg Cu is leached every year from the deposit [11]. Due to large quantities of pyrite remain in the flooded mine and in the surrounding rock complexes, this process is expected to continue to contaminate the territory in the long term [12, 13]. The AMD from the flooded underground mine flows to the surface by the shaft Pech without any pre-treatment and consequently is mixing with water in the Smolnik Creek (Figure 1) [14].

Figure 1. The shaft Pech effluent into the Smolnik Creek.

2.2. Characterisation of sampling sites

Water from the Smolnik creek was periodically sampled from 2006 to 2017. The water sampling sites are shown in Figure 2. The sampling sites 1 and 2 are situated in the upper part of the Smolnik creek as a background spots not contaminated by AMD. The outflow of AMD from the Pech shaft (Smolnik mine) signed as the site number 3. The sampling localities 4 and 5 are located under the shaft. Samples were collected once a year in the triplicate sampling from each sample sites.
Samples were collected according to ISO 5667-6-2005 "Water quality-Sampling-Part 6: Guidance on sampling of rivers and streams" [15]. The concentrations of heavy metals in the water samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Varian Vista, MPX, Australia). The concentration of sulphates was determined by colorimetric method by Colorimeter DR 890 (Hach, USA). The pH values were measured by pH meter inoLab pH 730 (WTW, Germany) directly in-situ. The results of the chemical analyses of the water samples ($(SO)_4^{2-}$, Ca, Mg, Fe, Mn, Al, Cu, Zn, As, Cd, and Pb) were compared with the allowed limit values according

to Regulation of the Government of the Slovak Republic no. 269/2010, which lays down the requirements for achieving good condition of waters [16].

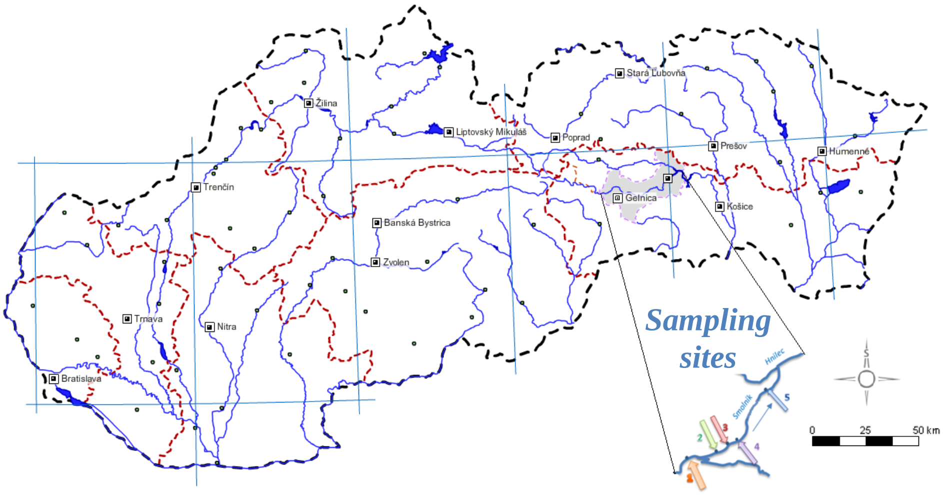

Figure 2. The location of water sampling sites in the river network of Slovakia.

3. Results and discussion

The mean values of the total concentration of metals, sulphates, and pH values in the surface water (sampling sites 1, 2, 4 and 5 - Smolnik Creek; 3 - AMD outflow from the shaft Pech) over 12 years are shown in Table1. From the results compared with the limits allowed in the surface waters (according to Regulation of the Government of the Slovak Republic no. 269/2010), it can be seen that AMD effluents of the shaft Pech has a permanent negative effect on the surface water quality in the Smolnik Creek. All monitored pollutants have exceeded the limits. The high level of contamination is also reflected in the low pH values of AMD discharges from the shaft Pech that are reflected into the lower pH values in the Smolnik Creek after contamination (sampling sites 4 and 5). The authors [17] report that the optimal pH values in the Smolnik Creek after the contact with AMD was only observed at the time of elevated water level (e.g. in years 2011-2014). The chemical analysis of AMD (sampling site 3) shows that all monitored parameters had the exceed limits. After the dilution of AMD with surface water in the Smolnik Creek, the increased concentrations of sulphates, iron, manganese, aluminium, copper and zinc were revealed.

Table 1. The results of chemical analysis of water in 2006 - 2017 - Smolnik Creek and shaft Pech.

Parameters		**Sampling site**					**Limits**
		1	**2**	**3**	**4**	**5**	
$(\mathbf{SO})_4^{2-}$	[mg/l]	13.7 ± 1.2	35.6 ± 38.7	**2902.0 ± 790.0**	129.9 ± 81.6	115.5 ± 62.9	**250.0**
Ca	[mg/l]	9.99 ± 1.34	12.1 ± 2.0	**158.1 ± 19.1**	20.6 ± 5.9	20.0 ± 5.9	**100.0**
Mg	[mg/l]	3.54 ± 0.28	4.74 ± 1.30	**249.6 ± 51.8**	15.9 ± 7.9	23.4 ± 31.8	**200.0**
Fe	[mg/l]	0.12 ± 0.19	0.83 ± 0.88	**322.70 ± 87.60**	**12.7 ± 8.9**	**5.46 ± 5.64**	**2.00**
Mn	[mg/l]	0.01 ± 0.01	0.12 ± 0.11	**25.30 ± 6.30**	**1.17 ± 0.74**	**0.91 ± 0.62**	**0.30**
Al	[mg/l]	0.03 ± 0.03	0.15 ± 0.21	**65.1 ± 19.4**	**1.17 ± 1.60**	**0.35 ± 0.72**	**0.20**
Cu	[µg/l]	4.09 ± 4.35	12.6 ± 7.5	**1512.0 ± 736.0**	**96.9 ± 116.1**	**43.0 ± 63.8**	**20.0**
Zn	[µg/l]	4.27 ± 1.35	40.6 ± 42.7	**7234.0 ± 2269.0**	**348.8 ± 250.1**	**254.3 ± 213.6**	**100.0**
As	[µg/l]	1.73 ± 1.27	1.36 ± 0.92	**37.40 ± 18.70**	1.55 ± 1.04	1.18 ± 0.60	**20.00**
Cd	[µg/l]	< 0.30	0.31 ± 0.03	**12.20 ± 8.80**	0.73 ± 0.58	0.41 ± 0.24	**1.50**
Pb	[µg/l]	< 5.00	< 5.00	**50.20 ± 16.90**	5.27 ± 0.91	< 5.00	**20.0**
pH		6.3 ± 0.8	6.4 ± 0.9	**4.0 ± 0.1**	5.8 ± 1.1	6.1 ± 1.1	**6.0 - 8.5**

Based on the results from the Table 1, the heavy metals contamination by iron, manganese, aluminium, copper, and zinc of the Smolnik creek was revealed. From this reason was detailed study the change of the concentrations of these elements in AMD during of the period years 2006-2017 (Figure 3). The monitored concentrations of heavy metals are affected by hydrogeological conditions [6]. As is clearly from the Figure 3, Fe, Mn, Al, Cu, and Zn concentrations oscillate irregularly. In addition, iron, manganese, aluminium, and zinc during 12 years reduced the concentration of almost half in the outflowing AMD. The concentrations of copper were deceased almost 5 times but the limits were still exceed for the surface water.

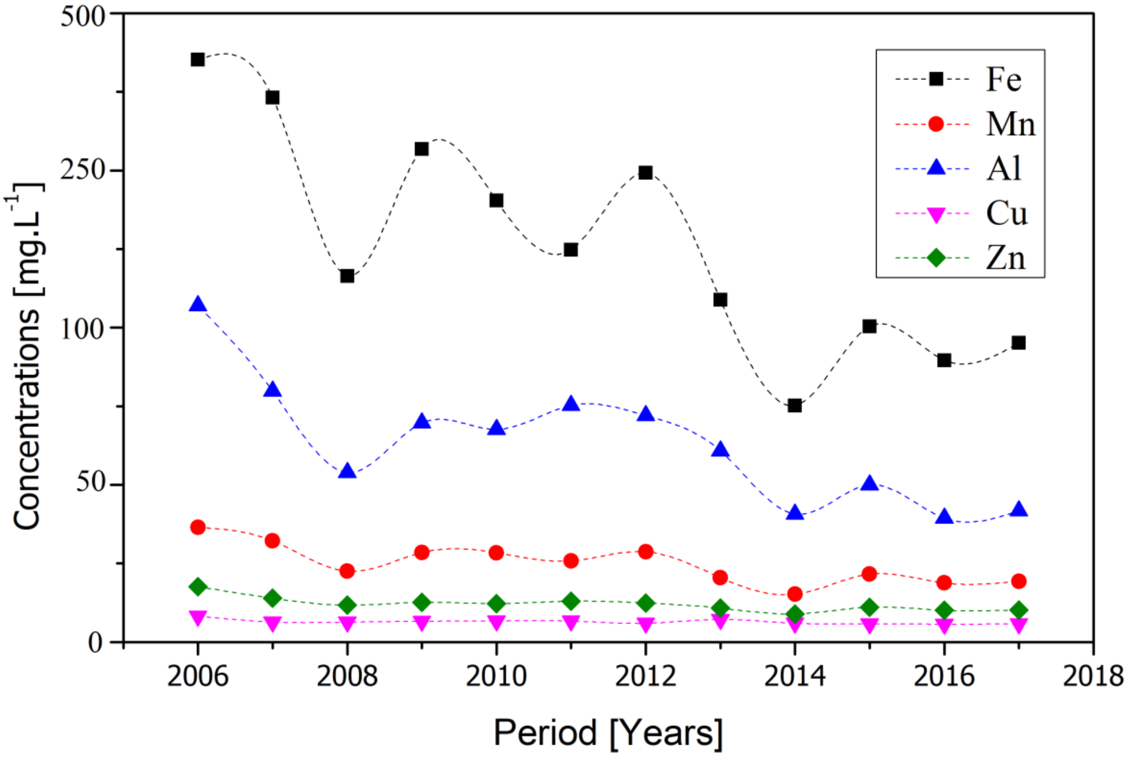

Figure 3. The change of selected heavy metals concentrations from AMD in 2006 - 2017.

4. Conclusion

The formation of AMD can take place either naturally or by anthropogenic activities. Naturally as a part of the rock weathering process, whereas anthropogenic activities such as mining activities bring effluents and artificially introduce the sulphates and heavy metals into the ecosystems. Therefore, necessary monitoring is mandatory of the contaminant concentrations of the effluents released to the environment.

Despite the decrease of the heavy metals concentrations in AMD for 12 years it still needs to monitor the locality of an abandoned mine Smolnik, because heavy metal concentrations still exceed the limits. Therefore, it is necessary to find a sustainable solution not only for this site but also for many similar people around the world.

Acknowledgments

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