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Chapter 2

AN OVERVIEW OF OCCURRENCE AND EVOLUTION OF ACID MINE DRAINAGE IN THE SLOVAK REPUBLIC

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Abstract: Acid mine drainage (AMD) is one of the worst environmental problems associated with mining activity. Both at the beginning and in the middle of the 20th C., the attenuation of mining activity in the Slovak Republic gave rise to the extensive closing of deposits using wet conservation i.e. flooding. The negative results of AMD activity can be observed mainly at those locations where sulphide ores and raw materials containing sulphides were mined. At the deposits in Roznava, Pezinok and Rudnany, the surrounding carbonate system partly buffers the AMD evolution. During the last decade various remediation methods were applied at the Sobov location aimed at reducing the environmental impact of AMD but without marked success. From the point of occurrence and generation of AMD, the deposits at Smolnik represent the classic example. The whole area of deposit is markedly affected by AMD activity. The mine waters have pH 3.8, high concentrations of sulphates, Fe, Mn, Cu, Zn, Al, and discharge straight into the Smolnik river. In order to propose an effective and economic method for the prevention of the negative influence of AMD at this location, it was necessary to understand the reasons for changes in the evolution of the mine water composition and provide a real estimation of their long-time evolution. The article presents the results of the monitoring of AMD quality at Smolnik from 1986 to 2005. In order to better understand the processes obtaining at the site, a geochemical modeling of AMD quality evolution during its gradual ascent to the surface was created.

Key words: Acid mine drainage; monitoring; trends; geochemical modeling.

1. INTRODUCTION

The drainage of acidic, high-mineralized mining water known as Acid Mine Drainage causes some of the most negative effects of mining activity. Acid mine drainage (AMD) is the term use to describe the drainage that occurs as a result of the natural oxidation of sulphide minerals contained in rocks when exposed to the combined action of water and atmospheric oxygen. The common sources of AMD are underground or open-pit mining works, mining waste rock or overburden dumps, processing tailings, and temporary or permanent heaps of sulphidic concentrates, notably pyrites. These sources may remain active for decades or even centuries after mine closure. Generation of AMD is observed in almost by all kinds of deposits with sulphide content. It is particularly related to coal, lignite and polymetallic sulphide mining. AMD solutions usually have a characteristic brown-red color attributed to the increased contents of Fe³⁺, and negatively impact the surrounding environment (Kontopoulos, 1998).

The main reason of AMD generation is the oxidation of sulphide minerals, especially pyrite (FeS₂). Normally, pyrite is a stable, insoluble mineral as long as it does not come into the contact with air and water. However, as a result of mining, it becomes exposed and is partially solubilized. The chemical oxidation of pyrite is expressed as (Postgase, 1959; Karavajko et al., 1972; Kontopoulos, 1998):
2FeS₂ (s) + 7O₂ (aq) + 2H₂O → 2Fe²⁺ + 4H⁺ + 4SO₄²⁻  \hspace{1cm} (1)

One of the important factors with regard to sulphide oxidation is the activity of bacteria. *In situ* oxidation processes of sulphides at the deposits of sulphide minerals are generally catalyzed by activity of autochthonous sulfur and iron oxidizing bacteria, e.g. *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, or *Leptospirillum ferrooxidans* (Kusnierova and Fecko, 2001).

Through the oxidation of pyrite or other sulphide minerals, the concentrations of Fe and elements such as Mn, Ni, Zn, Al, Cu, Co, As, Pb, etc. increase in AMD. Another result of pyrite oxidation is the increase of sulphate concentrations, which results in increasing mineralization and decreasing pH. In consequence AMD negatively affects the whole ecology of environment in the vicinity of mining plants. Where AMD is well-developed and extensive, the costs of remediation can be very high (Bethke, 1996; Younger et al., 2002).

Mining activity has in the Slovak Republic is a long-standing tradition. At the beginning and in the middle of the 20th C., the attenuation of mining activity gave rise to extensive closing of deposits using wet conservation i.e. flooding. Thereby were formed the suitable conditions for generation of AMD. The negative results of AMD influence can be observed mainly at locations such as Smolnik, Sobov, Hodrusa, Pezinok, Rudnany, Roznava, Slovinky where sulphide ores and raw materials containing sulphides have been mined.

### 2. MATERIALS AND METHODS

Water samples for chemical analyses of anions and cations were collected and filtered with 0.45 μm cellulose membrane filters, stored in 1.5 l-polyethylene bottles and acidified down to pH < 2 with concentrate HNO₃. Field parameters such as pH, Eh and temperature of the water samples were measured *in situ*. Cations were analyzed by atomic absorption spectrometry (AAS). Anions were analyzed by ion chromatography (IC). TDS were determined by gravimetric analysis.

The Geochemist’s Workbench® (Rockware, Inc., Golden, CO, USA) (Bethke, 1996; Bethke, 2004) was used for geochemical modeling. It is a set of interactive software tools for solving problems in aqueous geochemistry, including those encountered in environmental protection and remediation, the petroleum industry, and economic geology.

### 3. ACID MINE DRAINAGE IN THE SLOVAK REPUBLIC

The locations where AMD influence is very marked, or where there is a high assumption of AMD intensive generation, are as follows: Pezinok, Rudnany, Roznava, Sobov, and Smolnik (Fig. 1).

Pezinok deposit (Figure 1) is situated in Male Karpata Mts. It is the locality with Sb-Au mineralization and main minerals: antimony, berthierite, kermisite, pyrite, arzenopyrite, quartz, and carbonates (Rojkovic, 2003). In 2004, draining mine waters had pH within the limits 4 – 6 and contained increased concentrations of Fe and sulphates (Table 1) (Grant No. 2/2106/22). Considering the polymetallic mineralization of deposit, it is assumed that oxidation of sulphidic material is constantly ongoing and probably a largely presented carbonate system buffers the generating acidity.
Rudnany (Figure 1) is situated in the Ore Mountains. It is the locality with siderite-baryte mineralization and represents one of the largest accumulations of siderite having a significant share of baryte and sulphide ores (tetrahedrite, chalcopyrite, pyrite and mercury sulphide) in the Slovak Republic (Rojkovic, 2003). In 2004, an increased content of sulphates was observed. (Table 1) (Grant No. 2/2106/22). Considering the deposit mineralization, the oxidation processes of sulphides were considerably buffered through the surrounding carbonate system until now. Currently, the deposit is partially flooded. It will be interesting to observe and study the water quality in terms of Fe, Hg and other heavy metals concentrations when flooding is complete.

Roznava (Figure 1) represents a significant source of AMD. It is situated in Ore Mountains. Main minerals are: siderite, quartz, pyrite, tetrahedrite, and chalcopyrite (Rojkovic, 2003). Since the beginning of 2006, significant seepages of mine waters with pH 2.8 and increased concentrations of sulphates and Fe have been observed at this location. Despite of low concentrations of the other monitored species and the neutralization capacity of carbonate system, it is obvious that the process of AMD generation is intensive (Table 1).

Sobov (Figure 1) which is situated close to the city of Banska Stiavnica, represents a much endangered area. It is a quartzite open-pit mine where pyrite occurs as unusable raw material in clay material and is then deposited at the pile. Very acidic water of deep purple color with pH 2 and high concentrations of Fe, Zn, Cu, and As drains from below the pile (Table 1) (Grant No. 2/2106/22). Draining AMD water from the open pit mine and pile is diverted into the basin from where the water is discharged into the abandoned mines. Various remediation and restoration methods, such as a pilot project of wetland systems aimed at reducing the environmental impact of AMD, were applied at the site without marked success (Sottnik and Sucha, 2001).

The influence of AMD is the most visible at the Smolnik location (Figure 1). The Smolnik deposit is one of the best known, richest Cu-Fe ore deposits in the Slovak Republic. It is situated in Ore Mountains. The main minerals of the deposit are pyrite and chalcopyrite. The original relief and surrounding area of the former mining plant is loaded with mining activity occurring over a seven hundred and thirty five year period (Rojkovic, 2003). AMD at this site contains high concentrations of sulphates, Fe, Mn, Cu, Zn, Al, and negatively affects the waters of the Smolnik stream.
Within the framework of proposals for effective and economically available methods for the prevention of negative AMD influence at the Smolnik site, it is necessary to understand the reasons for changes in the evolution of AMD composition and to provide a real estimation of their long-time evolution. A periodic monitoring of AMD quality, which provides the data for estimation of long-time evolution of AMD quality is realized. The article presents the results of the monitoring of the AMD quality at the Smolnik during the years 1986 – 2005. The geochemical modeling is used to understand processes taking place at the location in detail. It was utilized to simulate the evolution of AMD quality during its gradual ascent to the surface and the achievement of equilibrium with the atmosphere.

<table>
<thead>
<tr>
<th>Localities</th>
<th>pH</th>
<th>SO42- [mg/l]</th>
<th>Fe [mg/l]</th>
<th>Cu [mg/l]</th>
<th>Zn [mg/l]</th>
<th>As [mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smolnik (2004)</td>
<td>6.45</td>
<td>400</td>
<td>31.2</td>
<td>&lt;0.02</td>
<td>0.12</td>
<td>0.005</td>
</tr>
<tr>
<td>Rudnany (2004)</td>
<td>6.99</td>
<td>1 340</td>
<td>&lt;0.05</td>
<td>&lt;0.02</td>
<td>0.03</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Roznava (2006)</td>
<td>2.8</td>
<td>940</td>
<td>66.3</td>
<td>0.44</td>
<td>0.09</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Sobov (2004)</td>
<td>2.18</td>
<td>-</td>
<td>2 226</td>
<td>6.15</td>
<td>6.47</td>
<td>0.5</td>
</tr>
</tbody>
</table>

4. RESULTS AND DISCUSSION

4.1 Basic trends in evolution of AMD quality at the locality of Smolnik

Trends in the evolution of AMD quality at the locality of Smolnik and the evolution of concentrations of monitored AMD components are displayed in the Figure 2. In 1990, mining activity at this location was terminated. The area of deposit was gradually flooded with water from December 1990 till May 1994. The first marked changes occurred soon after the end of the flooding. In June 1994, a sudden change in the composition of draining mine waters occurred and fish kill was reported in the Smolnik stream. An intense increase in concentrations of sulphates, TDS, Fe, Mn, Cu, and Zn resulted in a massive deterioration of the ecological situation. After the rapid increase of concentrations of individual monitored species, a gradual but various decrease was observed. After the rapid increase, concentrations of Zn, Cu and Mn (Figure 2) immediately decreased. The present evolution of these components is linear. The concentrations of sulphates, TDS and Fe (Figure 3) decreased less markedly compared to concentrations of Zn, Cu and Mn. At the present time a moderate decrease of sulphates and TDS concentrations is observed. As for iron, a repeated increase of concentrations compared to 2001-2002 was followed by a recent moderate decrease.
In the case of pH, values were within the limits 2.5 – 3.2 during flooding and after the end of flooding. During the past five years the values of pH were within the limits 3.5 – 4.

On the basis of evaluation of the evolution trends of individual monitored components, it has been observed that in recent years, AMD evolution has stabilized with a moderate decrease in concentrations of individual monitored components (in the case of pH, a moderate increase of values within the limits 3.5 – 4). While this trend signals certain stability, the values of concentrations of individual monitored components from May 2006 (Table 2) hint that the situation at the site is at all the time critical.
In recent years the similar behavior of mine waters has been observed at various ore or coal deposits in the world without reference to their type and geological structure (Geller et al., 1998; Ladwig et al., 1984; Marsden et al., 1997; Zeman and Kopriva, 2002; Kopriva et al., 2004; Zeman, 2005). Adequate explanations for the reasons and mechanisms of this behavior have not been given until now.

Table 2. Chemical characteristics of AMD at the locality of Smolnik in May 2006

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>pH</th>
<th>Eh</th>
<th>SO42-</th>
<th>TDS</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Al</th>
<th>Mn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.80</td>
<td>513</td>
<td>2960</td>
<td>4053</td>
<td>257</td>
<td>3.72</td>
<td>7.45</td>
<td>64.6</td>
<td>23</td>
<td>280</td>
</tr>
</tbody>
</table>

4.2 Geochemical modeling

Geochemical modeling software is being utilized ever more frequently to solve complex geochemical systems evolution, e.g. the interaction of AMD with wall rocks, migration of individual monitored components in a studied environment (Kopriva, 2002). Besides in situ field measurements, samples taking, their analyses, and evaluation, geochemical modeling belongs among the most effective methods of AMD-generation study. The aim of modeling is not to create the ideal model of reality but to better understand processes running within AMD and determine changes in conditions which are interesting and necessary for us to study (Zeman, 2005; Slesarova and Zeman, 2006).

On the basis of this approach, the simulation of AMD quality evolution during its gradual ascent to the surface and its achievement of entire contact with the atmosphere was realized by means of the Geochemist’s Workbench®, a geochemical modeling software. Modeling was performed with values listed in Table 3.

AMD during its ascent of surface was lead to the contact with gas phase. Gradually the increase of oxygen partial pressure to value 0.2 occurred. Simultaneously, CO₂ partial pressure decreased to value 0.0003. During this process the intense decrease of pH by hydrolysis of originating Fe³⁺ to value 3.3 (Figure 4) and precipitation of Fe compounds in form of jarosite-Na, jarosite-K, amorphous ferric hydroxide, and pyrolusite (Figure 5) should occur.

Table 3. Chemical composition of AMD used in geochemical modeling at 14°C

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentrations</th>
<th>Component</th>
<th>Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.9</td>
<td>Li</td>
<td>mg/l</td>
</tr>
<tr>
<td>Eh</td>
<td>mV</td>
<td>Mn</td>
<td>mg/l</td>
</tr>
<tr>
<td>TDS</td>
<td>mg/l</td>
<td>SO42-</td>
<td>mg/l</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>mg/l</td>
<td>Cl⁻</td>
<td>mg/l</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>mg/l</td>
<td>F⁻</td>
<td>mg/l</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>mg/l</td>
<td>HCO₃⁻</td>
<td>mg/l</td>
</tr>
<tr>
<td>Na⁺</td>
<td>mg/l</td>
<td>NO₃⁻</td>
<td>mg/l</td>
</tr>
<tr>
<td>K⁺</td>
<td>mg/l</td>
<td>SiO₂</td>
<td>mg/l</td>
</tr>
</tbody>
</table>
Figure 4. The change of pH during gradual mine water ascent of surface and its achievement of equilibrium with atmosphere.

Figure 5. The precipitated minerals originated during gradual mine water ascent of surface.

The presented results of modeling are in accordance with results of analyses realized by other authors (Jasko et al., 1996; Lintnerova and Sefcikova, 2002; Lintnerova et al., 2004).
5. CONCLUSIONS

Acid mine drainage is considered one of the worst environmental problems associated with mining activity. The results of AMD activity are evident in the Slovak Republic, most markedly in the Smolnik area.

The quality of mine waters at Smolnik is always critical. But AMD quality evolution trends of individual monitored components show that in the past three years the situation is gently stabilizing particularly in the case of Cu, Zn and Mn concentrations. However, the evolution trends of pH, sulphates and TDS hint that the oxidation processes of sulphide material are running very intensively and a marked improvement of the ecological situation was not observed. The continued negative effect of mine waters on the surrounding environment is expected to continue for decades without a distinct improvement in quality.

The geochemical modeling of AMD can provide important and valuable data to understand the mechanism of natural processes taking place at Smolnik and data for engineering practice. Appropriate continuing monitoring of geochemical evolution of AMD quality, together with the utilization of modern evaluation methods and modeling tools can facilitate long-time and seasonal prediction of AMD quality evolution at Smolnik for decades. Based on those studies it will be possible to propose the effective methods of AMD remediation at Smolnik.

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REFERENCES


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