Acid Waters Impact on the Environment

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The paper presents aspects of water contamination in the mining complex “Boita” from Romania. The mining complex included horizontal galleries, vertical wells and related galleries. Also, nearby was built the preparation station of ore and at few hundred meters is situated the mining settling pit which served as preparation station. In that area it was studied: the quality of groundwater from galleries, stabilization of dirt-heaps, stabilization and composition of the mining settling and the influence of all mining operations on the land. This work is a case study about the anthrop changes of “Boita” locality.

Keywords: mining activities, waste water, acid reactions, acid drainage, treatment station

At “Boita” can be seen very easy the way of the mineralization forming through the metal-genetic complex, which started in the Superior Anteprotuberzoic and finalized in Quaternary. In the area, the crystalline rocks series of “Sebes” Mountains is present through the sericite–quartiles phylite with chlorite and is closed with the complex of the actinolite schist, which are formed by muscovite with garnet and graphitic pigment. In the inferior part were identified lens intercalations with amphibolites shale and crystalline calc, dolomite.

At “Boita” village, the siderite and ankerit are impregnate in that lens. Those forms come from the area metamorphosing of the faces of the green shale which are formed by:

- chlorite \( [(\text{MgFe})_6(\text{AlFe})_2(\text{OH})_8\text{Si}_4\text{Al}_2\text{O}_{10}] \)
- albite \([\text{NaAlSi}_3\text{O}_8]\)
- quartz \(\text{SiO}_2\)
- almandine \([\text{Fe}_3\text{Al}_2(\text{SiO}_4)]\)
- muscovite \([\text{KAl}_2(\text{AlSi}_3\text{O}_10)(\text{OH})_2]\)
- chlorite \([ (\text{MgFe})_6(\text{AlFe})_2(\text{OH})_8\text{Si}_4\text{Al}_2\text{O}_{10}] \)

The mining exploitation from “Boita” is located up from “Boita”. The “Boita”–“Hateg” fault is the tectonic board of the Paleogene deposit from the Piedmont’s Hateg. In the north area of the tectonic contact can be found the “Boita” complex ore deposit. The goal of the mining activities, in 1949 was to extract the iron ore gossans. The exploitation was well developed until 1966 when all mining activities were stopped and the mines were conserved until 1969. The medium production was around 6000 – 8000 t/month. First all ore was transported with auto means to the “Subcetate” railway and from there to “Gura Barza”–“Brad” by train. The beginning of the mining activities for the complex ore (S, Zn, Pb, Mo, Ca), made necessary the construction of a Flotation Station for the first processing of the exploited ore.

The proportion of polluted waters inside old mines, especially goldmines, represents approximately 30 % of the total. The Cu content in mg/dm³ varies from 1 to 500, Pb from 0.1 to 94 and Fe from 0.5 to 5200. The method of producing acid mine water is very well known [11.]. Pyrite and other sulphurous minerals, when exposed to oxygen and water, oxidize in order to produce dissolved metals, sulphates and water. The processes are catalyzed by bacteria which oxidize the iron, such as Thiobacillus ferrooxidans. The resulted solution reacts with other constituents inside the mineral waste such as neutralizations, ion change and metal dissolving with acids. Consequently, mine waters may comprise a high quantity of sulphate according to the classical mine acid water formula representing high acidity values and metal and sulphate concentration up to a neutralized version.

The acid water drainage from the mining works is made through several ways.

The drainage from the “120” gallery (fig. 1) is made through the Treatment Station (fig. 2 and 3) nearby the former Flotation: the water from the gallery comes with a 6 to 7 pH, never constant. The rain and snow change the pH. The debit is around 2,700 m²/12 h. Inside the Treatment Station the water is treated with white lime and leave the station with a 8.5–10 pH in to the “Galbena” Stream through an 4 km underground pipe. The drainage mouth is located in the “Densus” village area. The slimes resulted from mine waters treatment are decanted in two phases in two open concrete basins (fig. 4).

a. The resulted dry slime is transported with mechanic means into a deposit up in front of the “10” gallery.

b. “10” gallery is closed with a concrete wall with drainage system on the base and a ventilation mouth in the superior side. The water has a 7.5–8 pH.

Fig. 1. Drainage from 120 gallery
c. The “+10” West gallery and “11” gallery have no drainage system only the rain water wash the sterile waste dump.

d. The natural drainage in the Flotation perimeter (fig. 5) is very well marked but is not controlled. All drainage flow over in the nearby stream which crosses “Boita” village.

The evacuation of acid waters is a persistent problem of most abandoned or recently closed mines. Acid mine water evacuation effect may be really impressive. The worst scenario is that all underwater life disappears, the bottom of the rivers covers with particles from acid water and pH drops dramatically. As a comparison, acid rain has a titrate acidity of 10-15 mg/L (measurement reflecting the alkaline material quantity, CaCO₃ necessary for the neutralization). Mine acid waters have an acidity of 20 up to 300 times higher. It results thus that acid rain is a real problem there where the rocks and ground contain allow amount of alkalinity. Mine acid waters, when their discharge is localized and when the flow is important, may overpass the dilution capacity of any water stream. Together with a low pH and high acidity, waters discharged from mines may also contain heavy metals within toxic limits. The production process of these waters is natural and it is more rapid during the mining activity. Mine discharged water appear from rapid oxidation of sulphurous minerals in open pit mines exposed to the atmosphere and following the mine activity. Civil engineering works, quarries or other excavations expose these minerals, but metalliferous mines are the primary source of such waters, mines exploiting concentrate metallic sulphur ore (e.g. pyrite, chalcopyrite, lead ore etc.).

Material and methods

Information about the site
Topography, History, Geology and Soils, Climatology, Hydrology, Vegetation, anthropic and entropic modifications, radionuclide and heavy metals circuit in the nature (the studied exposure ways), stages in the process of the metal extraction, the site for the sterile material, abandoned sites, problems and solutions.

Methodology
Collecting samples, analyses, mechanic and biologic stabilization of the site: goal, methods, species selection, planting techniques, management of wastes. This study was made on the base of own research. It is useful to identify and the history of mining work to understand all the phenomena which take place and are into independence bond. The working methods have been interdisciplinary and had the following stages:
- the zone identification on maps using the technique partial aeration;
- discussions with locals and authorities who worked in the area;
- measurements on the field and laboratories in the country and abroad;
- questionnaires applied inhabitants.

Materials- NBC (nuclear- bacteriological- chemical) autolaboratory provided with radiopolymeter and fast analysis putty.

Results and discussions
The chemistry of the industrial waste water treatment process

The factors controlling the formation of mine acid waters may be classified as primary, secondary and tertiary. Primary factors are directly involved in producing acid waters. Secondary factors control the consummation or alternation of products through acid producing reactions, while tertiary factors are only physical aspects for the determination of mineral waste or mineral sites which influence the developing and migration of acid waters.

Primary factors consist of pyrite and other sulphurous minerals, oxygen, iron, and bacteria and they play an important part in mine acid waters development reactions. The following four equations describe the development of acids in mine water out of pyrite. The first equation is developed without any oxygen by catalyzing the Thiobacillus ferrooxidans.
Galvanic corrosion may as well appear during sulphurous mineral bacterial soaking, where complex sulphurs are influenced differently by the soaking process, depending on their reactivity degree. For example, pyrite does not react that actively when associated to chalcopyrite than when it is isolated. Anodic reactions of chalcopyrite are illustrated in equation (5) [14]:

\[
\text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + 4 \text{e}^{-}
\]

The reactions corresponding to the attack of the bacterial environment and ferric ions for other sulphurous minerals are presented in the following equations:

- for chalcopyrite [5, 14]:
  \[
  \text{CuFeS}_2 + 4 \text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 5 \text{Fe}^{2+} + 2 \text{SO}_4^{2-}
  \]  
- for chalcocite [5]:
  \[
  \text{Cu}_2\text{S} + 4 \text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 4 \text{Fe}^{2+} + \text{S}^{0}
  \]  
- for blenda [5]:
  \[
  \text{ZnS} + 2 \text{Fe}^{3+} \rightarrow \text{Zn}^{2+} + 2 \text{Fe}^{2+} + \text{S}^{0}
  \]  
- for lead glance [5]:
  \[
  \text{PbS} + \text{Fe}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + 2 \text{Fe}^{2+} + \text{S}^{0}
  \]  
- for millerite [1]:
  \[
  \text{NiS} + 2 \text{O}_2 \rightarrow \text{NiSO}_4
  \]

Regarding the presence of pyrite inside other sulphurous minerals, mine acid waters cannot be present on a mine site due to secondary factors. The most important secondary factor is the neutralisation of the acidity from the alkalinity developed by mine carbonates, such as calcite (CaCO₃) and dolomite (CaMg (CO₃)₂). Calcite neutralisation of the acidity coming from pyrite oxidation may be represented as follows [18]:

\[
\text{FeS}_2(s) + 2\text{CuCO}_3(s) + 13/4 \text{O}_2(g) + 3/2 \text{H}_2\text{O} \rightarrow
\rightarrow \text{Fe(OH)}_3(s) + 2 \text{SO}_4^{2-} + 2\text{Cu}^{2+} + 2\text{CO}_2(g)
\]

It is obvious that carbonate minerals may as well inhibit sulphur oxidation and thus may act as primary factors. The dissolution of carbonate minerals produced alkalinity correlated to the balance of the complex solution which depends on the partial pressure carbon dioxide, temperature, the shape of the minerals and the composition of the solution.

Another secondary factor includes the alteration of oxidizing products by reaction, such as ions change on the surface of clays, precipitation of gypsum and the dissolution induced by the acids of other minerals. These reactions change the character of mine water adding different heavy metals (such as: Al, Mn, Cu, Pb, Zn) replacing the iron with alkaline basic ions and carbonates.

The main characteristic of mine acid waters is a low pH and high iron concentrations in sulphates, as well as other metals. The acidity dissolves carbonate minerals and consumes a series of minerals such as aluminium and
magnesium hydroxides as well as other metallic oxides present in rocks and earth. These reactions add calcium, magnesium, aluminium to mine acid waters. Iron oxide mineral precipitations are often visible in orange, yellow and red on the runway of mine acid waters. The common minerals are ferric hydroxide FeO(OH)₃, brown iron ore FeO(Oh), jarosite KFe₃(SO₄)₂(OH)₆.

Physical characteristics of rocks and disaggregate useful mineral substances and hoarded into the cavities made through the exploitation, communication spaces between excavations and the hydrological schedule, are several factor affecting mine acid waters development. The most important physical characteristics include the size of the particles, their predisposition to physical change, rocks permeability and useful mineral substances from the excavated area. The acid development degree depends on the total surface of the particles, while the properties of mineral particles reflect the quality of sulphurs reacting. In the first stage of the process, the acid production rate is linear, depending on the mineral particles surface exposed [7]. Moreover, larger mineral particles ensure the integration of a larger amount of oxygen between them and consequently a more accentuated production of acids, compared to the fine mineral particles. The exposed surfaces of the mines and sulphurous minerals on the contour of works and mining excavations constitute the alteration process. Also the greatest acid formation source of mine waters is the minerals from the site especially in the case of technologies which deposit the ore on site. The permeability of this mineral on deposit on site influences the flow of water and oxygen. Acid formation in mine waters is reduced when permeability decreases. Acid formation may be reduced with the increase of the alkalinity of infiltrated water by exploiting in the environment, the neutralisation reactions is made under or open cast mines calciferous minerals and alkalinity of infiltrated water by exploiting in the formation may be reduced with the increase of the permeability of this mineral on deposit on site influences the flow of water and oxygen. Acid formation in mine waters is reduced when permeability decreases. Moreover, acid mine water is discharged into the environment and the neutralisation reactions is made between the acid solution and carbonate minerals, such as calcite (CaCO₃), in the sediments of surface waters. The calcite resulted from neutralizing reaction combines with the sulphate resulting the gypsum:

\[ \text{CaCO}_3 + 2H^+ + SO_4^{2-} = CaSO_4 + H_2O + CO_2 \]  

(17)

Water infiltrated between the disaggregated minerals constitutes the primary factor within the mine water acid production inside unsaturated areas. Table 1 represents the sequences inside a mine waters treatment plant.

Conclusions

Each of the basic steps of the mining processes is able to expose metallic sulphur which may be a source of contamination of waters resulted from the mining activity. The flow of waters through the excavations also contributes to their contamination.

The prevention of mine acid waters resulted from these sources are the key element of the strategy and control of the pollution generated by mining operations.

References

2. DUGAN, P. R. Bacterial ecology of strip mine areas and its relationship to the production of acidic mine drainage. Ohio J. Sci., 75, no. 6, 1975, p. 266.

Table 1

<table>
<thead>
<tr>
<th>Table 1</th>
<th>MINE WATER TREATMENT PLANT FROM ‘BOITA’ LOCALITY</th>
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</thead>
<tbody>
<tr>
<td>Physical and chemical characteristics</td>
<td>Treatment plant’s outlet</td>
</tr>
<tr>
<td>Q(debit)= 1000 m³/day</td>
<td>pH= 6.5-8.5</td>
</tr>
<tr>
<td>pH= 3</td>
<td>suspensions= 60 mg/l</td>
</tr>
<tr>
<td>suspensions= 0.4 mg/l</td>
<td>fix residuum = 2000 mg/l</td>
</tr>
<tr>
<td>fix residuum = 3516 mg/l</td>
<td>Fe= 5.0 mg/l</td>
</tr>
<tr>
<td>Fe= 21.67 mg/l</td>
<td>Zn= 0.5 mg/l</td>
</tr>
<tr>
<td>Zn= 45.84 mg/l</td>
<td>Mn= 1.0 mg/l</td>
</tr>
<tr>
<td>Mn= 2.2 mg/l</td>
<td>sulphates= 400 mg/l</td>
</tr>
<tr>
<td>sulphates= 2390 mg/l</td>
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