# Use of Aquatic Vegetation for the Treatment of Mine Acid Waters in the Mine Brad

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*Abstract*

*Polluted mine waters contain chemical substances, heavy metal ions, solid suspensions, a very low pH, and are discharged into the hydrographic network, often above cross-border levels. Regardless of the aggregation state, the residues of the mining industry affect all components of the environment: soil, water and air. The emphasis in the past on achieving high production levels and neglecting environmental impacts has in the meantime led to the accumulation of serious environmental damage. As a result of the cross-border effect of pollution, environmental problems have overtaken local character, being pursued by local, regional and global stakeholders. The paper aims to find solutions to the use of aquatic vegetation for the treatment of mine acid waters.*

*Keywords: mine waters, heavy metal, environmental impact, mine acid waters, aquatic vegetation*

**1. Introduction**

Polluted mine waters, which contain chemicals, heavy metal ions, solid suspensions, are discharged into the hydrographic network, sometimes above cross-border levels. Regardless of the aggregation state, the residues of the mining industry affect all components of the environment: soil, water and air.

The emphasis in the past on achieving high production levels and neglecting environmental impacts has in the meantime led to the accumulation of serious environmental damage. As a result of the cross-border effect of pollution, environmental problems have overtaken local character, being pursued by local, regional and global stakeholders.

Romania, being a signatory to the international conventions on cross-border pollution, has undertaken obligations and strives for compliance with international environmental standards.

In conclusion, it is imperative to purify these polluted waters given that the effect is catastrophic for aquatic biocenosis in the waters where they are discharged, it is necessary to eliminate the pollution from the downstream alluviums of the solid waste polluted wastewater treatment plants deposited in time until the confluence with the clean, unpolluted emissary.

The general objective of the paper is to passively clean the mine water and to evacuate it to the Barza river.

**2. Location mining perimeter brad**

The mining perimeter Brad, which administratively belongs to MINVEST - Deva, is located within the Metaliferi Mountains (Figure 1) on the territory of Hunedoara County. Inside it there were underground, open-air and preparatory activities.

The exploitation of gold-silver ores in the Barza mine took place in the Barza mine, located in the Barza village, Crişcior commune, about 6 km S-E from the city of Brad. The activity of extracting the cuprifer miner in Valea Morii pit, located on the territory of Crişcior commune at approx. 7.0 km S-E from Brad.

Mine waters result from the former underground mining of gold-silver E.M. Barza. The barrage was closed in 2006. The mine acid waters run from the underground through the main galley channel, unite with the Barza river and wash the tailings heap located in the proximity of the Barza river.

The mine water flow is approx. 83 l/s, that is Q = 300 $m^3/h$ or 7,200 $m^3$/day, which shows an advanced degree of contamination with heavy metal ions and a very low pH. At present, these waters are directed to a channel in two mechanical decanters located downstream of the Barza mine.

Mine waters, characterized by a pH of 3.6 unpurified units, are discharged to the Crişul Alb, in the locality of Gurabarza, downstream of the Criscior section. Mine and seepage water purification is currently achieved through two vertical decanters, outdated as flow rates. There were exceedances of the indicators: pH, sulphates, total ionic iron, manganese, copper and zinc.

**3. Description of the passive treatment system**

After passing through the two vectant decanters the mine water is discharged into the Barza brook. Since the water flow rate is relatively high, the capacity of the decanters does not allow the water to stand for sufficient time to decant the slurry, so the mechanical treatment is unsatisfactory and the chemical is non-existent because no precipitating reagent is used. The design and construction of the mine water transport channel to the two physical purification decanters will be made in the form of lines, forming alternate angles (zigzag) to reduce the velocity of mine water in periods of heavy rainfall. (7)

These decanters are currently clogged with suspensions and require permanent cleaning to be used optimally in the mechanical purification step. Then these mine waters will be

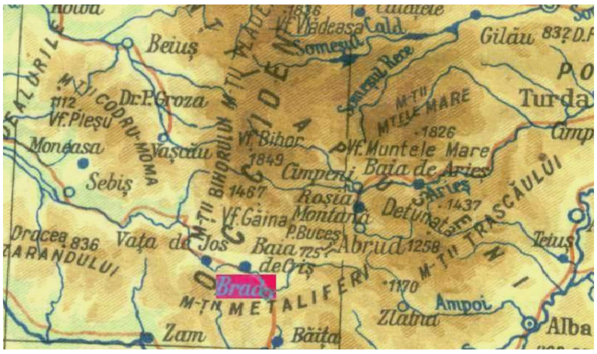

Fig. 1. The location of the mining perimeter Brad (2, 3)
Rys. 1. Lokalizacja obszaru górniczego Brad (2, 3)

routed through a filter to hold the suspension and from here will be directed to the pond treatment system (passive treatment system).

Mechanisms for removing and retaining metals in passive treatment systems are varied and include:

- oxidation
- precipitation as hydroxides and carbonates under aerobic conditions
- precipitation in the form of sulphides and hydrogen sulfate under anaerobic conditions complexation and adsorption on organic matter
- exchange of ions with organic matter
- plant uptake (phyto-remediation)

The environmental conditions of the passive treatment systems will dictate the dominant mechanisms of metal removal. Research in the field suggests that passive treatment is more effective if acidity loading is lower. (5)

### *3.1. Passive treatment of mine acid waters*

Passive treatment systems for mine acid waters are designed to purify and improve the quality of the waters that pass through them. These systems are designed in the form of wetlands with natural processes, with changes aimed at meeting the specific treatment objectives. Research calls for the investigation of natural wetlands that will receive mine acid waters with low pH and high concentrations of Fe and heavy metals. (5)

A critical step in designing the passive treatment system is to know the characteristics of the waters to be treated. This can be done by measuring the flows or flow rates of these waters and water quality constituent concentrations that raise concerns over an extended period – ideally at least one year – to determine how these quantities vary seasonally. Based on this information plus knowledge of the purpose of the system, we determine the elementary concentrations and the flow of mine water to be treated, these are the design conditions. Site features, especially land availability, also influence the choice and design of the passive treatment system.

### *3.2. Anaerobic wetlands*

Wet aerobic areas allow passive treatment systems to increase the alkalinity of the water, by making acidification of acidic waters more efficient (Figure 3).

Wet aerobic areas include the addition of a limestone layer underneath or mixed with an organic substrate that encourages the generation of alkalinity as bicarbonate ($HCO_3^-$). Reduced sulfate is a microbial process that occurs under anoxic conditions (low $O_2$) when organic sulfates and biodegradable are present. (6) Sulfate reducing bacteria use $O_2$ that enters the anoxic environment as a sulphate component ($SO_4^{2-}$) for the metabolic processing of biodegradable organisms, converting sulfur associated with either hydrogen sulphide ($H_2S$) or solid phase sulphide. The reduction of the sulfide $H_2S$ generated and bicarbonate alkalinity:

$$SO_4^{2-} + 2\ CH_2O \rightarrow H_2S + 2\ HCO_3^-$$

Sulfate reduction is common in both wet and wet wetlands, where their appearance can often be detected as visible bubbles coming out of the substrate, accompanied by the smell of „broken egg" of $H_2S$ gas. When soluble metals in the medium are in solution, sulphate reduction can form solid-phase metal sulphides as an alternative finite product, which removes the metals from the solution and deposits them in the substrate. In the following, „M" represents a sulfide-forming metal and „MS" is a metal sulfide.

$$M + SO_4^{2-} + CH_2O \rightarrow MS + HCO_3^-$$

Generating alkalinity by dissolving limestone inside or under the organic substrate:

$$CaCO_3 + H^+ \rightarrow Ca_2+ + HCO_3^-$$

Bicarbonate ($HCO_3^-$) is a source of alkalinity and can neutralize H+ and/or increase pH to increase precipitation of acid-soluble metals:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2\ (aq)$$

These systems are also referred to as „wetlands with compost" because the substrate layer generates alkalinity.

High density calcium alloys with $CaCO_3$ of more than 90% are preferred for passive use because they are more soluble than impure limestone or those containing a higher proportion of total carbonates such as $MgCO_3$ (dolomite limestone).

The limestone is placed so that the water has to travel through the organic substrate before it is reached, which allows bacteria in the organic material to remove $O_2$ from

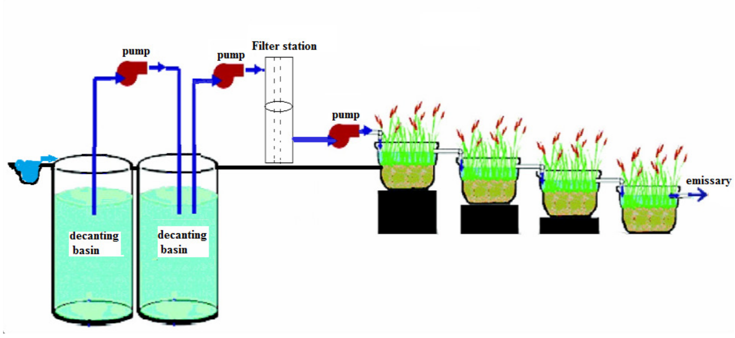


Fig. 2. The phyto-treatment acid mine water
Rys. 2. woda kopalniana do fitouzdatniania

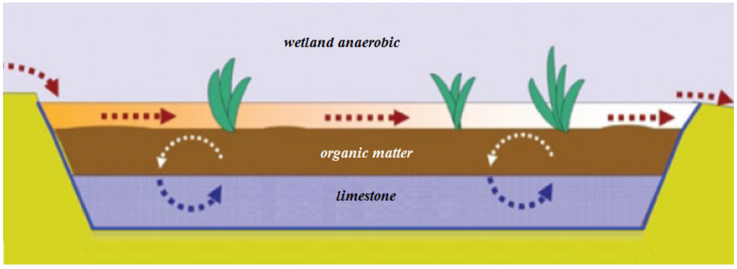


Fig. 3. Cross-section of an anaerobic wetlands (7)
Rys. 3. Przekrój beztlenowych mokradeł (7)

the percolation waters. This process helps prevent limescale spoilage. The term alteration refers to the Fe coating of limestone surfaces, which makes these surfaces less reactive.

Anaerobic wetlands are able to remove acid-soluble metals, especially Fe and Al, and produce alkalinity. However, their effectiveness is limited by the slow mixing of the alkaline substrate water with acidic waters close to the surface. Thus, these systems frequently require large areas and long retention times. As with other passive treatment systems, their efficacy in Mn removal is limited, unless very large areas are used.

Research (reported by Skousen) demonstrates that substrate processes – the generation of alkalinity to stimulate oxidation and hydrolysis and metal sulfide formation – are the main engines of long-term water purification. When systems are built for the first time, mechanisms such as the absorption and sorption of plants by organic materials can contribute to metal removal, but the ability of these mechanisms to remove metals is soon exhausted because absorption sites are filled.

General instructions for the construction of an anaerobic wetland area support the use of a layer of 30–60 cm organic matter over 15–30 cm of limestone or the introduction of a mixture of organic matter and limestone at a depth of 50–100 cm. The organic substance must be permeable to water and biodegradable.

Materials such as compost of used mushrooms have been successfully used in several sites (in the northern Appalachia). Hake (Typha sp.) Or other aquatic vegetation can be planted throughout the wetland to provide additional organic matter for $O_2$-consuming bacteria and to promote metal oxidation by releasing oxygen from their root system. If sediments or easily hydrolyzable Fe are present in the waters to be treated, a pre-treatment basin may be included in the design of the system. (5)

The depth of water design over the organic/limestone mixture varies. Some models of wet anaerobic areas maintain water depths of 10–30 cm to encourage aquatic vegetation that prevents canalization and adds fresh organic material to the substrate.

Instructions available for system sizing recommend that you plan the acid removal rate of 3.5 g/m²/day when the system is designed for compliance and 7 g/m²/day otherwise. However, performance data demonstrates that the anaerobic performance of wetlands is very variable and that these systems tend to neutralize acidity more efficiently when they get higher concentrations and influences of acidic influences.

The substrate may be composed of biodegradable organic materials which are placed over the limestone as represented, or as an organic-limestone mixture. Circular arrows are the diffusion of treatment waters through the substrate that generates alkalinity.

Proven application of passive treatment technology is in the field of reduced flow. The most successful passive treatment projects are treating less than 1,000 m³ per day.

A passive treatment system has to operate for several years without a major upgrading to fill up with sediment and should be able to operate without the use of electricity.

The four wetlands will be constructed in the proximity of the two existing mechanical cleaning decanters (Figure 3). Each pool will have the dimensions of 480 x 60 x 60 m (L x L x A) and a 2 per cent inclination and limestone-lined. The underground surface of the substrate consisted of a layer of 40 cm of soil. In each pool, plants are planted with 32 plants per rows to maximize overcrowding of wetlands, harvested from other worthy areas.

Tab. 1. The quality of mine water discharged into Gallery 1

Tab. 1. Jakość wody kopalnianej odprowadzanej do Galerii 1

| Indicator analyzed | U.M. | Determined values | CMA NTPA 001 | Test method |
|---|---|---|---|---|
| Ammoniacal nitrogen ($N-NH_4^+$) | mg/dm³ | 0,55 | 2 (3) | SR ISO 7150-1 2001 |
| Calcium | mg/dm³ | 560 | 300 | SR EN ISO 7980 2002 |
| Biochemical oxygen consumption ($CBO_5$) | mg $O_2$/dm³ | < 7,9 | 25 | SR EN ISO 1899-1 2003<br>SR EN ISO 1899-2 2002 |
| Consum chimic de oxigen (CCO) | mg $O_2$/dm³ | < 30 | 125 | SR ISO 6060: 1996 |
| Conductivity | µS/cm | 3860 | | SR ISO 27888: 1997 |
| pH at 19,5 °C | unit. pH | 3,6 | 6,5-8,5 | SR EN ISO 10523-2012 |
| Sulphates | mg/dm³ | 1425 | 600 | PSL-10, ed. 1/rev.0,<br>SM 4500-SO42-E |
| Cyanides | mg/dm³ | < 0,014 | | SR ISO 8703-1:1998 |
| Total cyanides | mg/dm³ | < 0,005 | 1,0 | CSN 757415<br>CSN EN ISO 14403-2 |
| Arsenic | mg/dm³ | 1,40 | 0,1 | US EPA 200.7<br>ISO 11885<br>CSN EN 16192<br>US EPA 6010<br>SM 3120<br>CSN 757358 |
| Cadmium | mg/dm³ | 0,0156 | 0,2 | |
| Copper | mg/dm³ | 1,06 | 0,1 | |
| Total iron | mg/dm³ | 2020 | 5,0 | |
| Total Manganese | mg/dm³ | 36,5 | 1,0 | |
| Nickel | mg/dm³ | 0,210 | 0,5 | |
| Lead | mg/dm³ | 0,124 | 0,2 | |
| Mercury | mg/dm³ | < 0,050 | 0,05 | |
| Selenium | mg/dm³ | < 0,150 | 0,1 | |
| Zinc | mg/l | 10,0 | 0,5 | |

### *3.3. The quantities of contaminated storm water*

The amount of polluted meteorological water is directly related to the intensity of precipitation.

In the construction phase, the disturbed surfaces will also be very variable in size and therefore the quantities of polluted meteoric waters will vary, making a more accurate estimation difficult.

During the exploitation phase, the meteorological streams from the different installations of the project will be included in the water balance.

## 4. Determination of the physico-chemical properties of the water environmental component

### *4.1. The quality of mine waters discharged on Gal. 1st May*

In order to highlight the degree of pollution of mine waters, their quality indicators were determined: pH, Ca, CCO-, $SO_4^{2-}$, Fe, Mn, Cu, Zn, Pb etc. (Table 1).

The results of physicochemical analyzes must and will demonstrate that the passive treatment system is able to stabilize all parameters analyzed within the normed limits and indicated by the legislation in force (NTPA 001).

### *4.2. The quality of the Barza brook after treatment*

Samples of acid water were taken and analyzed in the RENAR accredited laboratory, ALS Life Sciences Romania, Environmental Laboratory, Ploieşti (Table 1).

Acidic water intakes, coming from Valea Morii and Mina Barza, drastically affect the ecological status of the tributaries of the Crisul Alb River. The acid pH and high concentrations of heavy metals dissolved in these mine waters lead to a degradation of these brooks, which far exceeds the good environmental status required by the EU Surface Water Directive. The pollution level of the tributaries can be found at the level of the entire basin of the Crisul Alb River.

The content of heavy metals Zn and Cu in the sediments of the Crisul Alb River increases significantly after the confluence with the tributaries flowing through the mining areas, the polluted mine waters come from the two brooks Valea Arsului and Valea Barza (M. Sima, s.a., 2008). The sediment content of Pb can be met with a high concentration of 73 km from the Brad area, which can be attributed to these sources of pollution. The other metals, Ni, Cr and Cd are present in sediments but do not show significant concentrations over long distances.

To reduce the pressure on the aquatic environment and to eliminate the historical pollution cantonated in the brooks of Barza, Valea Arsului and Crişul Alb, the banks of the brooks and the Crisul Alb River will be excavated before the passive mine water treatment system is put into operation.

## Conclusion

When systems are built for the first time, mechanisms such as absorption and sorption of plants through organic materials can contribute to metal removal, but the ability of these mechanisms to remove metals is soon exhausted because absorption sites are filled.

The anaerobic performance of wetlands is very variable and these systems tend to neutralize acidity more efficiently when they get higher concentrations and influences of acidic influences.

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## *Wykorzystanie roślinności wodnej do oczyszczania kwaśnych wód kopalnianych w Kopalni Brad*

*Zanieczyszczone wody kopalniane zawierają substancje chemiczne, jony metali ciężkich, zawiesiny stałe, bardzo niskie pH i są odprowadzane do sieci hydrograficznej, często powyżej poziomów transgranicznych. Niezależnie od stanu skupienia pozostałości przemysłu wydobywczego wpływają na wszystkie elementy środowiska: glebę, wodę i powietrze. Nacisk na osiągnięcie wysokich poziomów produkcji i zaniedbanie wpływu na środowisko doprowadził do poważnych szkód w środowisku. W wyniku oddziaływania transgranicznego problemy zanieczyszczenia środowiska przyjęły charakter lokalny, problem zanieczyszczenia jest rozwiązywane przez lokalne, regionalne i globalne zainteresowane strony. Artykuł pokazuje możliwości znalezienia rozwiązań w zakresie wykorzystania roślinności wodnej do oczyszczania kwaśnych wód kopalnianych.*

*Słowa kluczowe: wody kopalniane, metale ciężkie, wpływ na środowisko, kwaśne wody kopalniane, roślinność wodna*