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PASSIVE REMEDY TECHNIQUES FOR ACID MINING WATERS USING LIMESTONE AND PLANTS

DOCTORAL THESIS

ABSTRACT

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Content

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Chapter 1 – Formation of acid waters and their effect over the environment

Chapter 1 presents the concern of acid waters, starting with the method and causes of their generation and continuing with the effects that these waters have over the environment.

1.1 Acid water generation

Since man began building stone tools and until now, approximately 1,150 million tons of metals such as copper, lead, cobalt, zinc, cadmium and chromium have been exploited (Sheoran & Sheoran, 2006). With the doubling of the world's population between 1956- 1990, the production of non-ferrous metals (zinc, copper, tin, lead, nickel, aluminum) increased eight times. A serious problem currently facing the mining industry, is the huge mass of tailings deposited in tailings ponds. Since the early 2000s, this amount was about 18 billion m^3/year and was expected to double within the next 20-30 years (Aswathanarayana, 2003). The water that infiltrates through the tailings from the ponds becomes acidic and this acidic nature of the solution allows the mobilization of metals and their transition into a soluble form (Sheoran & Sheoran, 2006).

In the absence of remediation programs, acidic water sources can remain active for decades or even centuries after the termination of mining activity (Modis et al., 1998). In the active period of a mine, acidic water are maintained at low levels by pumping and sewage treatment stations. The problem of acid water management occurs especially after the cessation of mining activity, when the water recirculation pumps are stopped and the mines abandoned (Simate & Ndlovu, 2014).

The chemistry of acid waters is determined by the geology of the mining region, the activity of microorganisms, temperature and the availability of water and oxygen. These factors are highly variable from one region to another and for this reason, the prediction, prevention, isolation and treatment of acidic waters must be considered carefully and with great specificity (Manders et al. 2009).

Acidic waters are formed when minerals from the sulfides group, especially pyrite, are exposed to oxidation conditions (Simate & Ndlovu, 2014; J. Skousen et al., 1998; US Environmental Protection Agency, 1994). Acidic water generation is not limited to the mining industry, but can also occur in the case of sulfides exposure through other activities, such as the construction of highways and tunnels and other deep excavations (J. Skousen et al., 1998). Acidic waters are characterized by low pH, high concentrations of iron, sulfates and heavy metals in varying proportions (Peppas et al.

2000). The metallic load of water is worrying, as is its acidity, in terms of environmental damage (Filipek et al., 2003; Kuyucak, 2002).

The main components behind the generation of acidic water are sulfides, moisture and an oxidant, which is either oxygen or the trivalent iron. In the majority of cases, bacterias play a major role in accelerating the generation of acidic water (Akcil & Koldas, 2006; Gónzalez-Toril et al., 2003).

Chemical, biological and physical factors are important for the generation of acidic water. According to Akcil and Koldas (2006), these factors are: pH, temperature, oxygen in the gas phase, oxygen in the aqueous phase, degree of water saturation, chemical activity of ferric iron (Fe^{3+}), energy of chemical activity, exposure surface of metal sulfides and bacterial activity. In addition to these factors, the permeability of tailings dumps is another very important factor. A high permeability causes the penetration of oxygen through the tailings, causing an acceleration of chemical reactions generating acidity (Akcil & Koldas, 2006).

The best known specie of active bacterias in acidic waters is *Acidithiobacillus ferrooxidans*. This bacteria is involved in the oxidation of pyrite (Jennings et al., 2008; Singer & Stumm, 1970). In addition to the oxidation of pyrite, *A. ferrooxidans* also contributes to the oxidation of other sulphides, such as arsenic, copper, cadmium, cobalt, nickel, lead, zinc, molybdenum and antimony.

Due to their diffuse nature and water mobility, this is the main way of transporting contaminants in the environment. Therefore, all measures aimed to controlling acid water migration refer to water flow control (Akcil and Koldas 2006; Vila et al. 2008).

1.2 Effects of acidic waters over the environment

The oxidation of sulfide minerals results in sulfuric acid formation, which subsequently determines the mobilization of metals. Thus, acidic waters contain high concentrations of acid and dissolved metals. Environmental problems occur when this complex of pollutants reaches groundwater or surface watercourses (Simate & Ndlovu, 2014).

Heavy metal contamination in water affects humans and animals in two ways (Akpor & Muchie, 2010). Firstly, heavy metals have the ability to persist in natural ecosystems for a long time. Secondly, they have the ability to accumulate successively in the trophic chain, thus causing acute and chronic diseases. Heavy metals affect metabolic functions in two ways: (1) they accumulate in vital organs and glands (heart, brain, kidneys, bones, liver) affecting their normal functioning and (2) they inhibit absorption, interfering with or replacing nutrient minerals, thereby obstructing their biological functioning (Singh et al. 2011).

Acidity, also, has a very toxic effect on humans and animals. At first, acidic waters are very clear, but gradually acquire a bright orange color, due to the neutralization and precipitation of iron oxides (Cotter & Brigden, 2006). This precipitate is very fine and is deposited on the substrate of rivers, in watercourses and oceans (Simate & Ndlovu, 2014).

Aquatic organisms, such as fish, accumulate heavy metals directly from contaminated water and indirectly through the trophic chain (Khayatzadeh & Abbasi, 2010). Because heavy metals are very persistent and toxic even in small amounts, they can cause severe oxidative stress in aquatic organisms (J. Singh & Kalamdhad, 2011). Cadmium, copper, lead and zinc are metals of particular interest due to their severe toxicity to aquatic organisms (Lewis & Clark, 1997).

Chapter 2 Acidic water treatment methods

As the effects of acid waters on the environment have become more visible over the years, a lot of research has focused on the development of remediation techniques, and, respectively, control of the source of acid water generation and their migration route (Johnson and Hallberg 2005). Source control methods are focused on controlling the generation of acidic water at the site of its formation (Egiebor & Oni, 2007; Luptakova et al., 2010).

Acidic waters can be neutralized using chemicals such as lime, calcium carbonate, hydrated lime, natrium hydroxyde, calcined soda, etc., which lead to the production of bulky sludge. The management of these sludges is an environmental issue that involves additional costs (Fiset et al., 2002). Thus, the high costs of conventional acid water treatment technologies have generated economic pressures and led engineers to look for creative, cost-effective and environmentally friendly ways (Sheoran & Sheoran, 2006).

These techniques can be classified into two categories: active and passive. A useful classification of these methods can be made based on biological activity (abiotic / biotic) (Johnson and Hallberg 2005).

Active techniques are more suitable for use in mines that are under exploitation. This is due to the fact that during the active period of a mine, the amount of water generated to be treated is very large. Passive techniques are a more realistic solution when treating acidic water in abandoned mines. Ecologically sustainable and low-cost treatment options are needed in these areas. In order for these costs to be low, treatment techniques must operate independently and without a source of electricity (PIRAMID Consortium, 2003).

2.1 Active methods

Active technologies are very efficient, but in contrast to passive technologies, they require continuous maintenance, can be dangerous and are also very expensive. Active technologies consist of mechanized procedures, in which various chemicals such as lime are added, to increase the pH and to promote the precipitation of metals in the form of hydroxides and carbonates (Tünay and Kabdaşli 1994; Matlock et al. 2002; Herrera et al. 2007 ; Harvey et al. 2011).

An example of active technology is that in which high density sludge (HDS) is used in treatment plants (Coulton et al., 2003). Another example is the ion exchange (cation-anion) processes (Schoeman & Steyn, 2001) and membrane flotation (Sudilovskiy et al., 2008).

One of the major advantages of the active treatment process is that, unlike passive treatment systems, it does not require additional space or construction. In addition, the active treatment process is fast and efficient in neutralizing acidic waters and removing metals. Another advantage of the active treatment technique is the lower cost associated with handling and disposing of sludge compared to passive treatment techniques (Coulton et al. 2003).

The major disadvantage of active treatments is that they require a continuous supply of chemicals and energy for the effectiveness of the treatment. Costs on chemicals and personnel employed to operate the systems significantly increase the total costs of these technologies. The efficiency of these systems depends entirely on the permanent maintenance and supply of chemicals, which makes it difficult to control for most abandoned and long-distance mining sites (RoyChowdhury et al. 2015).

2.2 Passive methods

Passive technologies are accessible economically and require little maintenance activities. Also, few chemical or biological substances are used, which allows the development of living organisms that help reduce the concentrations of contaminants (Jiménez-Castañeda, 2014). At the same time, the pH value of the water passing through the treatment system increases to a neutral value. Some of the most commonly applied passive treatment technologies are those that use limestone to neutralize water and precipitate heavy metals.

Passive acid water treatment technologies can be classified into two groups: conventional and emerging technologies. Conventional passive treatment technologies are constructed wetlands and anaerobic sulfate reduction bioreactors. Phytoremediation falls into the category of emerging technologies (RoyChowdhury et al. 2015).

2.2.1 Built Wetlands ("Wetlands")

Built wetlands are the most common passive technologies used to treat acidic waters (Hallberg & Johnson, 2005; Mays & Edwards, 2001; Mitsch & Wise, 1998). In addition to domestic, commercial and industrial wastewater treatment, in recent decades, research efforts have been directed towards wetlands as low-cost means of reducing heavy metals from acidic waters (Matagi et al., 1998, Fyson et al. , 1994). There are two types of wetlands: aerobic and anaerobic. Aerobically constructed wetlands are shallow water building (<30 cm), which provide sufficient retention time for the oxidation and precipitation of metal hydroxides. Plants such as *Typha sp., Juncus sp.* and *Scirpus sp*. have the role of regulating the flow of water, stabilizing and accumulating metals. At the same time, they maintain the microbial population and increase the aesthetic value of the contaminated site (Johnson and Hallberg 2005; Skousen and Ziemkiewicz 2005).

Anaerobic systems contain substrates rich in organic matter, which provide reducing conditions and neutralizing agents (limestone). Often, wetlands built anaerobically are underground and devoid of vegetation. In this type of system, the acidity of the water is reduced by the neutralizing effect of limestone and the metabolism of iron and sulfate-reducing bacteria. Substrates rich in organic products consist of mixtures of biodegradable products, such as straw manure, peat and sawdust. This mixture serves as a food source for iron and sulfate-reducing anaerobic bacteria. Manure or mushroom compost is used as a substrate for microbial communities (Skousen et al. 2000; Johnson and Hallberg 2005; Wieder 1992).

2.2.2 Bioreactors

Another commonly used passive technology is the one based on compost bioreactors, which generate alkalinity. Sulfate-reducing bacteria and organic matter are used in these reactors (Choudhary & Sheoran, 2012; Cole et al., 2011; Gibert et al., 2005).

Sulfur-reducing bacteria are a group of chemoorganotrophic and strictly anaerobic bacteria, represented primarily by the genera *Desulfovibrio*, *Desulfomicrobium*, *Desulfobacter* and *Desulfotomaculum* (RoyChowdhury et al. 2015).

Bioreactors help to improve water quality by reducing sulphate, acidity and metal concentration in acidic waters. Numerous studies have been performed to test the efficiency of bacteria that reduce sulfate to different pH values. The results showed that the best efficiency of sulfate-reducing bacteria is at a pH value between 5 and 8. A low pH value reduces the activity of sulfate-reducing bacteria and promotes increased solubility of metal sulfides (Neculita et al 2007; Dvorak et al. 1992; Willow and Cohen 2003).

2.2.3 Limestone drains

Limestone drains are used both in anoxic environments (closed systems) and in environments in the presence of oxygen (open systems). *Anoxic limestone drains* (ALD) are the most common passive acid water treatment systems using limestone. Most often these are underground systems, 30 m long, 1.5 m deep and 0.6-20 m wide filled with limestone. In these drains the limestone reacts with acidic water resulting carbon dioxide (CO_2), which favors increase of alkalinity (Watzlaf et al. 2004). Due to the lack of oxygen in the system and a pH value less than 6, iron remains in reduced form, not precipitating in the form of iron hydroxide (Skousen 1997; Johnson and Hallberg 2005).

Typically, anoxic drains are used in conjunction with aerobic and anaerobic constructed wetlands (Skousen et al. 2000; Johnson and Hallberg 2005; Kleinmann et al. 1998).

Open limestone channels (OLC) increase the alkalinity of acidic water in open channels or in ditches lined with limestone (Ziemkiewicz et al. 1994). Acidic water drains through these ditches and by dissolving the limestone, the water is treated. Due to the presence of oxygen, iron and aluminum precipitate in the form of hydroxides, covering the surface of the limestone.

Projection factors that can be modified for an optimal performance of the open limestone channels are length and gradient of channel, which affect turbulence and coverage rate. Optimal performance is achieved on slopes that exceed 20%, because the speed of the water keeps the precipitated hydroxides in suspension and keeps the limestone surfaces clean (Skousen 1997).

Open limestone channels can remove acidity from acidic waters by up to 69%, iron by 72%, manganese and aluminum by 20% (Skousen et al. 2000; Skousen and Ziemkiewicz 2005;

Ziemkiewicz et al. 1997). To maximize treatment efficiency and metal removal from acidic waters, open limestone channels are used simultaneously with other passive systems (Skousen 1997). The major advantage of these channels is the low cost, because once built, they do not require maintenance, except for refilling with limestone, as it is consumed (Skousen et al. 2000).

2.2.4 Phytoremediation

Phytoremediation is a passive technology for treating acidic water. Phytoremediation can be applied to both soils and acidic waters. Phytoremediation of contaminated sites mainly involves two mechanisms: phytoextraction and phytostabilization. In the phytoextraction process, plants extract heavy metals from contaminated soils and waters and store them in their biomass. On the other hand, phytostabilization ensures a vegetative cover of acidic and contaminated soils (Baker and Brooks 1989; Salt et al. 1995; Cunningham et al. 1997; Tordoff et al. 2000; Padmavathiamma and Li 2007).

Passive treatment technologies depend on several factors: water flow, built-up area size, waste characteristics, local topography and environment. In most cases, in order for acidic water to be discharged into the environment after treatment, the above-mentioned systems must be used in combination. The construction costs of passive treatment systems are very high, and these systems also require regular monitoring and maintenance (Gusek, 2013). Passive treatment systems also generate a considerable amount of sludge, and the cost of disposing of it is significant (RoyChowdhury et al. 2015).

2.3 Recovery of waste after applied treatment and recovery of metals from acid waters

Waste recovery and metal recovery aim to reduce residual sludge, generate income to recover treatment costs and also contribute to the long-term sustainability of water treatment projects (Simate & Ndlovu, 2014).

Particular attention must be paid to the recovery of industrially useful materials. Therefore, the recovery of useful products from waste streams after treatment processes may include the following: recovery of metals; recovery of salable products (sulfur, sulfuric acid or sulphate); electricity production; alkaline recovery (calcium carbonate); building materials (plaster and cement); agricultural use (fertilizer); adsorbents used in municipal and industrial wastewater treatment (Simate

& Ndlovu, 2014); pigments (ferihidrit) (R.S. Hedin, 2003); plants recovery (Rahman & Hasegawa, 2011).

2.3.1 Valorisation of plants

Plant management after the process of extracting contaminants and harvesting them is an important issue. The feasibility of application from an economical and environmental point of view is taken into account when choosing the method of disposal for these plants. Thus, in the study conducted by Rahman and Hasegawa (2011) are presented some options for the management of harvested plants. A first method proposed by Thomas and Eden (1990) is that of incineration and use of ash as a fertilizer or transformation into coal.

Liquid fuels, such as ethanol, can be produced from aquatic plants by hydrolysis along with fermentation, which would make plants a good substrate (Gunnarsson & Petersen, 2007).

Briquetting would be a good option for the treatment of bioaccumulating aquatic plants. Thomas and Eden (1990) reported that briquetting the water hyacinth is a viable method. After drying, the water hyacinth, can be pressed and turned into briquettes or pellets. The obtained material has an energy that is close to that of coal (Gunnarsson & Petersen, 2007; Thomas & Eden, 1990).

Anaerobic decomposition is a biological process in which organic matter is degraded in the absence of oxygen, resulting a byproduct, biogas. Biogas production would be a viable, interesting, and at the same time, ecological idea for the management of the plants that carried out the phytoremediation.

2.3.2 Metal recovery

Acid mine waters are characterized by a different composition of heavy metals depending on the type of mining deposit (Sheoran & Sheoran, 2006). The commercial benefit of dissolved metals can only be achieved if they are selectively extracted or concentrated.

The most generally applied treatment of acidic water involves the addition of alkaline reagents to increase the pH and precipitation of dissolved metals as hydroxides (Menezes et al., 2009). This step is usually followed by the collection and processing of sludge containing heavy metals. Most often, it is buried in specially arranged warehouses (Brown & CLF Technologies, 1996). Although this treatment can provide an efficient remedy, the major disadvantage is the high operating costs and the problems related to the disposal of the resulting bulky sludge (DB Johnson and Hallberg 2005; J. Skousen et al. 1998; Menezes et al. 2009; Matlock et al. 2002). ; Sampaio et al. 2009). In addition, the selective extraction of heavy metals is very difficult to achieve (Simate & Ndlovu, 2014). A more sustainable option should be based on the recovery and use of heavy metals. Using chemical and biological methods, MacIngova and Luptakova (2012) managed the selective removal of Fe, Cu, Al, Zn and Mn from acidic waters through a selective sequential precipitation process (SSP).

2.3.3 Pigments

Studies have shown that sludge obtained from acidic waters can be used to produce anorganic pigments (R.S. Hedin, 2003; Marcello et al., 2008; Michalková et al., 2013) and magnetic particles such as ferrites (Wei et al. 2008). In order to produce iron oxides usable as a raw material for the production of pigments or additives in the ceramics industry, an acid water treatment was developed using a two-stage selective precipitation process (R.S. Hedin, 2003).

Research conducted by Cheng et al. (2007; 2011) showed that combustion cell technologies can not only be used for the simultaneous treatment of acidic water and energy generation, but also to generate iron oxide particles with suitable size for use as pigments in other applications. . The particle diameter of iron oxides can be controlled by changing the conditions in the combustion cell, in particular the current density, pH and initial iron concentration. After drying, the iron oxide particles are then converted to goethite (α-FeOOH) (Simate & Ndlovu, 2014).

2.3.4 Construction materials

Many of the components in sludge resulted from acidic water treatment are the same as those used in the manufacture of cement. For example: calcite, gypsum, silica, Al, Fe and Mn are raw materials for the manufacture of cement. Therefore, these components can be used as raw materials for the manufacture of construction materials and other products.

Chapter 3 Study objectives and areas studied

The first and second parts of this chapter present the main objectives of the thesis and the sites studied or visited, in which the impact of acidic waters on the environment was observed or in which passive methods of acidic water treatment were applied. During the thesis preparation, I did a research internship at the University of Porto, Portugal (01.09.2015 - 30.09.2015). The last part of this chapter presents the studied mining areas, in terms of geography, geology and the impact that mining activities have had on the environment in the area.

3.1 The objectives of the study and the motivation for choosing the topic

The post-mining impact on the environment was negative, having a visible effect especially on water resources. After the cessation of mining activities in Romania (2006), acid waters continued to be a problem in former mining areas.

The three general objectives of the thesis are:

1. Identifying the potential for neutralization of acidic waters with limestone.
2. Identification of plants that have the potential to accumulate heavy metals in their tissues.
3. Building and installation of a pilot station in the field.

3.2 Examples of the application of passive techniques - Reiner Gallery (Maramureș) and Jales Mine (Portugal)

3.2.1 Reiner Adit – Cavnic

Reiner Adit is located near the Cavnic town in Maramureș County. This adit draws attention especially from the point of view of the management of the acidic water that was generated.

The study conducted by Neamțu and Pică (2014) highlights the positive results regarding the use of limestone as a passive method of acidic water treatment applied in the case of Reiner Adit. In the greening process of this gallery, the pH was fully neutralized with the limestone cladding of the gallery walls. A layer of filter material was used for the precipitated metal ions. According to the above-mentioned study, the water quality improves considerably after passing through the limestone and the filter layer. Subsequently, the water is discharged into a natural receptor.

In March 2016, a water sample was taken from the Reiner Adit. Like the study presented above, the results showed a very good water quality. Thus, the pH value was 6.82. The value of the concentration of heavy metals was: Cu - 0.0564 mg/L, Cr - 0.0038 mg/L, Zn - 4.741 mg/L, Cd - 0.2114 mg/L. The Fe and Ni concentration was below the detection limit of the device. The value of SO_4^{2-} concentration was 268.0 mg/L.

3.2.2 Jales Mine - Portugal

As mentioned in the introduction to this chapter, in 2015 I did a research internship at the University of Porto, Portugal, between 01.09.2015 - 30.09.2015. The main objective of the internship conducted in doctoral studies was to expand the knowledge in the field of geochemistry, more precisely to understand the behavior of heavy metals/metalloids in the environment.

The Jales Mine is located in the Vila Real District in northern Portugal, about 150 km from Porto. From a geological point of view, the mine is located in the region known as Campo. Together with the Gralheira and Tres mines they form the Jales mining district. The region is an auriferous one, characterized by the presence of metasedimentary rocks in the N-NE part, while in the S-SW part there are granitic rocks (Neiva and Neiva 1990).

For neutralization, limestone blocks were used in the collection basin and along the drainage channel, which carried water to the primary neutralization and aeration basin. The treatment of acidic water was based on three processes: chemical oxidation of Fe^{2+}, neutralization of acidic water with limestone and precipitation of iron oxides with consequent adsorption of other contaminants. The last basin in the treatment system was intended for the passive method, which uses plants to extract metals. The plants used were *Typha* (rush) and *Juncus* (sedge) (Boboș et al., 2010).

3.3 Description of the studied areas

3.3.1 Roșia Montană mining area

Roșia Montană is located in the Southern Apuseni Mountains and is one of the richest gold regions in Europe, belonging to the Golden Quadrangle. Roșia Montană is part of the northernmost belt of this metallogenetic district, in which other deposits of precious metals and copper are known (Bucium, Roșia Poieni) (Baciu et al., 2012).

Hydrographically, the main watercourse in the area that is affected by pollution is the Abrud River. Three tributaries of this river form the hydrographic network of the Roșia Montană area, the Roșia, Corna and Săliște streams (RMGC, 2006; Baciu et al. 2012).

Of the three valleys mentioned above, the most affected is Valea Roșia. Contaminated water from the network of underground galleries is discharged through several outlets in the Valea Roșia. The main evacuation galleries are Adit 714 and Adit Racoși. The water discharged from the two galleries has an acidic character, with a pH value between 2.5 and 3. In addition to the acidic character, the studies also indicated high concentrations of heavy metals and other chemicals such as: As , Cd, Ni, Pb, Cr, Se and SO_4 (RMGC, 2006; Baciu et al. 2012).

As a result of the mining activities in Roșia Montană, in addition to water pollution in the area, significant amounts of mining waste were generated. These are in the form of several tailings dumps of different sizes, located near the exploitation area and in the form of flotation tailings dumps, which have been placed in tailings ponds (RMGC, 2006; Baciu et al. 2012).

3.3.2 Baia Mare mining area

The Maramureș region has a long history of precious and non-ferrous metal mining (Bailly et al. 2002). Mining has been documented since the 14th century and is thought to have begun in the Roman period. Mining in the region was based on the extraction of non-ferrous metals, Cu, Pb, Zn, as well as precious metals, Ag, Au from veins of hydrothermal origin of Neogene age (Macklin et al., 2003).

Regarding the hydrography of the area, the Baia Mare depression is part of the Someș river basin (lower Someș sub-basin). The main tributaries are: Lăpuș, Cavnic and Săsar.

The study by Macklin et al. (2003) showed that the Lapuș and Someș rivers are contaminated with heavy metals from the mining activity of the past, which experienced a sharp decline after 2000, ceasing almost completely after 2006. Apart from the presence of heavy metals, another source of river contamination are industrial and urban waste coming mainly from the cities of Baia Mare and Baia Sprie (Macklin et al., 2003).

The field experiment took place on the Aurul tailings pond. It is located about 2.9 km from Baia Mare. The pond has in its vicinity (E part) a surplus water treatment plant, which after treatment is discharged into the Lăpuş River. The pond was built in 1999 and had the role of storage of tailings resulting from the activity of the tailings reprocessing plant.

3.4 Choice and description of the types of limestone used in the study

For the laboratory experiments, five types of limestone from five different areas were chosen: Viştea, Săndulești, Geomal, Buciumi and Cuciulat. Viştea and Sandulesti quarries are located in Cluj County, approximately 20 km and 35 km from Cluj-Napoca, respectively. Geomal Quarry is located in Alba County, about 25 km from Alba Iulia. Cuciulat Quarry is located near Cuciulat locality from Sălaj county. It is about 45 km from Zalău and about 55 km from Baia Mare. Buciumi Quarry is located in Maramureș County, about 30 km from Baia Mare. Given the proximity to the Aurul Pond, limestone from this quarry was used for the field experiment.

Chapter 4 Methodology of laboratory and field experiments

4.1 Laboratory experiments in which limestone was used

4.1.1 Column experiment

The purpose of the column experiment was to observe the effect of limestone on neutralizing acidic waters. The limestone was taken from the area of Cluj-Napoca (Donath Street), on the left slope of the Someş river. Before the experiment, the limestone was dried for 24 hours at a temperature of 105oC. Prior to drying, the limestone was crushed and sieved to obtain granules of 6 - 10 and 10 - 20 mm. For the experiment, an amount of 972 g of limestone (6-10 mm) was used in a cylindrical column with a volume of 800 ml.

An 800 ml cylinder was used for the closed system, in which the limestone was inserted. In the case of the open system, a gutter (PVC) with a length of 100 cm and a diameter of 5 cm at an inclination of 5 degrees was used.

In each experiment, 2 l of water from Adit 714 - Roșia Montană, a sample with the same volume from the Central Pond - Baia Mare and a control sample were used. The control sample solution had an initial pH of 2.73, close to that of the sample from Roșia Montană and the one from Central Pond.

In both systems, the 2 l of water were filtered 4 times through the column or limestone gutter, and the pH value was measured at intervals of 0, 30, 60, 120 and 180 s, with the multiparameter WTW 320i.

4.1.2 Static experiment

The static experiment was initiated to determine the efficiency of four types of limestone: Sandulesti, Geomal, Viştea and Cuciulat. The limestone was taken from the quarries and dried at room temperature for 24 hours. To obtain a granulation of 6 - 10 mm, the limestone was sieved with a vibrating sieve Retsch AS 200 basic.

In the experiment, Erlenmeyer flasks were used, in which a quantity of 120 ml of water from Roșia Montană or Băița (Maramureș) and a quantity of 150 g of limestone from the above mentioned areas were introduced. The duration of the experiment was 60 minutes. Previous studies have shown that a key parameter that determines the efficiency of neutralizing acidic water is the chemistry of the water used. For this reason, water from two distinct areas was handled in the experiment - Roșia Montană (Adit 714) and Băița (Maramureș) (Truță et al., 2017).

4.1.3 Dynamic experiment

The dynamic experiment was initiated in order to observe the behavior of the limestone by modifying parameters such as: drain length, water flow, amount of limestone, type of limestone. Open and closed systems were used. The limestone was crushed, dried at room temperature and sieved. The size of the limestone granules used in the experiments was 5-10 mm and 20-40 mm.

Water samples were collected at one-hour intervals, and the experiments lasted 5 hours (R2, R3 and R5), 8 hours (R6 and R7 experiments) and 12 hours (R9 experiment). For all experiments, the size of the limestone was 5-10 mm, except for experiment R7, where the size of the limestone granules was 20-40 mm.

In the first experiments, two open system drains with different lengths were built, of 1 m and 2 m, respectively. The drains were built of a PVC tube with a diameter of 10 cm, sectioned longitudinally.

A 5 cm diameter PVC tube was used for the closed system. The feed water was stored in a 20 l container, provided at the base with a drain and flow control valve.

Following the first experiments, it was established that the efficiency of limestone for water neutralization was better in the system with a length of 2 m, a water flow of 25 mL/min and a granulation of 5 - 10 mm. Thus, these parameters were used in the following experiments.

As mentioned above, different types of limestone were used. Thus, Geomal limestone was used in the R9 experiment.

For the application of the passive limestone treatment system in the field, two experiments were performed (R15, R16) in which limestone from the Buciumi quarry and water from the Aurul tailings pond were used. Table 4.1 presents the parameters of the drains from the 13 experiments performed in the laboratory.

Tabel 4.1 Physical parameters of the systems used in the experiments

Experiment	Drain length (m)	Flow (mL/min)	Quantity of limestone (kg)	Size of limestone (mm)	Sampling quarry	Water	System
R2	1	50	2,6	5-10	Sandulesti	Roșia Montană	Open
R3	1	25	2,6	5-10	Sandulesti	Roșia Montană	Open
R5	2	50	5,2	5-10	Sandulesti	Roșia Montană	Open
R6	2	25	5,2	5-10	Sandulesti	Roșia Montană	Open
R7	2	25	5,2	20-40	Sandulesti	Roșia Montană	Open
R9	2	25	5,2	5-10	Geomal	Roșia Montană	Open
R11	2	25	5,2	5-10	Viștea	Roșia Montană	Close
R12	2	25	5,2	5-10	Geomal	Roșia Montană	Close
R13	2	25	5,2	5-10	Viștea	Roșia Montană	Open
R14	2	25	5,2	5-10	Buciumi	Roșia Montană	Open
R15	2	25	5,2	5-10	Buciumi	Baia Mare	Open
R16	2	25	4,3	5-10	Buciumi	Baia Mare	Close
R17	2	25	5,0	5-10	Sănduleşti	Roșia Montană	Close

In all experiments, samples were collected at one-hour intervals. Samples taken for heavy metal analysis were filtered through a 0.45 µm filter, acidified to pH <2 with HNO_3 and stored in 50 ml containers at 4 ° C. At the same time, samples were taken for SO_4^{2-} analysis. These were filtered and stored in 50 ml containers at the same temperature. The analysis of heavy metals (Cd, Fe, Pb, Cr, Zn, Cu, Ni) was performed using the ZEEnit 700 Analytik Jena atomic absorption spectrometer.

The Dionex ICS1500 ion chromatograph was used for the analysis of cations and anions. The physico-chemical parameters of the water for all samples were measured with the WTW 320i multiparameter.

The mineralogical analysis of the sediments taken from the laboratory experiments was performed using the X-ray diffractometer (Bruker D8Advance).

4.1.4 Field experiment

In order to highlight the efficiency of the passive systems in the field, a pilot mini-station was built on Aurul Pond (Baia Mare). The experiment took place over a period of 17 days, from May 12 to May 29, 2016. The pilot station was built on the surface of the pond itself.

The first objective of the experiment was to neutralize the acid water by using a limestone drain. The second objective was to test the phytoextraction capacity of four different plant species (L*emna minor, Vallisneria spiralis, Juncus effusus, Phragmites australis* (reed)). The pilot mini-station was composed of two parts:

1. Limestone drain - with a role in neutralizing acidic water and reducing the concentration of heavy metals;
2. Pond with plants ("wetland") - with the role of phytoextraction of heavy metals from water.

The limestone drain was made on a length of 50 m, with trapezoidal section, having 0.25 m at the base and 0.35 m at the top. The pond with plants had a length of 3 m, a width of 2 m, with an average depth of 0.3 m. For the limestone drain was used a quantity of 1.0 t with a grain size of 40-60 mm. The limestone came from the Buciumi quarry (Maramureș County). Plants used for the pond experiment were: *L. minor, V. spiralis, J. effusus, P. australis* (common reed).

During the 17 days of the experiment, the physico-chemical parameters of the water at the entrance to the drain, at the exit from the drain and at the exit from the plant pond were monitored. At the same time, samples were taken from the same points in order to analyze ions and heavy metals. Monitoring and sampling was done every 24 hours. The samples were filtered with 0.45 µm filters in

50 ml plastic containers. The samples for heavy metals were acidified with HNO_3 to a pH value below 2.

Also, in order to analyze the heavy metals, at the end of the 17 days of the experiment, sediment samples were taken from the limestone drain from the first 10 m, 25 m and 50 m and limestone from the same distances. The sampled limestone was dried at room temperature and crust samples were taken from its surface.

For the analysis of heavy metals in plant tissue, they were dried at 105°C for 24 h, afterwards being ground with a grinder with stainless steel knives. 3 g subsamples were prepared from each vegetation sample.

4.2 Laboratory experiments in which plants were used

The working method included the analysis of quality parameters and heavy metal content of water samples and plant tissue, before and after the phytoextraction process. Over three weeks, plant species were monitored. Three types of samples were used in the laboratory: a control sample, consisting of commercially purchased bottled flat water, a water sample with a content of 50% drinking water and 50% water from Adit 714 - Roșia Montană, as well as a sample with a content of 75% drinking water and 25% water from Adit 714.

Chapter 5 Results and their interpretation

5.1 Dynamic experiment with closed / open system with multiple filtrations

In order to test the interaction between mine water and limestone, dynamic laboratory experiments were performed, based on the use of two types of systems built from limestone collected from the left bank of the Someș river, Donath Street, Cluj-Napoca. Therefore, an open system and a closed system were built, through which blank water samples, water samples from Roșia Montană and from the Central Pond (Baia Mare) were filtered several times.

1. Closed system

Following the laboratory experiment in which the closed system was used, a better efficiency of the limestone was observed in neutralizing the blank water sample (distilled water + HNO_3), compared to the natural acid water sample (Table 5.1).

Table 5.1 pH value depending on time and number of filtrations for the three water samples

Filtration	*I*			*II*		
Time (s)	*Blank pH*	*Rosia Montana*	*Central Pond*	*Blank*	*Rosia Montana*	*Central Pond*
0	2.734	2.817	3.017	6.885	3.29	6.085
30	7.255	3.49	6.24	7.499	4.027	6.205
60	6.303	3.178	5.91	7.417	3.551	6.113
120	6.331	3.19	5.595	7.419	3.512	6.17
180	6.738	4.403	5.43	7.521	3.508	6.206

Filtration	*III*			*IV*		
Time (s)	*Blank*	*Rosia Montana*	*Central Pond*	*Blank*	*Rosia Montana*	*Central Pond*
0	7.58	4.165	6.24	7.75	4.581	6.308
30	7.684	4.546	6.278	7.824	4.663	6.327
60	7.65	4.557	6.218	7.818	4.653	6.235
120	7.627	4.458	6.132	7.816	4.651	6.213
180	7.721	4.51	6.316	7.949	4.935	6.333

The Table 5.2 shows the final pH values of the waters, depending on the number of filtrations, for the three water samples tested (Blank sample, Roșia Montană sample and Central Pond sample).

Table 5.2 Final pH value depending on number of filtrations for the three water samples

Filtration	*Blank*	*Roșia Montană*	*Central Pond*
0	2.734	2.817	3.017
1	6.885	3.29	6.085
2	7.58	4.165	6.24
3	7.75	4.581	6.308
4	7.801	4.686	6.333

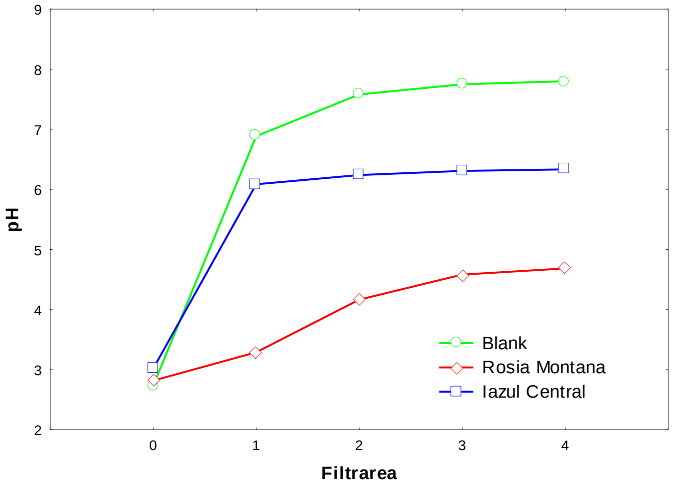


Figure 5.1 pH value depending on number of filtrations for the three water samples.

2. Open system

a. Blank sample

The Table 5.3 shows the results of pH and Eh values according to the number of filtrations for the blank water sample. A rapid neutralization of the water can be observed, even after the first filtration, the pH value reaching 7.46. After four filtration steps, the pH reaches a value of 8.52.

Table 5.3 pH and redox potential value depending on time and number of filtrations

Filtration	*I*		*II*		*III*		*IV*	
t(s)	pH	Eh (mV)	pH	Eh (mV)	pH	Eh (mV)	pH	Eh (mV)
0	2.749	196.1	8.276	-82	8.508	-93.7	8.537	-95
30	8.388	-87.4	8.598	-98.1	8.573	-96.9	8.542	-95.4
60	8.074	-71.6	8.521	-94.5	8.511	-93.8	8.518	-94.1
120	7.525	-43.5	8.494	-92.8	8.562	-96.4	8.52	-94.3
180	7.463	-40.6	8.498	-93.2	8.558	-96.2	8.521	-94.3

b. Water sample from Roșia Montană

The Table 5.4 shows the pH and Eh values according to the number of filtration steps for the water sample from Roșia Montană. A relatively slow evolution of water neutralization can be observed. After the first filtration, the pH value reaches 2.29. After four consecutive filtrations, the pH remains acidic, having a value of 4.01.

Table 5.4 pH and redox potential value depending on number of filtrations

Filtration	*I*		*II*		*III*		*IV*	
t(s)	pH	Eh (mV)	pH	Eh (mV)	pH	Eh (mV)	pH	Eh (mV)
0	1.95	236.1	2.385	216.2	3.174	176.4	3.763	146.7
30	2.471	211.6	3.157	177	3.817	143.7	3.936	137.9
60	2.289	220.8	2.973	186.2	3.702	149.5	3.911	139.2
120	2.241	223.3	2.892	190.5	3.703	149.6	3.927	138.4
180	2.29	220.8	2.988	185.7	3.808	144.3	4.012	134

c. Water sample from the Central Pond

The Table 5.5 shows the pH and Eh values according to the number of filtrations for the water sample from the Central Pond. It can be seen that after the first and second filtration steps, the pH value approaches a neutral value, reaching 6.52. After four filtrations, the pH indicates a value of 7.03.

Table 5.5 pH and redox potential value depending on number of filtrations

Filtration	*I*		*II*		*III*		*IV*	
t(s)	pH	Eh (mV)	pH	Eh (mV)	pH	Eh (mV)	pH	Eh (mV)
0	2.36	217.8	6.385	14.1	6.748	-4.3	6.999	-17.2
30	6.03	31.6	6.586	3.7	6.863	-10.3	7.055	-20.3
60	5.352	66.6	6.463	10.2	6.834	-8.9	7.004	-17.5
120	4.759	96.7	6.448	10.8	6.864	-10.3	7.008	-17.6
180	5.613	53.3	6.524	7.1	6.856	-10	7.032	-19

5.2 Static experiment

In the following, the mineralogical structure of the limestones taken from Sănduleşti, Vişțea, Geomal and Buciumi will be presented. The mineralogical analysis was performed with the support of the Department of Geology - UBB.

Table 5.6 Mineralogical analysis of limestones used in experiments

Sănduleşti		Vişțea		Geomal		Buciumi	
Mineral	Percent (%)	Mineral	Percent (%)	Mineral	Percent (%)	Mineral	Percent (%)
Calcite $CaCO_3$	96,2	Calcite $CaCO_3$	96,1	Calcite $CaCO_3$	98,3	Calcite $CaCO_3$	92,8
Kaolinite $Al_2Si_2O_5(OH)_4)$	2,4	Quartz SiO_2	3,9	Quartz SiO_2	1,7	Illite $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	7,2
Illite $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	1,4	-	-	-	-	-	-

In the first static experiment, a water sample from Roșia Montană was used (Adit 714). Table 5.7 shows the values of physico-chemical parameters depending on the type of limestone used. The highest efficiency in terms of water neutralization was recorded for the water in which Vişțea limestone was used, followed by the samples that required the use of Geomal, Cuciulat and Sănduleşti limestone. In Table 5.8 you can see the values of Pb, Ni, Cr, Zn, Fe, Cu and Cd concentrations after applying the static experiment.

Table 5.7. Physico-chemical parameters of water samples (Roșia Montană) after applying the static test

	pH	Eh (mV)	T (°C)	TDS (mg/l)	EC(µS/cm)	Salinity(‰)
R-Initial	2.6	236.6	19	3244.8	5070	2.7
R-Viștea	6.18	27.6	19	3321.6	5190	2.8
R-Geomal	6.06	34.9	19	3296	5150	2.7
R-Săndulești	5.907	44.2	19	3334.4	5210	2.8
R-Cuciulat	5.954	41.4	19	3424	5350	2.8

Table 5.8 Concentration of heavy metals from water (Roșia Montană) after application of the static test

	Pb (mg/l)	Ni (mg/l)	Cr (mg/l)	Zn (mg/l)	Fe (mg/l)	Cu (mg/l)	Cd (mg/l)
Limit	0.2	0.5	1	0.50	5.00	0.1	0.20
R0-Initial	**0.2142**	**0.9299**	0.0565	**61.11**	**2853.07**	**1.448**	**0.2889**
R-Viștea	0.1708	**0.5081**	0.03902	**44.48**	0.1818	0.03064	0.1195
R-Geomal	0.0925	**0.8322**	0.06427	**50.55**	0.4111	0.0705	**0.2316**
R-Săndulești	0.0588	0.4986	0.0171	**50.96**	0.3407	0.05269	**0.2139**
R-Cuciulat	**0.2152**	0.4088	0.02834	**51.11**	0.1813	0.04074	0.1639

In the second static experiment, a water sample from Băița - Maramureș was used. Table 5.9 shows the values of physico-chemical parameters depending on the type of limestone handled in the static experiment. As in the experiment based on the use of water from Roșia Montană, in this experiment the highest efficiency in terms of neutralizing the acidity of the water was recorded for the experiment in which Viştea limestone was used. Table 5.10 shows the values of Pb, Ni, Cr, Zn, Fe, Cu and Cd concentrations after applying the static experiment. In this experiment, the only exceedances compared to the allowed limit values were recorded in the case of Zn concentration. Otherwise, all other values, including those from the initial sample, were below the maximum legal limit.

Table 5.9 Physico-chemical parameters of water samples (Băița) after application of the static test

	pH	Eh (mV)	T (°C)	TDS (mg/l)	EC(µS/cm)	Salinity(‰)
B-Initial	2.87	220.7	19	1220	2770	1.3
B-Vistea	6.794	-7.6	19	1148	2610	1.2
B-Geomal	6.607	3.5	19	1173	2670	1.2
B-Sandulesti	6.652	0.8	19	1169	2660	1.2
B-Cuciulat	6.748	-4.8	19	1254	2850	1.3

Table 5.10 Concentration of heavy metals from water (Băița) after application of static test

	Pb (mg/l)	Ni (mg/l)	Cr (mg/l)	Zn (mg/l)	Fe (mg/l)	Cu (mg/l)	Cd (mg/l)
Limit	0.2	0.5	1	0.50	5.00	0.1	0.20
B0-Initial	0.10386	0.1609	0.01364	**67.78**	**2161.25**	0.6097	0.1741
B-Viștea	0.0996	0.1503	0.03583	**40.27**	0.07789	0.01119	0.07869
B-Geomal	0.09683	0.1267	0.0672	**52.67**	0	0.005789	0.109
B-Săndulești	0.20242	0.1697	0.174	**55.03**	0	0.004088	0.1054
B-Cuciulat	0.09251	0.1696	0.08651	**52.32**	0.6189	0.01418	0.08618

5.3 Dynamic experiment in continuous flow

The tables below show the values of the physico-chemical parameters, the concentrations of the metals Fe, Cd, Cr, Cu, Ni, Pb and Zn and of the SO42- anion. All the graphs illustrate the positive effect of the limestone channel on the acid waters from Roșia Montană (Adit 714) and Baia Mare (Auru Pond). The pH values of the water increased to a neutral value within the first hour, following a downward trend later. This phenomenon can also be observed in the case of the SO42- anion. In the case of iron, the decrease in the concentration value is much more noticeable compared to the decrease in the cadmium concentration value.

Table 5.11 The values of the physico-chemical parameters in the case of the drain of 1 m length, flow of 50 mL / min and grain size 5-10 mm (Săndulești limestone, Roșia Montană water).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (°C)
R2-i	0	2.73	228.6	4290	1886	19
R2-1	60	4.04	153	4230	1863	19
R2-2	120	3.33	194.1	4200	1849	19
R2-3	180	3.16	203.5	4190	1844	19
R2-4	240	3.1	207.1	4180	1838	19
R2-5	300	3.04	210.5	4180	1840	19

Table 5.12 The values of the physico-chemical parameters in the case of the drain of 1 m length, flow of 25 mL / min and grain size 5-10 mm (Săndulești limestone, Roșia Montană water).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (°C)
R3-i	0	2.74	228.3	4350	1914	19
R3-1	60	5.99	39	4600	2944	19
R3-2	120	5.82	49	4500	1979	19
R3-3	180	5.17	86.9	4390	1935	19
R3-4	240	4.62	118.5	4340	1909	19
R3-5	300	3.47	185.5	4300	1892	19

Table 5.13 The values of the physico-chemical parameters in the case of the drain of 2 m length, flow of 50 mL / min and grain size 5-10 mm (Săndulești limestone, Roșia Montană water).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (°C)
R5-i	0	2.83	232.2	4360	2790	20.3
R5-1	60	6.02	46.2	4680	2990	20.3
R5-2	120	5.02	107.5	4460	2860	20.1
R5-3	180	4.38	142.6	4280	2740	20.4
R5-4	240	3.48	196.3	4310	2760	20.4
R5-5	300	3.37	201	4250	2720	20.2

Table 5.14 The values of the physico-chemical parameters in the case of the drain of 2 m length, flow of 25 mL / min and grain size 5-10 mm (Sândulești limestone, Roșia Montană water).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (°C)
R6-i	0	2.8	233.5	4480	2870	19.4
R6-1	71	6.26	33.3	4760	3050	19.5
R6-2	120	6.25	34.4	4690	3000	19.2
R6-3	180	6.11	41.8	4620	2950	19.3
R6-4	240	6.01	48.2	4530	2900	19.5
R6-5	300	5.82	59.8	4490	2880	19.5
R6-6	360	5.32	88.2	4410	2820	19.5
R6-7	420	4.75	120.6	4340	2780	19.1
R6-8	480	4.55	132.3	4280	2740	19.4

Table 5.15 The values of the physico-chemical parameters in the case of the drain of 2 m length, flow of 25 mL / min and grain size 20-40 mm (Sândulești limestone, Roșia Montană water).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (°C)
R7-i	0	2.64	233.9	4520	1989	19
R7-1	60	4.76	110.3	4510	1984	19
R7-2	120	4.09	149.7	4330	1906	19
R7-3	180	3.78	167.4	4260	1874	19
R7-4	240	3.62	177.1	4210	1850	19
R7-5	300	3.35	192.5	4200	1849	19
R7-6	360	3.33	194	4230	1860	19
R7-7	420	3.34	193.1	4220	1855	19
R7-8	480	3.36	192.1	4200	1847	19

Table 5.16 The values of the physico-chemical parameters in the case of the drain of 2 m length, flow of 25 mL / min and grain size 5-10 mm (Geomal limestone, Roșia Montană water).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (°C)
R9-i	0	2.64	233.8	4530	1993	19
R9-1	86	6.45	12.2	4640	2969.6	19
R9-2	120	6.16	29.2	4640	2969.6	19
R9-3	180	6.01	37.8	4600	2944	19
R9-4	240	5.91	43.8	4540	1998	19
R9-5	300	5.79	50.5	4490	1975	19
R9-6	360	5.44	71.3	4430	1948	19
R9-7	420	4.78	109.3	4360	1920	19
R9-8	480	4.89	102.9	4410	1942	19
R9-9	540	4.65	117.1	4330	1904	19
R9-10	600	4.5	125.7	4290	1889	19
R9-11	660	4.65	116.8	4360	1916	19
R9-12	720	3.96	157.3	4240	1864	19

Table 5.17 Concentration of Cd, Fe, Cr, Cu, Ni, Pb, Zn and SO42- a. 1 m long channel, flow rate of 50 mL / min and granulation of 5-10 mm; b. 1 m long channel, flow rate of 25 mL / min and granulation of 5-10 mm; c. 2 m long canal, flow rate of 50 mL / min and granulation of 5-10 mm (Sănduleşti limestone).

Timp (min)	**a.**	Cd (mg/L)	Fe (mg/L)	Cr (mg/L)	Cu (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)	SO_4^2 (mg/L)	Timp (min)	**b.**	Cd (mg/L)	Fe (mg/L)	Cr (mg/L)	Cu (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)	SO_4^2 (mg/L)	Timp (min)	**c.**	Cd (mg/L)	Fe (mg/L)	Cr (mg/L)	Cu (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)	SO_4^2 (mg/L)
0	R2-i	0.236	1353.68	0.03535	0.863	0.6841	0.1579	197.65	5410.2	0	R3-i	0.210	1366.33	0.03611	1.139	0.6757	0.2435	206.14	5583.7	0	R5-i	0.206	1351.69	0.06895	1.119	0.461	0.2059	204.57	5500.8
60	R2-1	0.247	530.16	0.01812	3.194	1.15	0.2103	216.10	4425.0	60	R3-1	0.174	823.52	0.0244	1.644	1.582	0.26	211.57	5230.4	60	R5-1	0.175	589.50	0.1143	1.488	0.7453	0.1277	218.88	2839.1
120	R2-2	0.234	1078.96	0.03275	3.229	1.064	0.3034	214.92	5070.7	120	R3-2	0.209	856.11	0.02767	2.126	1.473	0.316	228.02	2882.6	120	R5-2	0.192	482.80	0.07974	2.618	0.6823	0.122	216.79	4156.3
180	R2-3	0.234	1179.40	0.02812	3.35	1.077	0.3766	216.92	6725.2	180	R3-3	0.220	930.62	0.02953	2.564	1.4	0.28	229.87	3237.4	180	R5-3	0.199	6.43	0.1081	3.075	0.9147	0.1971	215.41	3120.0
240	R2-4	0.249	1217.98	0.05808	3.476	1.015	0.3232	215.28	5705.2	240	R3-4	0.204	806.22	0.0313	3.158	1.489	0.3176	227.50	3905.1	240	R5-4	0.234	894.03	0.06374	2.985	0.9378	0.3618	20.86	5189.9
300	R2-5	0.232	1246.58	0.03417	2.764	0.9542	0.2794	213.19	5885.0	300	R3-5	0.196	887.38	fara proba	3.662	1.402	0.5432	225.57	4984.3	300	R5-5	0.231	1127.52	0.06067	2.843	0.9412	0.3846	20.89	5677.5

Table 5.18 Concentration of Cd, Fe, Cr, Cu, Ni, Pb, Zn and SO_4^{2-} a. drain of 2 m length, flow rate of 25 mL / min and granulation of 5-10 mm; b. Drain of 2 m length, flow rate of 25 mL / min and granulation of 20-40 mm; c. Drain 2 m long, flow rate of 25 mL / min and granulation 5-10 mm (Geomal limestone)

Timp (min)	a.	Cd (mg/L)	Fe (mg/L)	Cr (mg/L)	Cu (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)	SO_4^2 (mg/L)	Timp (min)	b.	Cd (mg/L)	Fe (mg/L)	Cr (mg/L)	Cu (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)	SO_4^2 (mg/L)	Timp (min)	c.	Cd (mg/L)	Fe (mg/L)	Cr (mg/L)	Cu (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)	SO_4^2 (mg/L)
0	R6-i	0.214	1381.63	0.0749	0.6286	0.4814	0.2435	219.18	5772.4	0	R7-i	0.241	1360.31	0.06707	1.058	0.599	0.186	230.34	5271.8	0	R9-i	0.220	1359.68	0.04764	1.033	0.5825	0.1382	213.76	5025.5
71	R6-1	0.076	3.98	0.07214	0.267	1.662	0.1777	256.09	2942.2	60	R7-1	0.152	517.53	0.08238	3.448	1.786	0.125	274.23	3030.2	86	R9-1	0.053	3.48	0.01781	0.4505	1.409	0.1235	227.42	3406.3
120	R6-2	0.138	462.18	0.07886	0.9234	0.5709	0.1303	250.72	2837.0	120	R7-2	0.221	686.49	0.1051	5.939	0.867	0.253	259.30	4304.2	120	R9-2	0.123	505.82	0.01325	1.161	0.8995	0.125	225.72	3376.3
180	R6-3	0.227	619.43	0.124	2.341	0.6622	0.1558	280.75	2866.9	180	R7-3	0.197	781.61	0.12	5.822	0.8315	0.353	254.82	4454.7	180	R9-3	0.178	764.98	0.0096	2.875	0.8008	0.1265	229.80	3524.9
240	R6-4	0.211	623.43	0.2586	2.481	0.6467	0.1418	252.47	2886.5	240	R7-4	0.211	931.95	0.08836	5.025	0.8265	0.254	259.84	4756.1	240	R9-4	0.196	769.64	0	3.208	0.7259	0.1878	224.86	2650.5
300	R6-5	0.213	675.18	0.3227	2.455	0.7072	0.1162	252.04	3028.5	300	R7-5	0.235	1099.58	0.1032	4.86	0.7848	0.276	260.71	4830.7	300	R9-5	0.206	750.35	0.01136	3.473	0.6928	0.1597	226.40	3447.3
360	R6-6	0.205	678.50	0.2762	2.666	0.8242	0.1729	256.20	3166.9	360	R7-6	0.215	1059.66	0.1447	3.236	0.821	0.4	256.12	4558.5	360	R9-6	0.216	755.67	0.02224	2.668	0.6021	0.1878	228.28	3699.4
420	R6-7	0.209	729.06	0.3974	2.862	0.8621	0.221	255.01	3318.1	420	R7-7	0.221	1086.94	0.1181	3.251	0.8166	0.42	256.04	4942.0	420	R9-7	0.242	579.26	0.03497	2.33	0.6224	0.2027	229.14	3660.3
480	R6-8	0.222	530.16	0.5724	3.063	0.8771	0.1819	244.18	3716.5	480	R7-8	0.215	1066.98	0.1252	3.692	0.8173	0.34	252.21	4925.1	480	R9-8	0.223	697.86	0.03407	2.742	0.5724	0.197	214.71	4031.9
																				540	R9-9	0.188	722.41	0.03112	3.348	0.5332	0.2223	218.00	3606.5
																				600	R9-10	0.180	680.50	0.03525	2.989	0.5929	0.2161	214.61	4248.4
																				660	R9-11	0.190	716.42	0.02218	2.483	0.5339	0.2042	215.90	4098.9
																				720	R9-12	0.186	909.33	0.03202	4.549	0.4143	0.2933	214.09	4638.7

Following the first experiments, it was observed that the drain parameters with the best results in terms of neutralizing the pH and decreasing the concentration of heavy metals and SO_4^{2-} are the following: limestone grain size - 5-10 mm, drain length - 2 m, water flow - 25 mL/min. After establishing the parameters of the experimental drain, limestone tests were performed in other areas: Viştea, Buciumi and Geomal.

In the first six experiments only the systems in oxidizing environment (open) were used, whereas in the following experiments were applied systems in anoxic environment (closed) with Viştea, Geomal, Buciumi and Săndulești limestone.

The values of the physico-chemical parameters are presented in Tables 5.19 - 5.25. In these experiments, water from Roșia Montană and the Aurul tailings pond were used.

Table 5.19 The values of the physico-chemical parameters in the case of the drain of 2 m length, flow of 25 mL/min, grain size 5-10 mm and anoxic medium (Viștea limestone and water from Roșia Montană).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (⁰C)
R11-i	0	2.61	233.3	4560	2918.4	20.1
R11-1	120	6.29	21.9	4680	2995.2	19.1
R11-2	180	6.17	28.5	4740	2607.36	19.7
R11-3	240	6.12	31.2	4730	2606.72	19.7
R11-4	300	6.1	32.8	4720	3020.8	19.9
R11-5	360	6.03	34.9	4710	3014.4	19.8
R11-6	420	6.08	33.9	4700	3008	19.9
R11-7	480	5.9	43.9	4620	2956.8	20.1
R11-8	540	5.87	45.9	4620	2956.8	19.9
R11-9	600	5.91	43.4	4620	2956.8	19.7
R11-10	660	5.74	53.4	4530	1993	19.6
R11-11	720	5.66	57.8	4500	1982	19.7

Table 5.20 The values of the physico-chemical parameters in the case of the drain of 2 m length, flow of 25 mL/min, grain size 5-10 mm and anoxic medium (Geomal limestone and water from Roșia Montană).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (⁰C)
R12-i	0	2.77	223.7	4570	2010.8	18.9
R12-1	120	5.98	39.5	5080	2235.2	19.7
R12-2	180	5.66	58	5010	2204.4	19.6
R12-3	240	5.28	79.9	4890	2151.6	19.5
R12-4	300	4.78	108.7	4800	2112	19.4
R12-5	360	4.48	125.6	4720	2076.8	9.5
R12-6	420	4.26	138.3	4640	2041.6	19.5
R12-7	480	3.7	170.6	4630	2037.2	19.5
R12-8	540	3.32	192.2	4660	2050.4	19.5
R12-9	600	3.17	201.3	4650	2046	19.5
R12-10	660	3.13	203.3	4630	2037.2	19.5
R12-11	720	3.05	207.6	4620	2032.8	19.5

Table 5.21 The values of the physico-chemical parameters in the case of the drain of 2 m length, flow of 25 mL / min, grain size 5-10 mm and oxidizing medium (Viștea limestone and Roșia Montană water).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (^{0}C)
R13-i	0	2.68	23.4	5020	2208.8	20.1
R13-1	120	6.29	22.4	5230	2301.2	18.9
R13-2	180	6.044	36.9	5260	2314.4	18.8
R13-3	240	5.947	42.5	5210	2292.4	18.9
R13-4	300	5.687	57.7	5130	2257.2	19
R13-5	360	4.757	112.3	4990	2195.6	19
R13-6	420	4.538	125.1	4930	2169.2	19
R13-7	480	4.726	114.2	4940	2173.6	19
R13-8	540	4.263	141.2	4840	2129.6	19
R13-9	600	3.712	173.6	4840	2129.6	18.9
R13-10	660	3.405	191.5	4830	2125.2	18.9
R13-11	720	3.703	174	4790	2107.6	18.8

Table 5.22 The values of the physico-chemical parameters in the case of the drain of 2 m length, flow of 25 mL / min, grain size 5-10 mm and oxidizing medium (Buciumi limestone and Roșia Montană water).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (°C)
R14-i	0	2.691	233.2	5050	2222	18.8
R14-1	120	5.92	43.7	5240	2305.6	17.4
R14-2	180	4.716	114.7	5010	2204.4	17.3
R14-3	240	5.672	53.3	5110	2248.4	17.4
R14-4	300	5.583	63.8	5020	2208.8	17.4
R14-5	360	5.285	81.3	4950	2178	17.4
R14-6	420	4.754	112.3	4870	2142.8	17.4
R14-7	480	4.561	123.7	4810	2116.4	17.4
R14-8	540	4.322	137.8	4740	2085.6	17.4
R14-9	600	3.945	159.8	4720	2076.8	17.4
R14-10	660	3.576	181.5	4730	2081.2	17.4
R14-11	720	3.51	185.3	4740	2085.6	17.3

Table 5.23 The values of the physico-chemical parameters in the case of the drain of 2 m length, flow of 25 mL / min, grain size 5-10 mm and oxidizing medium (Buciumi limestone and Auru Pond water).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (°C)
R15-i	0	2.917	220	5400	2376	17.1
R15-1	120	6.62	3.7	5090	2239.6	16.4
R15-2	180	6.616	3.1	5090	2239.6	17.3
R15-3	240	6.6	3.9	5090	2239.6	17.3
R15-4	300	6.58	4.8	5090	2239.6	17.3
R15-5	360	6.563	6.5	5080	2235.2	17.3
R15-6	420	6.54	7.7	5080	2235.2	17.3
R15-7	480	6.54	7.7	5080	2235.2	17.3
R15-8	540	6.55	7.2	5080	2235.2	17.5
R15-9	600	6.53	8	5080	2235.2	17.9
R15-10	660	6.53	8	5080	2235.2	17.9
R15-11	720	6.49	10.1	5080	2235.2	17.7

Table 5.24 The values of the physico-chemical parameters in the case of the drain of 2 m length, flow of 25 mL / min, grain size 5-10 mm and anoxic medium (Buciumi limestone and Auru Pond water).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (°C)
R16-i	0	2.899	221.2	5410	2380.4	18.3
R16-1	120	6.44	13.6	5130	2257.2	19.1
R16-2	180	6.32	20.5	5130	2257.2	19.8
R16-3	240	6.31	21	5130	2257.2	19.3
R16-4	300	6.348	19	5120	2252.8	18.8
R16-5	360	6.334	19.8	5130	2257.2	18.6
R16-6	420	6.3	21.9	5110	2248.4	19
R16-7	480	6.301	21.8	5100	2244	19.1
R16-8	540	6.303	21.7	5090	2239.6	19.2
R16-9	600	6.285	22.7	5100	2244	19.3
R16-10	660	6.338	19.6	5100	2244	19.2
R16-11	720	6.28	23	5080	2235.2	19.2

Table 5.25 The values of the physico-chemical parameters in the case of the drain of 2 m length, flow of 25 mL / min, grain size 5-10 mm and anoxic environment (Sandulesti limestone and Roșia Montană water).

	Time (min)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)	T (°C)
R17-i	0	2.66	235.1	5140	2261.6	18.4
R17-1	120	5.7	57.1	5150	2266	17.9
R17-2	180	5.523	67.4	5030	2213.2	18.2
R17-3	240	5.387	75.4	4970	2186.8	18.3
R17-4	300	5.04	95.7	4890	2151.6	18.2
R17-5	360	4.514	126.6	4750	2090	18.8
R17-6	420	4.377	134.6	4690	2063.6	19.1
R17-7	480	4.279	140.2	4630	2037.2	19.2
R17-8	540	4.231	143.1	4590	2019.6	19.2
R17-9	600	4.147	148	4580	2015.2	19.2
R17-10	660	4.209	144.4	4550	2002	19.3
R17-11	720	4.189	145.5	4530	1993.2	19.1

Previous experiments from R11 to R17 demonstrate that the neutralization of acidic waters in the two areas studied (Roșia Montană and Baia Mare) can be achieved using different types of limestone in different media (anoxic / oxidant).

In relation to experiments R11 and R13, in which Viştea limestone was used to reduce the concentrations of heavy metals in the water sample from Roșia Montană, it can be observed that the closed system is more efficient. In the first 120 minutes, the decrease in the concentration of heavy metals was higher in the case of Fe, Cd and Pb metals. In the case of decreased SO_4^{2-} concentration, the two systems were equally effective until the 360th minute, when the closed system kept its efficiency constant compared to the open system.

If Geomal limestone and water from Roșia Montană were used, it can be seen that the two systems were effective in decreasing the Fe concentration throughout the experiments. The decrease of the Cd concentration was registered especially in the first 240 minutes with a better efficiency for the closed system. In decreasing the Pb concentration, the closed system was more efficient compared to the open one. The open system was effective in the first 180 minutes. The two systems were also effective in decreasing the concentration of SO_4^{2-} throughout the experiments.

In the experiments (R15 and R16) in which limestone from the Bucumi quarry (Maramureș) and water from the Aurul Pond were used, both systems used were effective in reducing the concentration of Fe, Cd, Cu, Pb and Zn.

In the R17 and R6 experiments in which Săndulești limestone and water from Roșia Montană were used, the two systems were effective in causing the decrease of the concentration of Fe, Pb and SO_4^{2-}.

5.4 The mineralogical analysis of sediments

The mineralogical analysis of the sediments taken at the end of each experiment is presented in Table 5.26. From this table it can be seen that the predominant mineral in the sediments is gypsum (CaSO4 · 2H2O). Exceptions are experiments R15 and R16, in which the water from the Aurul Pond was used. The predominant mineral in these sediments was calcite ($CaCO_3$).

Table 5.26 Mineralogical analysis of sediments

Experiment / Mineral	**R2** (%)	**R3** (%)	**R5** (%)	**R6** (%)	**R7** (%)	**R9** (%)	**R11** (%)	**R12** (%)	**R13** (%)	**R14** (%)	**R15** (%)	**R16** (%)	**R17** (%)
Gypsum	85,8	93,6	85,7	96,7	98,0	96,8	55,5	90,8	60,3	100	45,4	37,8	68,0
Calcite	14,2	6,4	14,3	3,3	2,0	3,2	44,5	9,2	39,7	-	54,6	59,9	32,0
Quartz	-	-	-	-	-	-	-	-	-	-	-	2,3	-

5.5 Laboratory experiments in which plants were used

5.5.1 Analysis of physico-chemical parameters and heavy metals in water before and after the experiment

In the phytoremediation experiment, the physico-chemical parameters of water quality, heavy metals (Pb, Cu, Zn, Ni, Fe, Cr, Cd), metalloids (As) were analyzed. For the pH value, the efficiency was established in procentage (Figure 5.2).

After the phytoremediation process, it was observed that all plants had a neutralizing effect on acidity.

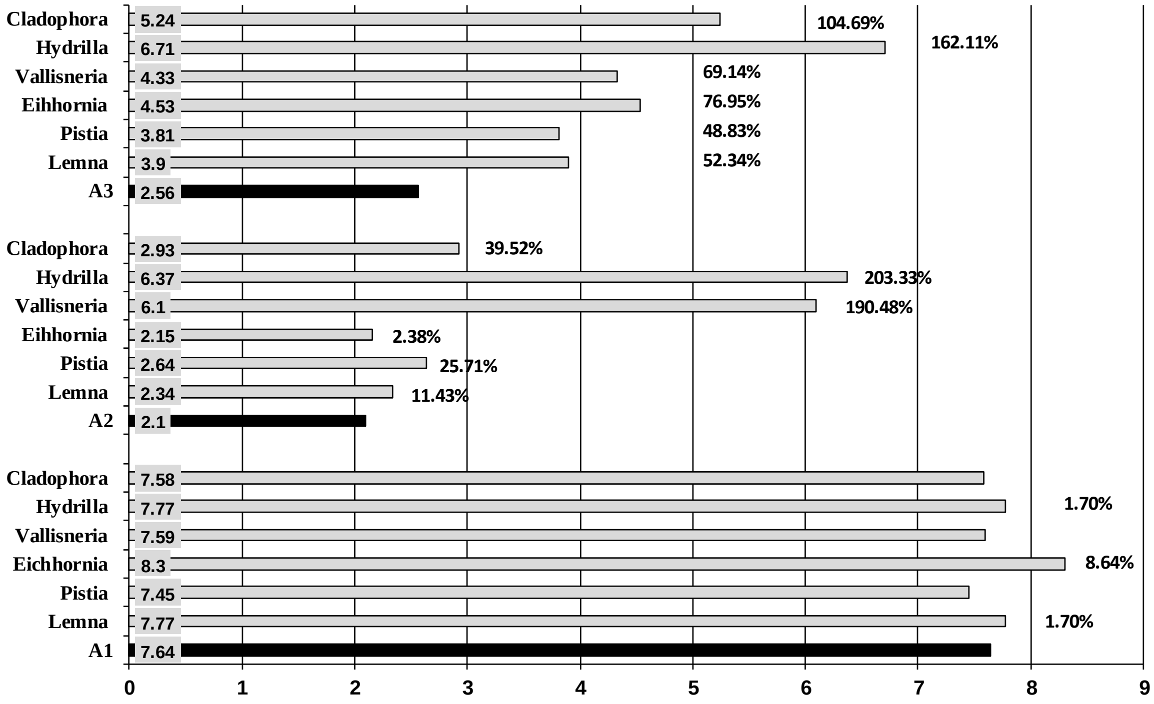


Figure 5.1 Phytoremediation laboratory tests for acid mine water – pH value (Rosia Montana, Adit 714). A = Before phytoremediation (04/03/2015) B = After phytoremediation (04/29/2015). Variants: 1 = unpolluted water (flat); 2 = water to dilute 50% 714 Gallery; 3 = water to dilute 25% 714 Gallery.

Most plants manage to reduce the concentration of Fe in water. In contrast, for Ni, only *Vallisneria* and *Hydrilla* showed this reducing effect. For Zn and Cu the plants that have a reducing effect are *Vallisneria* and *Hydrilla*. Most plants manage to reduce the concentration of As in the water, and instead Cr is reduced by *Pistia*, *Eichornia*, *Valisneria* and *Hydrilla*. Cd is reduced by *Eichornia*, *Vallisneria* and *Hydrilla*, and Pb is reduced by all plants (*Lemna, Pistia*, *Eichornia*, *Vallisneria*, *Hydrilla* and *Cladophora*).

In the Table 5.27 it is calculated the efficiency of plants for extracting heavy metals from water.

Table 5.27 Efficiency of plants for the extraction of heavy metals from water

Plants	Adit 714 RM	Fe	Cu	Zn	Pb	Cd	Ni	Cr
Lemna	Dilution ½ (50%)	50,3%	-	-	9,33%	-	-	4,37%
	Dilution ¼ (25%)	86,0%	-	-	63,67%	-	-	-
Pistia	Dilution ½ (50%)	94,2%	-	-	80,60%	-	-	65,16%
	Dilution ¼ (25%)	92,3%	-	-	73,19%	-	-	66,00%
Eichhornia	Dilution ½ (50%)	3,1%	-	-	46,03%	-	-	-
	Dilution ¼ (25%)	91,6%	5,3%	1,29%	81,81%	47,79%	2,17%	100,00%
Vallisneria	Dilution ½ (50%)	99,4%	100,0%	44,80%	99,32%	38,00%	22,02%	89,57%
	Dilution ¼ (25%)	91,5%	99,4%	25,13%	74,92%	35,96%	21,35%	100,00%
Hydrilla	Dilution ½ (50%)	99,3%	100,0%	51,20%	96,19%	50,46%	30,82%	100,00%
	Dilution ¼ (25%)	90,2%	100,0%	91,23%	78,44%	93,86%	70,69%	100,00%
Cladophora	Dilution ½ (50%)	-	-	-	28,61%	-	-	64,52%
	Dilution ¼ (25%)	63,1%	100,0%	93,28%	89,35%	98,65%	17,09%	-

5.5.2 Analysis of heavy metals from plants

In the previous subchapter, the concentrations of heavy metals in the water from Roșia Montană were analyzed before and after the experiment. This subchapter presents the results of the analysis of heavy metals from plant tissue to observe their bioaccumulation capacity. Table 5.28 shows the concentrations of heavy metals in the plant tissue of *Lemna minor, Pistia stratiotes, Eichhornia crasipes, Vallisneria spirallis, Hydrilla verticilata* and green alga *Cladophora glomerata*.

Table 5.28 Concentration of heavy metals in plant tissue after experiment

	Lemna			Pistia			Eichornia		
mg/ kg	Tap water	Dil.50%	Dil.25%	Tap water	Dil.50%	Dil.25%	Tap water	Dil.50%	Dil.25%
Fe*	*882.40*	*62003.36*	*19976.35*	*343.55*	*16581.87*	*5884.64*	*2455.11*	*13152.32*	*1533.45*
Pb	3.85	8.30	6.03	0.62	3.80	1.67	1.01	2.04	2.08
Cd	0.40	1.66	2.10	0.13	0.92	0.39	0.51	0.91	0.20
Cr	2.45	10.40	5.20	1.06	2.12	1.20	1.42	1.62	1.55
Ni	4.26	9.00	7.89	5.32	7.53	11.53	3.34	5.55	8.01
Cu	22.81	47.86	88.83	29.13	27.73	20.99	54.64	31.78	217.50
Zn	63.46	240.54	229.12	75.23	138.30	69.35	91.11	136.24	176.72
	Vallisneria			Hydrilla			Cladophora		
mg/ kg	Tap water	Dil.50%	Dil.25%	Tap water	Dil.50%	Dil.25%	Tap water	Dil.50%	Dil.25%
Fe*	*170.43*	*4163.71*	*3106.37*	*322.95*	*7992.08*	*3686.84*	*894.43*	*9211.52*	*6060.77*
Pb	0.43	1.59	1.85	0.46	2.88	1.27	1.51	3.22	2.54
Cd	0.27	1.78	0.81	0.07	2.32	4.86	0.07	0.51	2.32
Cr	5.34	2.48	2.74	1.50	5.95	2.70	1.82	3.64	2.67
Ni	4.28	5.08	4.32	3.94	18.21	8.96	3.80	5.21	5.90
Cu	32.60	57.26	60.63	16.15	62.89	49.14	25.81	39.08	44.56
Zn	39.62	126.32	96.93	45.01	223.16	222.97	19.73	75.75	295.51

5.4 Field experiment - Aurul pond (Baia Mare)

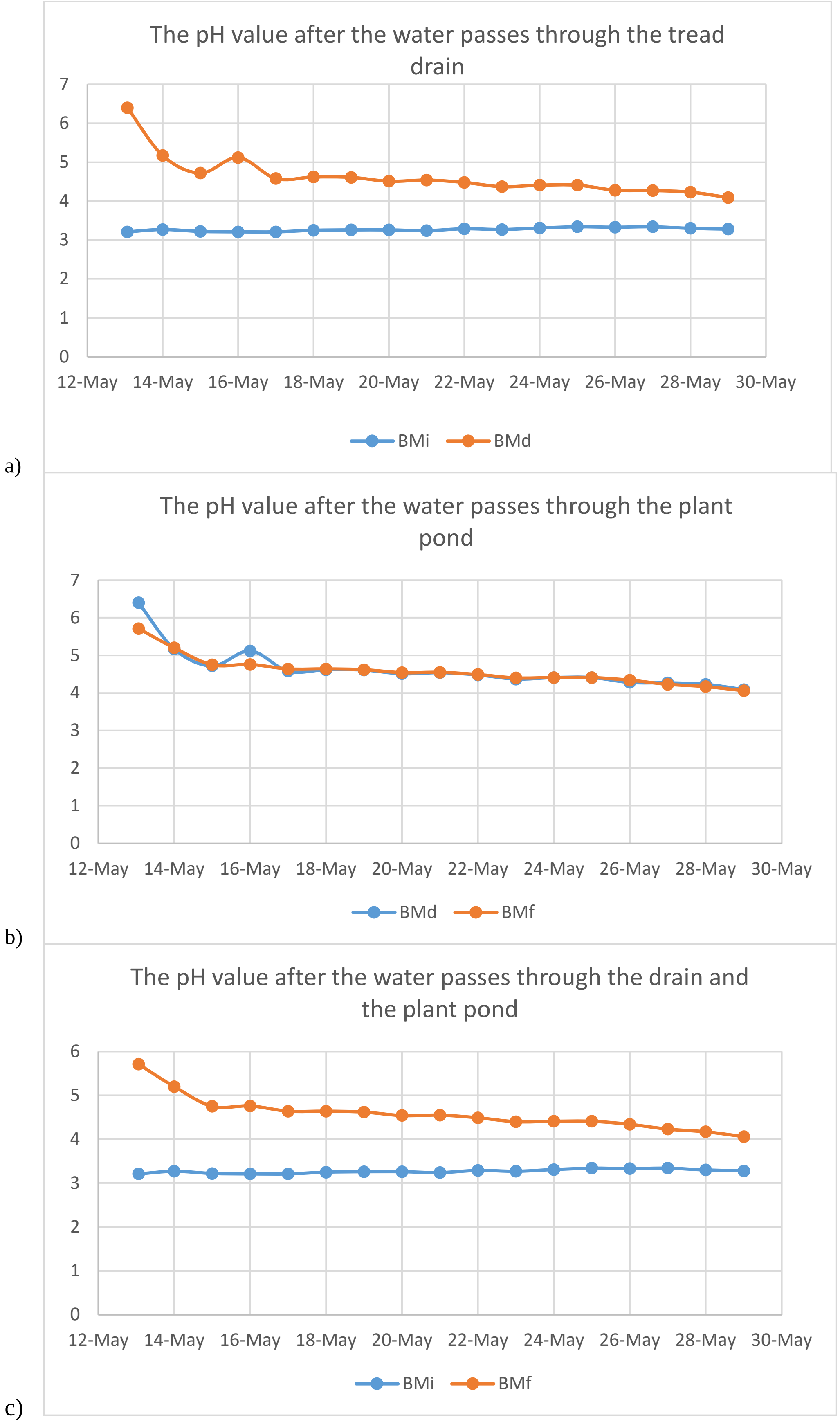
5.4.1 Monitoring of physico-chemical parameters and heavy metals during the pilot experiment

The Table 5.38 shows the values of the physico-chemical parameters and the concentrations of anions, cations and heavy metals for the samples collected during the 17 days of monitoring. As shown in Chapter 4 - Methodology, the samples were taken from 3 points - the entry of water into the limestone drain (BMi), the outflow of water from the limestone drain (BMd) and the outflow of water from the plant pond (BMf).

The Figure 5.2, presented in the form of three graphs, shows the pH values during the monitoring days. Analyzing as a whole the system installed in the field (limestone drain + pond with plants), it can be seen from Figure 5.2c that it was succesful in terms of decreasing the pH of the water.

Table 5.1 Results of physicochemical parameters, anions, cations and heavy metals for samples taken during the 17 days of monitoring

		Physico-chemical parameters								Cations				Anions		Heavy metals						
Date	**Sample**	**pH**	**Eh**	**EC**	**TDS**	**Salinity**	**O2**	**turbidity**	**Temperature**	**Na^+**	**K^+**	**Mg^+**	**Ca^+**	**SO_4^{2-}**	**Cl^-**	**Fe**	**Cd**	**Pb**	**Cu**	**Ni**	**Cr**	**Zn**
			mV	µS/cm	mg/L	‰	mg/L	FNU	°C	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
12.05.2016	BM1	3.19	199.6	6580.00	4211.20	3.5	5.79	4.48	16.2	304.41	131.92	402.57	462.33	6453.81	42.8671							
occurrence: 46min	BM 2	6.38	16.6	6890.00	4409.60	3.7	4.46	98.4	19.3	340.33	149.8	444.15	456.6	5517.114	56.8425							
12 ore		5.59	61.7	6450.00	4128.00	3.5	3.69		18.6													
13.05.2016	BM3i	3.21	198.5	6170.00	3948.80	3.3	4.7	12.2	19.3	324.04	119.55	427.29	481.5	7075.471	47.3971	1376.91	0.1934	0.1087	2.085	0.4173	0.07854	286.19
	BM3d	6.4	15.4	4200.00	1847.00	2.1	5.51	26.7	15.2	167.72	82.84	233.96	542.84	3681.303	24.6721	1243.15	0.1044	0.07971	0.05315	0.2921	0.03433	245.89
	BM3f	5.71	55	6100.00	3904.00	3.3	4.42	24.4	22.5	266.26	123.51	292.38	312.79	6438.527	43.0923	1314.85	0.1773	0.0729	0.0568	0.4585	0.06711	292.69
14.05.2016	BM4i	3.27	193.5	6020.00	3852.80	3.2	4.22	8.32	17.4	253.12	115.91	335.05	417.21	5045.72	36.0668	1293.90	0.1379	0.2325	2.068	0.3	0.04785	247.71
	BM4d	5.17	86.3	6420.00	4108.80	2.8	4.1	26.8	17.6	267.64	126.76	343.18	493.49	4187.792	40.0023	1230.18	0.1318	0.2876	0.1857	0.316	0.02625	255.44
	BM4f	5.2	84.5	6120.00	3916.80	3.3	4.62	32.4	17.6	220.22	117.59	288.51	490.61	4660.174	33.7427	1240.82	0.1268	0.2846	0.1843	0.3343	0.08668	256.17
15.05.2016	BM5i	3.22	197.6	5570.00	3564.80	2.9	5.47	7.48	15.7	286.01	115.45	385.32	451.48	6825.785	48.2214	1350.37	0.1564	0.1323	2.335	0.3799	0.1188	269.16
	BM5d	4.72	111.5	5480.00	3507.20	2.9	5.34	22.4	16	243.45	109.86	326.37	502.38	5210.542	35.3793	1303.74	0.1509	0.178	0.2444	0.3829	0.0818	274.51
	BM5f	4.75	110	5240.00	3353.60	2.7	5.72	20.6	15.1	226.11	104.64	302.29	476.29	5048.597	34.6849	1291.77	0.1372	0.09617	0.1902	0.3971	0.0688	266.44
16.05.2016	BM6i	3.21	194.7	5900.00	3776.00	3.1	4.92	16.8	11.4	269.86	129.02	358.16	418.29	5718.353	51.7027	1354.63	0.1831	0.2697	2.539	0.43	0.1123	280.48
	BM6d	5.12	91.3	5620.00	3596.80	2.9	5.56	25.4	11.6	265.3	115.18	357.11	479.18	5748.261	40.7455	1336.67	0.1777	0.3173	0.3366	0.4476	0.0867	288.09
	BM6f	4.76	110.3	5360.00	3430.40	3	5.12	31.6	11.6	255.79	111.48	348.37	533.78	5876.712	36.836	1300.75	0.136	0.2739	0.192	0.412	0.13	272.61
17.05.2016	BM7i	3.21	198.5	5750.00	3680.00	3.1	5.36	3.64	15.1	257.63	114.96	341.43	409.76	6136.847	36.6824	1366.60	0.163	0.2268	2.584	0.4415	0.05737	281.30
	BM7d	4.58	119.8	5780.00	3699.20	3.1	5.79	10.8	15.3	282.8	117.52	381.54	525.3	6148.694	38.7141	1350.37	0.1594	0.2089	0.3431	0.4433	0.06821	283.20
	BM7f	4.64	116.6	5680.00	3635.20	3	5.82	7.56	13.3	276.18	118.69	371.78	543.19	6339.129	42.2701	1319.11	0.1396	0.1982	0.2923	0.4363	0.07547	281.03
18.05.2016	BM8i	3.25	196.3	6020.00	3852.80	3.2	5.47	4.86	13.2	258.66	118.68	351.29	409.03	6288.544	41.0069	1361.08	0.1895	0.3405	2.815	0.4086	0.07055	290.79
	BM8d	4.62	117.9	5890.00	3769.60	3.1	7.25	2.46	14.2	261.51	118.61	349.9	489.02	6187.963	41.8133	1329.42	0.178	0.3648	0.369	0.436	0.04732	295.41
	BM8f	4.64	116.6	5480.00	3507.20	2.9	6.6	8.96	13.2	256.97	112.52	348.96	493.96	5992.387	40.5453	1303.28	0.1249	0.321	0.2727	0.3952	0.05877	284.29
19.05.2016	BM9i	3.26	195.5	5990.00	3833.60	3.2	5.65	62.1	12.7	268.52	109.84	365.27	440.05	6573.597	43.0564	1354.63	0.1575	0.2477	2.26	0.4073	0.1564	285.64
	BM9d	4.61	118.2	5940.00	3801.60	3.1	5.92	1.42	12.1	278.56	121.25	376.9	521.76	6810.493	44.5427	1339.26	0.1576	0.3634	0.3199	0.4522	0.1282	299.21
	BM9f	4.62	117.4	5650.00	3616.00	3	6.6	8.07	11.9	250.49	115.05	347.69	488.92	6135.034	39.1812	1308.86	0.1409	0.2961	0.2667	0.4247	0.07252	292.15
20.05.2016	BM10i	3.26	195.6	6060.00	3878.40	3.2	4.74	50.6	13.8	283.27	112.75	394.85	510.23	6993.75	47.07	1349.96	0.2157	0.2268	2.443	0.3895	0.1697	279.13
	BM10d	4.51	123.8	6000.00	3840.00	3.2	4.82	11.4	16.1	299.42	116.5	412.27	521.32	7310.01	49.13	1355.56	0.2069	0.2451	0.251	0.4259	0.02973	293.24
	BM10f	4.54	122.5	5790.00	3705.60	3	5.82	6.93	13.2	305.6	109.78	432.08	560.12	7317.09	48.09	1330.68	0.2153	0.2259	0.2566	0.4259	0.059	284.56
21.05.2016	BM11i	3.24	196.7	6510.00	4166.40	3.5	4.53	21.8	14.6	330.25	122.84	464.87	514.95	8189.17	51.92	1385.89	0.2292	0.2921	2.481	0.4266	0.05482	295.14
	BM11d	4.54	122.1	6370.00	4076.80	3.4	4.56	0.27	13.2	303.12	120.82	419.9	524.81	7672.14	46.95	1355.49	0.2211	0.3398	0.2444	0.451	0.01467	301.92
	BM11f	4.55	121.4	6130.00	3923.20	3.3	5.98	6.42	12.9	327.36	117.49	460.99	596.97	7878.14	50.56	1313.99	0.2159	0.3533	0.2131	0.4265	0.02378	296.22
22.05.2016	BM12i	3.29	194	6720.00	4300.80	3.6	4.55	8.8	15.3	367.98	125.73	508.56	631.71	8992.39	57.93	1391.41	0.2288	0.2271	2.126	0.4326	0.04733	306.81
	BM12d	4.48	125.8	6580.00	4211.20	3.5	4.56	<0.001	16	374.22	124.42	514.18	590.45	8832.71	58.71	1370.06	0.2208	0.2977	0.276	0.4537	0.0511	306.54
	BM12f	4.49	125	6440.00	4121.60	3.5	5.7	5.8	14.7	352.99	123.56	490.62	771.92	8345.41	58.88	1347.38	0.2203	0.2908	0.2432	0.4387	0.05629	305.45
23.05.2016	BM13i	3.27	194.9	6810.00	4358.40	3.7	4.11	7.47	17.7	338.48	131.82	460.13	1120.94	7956.49	53.78	1384.60	0.2187	0.1595	1.735	0.4323	0.1123	304.10
	BM13d	4.37	132.2	6620.00	4236.80	3.6	4.06	1.87	22	350.85	130.99	468.86	570.7	7108.58	349.52	1364.93	0.2236	0.2107	0.2326	0.4729	0.0717	305.45
	BM13f	4.4	130.1	6620.00	4236.80	3.6	5.06	7.35	18.3	299.44	129.96	404.09	566.61	7215.38	47.95	1355.94	0.2159	0.1321	0.1797	0.4111	0.01011	295.41
24.05.2016	BM14i	3.31	193	6930.00	4435.20	3.8	4.06	8.62	16.5	323.38	133.76	438.3	510.28	7856.69	54.07	1393.14	0.2254	0.3329	1.661	0.4495	0.1258	303.82
	BM14d	4.41	129.7	6800.00	4352.00	3.7	4.26	<0.01	18.7	343.91	130.48	465.7	614.84	8014.92	51.13	1371.34	0.2239	0.3348	0.2809	0.4731	0.1091	308.17
	BM14f	4.41	129.9	6780.00	4339.20	3.7	5.35	7.05	17.5	332.74	131.08	448.78	529.9	7728.57	51.25	1359.36	0.217	0.3398	0.2606	0.4254	0.07386	304.10
25.05.2016	BM15i	3.34	191.3	6530.00	4179.20	3.5	4.91	6.9	15.5	319.54	125.79	436.24	584.28	6826.21	52.23	1370.92	0.2065	0.2222	1.785	0.4042	0.09831	296.77
	BM15d	4.41	129.9	6390.00	4089.60	3.4	5.72	0.5	17.2	267.18	126.23	390.45	777.31	7229.21	871.45	1349.10	0.2131	0.2764	0.4889	0.3865	0.08204	288.09
	BM15f	4.41	130	6320.00	4044.80	3.4	6.82	6.81	16.6	304.83	213.8	409.58	546.57	6579.42	47.37	1334.13	0.2056	0.2188	0.4907	0.3943	0.1005	286.73
26.05.2016	BM16i	3.33	191.8	6620.00	4236.80	3.6	4.22	4.44	15.7	296.08	130.39	393.35	556.41	6686.6	47.56	1376.90	0.2279	0.1068	1.669	0.4423	0.1146	279.94
	BM16d	4.28	137.2	6500.00	4160.00	3.5	4.7	3.4	19	320.03	129.21	426.87	621.68	7261.47	52.85	1355.94	0.2183	0.1374	0.4931	0.4315	0.06638	293.24
	BM16f	4.34	133.8	6520.00	4172.80	3.5	6.48	6.72	16.1	356.83	127.78	482.18	580.31	7828.94	56.87	1343.54	0.2151	0.1194	0.476	0.3901	0.03253	311.16
27.05.2016	BM17i	3.34	191.3	6790.00	4345.60	3.7	3.73	6.13	17.3	336.19	133.51	436.1	538.17	7531.05	51.96	1346.11	0.2276	0.2139	1.607	0.39	0.0555	301.38
	BM17d	4.27	138.1	6690.00	4281.60	3.6	4.71	<0.01	21.8	327.58	131.99	427.55	557.76	7330.24	51.1	1313.12	0.226	0.2106	0.3359	0.3929	0.0623	309.25
	BM17f	4.23	140	6750.00	4320.00	3.7	5.98	4.65	18.2	324.59	135.48	432.7	522.84	7417.73	50.26	1293.90	0.2171	0.2116	0.3484	0.4201	0.07845	309.53
28.05.2016	BM18i	3.3	193.6	6930.00	4435.20	3.8	3.61	6.1	19.4	337.17	136.04	441.59	557.31	7768.97	54.74	1372.63	0.2303	0.2767	1.574	0.4491	0.07579	314.41
	BM18d	4.23	140.4	6760.00	4326.40	3.7	4.02	<0.01	23.3	334.45	134.7	439.42	565.85	7384.7	53.88	1346.53	0.2347	0.2874	0.3025	0.4827	0.05819	317.13
	BM18f	4.17	143.5	6830.00	4371.20	3.7	7.42	4.68	19.9	322.2	134.8	422.28	542.28	7255.58	48.59	1288.64	0.2248	0.2778	0.3271	0.4866	0.06926	322.02
29.05.2016	BM19i	3.28	194.3	6930.00	4435.20	3.8	3.56	7.96	20.5	337.8	136.17	448.74	547.59	7951.81	53.95	1334.94	0.2433	0.3431	1.514	0.4989	0.1145	316.59
	BM19d	4.09	148.1	6810.00	4358.40	3.8	3.42	0.15	27.8	351.44	136.2	462.61	534.61	7836.81	54.01	1297.34	0.237	0.3202	0.2836	0.5022	0.1001	318.21
	BM19f	4.06	150.1	6940.00	4441.60	3.8	6.75	3.73	24	337.83	137.46	442.67	550.04	7780.08	52.78	1219.92	0.2405	0.3115	0.399	0.5165	0.08597	323.37


The pH value after the water passes through the tread drain

The pH value after the water passes through the plant pond

The pH value after the water passes through the drain and the plant pond

Figure 5.3 pH value during the monitoring days - a) after the water passes through the limestone drain, b) after the water passes through the plant pond, c) after the water passes through the drain and the plant pond

5.4.2 Mineralogical analysis and heavy metals from limestone crust and sediments

The Table 5.30 shows the minerals present in the crust and sediments taken from the limestone drain from distances of 10, 25 and 50 meters.

Table 5.30 Minerals present in the crust and sediments taken from the limestone drain at distances of 10, 25 and 50 m

Sample Mineral	**C1** (%)	**C2** (%)	**C3** (%)	**T1** (%)	**T2** (%)	**T3** (%)
Gypsum	61,2	53,8	41,9	48,0	22,1	30,5
Calcite	9,8	4,1	22,6	-	5,3	33,4
Quartz	28,9	19,7	20,2	21,9	44,9	15,2
Orthoclase	-	22,5	14,5	-	9,0	12,7
Schwertmannite	-	-	-	18,3	18,8	8,3
Jarosite	-	-	-	8,7	-	-
Hematite	-	-	-	0,2	-	-
Goethite	-	-	-	3	-	-

The Table 5.31 shows the concentrations of heavy metals in the crust on the limestone taken from 10 m (C1), 25 m (C2) and 50 m (C3). At the same time, the concentrations of heavy metals from the sediments taken from the same distances are presented - 10 m (T1), 25 m (T2) and 50 m (T3).

Table 5.31 Concentration of heavy metals in crust on limestone from the first: 10 m (C1), 25 m (C2), 50 m (C3) and sediment from the first: 10 m (T1), 25 m (T2), 50 m (T3)

	Fe	Cd	Pb	Cu	Ni	Cr	Zn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
C1	52975.16	5.53	480.67	499.00	19.91	34.27	9376.43
C2	52119.66	5.93	586.67	538.33	19.54	31.65	8878.36
C3	51057.66	5.89	509.33	501.67	10.22	13.87	5729.00
T1	52798.16	2.68	673.70	423.33	17.34	22.78	6703.00
T2	51647.66	2.32	694.87	507.67	11.81	15.34	8498.33
T3	50925.00	8.73	488.20	324.33	16.43	8.06	9376.43

5.4.3 Heavy metals from the plants

The Table 5.32 shows the concentrations of heavy metals in the plant tissue of the plants used in the experiment.

Table 5.32 Concentration of heavy metals in plant tissue at the beginning and end of the experiment

	J. effusus-tulpini		*J. effusus-rădăcini*		*P. australis-tulpini*		*P. australis-rădăcini*		*V. spiralis-tulpini*		*V. spiralis-rădăcini*		*L. minor*	
mg / kg	Înainte	După	Înainte	După	Înainte	După	Înainte	După	Înainte	După	Înainte	După	Înainte	După
Fe	379.73	2875.14	2449.98	5843.15	946.03	8808.71	9585.97	20711.71	2527.87	25229.18	3611.11	25860.44	740.59	42343.17
Mn	219.34	1302.07	251.50	630.34	293.75	2744.67	821.24	1993.07	444.12	1258.56	421.83	1008.20	865.54	3353.95
Zn	50.89	194.36	43.72	137.82	75.63	542.92	234.27	201.65	206.49	239.44	394.32	305.47	41.35	720.62
Cr	9.49	3.14	6.85	17.80	16.50	384.71	10.92	1.45	3.81	7.16	5.13	7.13	4.74	19.57
Co	0.23	3.67	0.95	4.30	1.00	4.48	5.11	4.72	1.44	4.08	2.38	4.11	1.34	14.05
Ni	2.73	3.07	2.59	5.12	4.82	96.32	6.42	7.40	5.69	3.37	10.71	4.68	4.07	9.27
Cu	9.60	5.91	13.14	32.62	5.80	156.52	58.34	15.60	54.03	72.07	97.63	107.11	16.41	183.56
As	1.38	2.58	3.07	13.85	5.28	26.66	16.99	42.20	5.47	45.31	5.34	48.46	4.28	146.11
Cd	6.93	2.77	3.35	1.85	0.19	0.66	3.43	1.30	1.60	1.14	1.65	1.67	0.18	3.29
Pb	2.61	<0.15	<0.15	<0.15	2.80	13.13	<0.15	4.65	7.75	<0.15	7.85	<0.15	4.71	<0.15

Chapter 6 Discussions

The most important factors to be considered in the design of passive acid water treatment systems are: water chemistry (pH, concentration of heavy metals and sulphates, redox potential), residence time of water in the treatment system (directly dependent flow rate), the physico-chemical characteristics of the material used for neutralization and the physical characteristics of the drain (slope, profile, length, etc.) (Bernier et al., 2002; Robert S. Hedin & Watzlaf, 1994).

In order to highlight the importance of water chemistry, in the laboratory experiments carried out in this study, water was used from different areas such as Baia Mare (Central Pond, Aurul Pond), Roșia Montană (Adit 714), and for comparison a control sample using acid and drinking water. The residence time was controlled in the case of experiments by changing the water flow or the number of water filtrations through the column or limestone drain. The material used to neutralize the water was limestone. To highlight the importance of the type of limestone used in passive systems, it was collected, as described in Chapter 4, from several areas and geological formations (Cluj-Napoca, Viştea, Sandulesti, Geomal, Buciumi, Cuciulat). Physical characteristics, such as the length and diameter of the drains used in the experiments, were also modifed.

Comparing from the point of view of chemistry, the two types of water used in the dynamic experiments, it can be said that the water samples from Roșia Montană had an average pH of about 2.7, compared to the average pH of the water from the Aurul Pond, which had a value of 2.9. Also, the concentration of SO_4^{2-} anion was different, aspect mentioned in Chapter 5 (Results). Thus, the concentration of the SO_4^{2-} anion is higher in the water from Roșia Montană compared to the water from the Aurul pond.

In what concerns the concentration of heavy metals, it could be observed that the averages of the concentrations of Cd, Ni and Cr were higher in the water samples from Roșia Montană compared to the water samples from the Aurul Pond. Thus, the average Cd concentration was 0.22 mg / L, Ni was 0.58 mg / L and Cr was 0.07 mg / L in the water samples from Roșia Montană. Instead, for the water samples from the Aurul pond, the average concentrations were 0.20 mg / L, 0.43 mg / L, respectively 0.06 mg / L.

A higher average of the concentration of Fe, Pb, Cu and Zn was in the water samples from the Aurul tailings pond. The average Fe concentration was 2383 mg / L, Pb - 0.42 mg / L, Cu - 5.22 mg / L and Zn - 299.21 mg / L. For the water samples from Roșia Montană, the average concentrations for the four metals were as follows: Fe - 1945 mg / L, Pb - 0.31 mg / L, Cu - 2.40 mg / L and Zn - 228.98 mg /L.

On the limestone surface, in open drains, the oxidation of Fe^{2+} to Fe^{3+} is favored, which precipitates in the form of iron hydroxide. In addition, the capacity of neutralizing limestone is also affected by the precipitation of aluminum hydroxides and gypsum (Brăhaiţa et al., 2017). Once the surface of the limestone granules was covered with precipitate, in the laboratory experiments presented in this thesis, a reduction of the neutralization efficiency of the limestone was observed after the first hour. The study by Hammarstrom et al. (2003) showed that the pH value of water from a coal mine increased from 2.9 to 7. Due to the coating of limestone with precipitate, after 48 hours the pH dropped below 4.

In the majority of laboratory experiments, a decrease in SO_4 concentration was observed in the first hours, followed by an upward trend. The increase is due to the fact that $CaCO_3$ started to be less reactive due to the precipitation of gypsum on the limestone surface and with the decrease of the pH value, part of this gypsum started to dissolve (Brăhaiţa et al., 2017). This observation was also described in the study by Offeddu et al. (2015) who used a limestone column. In this study, two synthetic acid solutions (H2SO4) were used, one with a higher concentration of Fe at pH = 2 and the other with a higher concentration of Al at pH = 2 and 3.

Two presumed reasons for the high efficiency in the reducing of the concentration of Fe using limestone, are its surface, which functions as a support for the absorption of the metal ions and the presence of calcium carbonate dissolved, which increases the pH, leading to the precipitation of iron and of other metals in the form of oxides, hydroxides or carbonates (Brăhaiţa et al., 2017).

It was observed that the most important reductions in metal concentrations were recorded in the first 120 minutes. Table 6.2 shows the metals, for which, the concentrations decreased in the first 120 minutes depending on the type of limestone and the system used.

Table 6.2 Metals whose concentrations decreased in the first 120 minutes

	Vistea		Geomal		Buciumi		Sandulesti	
System Metal	Closed	Open	Closed	Open	Closed	Open	Closed	Open
Fe	x	x	x	x	x	x	x	x
Cd	x	x	x	x	x	x	x	x
Cr	-	-	x	x	x	-	-	-
Cu	x	x	x	-	x	x	-	-
Ni	-	-	-	-	-	x	-	-
Pb	x	x	x	x	x	x	x	x
Zn	x	x	x	-	x	x	-	-

The study by Soler et al. (2008) highlighted the effect of granulation on the process of decreasing Fe concentration. Thus, the use of small limestone grain (1-2 mm) determines a higher capacity to decrease the Fe concentration compared to larger grain (2-5 mm).

Most passive acid water treatment systems use several methods, often in series, to neutralize water and oxidize and precipitate metals (Jeff Skousen et al., 2017). Thus, if with the help of limestone drains an attempt was made to neutralize and decrease the concentrations of metals, the study also included the use of plants as a continuation of the acid water treatment process.

The effect of aquatic species on bioremediation has been highlighted in numerous studies. Therefore, the effect of bioaccumulation of metals for certain plant species such as *Vallisneria spiralis;* water hyacinth - *Eichhornia crassipes; Hydrilla verticillata*; water salad - *Pistia stratiotes* and green alga *Cladophora glomerata* has been demonstrated for metal accumulation and wastewater treatment (Buta et al., 2011; McCutcheon & Schnoor, 2003; Núñez et al., 2011; Sim et al., 2008; Stoica et al. , 2009, Malschi et al., 2015, Brăhaița et al., 2015a).

The effect of bioaccumulation of metals in the tissue of the three plant species and green algae could be observed in our study. Moreover, in the field study from the Aurul Pond, the bioaccumulation of metals in the tissue of the *Vallisneria spiralis* plant was observed.

Another plant species widely used in bioremediation studies is Lemna minor belnging to the Araceae family. Numerous results have highlighted its effect in the bioaccumulation of pollutants, metals and wastewater treatment (Dosnon-Olette et al., 2011; Malschi et al., 2013; Rahmani & Sternberg, 1999).

Chapter 7 Conclusions

The first experiments in which a column and a drain with limestone were used to neutralize the acidic water taken from Roșia Montană and Central Pond (Maramureș), pointed out that the use of limestone is a viable method. Also, the experiment showed that limestone is more efficient in neutralizing synthetic water compared to natural water. The difference in limestone efficiency for the types of water used is given, as studies have shown, by the chemistry of the waters (Brăhaița et al., 2015b).

The main objective of the first continuous flow experiments (R2-R9) was to determine the optimal parameters of the drain. Thus, in the process of treating the acidic water from Roșia Montană, the parameters followed were: the length of the drain, the water flow and the grain size of the limestone (Brăhaiţa et al., 2017).

It was observed that the efficiency of water neutralization with the help of limestone increases directly proportional to the increase in the length of the drain. In addition to the length of the drain, it was observed that the flow is also an important parameter. Thus, a low flow rate results in a higher efficiency in the treatment of acidic water.

Following the first dynamic experiments in continuous flow, it was observed that the drain parameters with the best results in terms of neutralizing the pH and decreasing the concentration of heavy metals and SO_4^{2-} are: limestone granulation - 5-10 mm, drain length - 2 m, water flow - 25 mL/min.

The following experiments from R11 to R17 demonstrate that the neutralization of acidic waters in the two studied areas (Roșia Montană and Baia Mare) can be achieved using different types of limestone in different environments (anoxic / oxidant).

Comparing the neutralization efficiency depending on the type of system, it can be concluded that the closed system was efficient for the experiment in which Viștea limestone and water from Roșia Montană were used. The open system was more efficient in neutralizing the water from Roșia Montană in the experiments in which Geomal and Viştea limestone was used. In the experiments in which Buciumi limestone and water from the Aurul Pond were analyzed, the open system was slightly more efficient in neutralizing the solution.

Regarding the decrease of heavy metal concentrations in the experiments in which Viștea and water limestone from Roșia Montană was used, the open system was more efficient in reducing Fe, Cd, Pb, Cu, Ni and Zn and less efficient in decreasing Cr. The closed system was more efficient in decreasing the concentration of Fe, Cd, Pb, Ni and Zn and less efficient in decreasing the concentration of Cu and Zn.

In the experiments in which Geomal limestone and water from Roșia Montană were used, the open system was more efficient in decreasing the concentration of Fe, Cd, Cr and less efficient in decreasing the concentration of Pb, Cu and Ni. The closed system was more efficient in decreasing the concentration of Fe, Cd, Pb and less effective in decreasing the concentration of Cr and Ni.

The experiments in which Sandulesti limestone and water from Roșia Montană were used, both the closed system and the open system were efficient in decreasing the concentration of Fe, Cd and Pb.

The experiments in which Buciumi limestone and water from the Aurul pond were used, the open system was effective in decreasing the concentration of Fe, Cd, Pb, Cu, Ni, Cr, Zn, and the closed system was more effective in reducing the concentration of Fe, Cd, Pb, Cu and Zn.

As in the case of the first experiments (R2-R9), the decrease of the SO_4^{2-} concentration could be observed as well for the experiments from R11 - R17.

When both closed and open systems were used, the efficiency of decreasing the concentration of SO_4^{2-} was relatively similar for all types of limestone used.

From the mineralogical analysis of the sediments taken at the end of each experiment, it can be seen that the predominant mineral in the sediments is gypsum ($CaSO_4 \cdot 2H_2O$). Exceptions are experiments R15 and R16, in which the water from the Aurul tailings pond was used. In this case, the predominant mineral in the sediments was calcite ($CaCO_3$).

Following the phytoremediation experiment in the laboratory, it could be observed that most of the plants managed to reduce the concentration of Fe from the water. Instead, for Ni, only *Vallisneria* and *Hydrilla* showed this ability. For Zn and Cu, the only plants with bioaccumulative effect were *Vallisneria* and *Hydrilla*. Most plants manage to reduce the concentration of As from the water, but instead Cr is reduced only by *Pistia, Eichornia, Valisneria* and *Hydrilla*. The concentration of Cd is reduced by *Eichornia, Vallisneria* and *Hydrilla*, and the concentration of Pb is reduced by all plants used in experiments (*Lemna, Pistia, Eichornia, Vallisneria, Hydrilla* and *Cladophora).*

Analysis of heavy metals from plant tissue indicated the fact that depending on the experimental water type - blank sample, water sample with a content of 50% tap water and 50% water from Adit 714 and the sample with a content of 75% tap water and 25% water from Adit 714 - the plants have bioaccumulated concentrations of Fe, Cd, Cr, Ni, Cu and Zn.

For the experiment performed in the field at the Aurul pond, from the point of view of water neutralization it can be concluded that the limestone drainage system + plant pond are efficient. The most pronounced neutralizing effect was given by limestone.

Through the results obtained in the laboratory experiments and in the field experiment from the Aurul Pond, the three proposed objectives were achieved. Thus, the potential for neutralization and reduction of metal concentrations was highlighted; as well as the ability of metals to bioaccumulate in the plant tissue of plants. The field experiment showed that passive techniques tested in the laboratory can also be implemented in the field. At the same time, this study contributes to the development and encouragement of studies on the use of passive techniques in acid water treatment in Romania as well.

Results dissemination

International Conferences and National Conferences with International Participation:

International U.A.B. – B.EN.A. Conference, May 25-27th, 2017, Use of limestone in open as well as in closed system for treating acidic water. Laboratory study, Dorian Ioan Brăhaița, Călin Baciu, Ionan Cristian Pop, Carmen Roba, Radu Mihaiescu, Cristina Modoi, Roxana Truță - oral presentation (poster).

ELSEDIMA, May 26-28th, 2016 - *The efficiency of limestone in neutralizing acid mine drainage – a laboratory study,* Dorian Ioan Brăhaița, Ioan-Cristian Pop, Călin Baciu, Radu Mihăiescu, Cristina Modoi, Gabriela Popita, Roxana-Maria Truța - oral presentation (poster).

ENVIRONMENT & PROGRESS, 29-30 OCTOMBRIE 2015 - *The Use of Aquatic Plants for the Treatment of Acidic Waters Polluted with Heavy Metals,* Ioan Dorian Brăhaița, Dana Malschi, Erika Andreea Levei, Claudiu Tanaselia, Carla Nicoară, Elena Rînba - oral presentation (poster).

ENVIRONMENT & PROGRESS, OCTOBER 29-30th, 2015 - *Passive Systems for Neutralizing the Acid Waters by Using Limestone,* Dorian Ioan Brăhaița, Călin Baciu - oral presentation (poster).

International U.A.B. – B.EN.A. Conference, May 28-30th, 2015 - *The efficiency of limestone in passive treatments of acid mine drainage – influence on the value of pH,* Dorian Ioan Brăhaița, Călin Baciu - oral presentation (poster).

ELSEDIMA, September 18-19th, 2014, Phytoremediation study of water polluted with heavy metals using floating macrophytes: *Lemna minor* and *Pistia stratiotes***,** Dorian Ioan Brăhaița, Dana Malschi, Gabriela Emilia Popița - oral presentation (poster).

Published articles

Brăhaița I. D., Pop I. C., Baciu C., Mihăiescu R., Modoi C., Popița G., Truță R. M., 2017, *The efficiency of limestone in neutralizing acid mine drainage – a laboratory study,* CARPATHIAN JOURNAL of EARTH and ENVIRONMENTAL SCIENCES

Truța R. M., **Brăhaița I. D.,** Pop C. I., Baciu C., Popița G., 2017 Batch experiment to test the limestone treatment on two types of acid mine water. AES Bioflux 9(1):92-98.

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Malschi Dana; Oprea Ioan C.; Ştefănescu Lucrina; Popiţa Gabriela E.; **Brăhaiţa Dorian Ioan**; Rînba Elena; Kadar Rozalia, *Research on wastewater bioremediation using aquatic species for heavy metals phytoextraction and bioaccumulation,* Environmental Engineering & Management Journal (EEMJ) . Nov2015, Vol. 14 Issue 11, p2577-2589. 13p.

Brăhaița I. D., Malschi D., Popița E. G., 2015 *Phytoremediation study of water polluted with heavy metals using floating macrophytes: Lemna minor and Pistia stratiotes*. AES Bioflux 7(2):155-162.

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