Batch experiment to test the limestone treatment on two types of acid mine water

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Abstract. Using limestone in passive acid water treatment systems has been proven to be efficient in numerous cases, and cost-effective. Limestone has the ability to increase the pH and to determine the precipitation of some heavy metals from the aqueous solutions. This research shows the efficiency of four distinct types of limestone in the treatment of water from Rosia Montana and Baia Mare mining areas. Limestone collected from four sites in Romania (Cuciulat, Sandulesti, Geomal and Vistea) was used in the laboratory experiment. The water samples were taken from the Baia Mare mining area – Adit Baita, and from Rosia Montana – Adit 714. In order to identify the most effective type of limestone for raising the pH, a sample of 120 mL of water and 150 g of limestone (grain size 5-10 mm) were stirred for 60 minutes. The results revealed that the most suitable type of limestone for increasing the pH is the one from Vistea, followed by Cuciulat, Geomal and Sandulesti. The heavy metal concentrations in water (Fe, Cd, Zn and Cu) were analyzed using atomic absorption spectroscopy (AAS). The results have shown that the heavy metal concentrations decreased for all types of limestone used.
Key Words: acid mine drainage, passive treatment system, heavy metals, alkalinity production.

Introduction. Mining, especially in the case of precious and base metals, but also of coal, is very often associated with acid drainage problems that can cause long-term impairment to watercourses and biodiversity. Furthermore, some effluents generated by metal mining industry contain large quantities of toxic substances, such as cyanides and heavy metals (Akcil & Koldas 2006).

Acid mine drainage (AMD) is generated by both active and abandoned mines, affecting the quality and potential uses of water supplies in mining regions worldwide. Metals in the mine drainage degrade the aquatic habitat and can be toxic to aquatic organism (Cravotta 2008). These acid waters are one of the biggest environmental problems caused by mining of sulpide-rich mineral deposits associated with coal and metal-bearing mineral deposits (Nieto et al 2013).

According to US EPA (1994), acid is generated at mines sites when metal sulphide minerals, which are present in the host rock, are oxidized. The oxidation of sulphide minerals consists of several reactions (Equations 1, 2):

$$2FeS_2(S) + 2H_2O + 7O_2 \rightarrow 4H^+ + 4SO_4^{2-} + 2\,Fe^{2+} \tag{1}$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \tag{2}$$

In the normal chemical processes that are taking place in the pH range between 3.5-4.5, the bacterial activity of *Metallogenium* catalyses the reaction (Equation 3; US EPA (1994)). When the pH drops below 3.5 *Thiobacillus ferrooxidans* dominate the bacteria assemblage.

$$2FeS_2\ (s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{3}$$

The ferric iron hydrates occur as an amorphous yellow, orange, or red precipitate on the stream bottoms, commonly known as „yellow boy" (U.S. EPA 1994) (Equation 4).

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3(s) + 3H^+ \qquad (4)$$

All these reactions generate significant amounts of acid that make the solution even more aggressive against the rock.

Due to high costs imposed by the traditional methods of treating acid water from mining sites, new passive methods have been developed. The main purpose of the new techniques is to use abundant resources, such as limestone, to design an effective and inexpensive method, as a viable solution to remedy environmental problems imposed by acid waters from mining areas.

During the recent decades, a series of studies were performed worldwide, in order to develop efficient passive methods for treating acid mine waters. Most researches use limestone in open channels or in anoxic drains, resulting in considerable reduction of water acidity and also in effective precipitation of most of the heavy metals present in water (Ziemkiewicz et al 1997; Hammarstrom et al 2003; Alcolea et al 2012; Ziemkiewicz et al 2003; Cravotta & Trahan 1999; Brahaita et al 2015).

Kusin et al (2013) have demonstrated in their study that limestone treatment of acid water is a method worth to be further investigated. The dissolution of calcite ($CaCO_3$) can neutralize acidity and increase pH, alkalinity ($HCO_3^- + OH^-$) and Ca^{2+} in acidic waters. As the pH increases to near-neutral values, concentration of Fe^{3+}, Al^{3+}, and other metals can decline consequently to their precipitation or adsorption (Kusin et al 2013).

The current contribution presents the results of the laboratory experiments using four different types of limestone to treat acid water from two mining areas from Romania: Rosia Montana- Adit 714, and Baia Mare- Adit Baita. The main purpose of this research is to highlight the most efficient type of limestone in removing heavy metals (Cd, Zn, Cu, and Fe) and increasing the value of residual water pH.

Material and Method. The sites chosen for collecting acid water for the experiments belong to representative mining areas in Romania. Rosia Montana is a gold mine exploited since pre-Roman times, both in the underground and open pit. The underground mining activities have ceased in 1985. Recent mining operations, combined with historical mining activities in the area have led to AMD generation at the surface and also in the underground. Disturbance from these historical activities is evident in several places along the Rosia Valley. Adit 714 collects and discharges acidic seepage from old underground mining works, acting as an underground passage way that resurfaces at 714 m elevation above sea level. Adit 714 flow ranges between 18 m^3 $hour^{-1}$ and about 63 m^3 $hour^{-1}$ (5 to 17.5 L s^{-1}), with an average flow of 51 m^3 h^{-1} (14.2 L s^{-1}) (RMGC, 2011).

The second sampling site for acid water is Baita Adit, located in Gutai Mountains, Maramures region, north-west of Romania. The region displays serious environmental issues due to intense pollution by sulphide leak, caused by ancient and recent mining of Pb-Zn-Cu-Au-Ag.

The limestone used for the tests was collected from active quarries in Geomal, Vistea, Sandulesti and Cuciulat sites. In order to remove the moisture, the limestone was dried for 24 hours at a temperature of 105°C before the experiment. Prior to drying limestone, it has been crushed and sieved to obtain a uniform fraction of 5-10 mm.

The experiments consisted in the use of 120 mL of acidic water from the two sources, Rosia Montana and Baita, in which 150 g of limestone was added. Every type of limestone was put into contact with each type of water in Erlenmeyer flasks.

After determining the physical and chemical parameters of the initial sample, the flasks were manually shaken for 60 min, which has proven to be sufficient for a good contact time between acid water and limestone. Then, the final physical parameters were measured.

Metals were analyzed by an atomic absorption spectrometer (ZEEnit 700 Analytik Jena), and physicochemical parameters were measured by using the Multiparameter WTW320i.

The graphs were built using Statistica 8.0 and Excel software packages.

Results and Discussion. The graphs and tables below are showing the results of the laboratory experiments using four different types of limestone on two types of acidic water from mining areas.

The initial quality of the water samples used in the experiments has been assessed by measuring the physicochemical parameters. As can be seen in Table 1, the water samples had very low pH (2.87 for water samples from Baia Mare, and 2.6 for samples from Rosia Montana), high conductivity imposed by the total of dissolved substances in the solution, and high concentration of heavy metals (Table 2). All these characteristics are representative for acid mine waters, and exceed the maximum admissible contents established by the Romanian legislation in HG 188/2002 (NTPA 001).

Table 1

Initial physicochemical parameters for each acidic water sample

Parameters	*M.U.*	*Baia Mare – Adit Baita*	*Rosia Montana – Adit 714*
pH	pH unit	2.87	2.6
Eh	mV	220.7	236.6
T	°C	19	19
TDS	mg/L	1220	3244.8
EC	μS/cm	2770	5070
Salinity	‰	1.3	2.7

Table 2

Initial concentration of metals in each acidic water sample

Parameters	*M.U.*	*Baia Mare- Adit Baita*	*Rosia Montana- Adit 714*
Zn	mg/L	67.78	61.11
Fe	mg/L	2161.25	2853.07
Cu	mg/L	0.6097	1.448
Cd	mg/L	0.1741	0.2889

Further on, each water sample has been treated with every type of limestone. As expected, the pH values have increased in both cases as a result of the contact with limestone, as shown in Figure 1. The water sample from Baia Mare, Baita Adit, proved to be more suitable for neutralizing with limestone, the pH rising to values close to 7, thereby falling in optimal limits for the aquatic life. The water sample from Rosia Montana, Adit 714 has been more refractory, reaching values of pH around 6 after the treatment under similar conditions as the Baia Mare sample. The Eh of both water samples is decreasing (Figure 1).

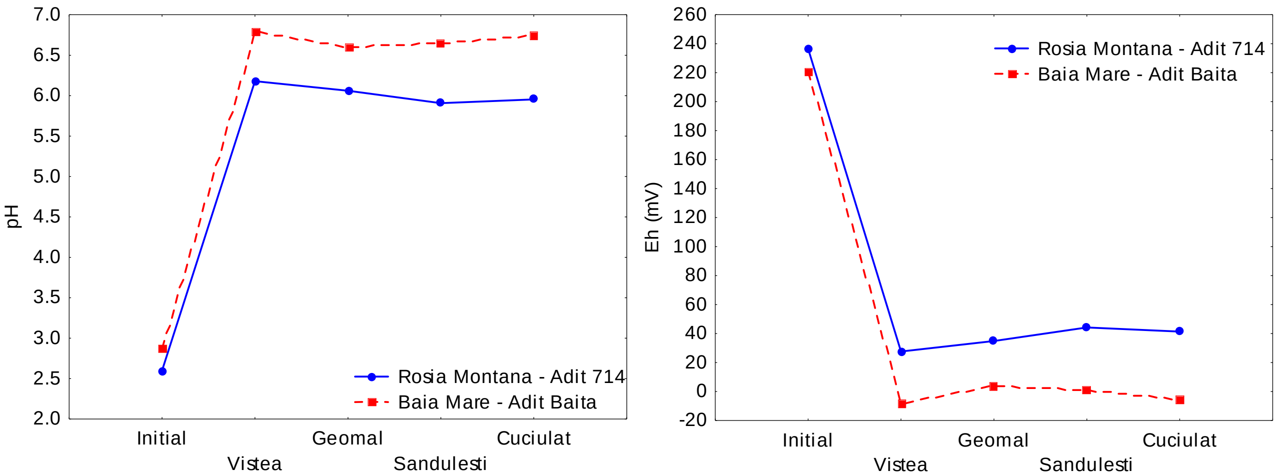

Figure 1. The evolution of pH and Eh depending on the limestone type.

Significant declines of the heavy metal concentrations were observed after the limestone treatment of the water samples, presumably due to adsorption on the surface of limestone grains, as shown in Figures 2 to 5. The removal efficiency rate of heavy metals depends on limestone porosity, dimension of the grains, and contact time between water and rock. A time interval of 60 minutes has been considered to be relevant for this experiment.

The electrical conductivity values are elevated, in correspondence with the high TDS content.

The Vistea and Cuciulat limestones, with a relatively high porosity, were the most effective for the removal of cadmium. After the laboratory experiments, for both water samples, the concentration of Cd decreased below 0.2 mg/L, which is the maximum allowable content- CMA- according to NTPA 001 (Figure 2).

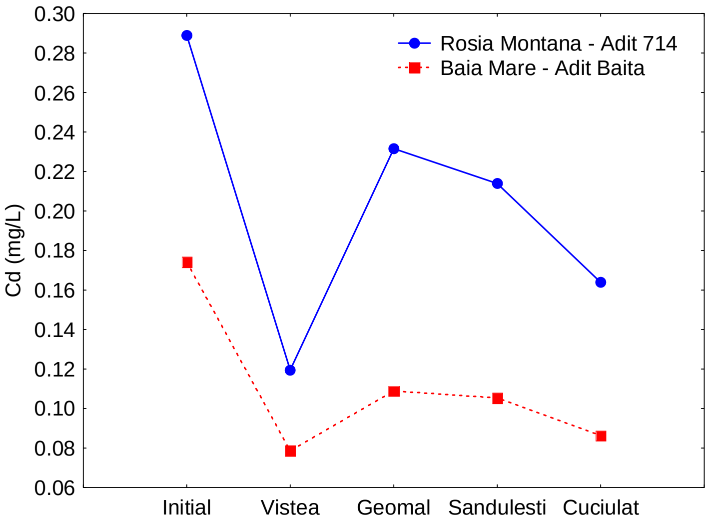

Figure 2. Effect of each type of limestone on the removal of Cd ions from AMD.

For copper removal, all limestone types were efficient (Figure 5), managing to decrease the Cu concentration in the AMD below 0.1 mg/L, the maximum admissible concentration established by NTPA 001.

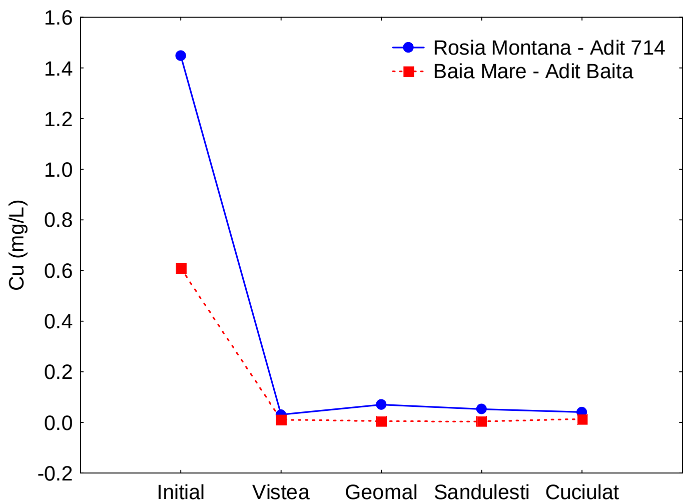

Figure 3. Effect of each type of limestone on the removal of Cu ions from AMD.

Also for iron removal (Figure 4), all limestone types were efficient, and the concentration obtained in the treated water after fulfilling the laboratory experiment are lower than 5 mg/L, the limit established by NTPA 001. The initial iron concentration for the water sample from Rosia Montana was 2853.07 mg/L, while for the Baia Mare water sample, the initial concentration was 2161.25 mg/L. After the experiment, the iron concentration in solution was lower than 0.41 mg/L for Rosia Montana water sample, and lower than 0.61 mg/L for Baia Mare water sample.

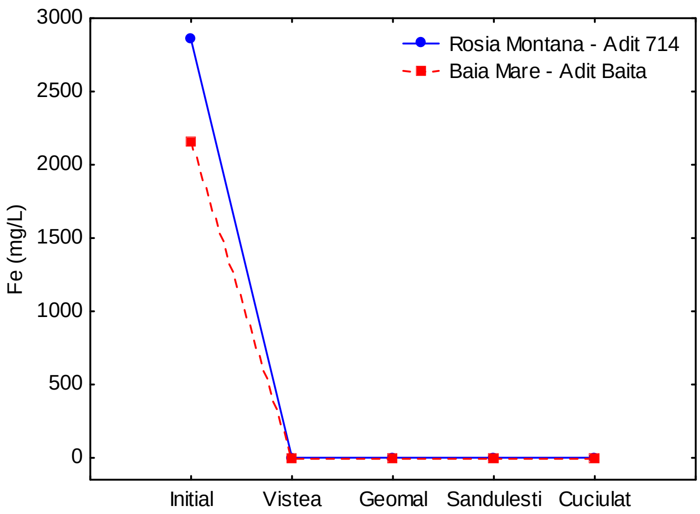

Figure 4. Effect of each type of limestone on the removal of Fe ions from AMD samples.

Our attempts were less successful in the case of zinc (Figure 5). Although a decrease of the Zn concentration has been noticed, the efficiency of the treatment is low for every limestone type, with some variations related to the characteristics of the limestone. The most effective for both water types was Vistea limestone.

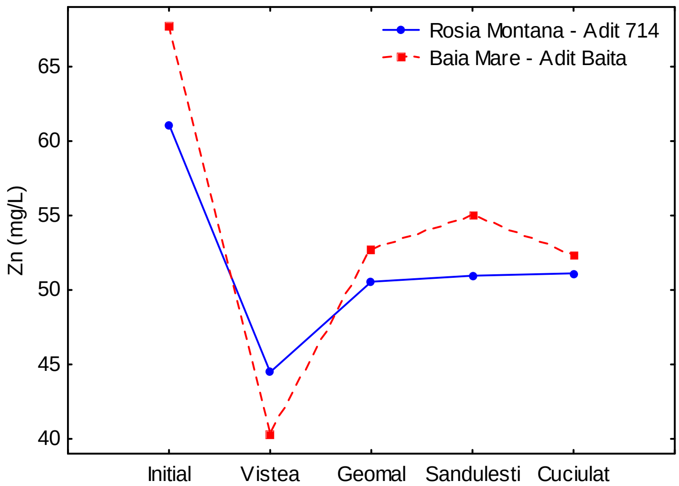

Figure 5. Effect of each type of limestone on the removal of Zn ions from AMD.

Conclusions. In the present study a natural and low-cost material, namely the limestone, was investigated in the laboratory experiments as a potential alternative in the treatment of acid mine drainage. The method proved to be effective in reducing the concentration of heavy metals by raising the pH of the solution, forcing them to precipitate.

The experiments have shown that the effectiveness of the method depends on the type of limestone, water characteristics, and the contact time between water and rock. The limestone method is a good alternative for neutralizing the acidic waters and reducing the concentration of heavy metals. The method was shown to be effective in reducing iron, copper, cadmium and zinc concentrations.

The limestone from Vistea, with a higher porosity than the other types, proved to be the most effective in treating AMD. All parameters considered in the study for both water samples, from Rosia Montana – Adit 714 and Baia Mare – Adit Baita, were improved. For the water sample from Rosia Montana, the limestone samples from Vistea and Cuciulat were effective in improving the water quality. The experiments with the water sample from Baia Mare have recorded improvements of the parameters, by using limestone from Vistea, Geomal and Sandulesti.

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