

THE EFFICIENCY OF LIMESTONE IN NEUTRALIZING ACID MINE DRAINAGE – A LABORATORY STUDY

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Abstract: The neutralization of acid mine drainage (AMD) by limestone proved to be effective in various laboratory tests and real-scale applications worldwide. The present contribution describes the results of an experimental approach intended to test the limestone's efficiency under laboratory conditions. Two open channels have been built, with the length of 1 and 2 m respectively. In the first channel (1 m long), 2.6 kg of limestone (granulometry 5-10 mm) were used at two different flow rates: 25 ml/min and 50 ml/min. For the second channel (2 m long), 5.2 kg of limestone were used at the same flow rates. In each experiment the samples were collected every hour for measuring the ion concentrations. The results of all the experiments have shown that in the first hour, the pH value increased from 2.3 up to 4.04-6.26. After 5 hours of contact, the pH value increased constantly between 3.04 and 5.82, in relation with the channel's length and flow rates. In regard to the flow rate, the highest efficiency in terms of neutralization was observed for the lower flow rate (25 mL / min) associated with a pH value of 6.26 for the first hour and 4.55 after 8 hours. Another important parameter associated with the experiments was the limestone grain size. The results showed that larger grain size (20-40 mm) are less effective in neutralizing acidic water compared to the case when a smaller grain size (5-10 mm) was used. The heavy metals (Cd, Fe) and sulphate concentration decreased in the first couple of hours of interaction. Following this study, it can be concluded that the contact time between water and limestone is of high importance. By adjusting the drain length and the water flow rate, there is an increase in the contact time. Efficiency of Cd and Fe retention was observed especially in the first hour of experiments. The same was also noticed for the ability of the limestone to remove SO_4^{2-} .

Key words: AMD neutralization, limestone, pH, heavy metals, Rosia Montana

1. INTRODUCTION

The environmental impact of mining, especially concerning the water resources, is very severe in many cases, even in the post-operational phase. The acid mine drainage (AMD) continues to represent a serious concern in Romania, although the majority of the mines have ceased their operation.

The AMD is characterised by low pH, high amount of dissolved solids, and the occurrence of heavy metals and metalloids, many of them harmful to the environment and human health (Ziemkiewicz et al., 1997; Peppas et al., 2000). The particular composition of the solution depends very much on the characteristics of the rocks/minerals that are dissolved, including their buffering capacity, as well as the availability of oxygen, local climate, etc.

Numerous treatment technologies have been setup for the remediation of mining polluted water; however this remains a challenging issue from an economic and technical point of view. Nevertheless, due to high costs and inadequate methods, a wide variety of acidic waters still remain untreated. Previous studies reveal that an efficient, yet inexpensive solution is represented by the usage of natural materials, which have the potential to raise the pH of the solution, and are able to decrease the concentration of dissolved metals by precipitation, adsorption, etc.

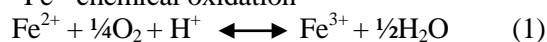
The use of limestone channels is one of the most common passive methods for acid mine water treatment. This method favours a rise of pH and also the removal of dissolved heavy metals through precipitation and oxidation reactions (Hugh et al., 2011). An advantage of this procedure is the simple

design and the relatively low maintenance costs, compared to other methods (Skousen et al., 1998, Sun et al., 2000, Cravotta, 2003, Hammarstrom et al., 2003).

However there are some significant shortcomings, including a quick coverage of the limestone grains with iron oxides, calcium sulphates and organic matter, that will inhibit the interaction between limestone and acid water (Akciil & Koldas, 2006). Although it is a cheap method that can give good results in particular cases, currently there are few attempts to use it in Romania, in spite of the high number of former mining sites that need environmental remediation.

Acid water treatment by using limestone, exhibits three stages (Bobos, 2007; Sun et al., 2000):

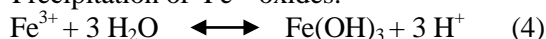
1. Fe^{2+} chemical oxidation



2. Acid water neutralization process by using limestone:



3. Precipitation of Fe^{3+} oxides:



As shown by equations 2 and 3, one mole of CaCO_3 can react with one to two moles of acidity (Garrels & Christ, 1965). As a consequence of this treatment, the pH of the initially acid solution may reach the circumneutral zone, (Pearson & McDonnell, 1975; Webb & Sasowsky, 1994; Brăhăița et al., 2015). This aspect confers the limestone a main role in acid water treatment, both in active and passive systems. Limestone passive treatment systems are mainly used in post closure of mining activities (Taylor & Waters, 2003).

The objective of this laboratory experiment was to assess the effectiveness of limestone in acid water treatment by modifying some parameters such as: drain length, water flow, limestone quantity, and the type of limestone.

2. MATERIALS AND METHODS

For the laboratory experiments, limestone samples from Sandulesti and Geomal quarries were used. These rocks belong to the Upper Jurassic – Lower Cretaceous carbonate platform developed on the eastern edge of the Apuseni Mountains. The limestone that has been used for the experiments corresponds to the Upper Jurassic Stramberk facies. In Sandulesti quarry, a 60-m thick sequence of coarse “reef” detrital deposits and bioconstructions is present (Sasaran, 2006). The limestone mainly consists of a

carbonate fraction (about 93%) formed by high magnesio-calcite (95-98%), and dolomite (2-5%). A minor siliciclastic fraction (7%), including clay minerals (illite, smectite, caolinite, chlorite, iron oxy-hydroxides), and other minerals as quartz, feldspars, apatite, etc., occurs mainly on fissures and in dissolution voids.

Composite limestone samples with a weight of 20 kg each have been collected from the pit. The limestone was grinded, dried at room temperature and then sieved. The grain size of the limestone used in experiments was 5-10 mm and 20-40 mm in the case of Sandulesti, and 5-10 mm for Geomal.

Two drains were built for laboratory experiments using PVC tubes with a diameter of 10 cm. At the end of each of the drains caps fitted with inlet and outlet valves for the water system were installed (Fig. 1). The length of the drains was 1 m and 2 m, respectively.

In the 1 m long channel an amount of 2.6 kg of limestone was used (Fig. 1a). The established flow rates were 50 mL/min (R2) and 25 mL/min (R3). In the 2 m long channel (Fig. 1b), an amount of 5.2 kg limestone was used, at the same flow rates (R5, R6). The flow rates were set using the bucket and stop watch method. Due to the decrease in the amount of water in the storage tank (20 L), and consequently of the hydrostatic pressure, a reduction of the flow rate was observed, therefore the flow rate had to be checked and adjusted every hour. The water sample used in the laboratory experiment was collected from the Adit 714, Rosia Montana mining area.

The porosity of the limestone grain assemblage was determined by measuring the volume of the water-filled voids and the total volume occupied by water and limestone (5).

$$P = \frac{V_v}{V_t} \times 100 \quad (5)$$

P – porosity (%)

V_v – voids volume (L)

V_t – total volume (L)

The porosity was computed to be approximately 45%. The channel's slope was set at 0.8%. The retention time represents the time required for the water to go through the entire length of the channel towards the exit. It was calculated using the formula (6) (Watzlaf et al., 2000):

$$t = P \times \frac{V_L}{Q} \quad (6)$$

where

t – retention time (min)

P – porosity (%)

V_L – limestone volume (L)

Q – flow rate (L/min)

Table 1. Physical parameters of the experiments

Experiment	Length (m)	Flow rate (ml/min)	Limestone quantity (kg)	Grain size (mm)	Type of limestone	Retention time (min)
R2	1	50	2.6	5-10	Sandulesti	9.36
R3	1	25	2.6	5-10	Sandulesti	18.72
R5	2	50	5.2	5-10	Sandulesti	18.72
R6	2	25	5.2	5-10	Sandulesti	37.44
R7	2	25	5.2	20-40	Sandulesti	37.44
R9	2	25	5.2	5-10	Geomal	37.44



Figure 1. Experimental drains: (a) 1 m long; (b) 2 m long.

The limestone volume was calculated using the density of limestone ($\rho=2489 \text{ kg/m}^3$). For 2.6 kg of limestone the volume was computed to be 1.04 L, and 2.08 L for 5.2 kg of limestone.

The physical parameters of the performed experiments are presented in table 1.

The purpose of the first laboratory experiments (R2, R3, R5, R6, R7) was to determine the optimum parameters (length, limestone amount, grain size, and water flow) in order to obtain the best treatment efficiency. Water samples were collected every hour for heavy metal and major ions analyses. Samples were filtered on $0.45 \mu\text{m}$ filters, and stored in 50 mL HDPE containers and refrigerated until analysis. A WTW Multi 350i portable multimeter (Germany) was used for measuring the physicochemical characteristics of the water samples. The major ion concentrations have been measured by a Dionex ICS1500 Ion Chromatograph. For the heavy metal

analyses, the samples were acidified with HNO_3 to a pH value below 2. The heavy metal concentrations were determined on a ZEEnit 700 atomic absorption spectrometer (AAS) Analytik Jena (Jena, Germany), using the flame AAS method. An initial analysis of the water has been performed prior to running each experiment, and the values were plotted on the graphs at the initial sampling time $t = 0$.

3. RESULTS AND DISCUSSION

Six experiments have been conducted, by adjusting the physical parameters of the treating system: drain length, water flow rate, limestone amount, and grain size. The parameters of the system used in each experiment are presented in table 1.

The water samples were collected on an hourly basis, and the experiments lasted for 5 hours (R2, R3, and R5), 8 hours (experiments R6 and R7), and 12 hours (experiment R9). For all experiments the grain size was 5-10 mm, excepting R7 experiment where the limestone grain size was 20-40 mm.

In the first experiment (R2) the channel had a length of 1 m at a flow rate of 50 mL/min. The pH value increased from 2.73 to 3.04 after 5 hours. The maximum efficiency of neutralization was recorded after the first hour, when the pH value reached 4.04. The following experiment (R3) proved to be more efficient because the water flow rate was reduced to 25 mL/min, therefore increasing the contact time. The pH value increased from 2.74 to 5.99 in the first hour, reaching a value of 3.47 after five hours.

The results of the experiment R5, with the drain length of 2 m and a water flow rate of 50 mL/min, are similar to R3 (drain length – 1 m, and flow rate – 25mL/min), the pH after 5 hours being 3.37.

The highest efficiency of neutralization has been observed during the experiment R6, in which a drain of 2 m and a water flow rate of 25 ml/min were used. In this situation, a maximum pH value of 6.26 was reached within the first hour. After 8 hours, the pH value was 4.55. Due to this efficiency of the neutralization, the same drain length and flow rate were used for the following experiments.

The 20-40 mm grain size (experiment R7) has

been less efficient in neutralizing the acid water, as the final pH value was 3.36. In the last experiment (R9) Geomal limestone was used and the neutralization efficiency was similar to experiment R6, in which Sandulesti limestone was used under analogous conditions.

Regarding the removal of Fe (III), the highest efficiency in all experiments was noticed within the first hour. In the experiments R6 and R9, with 2 m drain length, and 25 mL/min water flow, the iron removal efficiency was more than 99% (Table 3). It has been noticed that after 5 hours, the efficiency of limestone in removing the Fe was below 8%, in the experiment R2. In the situation when Geomal limestone was used (experiment R9), efficiency dropped to 33% after 12 hours. In this case the length of the drain and the water flow rate was 2 m, and 25 mL/min respectively.

The efficiency of removing the Cd (II) was the highest during the first hour. This reached the value of 75% for the experiment R9, with the drain having a length of 2 m and flow rate of 25 ml/min, using Geomal limestone.

In the experiment R6 (drain length – 2m, water flow rate – 25 mL/min), the SO_4^{2-} removal efficiency was higher than 50.8%. In the situation when a 1 m long drain and 50 mL/min flow rate was used (experiment R2), the efficiency of removing SO_4^{2-} was the lowest, approximately 18% after the first hour.

Open limestone channels are favouring the oxidation of Fe^{2+} to Fe^{3+} which precipitates as iron hydroxide on the surface of the limestone. Additionally, aluminium hydroxides and gypsum precipitate, decreasing limestone ability to neutralize water (Ziemkiewicz et al., 1997; Hammarstrom et al., 2003). Once the limestone granules are covered with precipitate, a reduction of the limestone neutralization efficiency was noticed after the first hour. Hammarstorm et al. (2003), have noticed in their experiment that the pH value increased from 2.9 to 7, but after 48 hours, due to the covering of the limestone with precipitate, it decreased below 4. In their experiment, it was used a reactor with limestone and water from a coal mine.

The tables 2 to 3 and figures 2 to 5 show the results of the physicochemical measurements, metal (Cd and Fe), and ion (SO_4^{2-} and Ca^{2+}) analyses. All graphs illustrate the positive effect of the limestone channel over the acidic waters. The pH values of the water samples increased to a circumneutral value within the first hour, followed by a descending trend due to the armouring of limestone (Fig. 2). This phenomenon can also be observed for the SO_4^{2-} anion (Fig. 5). Concerning the iron, the decrease of

concentration (Fig. 4) is more obvious compared to the cadmium concentration (Fig. 3).

Examining the Figure 2 (a), it appears that the pH value increases towards a circumneutral value when a lower granulation of the limestone is used. This is due to an increase in the specific surface area of the grains. Moreover, the concentration of Cd, Fe and SO_4^{2-} decreased when a 5-10 mm granulation was used (Fig. 3a, 4a, 5a).

During all experiments, the concentration of Ca^{2+} has increased from a minimum value of 359.33 mg / L to a maximum value of 1042.01 mg / L in the experiment R9. Dissolution of limestone due to acidic water leads to the release of Ca^{2+} in solution. The Ca^{2+} ion promotes gypsum, iron oxyhydroxysulphates, or iron oxyhydroxchlorides precipitation (Soler et al., 2008). The study of Soler et al., (2008) showed that using small grains (1-2 mm) the ability of the limestone to remove iron is much higher compared to the experiment that used larger grains (2-5 mm). In the experiment suggested by Soler et al., (2008) a column with limestone and a solution (HCl and H_2SO_4 , pH=2) were used, with a concentration of Fe (III) between 250 and 15,000 mg/L at a constant flow rate.

There are two presumed reasons for the high iron removal efficiency of the limestone. The first is represented by the rough surfaces of the limestone, that favour the sorption of metal ions, and the second is given by the presence of dissolved calcium carbonate which increases the value of the pH, therefore leading to the precipitation of iron and other metals as oxides, hydroxides, or carbonates (Aziz et al., 2008).

Alcolea et al. (2012) used a drain with a total length of 1986 m, and limestone blocks measuring 60-150 cm in length on the bottom of the channel, and between 30-40 cm on the drain walls. In the study of Alcolea et al. (2012) a significant growth in the concentration of Ca^{2+} was observed towards the outlet of the channel. The value of the pH increased at the same time as the Ca^{2+} concentration.

The high value of the electrical conductivity, as well as the high concentration of sulphates, indicate the presence of a large amount of ions. During the early hours of our experiments, there was a raise in the electrical conductivity, followed by a downward trend below the initial value. A similar trend was also observed in the aforementioned study (Alcolea et al., 2012). In most of our experiments, the total dissolved solids (TDS) value increases during the first hour, presumably due to the dissolution of limestone, followed later on by a decrease, as the grains surface is covered with precipitates.

Table 2. Variation of the concentration of Cd, Fe, Ca, and SO_4^{2-} during the experiments **a.** 1 m long channel, 50 mL/min flow rate and 5-10 mm grain size ; **b.** 1 m long channel, 25 mL/min flow rate and 5-10 mm grain size; **c.** 2 m long channel, 50 mL/min flow rate and 5-10 mm grain size.

Time (min)	a.	Cd (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)	b.	Cd (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)	c.	Cd (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)
0	R2-i	0.236	1353.68	5410.2	460.19	R3-i	0.210	1366.33	5583.7	461.5	R5-i	0.206	1351.69	5500.8	444.7
60	R2-1	0.247	530.16	4425.0	659.36	R3-1	0.174	823.52	5230.4	612.71	R5-1	0.175	589.50	2839.1	606.83
120	R2-2	0.234	1078.96	5070.7	707.18	R3-2	0.209	856.11	2882.6	579.07	R5-2	0.192	482.80	4156.3	557.17
180	R2-3	0.234	1179.40	6725.2	576.35	R3-3	0.220	930.62	3237.4	666.96	R5-3	0.199	6.43	3120.0	656.94
240	R2-4	0.249	1217.98	5705.2	637.6	R3-4	0.204	806.22	3905.1	604.67	R5-4	0.234	894.03	5189.9	699.71
300	R2-5	0.232	1246.58	5885.0	523.73	R3-5	0.196	887.38	4984.3	741.66	R5-5	0.231	1127.52	5677.5	1523.45

Table 3. The concentration of Cd, Fe and SO_4^{2-} **a.** 2 m long channel, 25 mL/min flow rate and 5-10 mm grain size; **b.** 2 m long channel, 25 mL/min flow rate and 20-40 mm grain size; **c.** 2 m long channel, 25 mL/min flow rate and 5-10 mm grain size.

Time (min)	a.	Cd (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)	b.	Cd (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)	c.	Cd (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)
0	R6-i	0.214	1381.63	5772.4	390.72	R7-i	0.241	1360.31	5271.8	452.28	R9-i	0.220	1359.68	5025.5	359.33
60	R6-1*	0.076	3.98	2942.2	697.58	R7-1	0.152	517.53	3030.2	487.13	R9-1**	0.053	3.48	3406.3	863.43
120	R6-2	0.138	462.18	2837.0	543.63	R7-2	0.221	686.49	4304.2	654.63	R9-2	0.123	505.82	3376.3	857.93
180	R6-3	0.227	619.43	2866.9	513.45	R7-3	0.197	781.61	4454.7	715.91	R9-3	0.178	764.98	3524.9	937.73
240	R6-4	0.211	623.43	2886.5	476.49	R7-4	0.211	931.95	4756.1	702.06	R9-4	0.196	769.64	2650.5	603.87
300	R6-5	0.213	675.18	3028.5	682.08	R7-5	0.235	1099.58	4830.7	709.04	R9-5	0.206	750.35	3447.3	678.21
360	R6-6	0.205	678.50	3166.9	608.08	R7-6	0.215	1059.66	4558.5	658.95	R9-6	0.216	755.67	3699.4	877.36
420	R6-7	0.209	729.06	3318.1	625.33	R7-7	0.221	1086.94	4942.0	628.81	R9-7	0.242	579.26	3660.3	956.87
480	R6-8	0.222	530.16	3716.5	675.92	R7-8	0.215	1066.98	4925.1	627.81	R9-8	0.223	697.86	4031.9	1042.01
540											R9-9	0.188	722.41	3606.5	618.48
600											R9-10	0.180	680.50	4248.4	962.35
660											R9-11	0.190	716.42	4098.9	958.26
720											R9-12	0.186	909.33	4638.7	864.64

* First occurrence time was 71 min

**First occurrence time was 86 min

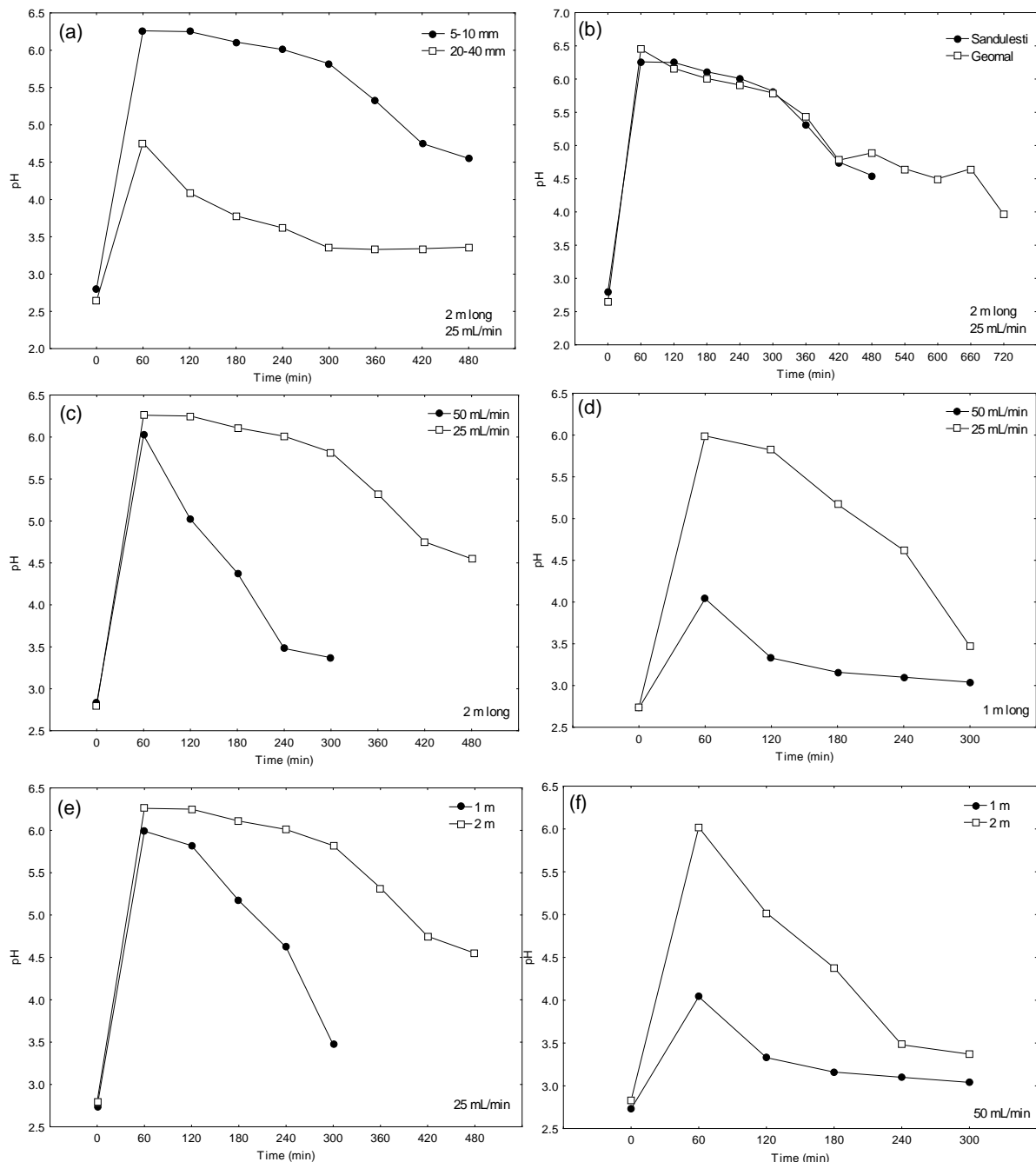


Figure 2. The pH value depending on the time, and (a) grain size (R6-R7); (b) type of limestone (R6-R9); (c, d) water flow rate (R2-R3, R5-R6); (e, f) length of the channel (R2-R5, R3-R6).

The SO_4^{2-} concentration decreased in the early hours, followed by an upward trend. This increase is due to the fact that CaCO_3 began to be less reactive, therefore the gypsum that precipitated previously was dissolved. These findings were noticed in the study of Offeduu et al., (2015) that used a limestone column. In this study, two synthetic acidic solutions (H_2SO_4) were used, one with a higher concentration of Fe (III) at pH=2 and the other with a higher concentration of Al at pH=2 and 3.

By comparing the performance of the system at two flow rates, it can be observed that the 25

mL/min is more efficient than the 50 mL/min flow rate. On the other hand, with a longer drain, a greater residence time, and an increased efficiency can be noticed (McDonald et al., 2001; Sdiri et al., 2012). In terms of channel length, analysing the figures 2, 3, 4, and 5, it can be observed that the 2 m long channel is more efficient than the 1 m channel (Figs. 2 to 5 (e and f)). As a result of these experiments, it has been shown that the 25 mL/min flow rate and the 2 m length are more suitable, and this regime was used in the experiments R6, R7, and R9.

4. CONCLUSIONS

The limestone channel usage is a method frequently applied in mining areas to reduce heavy metal concentrations and to increase the pH value of acid water. Taking into account the large number of such areas in Romania (e.g. Apuseni Mountains, Eastern Carpathians, etc.), the results of this study represent a basis for the development of future, more complex research in this field. The main objective of this study was to determine the optimum parameters, such as: drain length, flow rate, and limestone

quantity in the treatment process of acid water from Rosia Montana.

As a result of the experiments it was observed that the efficiency of water neutralization by using limestone increases proportionally with the drain length. Moreover, heavy metals (Fe, Cd) and sulphate (SO_4^{2-}) removal is also increased. Nevertheless, in addition to the length of the drain it was noted that the flow rate is also important. Thus, a low flow determines a higher efficiency of acidic water treatment.

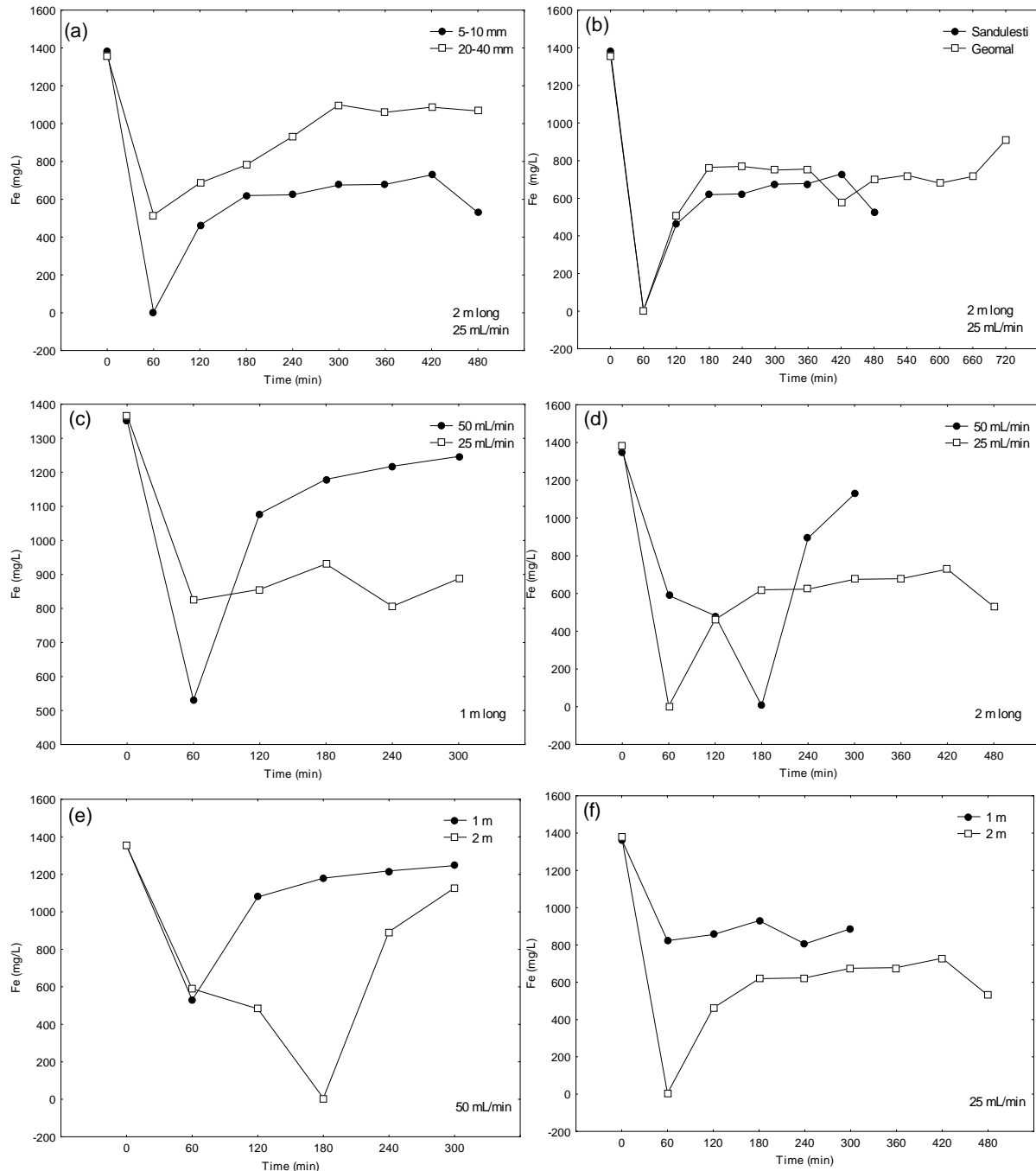


Figure 3. The concentration of Fe depending on time, and (a) grain size (R6-R7); (b) type of limestone (R6-R9); (c, d) water flow rate (R2-R3, R5-R6); (e, f) length of the channel (R2-R5, R3-R6).

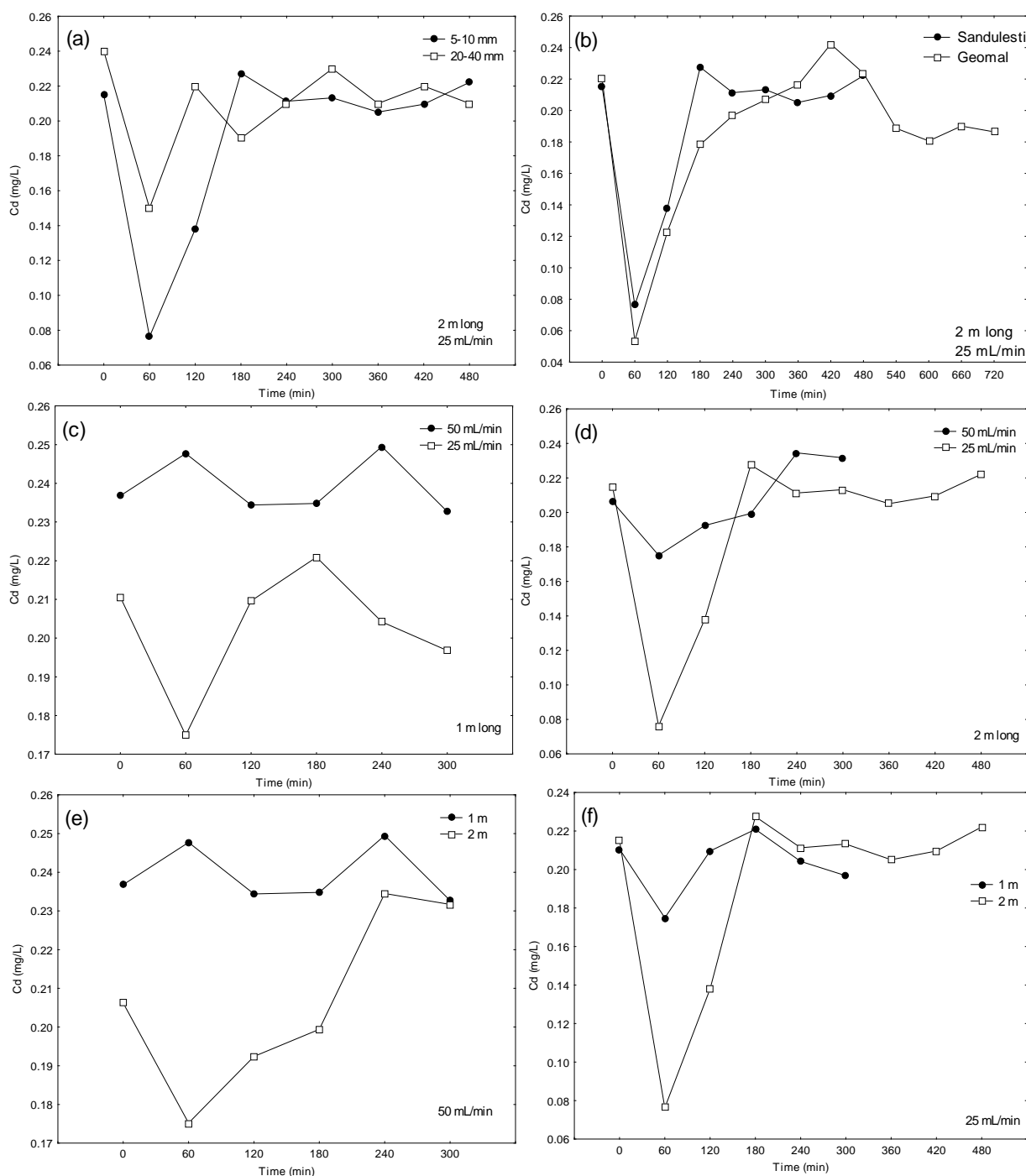


Figure 4. The concentration of Cd depending on time, and (a) grain size (R6-R7); (b) type of limestone (R6-R9); (c, d) water flow rate (R2-R3, R5-R6); (e, f) length of the channel (R2-R5, R3-R6).

It can be concluded that the most important factor in neutralizing the acid water is the contact time between water and limestone. This time of contact can be increased by using a longer channel, a lower water flow rate, and a larger amount of limestone. The limestone has the potential to immobilize heavy metals like Cd and Fe in the first couple of hours of interaction.

A finer granulation (5-10 mm) of the limestone is more effective compared to a coarser

granulation (20-40mm), both for acidic water neutralization, and for heavy metals or sulphate removal from acidic water. This is due to the larger specific surface area of the smaller grains.

The consumption of limestone can be correlated with the decrease of SO_4^{2-} , also observed in the laboratory experiments. The two types of limestone used demonstrate similar behaviour.

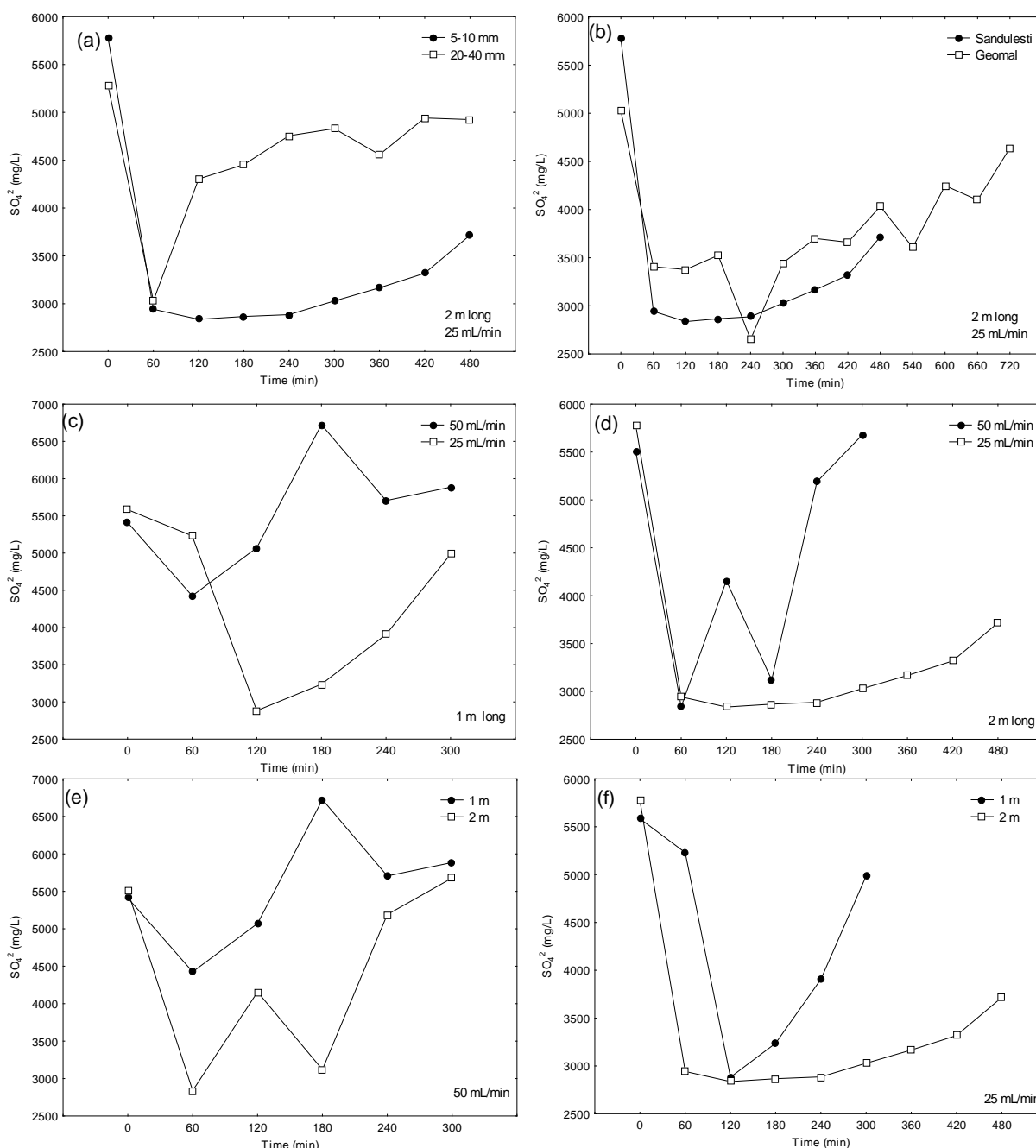


Figure 5. The concentration of SO_4^{2-} depending on time and (a) grain size (R6-R7); (b) type of limestone (R6-R9); (c, d) water flow rate (R2-R3, R5-R6); (e, f) length of channel (R2-R5, R3-R6).

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