

## REMOVAL OF HEAVY METALS FROM WASTEWATER BY USING ZEOLITIC TUFF

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**Abstract:** Zeolitic tuff (from the region of Barsana, Maramures, Romania) was used in the experimental determinations for retaining the Pb and Zn ions from industrial wastewater. The determination was performed in static regime using 10 g zeolitic tuff/100 cm<sup>3</sup> wastewater (from the slag granulation basin of the metallurgical factory S.C. Romplumb S.A. Baia Mare, Romania). The initial concentration of the metal ions in the wastewater was 3.806 mg Pb<sup>2+</sup>/l, respectively 129.20 mg Zn<sup>2+</sup>/l. We followed the evolution of the ion exchange process upon retaining the heavy metal ions in three types of particle size range from the zeolitic tuff sample, i.e. 0.4 – 0.2 mm (G04); 0.2 – 0.12 mm (G02); <0.012-mm (G012). The clinoptilolite was predominant in the zeolitic material used in this experiment and was identified by qualitative analysis with the electronic microscope (SEM) and quantitative analyses by spectral analyses (EDS). For the G012 set of samples, particle surface were analysed by the scanning electronic microscope (SEM) and local X-ray energy dispersive spectrometry (EDS). The zeolitic tuff which was in contact with the wastewater was separated by filtration, and the samples for determining the Pb and Zn ions were prelevated after 12 hours. The concentration of the Pb and Zn ions was determined by atomic absorption spectroscopy at a pH of 5.90. The determined ion exchange efficiency values for Pb were above 96%, with the maximum 99.17% for the G012 set of samples. For Zn, where the Zn ions had high concentrations in the initial sample, the maximum ion exchange efficiency was 52.95%.

**Key words:** Wastewaters; Heavy metals; Natural zeolites; Clinoptilolite

### 1. INTRODUCTION

The nonferrous metallurgical industry has been a continuous polluting source, affecting particularly water and soil. Surface waters and ground waters are mainly polluted by industrial waters containing nonferrous metals. Wastewater recycling should be increased, because it not only reduces fresh water consumption but it also restricts the pollutants that may be evacuated in the environment. Wastewater recirculation requires some heavy metals to be retained.

Latest worldwide researches on designing efficient wastewater treatment techniques suggested that the introduction of advanced water treatment stages based on physical-chemical processes, advanced oxidation, ultrafiltration, or inverse osmosis require increased costs and investments (Kim et al., 2000; Cincotti et al., 2001; Langella et

al., 2000). Within this context, employing unconventional methods to retain heavy metals from waters by using filters formed of natural or synthetic zeolites seems a fairly good solution.

All these investigations need to take into account the techniques of zeolite composition and structure. Clinoptilolite-rich volcanic tuffs have been employed in many researches in the processes of heavy metal cation retention from solutions. Kinetic studies have indicated that the Pb ions adsorbed on the natural zeolite in mono-component systems follow order I kinetics; adsorption is a diffusion process taking place in one stage, Pb<sup>2+</sup> following the adsorption model according to the Freundlich isotherm (Wang & Ariyanto, 2007). Pb<sup>2+</sup> ions prove a relatively high affinity and the selectivity of being adsorbed on the zeolite by following an order I kinetics. Pop et al., (2011b) presented modelling adsorption kinetic of Pb ions from wastewater in the

metallurgical industry as ion exchange using zeolite volcanic tuff from Barsana area.

Pb ions retention by natural zeolites in a wide range of pH (3, 4, 5) has been demonstrated by Ponizovski & Tsalidis (2003) and can be seen as an ion exchange reaction, high values for ion exchange capacity being obtained. Culfaz & Yagiz (2004) employed equilibrium calculation and obtained free exchange energy values for two systems: for the system Pb-Na,  $\Delta G^\circ=16.6$  KJ/eq,  $K_a=16.6$  KJ/eq and for the system Cd-Na  $\Delta G^\circ=2.27$  KJ/eq,  $K_a=0.16$  KJ/eq. Comparing the obtained data with the results from the literature, the ion exchange performance proved to be 100% for the  $Pb^{2+}$  ions and 54% for the  $Cd^{2+}$  ions. Aleksandrova et al., (2004) used a titanium phosphate-based adsorbent to modify the surface of the clinoptilolite by grafting it in order to increase the concentration of OH groups, which can exchange ions for cations of heavy metals. The stabilization of Cd ions in soil polluted with heavy metals with the help of clinoptilolite has been described by Mahabadi et al., (2007), the zeolite increase to 15% in the treated soil leading to a decrease in the Cd content to under 0.1 mg/l in the leaching solutions.

The ion exchange has become a specifically important method of reducing the heavy metal content in wastewaters. Natural and chemically modified zeolites have been employed in the ion exchange process, through kinetic studies which aimed to demonstrate the retention capacity of  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Mn^{2+}$  cations contained within waste discharge (Burtică et al., 2003). The increased immobilization capacity of cadmium has been proved through the use of nanoparticles obtained from chemically modified zeolite Na-tuff (Ghrais et al., 2009).

Adsorption and ion exchange, with the purpose of retaining heavy metals from wastewaters with the help of natural zeolites, can be successfully applied for wastewaters with low content of heavy metals or to enhance the efficiency of classical water treatment procedures (Stanca et al., 2006). Ion exchange through zeolites is a treatment procedure for both supply water and wastewaters. This method is based on the capacity of some materials to replace their ions with the ones in the solutions. The following removal efficiency has been recorded in the examined experimental conditions, (Inglezakis & Grigoropoulou, 2004):  $Pb^{2+}>Cr^{3+}>Fe^{3+}>Cu^{2+}$ . The ion exchange series is influenced by the studied parameters in the following order: concentration > volume flow > rate > particles sizes > material modification.

Ion exchangers can be inorganic (natural) aluminosilicates: glauconite, vermiculite, natural zeolite, chabazite, kaolinite, illite. Chantawong et

al., (2003) observed that adsorption increased with the pH, the adsorption model following both Langmuir and Freundlich isotherms. The adsorption series of metals in the kaolinite solutions were:  $Cr>Zn>Cu \approx Ni>Pb$ ; and for illite, they were:  $Cr>Zn>Cu \approx Pb>Ni$ . Pansini et al., (1996) obtained results in removal of Pb ions from wastewater by phillipsite.

Natural zeolites can be used as follows: soil remediation (Damian & Damian 2007). The available literature has also underlined the interest for employing new inorganic adsorbents (natural zeolites, clay minerals), and natural zeolites pre-treated with NaCl which lead to an increase in both the immobilization rate of ions from heavy metals and the distribution coefficients. This is just a guiding characteristic for the ion exchange process. Heavy metals are more tightly connected to the NaCl pre-treated zeolites, as compared to natural zeolite (Panayotova & Velikov, 2003). Peric et al., (2004) studied zinc, copper and lead retention in water solutions through the ion exchange on zeolitic tuff and observed that the removal efficiency is bigger for lead and copper than for zinc ions.

Natural zeolites have been used for the adsorption of Ag ions and antibacterial activities, Ag-clinoptilolite being used as antibacterial material (Top & Ulku, 2004).

## 2. MATERIAL AND METHODS

### 2.1. Zeolitic volcanic tuff

To determine the removal efficiency of the Pb and Zn ions in the wastewaters from the slag granulation basin of the S.C. Romplumb S.A Baia Mare metallurgical factory, a zeolitic tuffs sample has been collected from the outcrop area Barsana, Maramures (Cochemé et al., 2003).

The main criterion used in the selection of the zeolitic tuffs employed in our experimental researches has been its clinoptilolite-rich content. Due to its structure, this zeolite has a great affinity to the studied ions (Bedelean et al., 2007). Natural zeolites have been used in several domains, from industry to environment protection, and they have been rightfully named *la roca magica* by Mumpton (1999). The initial zeolitic tuff sample (Fig. 1) has been processed to optimal particle size range through crushing, ball milling and was realized size separation, less than 1mm, (Fig. 2).

The main component of zeolitic tuffs is the volcanic glass, present both as glass shard and as very small quantities of crystalloclasts and lithic

fragments. Volcanic glass usually has an over 90%, whereas crystalclasts and lithic fragments have a 10%. Glass shards are present as curved angular, globular and filiform fragments, usually with a size under 0.05 mm. Crystalclasts are represented by plagioclase feldspar, sanidine, quartz, mica (biotite and muscovite). Lithic fragments appear sporadically and are represented by quartzite fragments, eruptive rocks with pilotaxitic structure, represented by andesite.

Glass shards are devitrified in zeolites, smectites, seladonite. Zeolites are represented by clinoptilolite up to 75-85% (Damian et al., 2002). The zeolites are distributed in clusters or inside the contour of the glass shards.

The zeolitic volcanic tuff samples have been examined by scanning electron microscope (SEM) type and by spectral analyses (EDS).

The qualitative analysis of the zeolitic tuff

performed at the scanning electron microscope (SEM) showed that the predominant habitus of the clinoptilolite crystals is tabular (Fig. 3a and 3b). Figure 3 shows zeolites as microcrystals displayed in massive aggregates, in cavities or substituting glass fragments. Zeolites appear as tabular crystals of clinoptilolite (Fig. 3b), with 2-8 microns sizes, very rarely reaching 30 microns, in the cavities and pores (Fig. 3a).

The quantitative determinations obtained by EDX spectral analysis of the clinoptilolite crystals have showed the chemical composition displayed in table 1, presented in the spectrum in figure 4b as well as the map composition in figure 4c. Also, the overall chemical composition of the zeolitic tuff used within the experiment was determined, (Table 2). When analysing the values of the overall chemical composition of the zeolitic tuff as displayed in table 2, it can be noted that the elements slightly differ from the clinoptilolite crystals in terms of composition (Table 1)



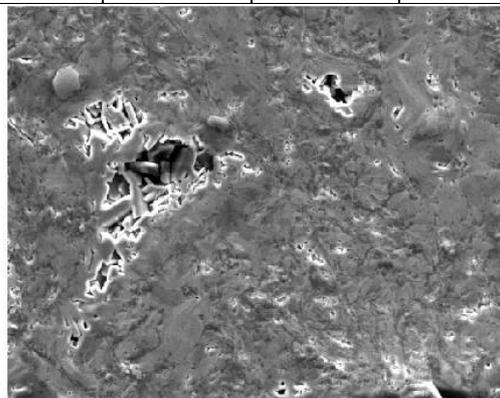
Figure 1. Zeolitic tuff samples from Barsana



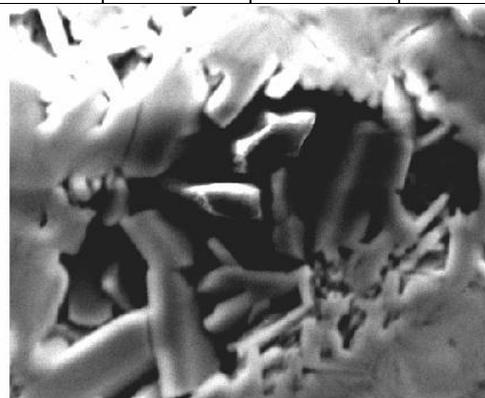
Figure 2. Zeolitic tuff crushed and milled at < 1 mm particle size range

Table 1. The chemical composition of a clinoptilolite crystal

Element	O	Na	Mg	Al	Si	K	Ca
% weight	59.71	3.6	0.16	6.59	27.55	1.54	0.85
% atomic	72.03	3.02	0.13	4.72	18.93	0.76	0.41



a)



b)

Figure 3. SEM Image of described zeolitic tuff: a) overall image; b) clinoptilolite composed of tabular crystals

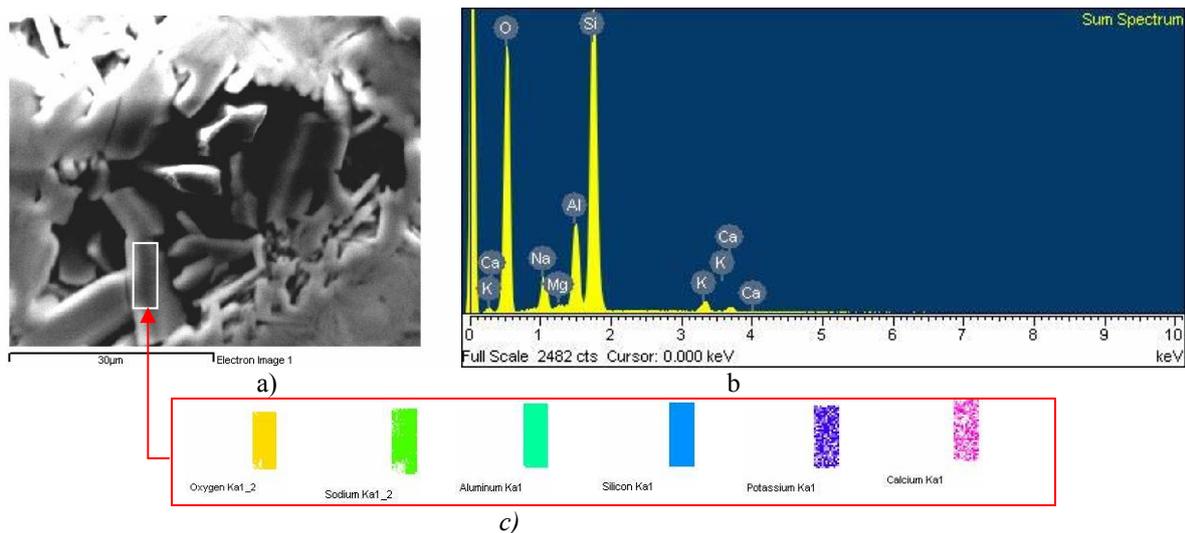


Figure 4. SEM image a) Clinoptilolite crystals, b) EDS Spectrum, c) map the composition in area of clinoptilolite crystal marked in frame (see fig.4a).

Table 2. The overall chemical composition of the volcanic tuff

Element	O	Na	Mg	Al	Si	K	Ca
% weight	60.13	2.36	0.16	5.86	29.18	1.70	0.60
% atomic	72.52	1.98	0.13	4.19	20.05	0.84	0.29

Table 3. The chemistry of zeolitic tuff (after Damian et al., 1991)

No	SiO <sub>2</sub> %	AlO <sub>2</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	FeO %	MnO %	MgO %	CaO %	Na <sub>2</sub> O %	K <sub>2</sub> O %	TiO <sub>2</sub> %	CO <sub>2</sub> %	H <sub>2</sub> O <sup>+</sup> %	H <sub>2</sub> O <sup>-</sup> %	Total %
1	66.90	13.92	0.68	0.27	0.06	1.40	1.40	2.88	2.17	0.33	-	8.85	2.15	100.95
2	66.68	14.35	0.76	0.21	0.05	0.42	0.42	3.37	2.58	-	1.00	4.98	4.38	99.28
3	67.72	11.20	0.70	0.14	0.07	0.84	1.12	2.88	2.48	-	1.90	6.06	4.42	99.53
4	67.00	13.00	0.80	0.32	-	1.10	2.73	1.51	2.04	0.21	0.24	6.79	4.17	99.91
5	67.2	12.50	0.80	0.39	-	1.48	2.86	0.57	2.02	0.16	0.06	7.50	4.01	99.49

The overall rock composition resulted from the EDX analysis is different in different points of analysis due to the fact that the rock is not homogenous. Therefore, the overall chemical analysis of the silicates is much more relevant, (Table 3). The comparative analysis of the three tables shows the high content of sodium, calcium, potassium, silicon and aluminium. The zeolite crystal analysis (Table 1, Fig. 4) shows that the clinoptilolite has much more sodium than the zeolitic rock. Sodium-rich clinoptilolite frequently has a cation exchange capacity higher than the one of calcium or potassium rich varieties.

Zeolitic tuffs used for heavy metal removal have an increased Na<sup>+</sup> exchange capacity (Damian et al., 2002). The exchange capacity for Na<sup>+</sup> varies between 8.05-118.49 mvali/g and an average value of 69.52 mvali/g. The values for K<sup>+</sup> are quite high, between 16.55 and 40.70 mvali/g, with an average value of 27.78 mvali/g. The values for the cation exchange capacity for Ca<sup>2+</sup> are quite high, between 20.90 and 87.78 mvali/g, with an average value of

40.34 mvali/g. The values for the cation exchange capacity for Mg<sup>2+</sup> varies between 0.49 and 13.93 mvali/g, with an average value of 4.63 mvali/g.

## 2.2. Wastewater

Treated wastewater samples with zeolitic tuffs were collected from the slag granulation basin of metallurgical factory.

Wastewater was analysed to determine the concentration of heavy metals ions and then put into contact with the zeolitic tuff sample in the established proportion.

## 2.3. Research method

The wastewater was stored in three reaction vessels and put in contact with the zeolitic material in static conditions. The zeolitic material was represented by three granulometric classes of particles: 4-0.2mm; 0.2-0.12mm; <0.012-mm, in the following proportion: 10g zeolitic tuff/100 cm<sup>3</sup> wastewater. During the 48 hour time interval,

sampling was performed every 12 hours through siphoning followed by filtration (using a filter paper with blue band). Samples were analysed by atomic absorption spectrophotometry. Zeolitic tuff samples from the set G012 were analyzed using scanning electron microscopy (SEM) and images were made of particle surface, and EDS spectrum of chemical elements.

The concentrations of heavy metal ions were determined by atomic absorption spectrophotometry. During the experiment, the atomic adsorption spectrometer was employed to determine Pb in the acetylene-air flame atomization and the primary radiation source for Pb was a hollow cathode lamp. The instrumental work conditions were  $\lambda = 217.0$  nm, and the following reactivities were used: calibration solution Merk Germania stock – traceable at NIST: SRM 682-1000mgPb/l, lot HC894645; azote acid Merk 65% and bidistilled water.

### 3. RESULTS AND DISCUSSIONS

Previous tests performed under static conditions, (Pop et al., 2011) using zeolitic tuff from Barsana region and the wastewater from the Romplumb factory (slag granulating basin) and it make the researchers to select as the best option the one with 10g zeolitic tuff/100 cm<sup>3</sup> of wastewater in order to monitor the efficiency of ion exchange process. Heavy metals removal is based on the cation exchange and the use of zeolites to achieve this objective is highlighted by frequent works, as it is showed in, (Pabalan & Bertetti, 1999 and Stanca et al., 2006).

In our research and in agreement with (Pop et al., 2011a) it was considered that the established report to be of 10g zeolitic tuff/100 cm<sup>3</sup> wastewater, because it leads to about 36 hours after equilibration for Pb's, except that lower Pb ion concentration occurs with a high speed in the first 12 hours (from 4.328 mg/l to 0.0586 mgPb/lPb). The process of ion exchange monitored by exchange efficiency in retaining Pb and Zn ions from wastewater by zeolitic tuff of Barsana presented in (Pop et al., 2011)

obtained the values 48h after exchange efficiencies 99.2028% Pb and 75.857% Zn.

The performed experiments studied the influence of the particle size proportion of the zeolitic tuff samples on the efficiency of the ion exchange process, resulting in three sets of samples with the following grain size: 0.4mm; 0.2mm and 0.012mm. Wastewater had an initial metallic ion concentration of 806mg Pb<sup>2+</sup>/l; 129,20 mg Zn<sup>2+</sup>/l and a pH=5.90. Research was performed on sets of samples. For each set, the focus was on a certain proportion, as follows:

- The G02 set of samples: 10g (zeolite tuff with 0.2 mm particle size)/100 cm<sup>3</sup> wastewater;
- The G04 set of samples: 10g (zeolite tuff with 0.4 mm particle size /100 cm<sup>3</sup> wastewater;
- The G012 set of samples: 10g (zeolite tuff with 0.012 mm particle size) /100 cm<sup>3</sup> wastewater.

The values of Pb and Zn ions concentrations determined by atomic absorption spectrophotometry are displayed for each set of samples in table 4.

As far as Pb ions are concerned, as shown in figure 5, the decrease of the cations concentration in the wastewater is more obvious in the case of the three sets after the first 12 hours, but, in the case of G012 set, it seemed to have suddenly decreased from the initial value of 3.806 to 0.1955 mg/l. After this moment, the decrease in the Pb ions concentration was almost linear, and a balance was reached after approximately 60 hours. As far as the G02 and G04 sets are concerned, the value of the Pb ion concentration in the wastewater was close to the wastewater concentration in the case of G012 set after 12 hours. These sets (G02, G04) registered a linear decrease of Pb ion concentration in wastewater after 20 hours. The efficiency of the ion exchange has been assessed in static conditions.

According to references data, metallic ion exchange can be performed within the following pH interval: 3-6. After Dyer & Zubair (1998) higher pH values (considered above 4) improve the adsorption of heavy metals, but there is a possibility for precipitation.

Table 4. The concentrations values of Pb and Zn heavy metals ions displayed by time and for samples G02, G04 and G012

Time, h	Concentrations, mg/l					
	Pb			Zn		
	G012	G02	G04	G012	G02	G04
0	3.806	3.806	3.806	129.20	129.20	129.20
12	0.1955	0.2953	0.4246	106.37	113.46	125.98
24	0.1007	0.1376	0.3590	89.79	94.91	107.40
36	0.0865	0.1219	0.3384	78.76	83.31	94.20
48	0.0731	0.1175	0.2407	76.86	81.32	92.73
60	0.0315	0.0927	0.1509	62.59	60.91	66.81

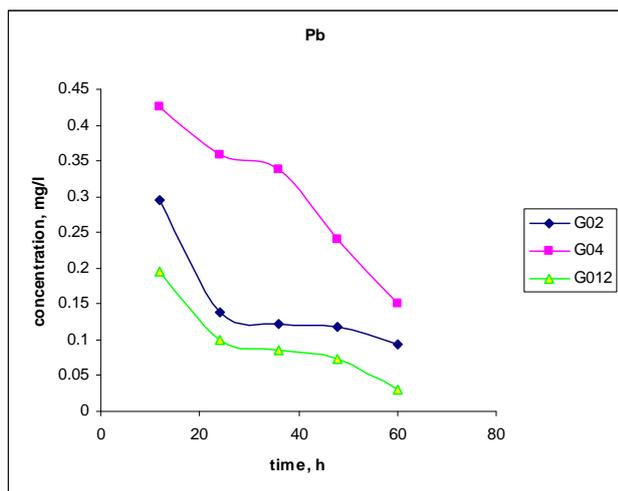


Figure 5. The variations of Pb ions concentrations by time for samples G02, G04 and G012

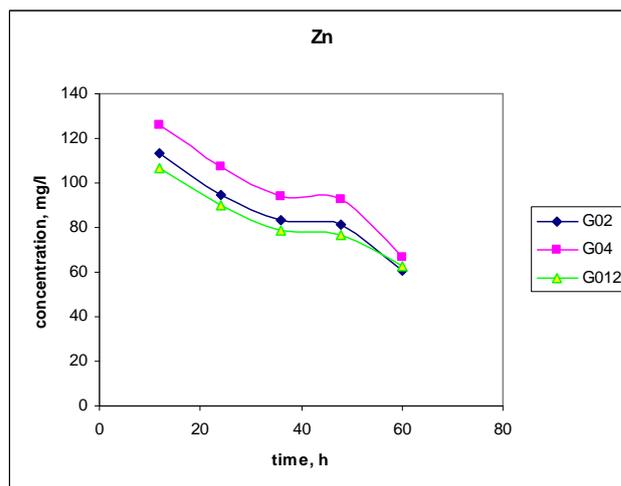
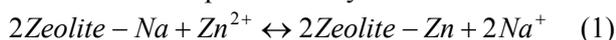


Figure 6. The variation of Zn ions concentration by time, for the G02, G04 and G012 samples

In our researches performed at pH higher than 5.90, for Pb and Zn, the selectivity series described in the references data, seemed to be respected, namely Pb>Zn. Selectivity for metal cations of the zeolitic materials with high content of clinoptilolite, vary with the solution pH and the concentration of metal ions. Selectivity for metal cations of zeolitic materials with high content of clinoptilolite, vary with the pH solution and concentration of metal ions used. There are several researches done in this direction.

Fujimori & Moriya (1973) and Semmens & Seyfarth (1978) established the following series of selectivity: Pb> Cd> with> Zn, respectively: Pb> Cd> Zn> Cu. Other research has established similar selectivity series: Blanchard et al., (1984) - Pb> Cu, Cd> Zn, Co> Ni> Hg, Zamzov et al., (1990) - Pb> Cd> with> Co> CR3 +> Zn> Ni> Hg; Horvathova & Kachanak, 1987) - Cs> Pb> Fe> with> Zn, C, Co> Ni> Mn> Cr; Kalita & Chelishchev, (1995) - Pb> with> Zn> Co> Ni. All these data are similar, the cations occupying the same position in the lead series and copper ions having a higher selectivity than zinc ions in most cases.

The efficiency of this process, of cationic exchange, was observed through the performance of ion exchange, in static conditions. The reactions taking place during the ion exchange process considered in the present study are as follows:



The value of the exchange efficiency has been calculated with the following relation (3) and displayed in table 5:

$$\eta = (C_i - C_{t,e}) / C_i * 100 \quad (3)$$

where:

$C_i$  is the considered ion concentration in

solution, expressed as  $\text{mg}/\text{dm}^3$

$C_{t,e}$  is the considered ion concentration at moment t, namely at equilibrium, expressed as  $\text{mg}/\text{dm}^3$  (Maicaneanu et al., 2008)

Figures 7 and 8 display the Pb and Zn ion exchange performance. Lead registers a maximum retention performance of 90% after the first 12 hours for the G012 and G02 sample sets and after the first 24 hours for the G04 set, as shown in (Fig. 7). Table 5 shows that the retention performance is over 96% for all the three sets after 60 hours, the maximum value, of 99.17%, being registered by the G012 set, a value close to the one obtained by Culfaz & Yagiz (2004), who used a chemically treated volcanic tuff.

The Zn ions retention performance proves to increase linearly for all the three sets, reaching the 50% value after 60 hours (Fig. 8), the G012 set being the one which registers a maximum value once again (Table 4). The process of underlining the role of zeolites in heavy metals retention has been performed through EDS spectral analyses on the zeolitic tuff particles from the tuff samples which were put into contact with heavy metal ions - rich wastewaters.

The ion exchange between the clinoptilolite and the  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  has been confirmed through EDS analyses and microprobe by Mozgawa (2000) and Damian & Damian (2007).

The cation exchange capacity of the zeolites, and especially the one of the clinoptilolite, has been demonstrated by the research performed by Langella et al., (2003), Sullivan et al., (2003), proving the highly efficient retention of lead and cadmium. Lead retention from wastewaters could also be the result of the direct addition of zeolitic materials containing clinoptilolite.

For the G012 Romplumb Baia Mare sample have been taken images of the particles surfaces, (Fig. 9) and the spectral EDS analysis of the chemical elements (Fig. 10) has been performed with the help of the scanning electron microscope (SEM). The resulted spectrum showed not only specific elements of the zeolite composition, but also other elements, such as Pb and Zn.

These elements appear in the zeolite as a result of the cation exchange with Na, K and Ca in the zeolites structure. This cation exchange is accounted for by the high affinity of the clinoptilolite for heavy metals, especially for lead (Langella et al., 2003).

Figure 10 displays the distribution of the ions of the heavy metals being retained in the zeolitic tuff particles. The overlap of Zn and Pb over Ca, K and Na can be, hereby, noted. This demonstrates that the cation exchange takes place predominantly with the zeolite clusters in the zeolitic tuff particles. Figure 3 shows that the clinoptilolite crystals appear as clusters and represent the areas were heavy metals are predominantly retained. This can also explain the non-homogenous distribution of heavy metals in the zeolitized tuff particles as compared with the elements in the chemical composition of the zeolites, the distribution of which is more homogenous, thus supporting the idea of heavy metals retention in the zeolite structure.

Table 5. The values of Pb and Zn ions retention performance by time for the G02, G04, G012 sample sets

Time, h	Performance, %					
	Pb			Zn		
	G012	G02	G04	G012	G02	G04
12	94.86337	92.2412	88.84393	17.67028	12.18266	2.49226
24	97.35418	96.38466	90.56752	30.5031	26.54025	16.87307
36	97.72727	96.79716	91.10878	39.04025	35.51858	27.08978
48	98.07935	96.91277	93.67578	40.51084	37.05882	28.22755
60	99.17236	97.56437	96.03521	52.85604	51.55573	48.28947

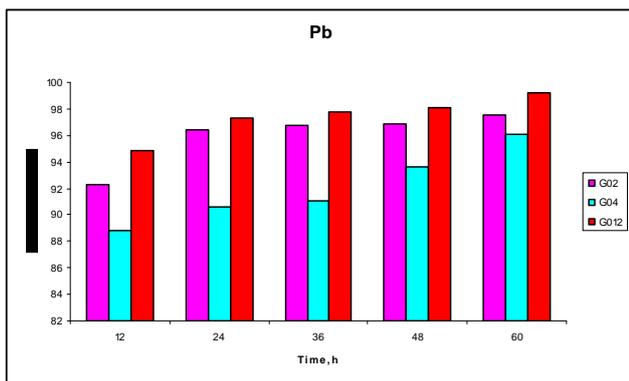


Figure 7. The Pb ions retention performance by time for the G02, G04, G012 sample sets in static conditions

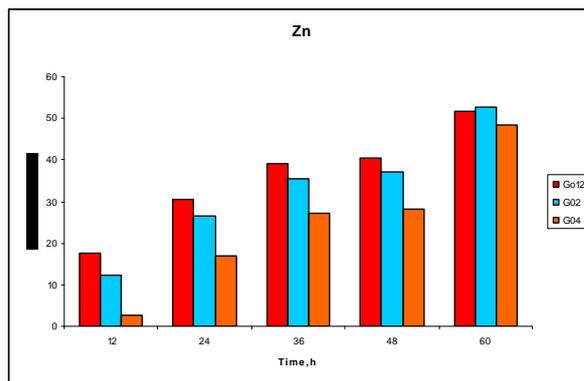
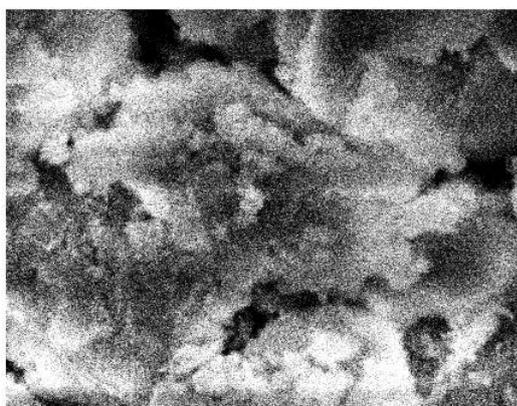
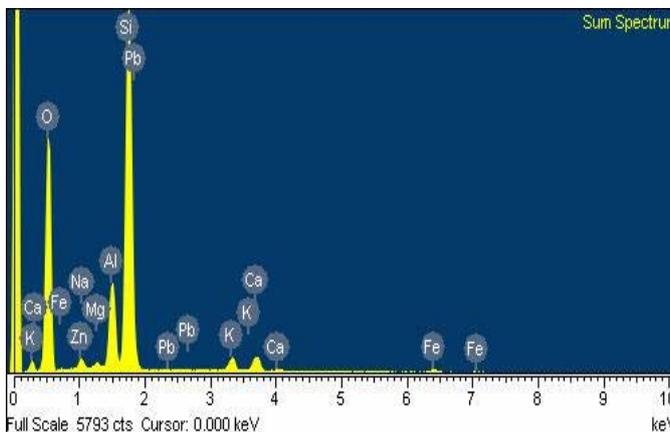


Figure 8. The Zn ions retention performance by time for the G02, G04, G012 sample sets in static conditions



a)



b)

Figure 9. SEM image of the zeolitic tuff particles in the G012 sample (a) and the EDS spectrum of the G012 sample zeolitic tuff particles retaining heavy metals (Pb, Zn, Fe).

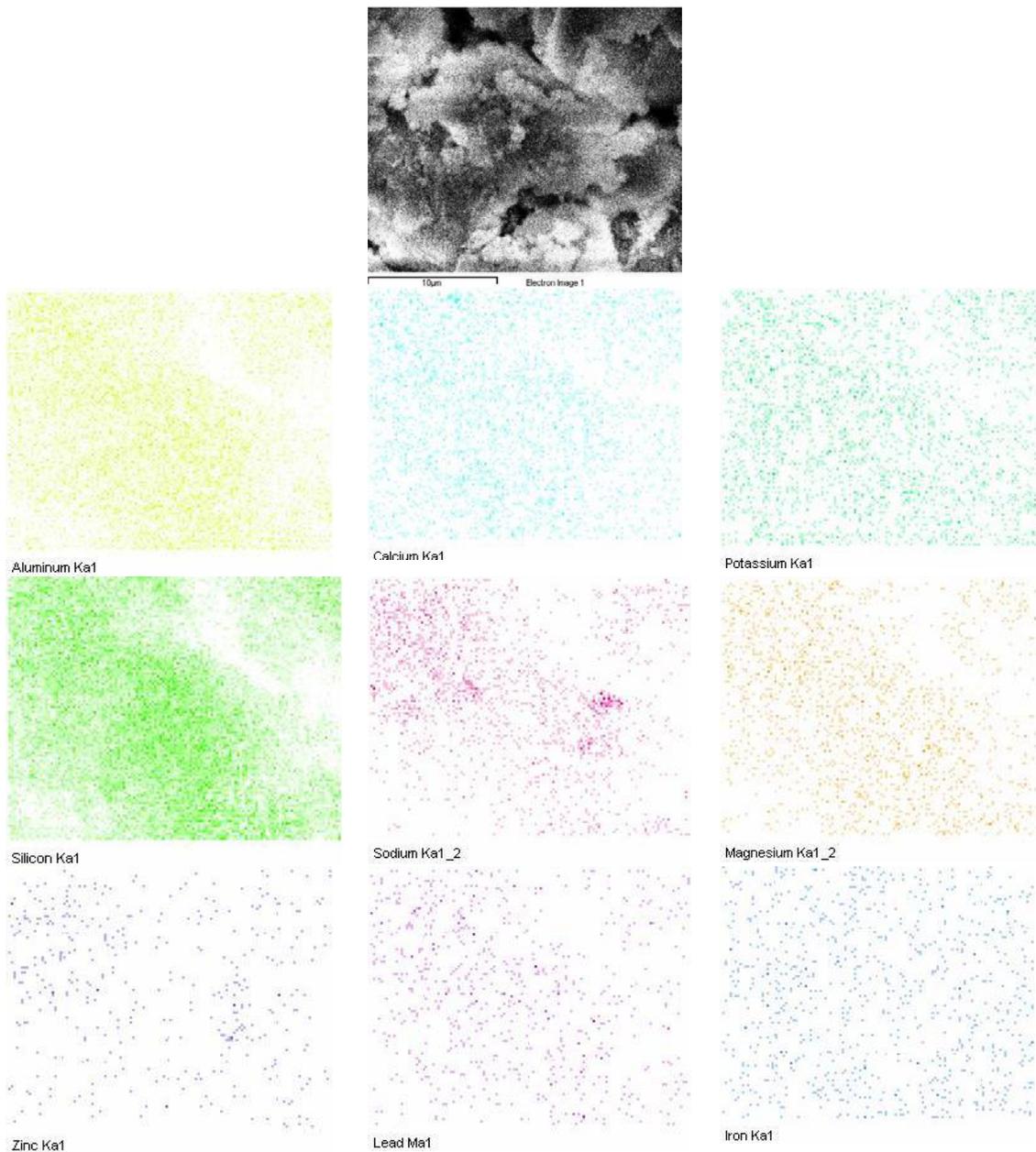


Figure 10. Maps of compositions for the described zeolitic tuff particles

## 5. CONCLUSIONS

The obtained results have demonstrated the fact that the ion exchange has a good outcome for the elements in question, the employed zeolitic tuff proving structural characteristics similar to those described by the literature, such as: the Maramures basin tuffs described by Damian et al., (1991; 2007) and the ones in the north-western part of Transylvania, described by Seghedi et al., (2000).

The data in Table 4 and their representation in Figure 5 prove that the Pb ions concentration undergoes a fast decrease in the first 12 hours, and reaches equilibrium only after approximately 48 hours for all the sample set employed. These results are easily accounted for by the high cation exchange

affinity of the clinoptilolite, demonstrated by Pansini (1996).

The efficiency of the process has been monitored through the ion exchange performance and the calculations have been displayed in Table 4 and graphically represented in Figures 7 and 8. The Pb ions register a maximum value, 99.17% for the G012 set as well as values close to this maximum one for other sets, such as: 97.56% for the G02 set and 96.03% for the G04 one.

Due to the fact that Zn ions in the initial sample seem to have a significantly high concentration value, retention is obvious, but more contact time and a bigger solid/liquid proportion are needed to reach equilibrium. Kallo, (2001) observed the high affinity of the clinoptilolite for the  $Zn^{2+}$  in

aqueous solutions. However, Erdem et al., (2004) showed that the capacity of natural zeolites to adsorb heavy metals species from industrial wastewater decreases as the metals concentration in aqueous solutions increases. This could explain the time needed for Zn retention in our research. However, retention advances slowly and exchange performance values around 50% are obtained for all the sets in the study (Table 5).

If the volume of wastewater used during the experiments is constant, the decrease in the particle size range of zeolite volcanic tuff samples proves to be associated with an increase in the retention of studied ions. The lowest concentration values are obtained for the G012 set, namely the set with a particle size range of the volcanic tuff of under 0.012 mm. This can be explained by the fact that the lower the particle size range, the higher the contact surface for the same quantity of zeolite.

A significant decrease in the metallic ions present within wastewater could be noted during our research, enabling treated wastewater to be re-introduced in the process or evacuated in the emissary. The zeolite tuff, widely met in our country, could be the main material to be used in technologies of industrial wastewater purification due to its special properties.

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