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STUDIES AND RESEARCH CONCERNING THE USAGE OF ZEOLITIC TUFFS FROM BÂRSANA AREA IN NONCONVENTIONAL TECHNOLOGIES OF WASTEWATER CLEANING

PhD Thesis

(Summary)

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CONTENTS

Keywords

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INTRODUCTION

The pronounced global economic development and exponential growth in consumption of materials and mineral resources in the last century, have attracted intense concerns in finding alternative methods for technological applications with a high consumption of fuel and energy. Thus, more intense steps and tries are made for finding methods and cleaner technologies for environment decontamination which will be based and promote the sustainable development principles.

The concept of this paper is based on a modern vision for finding the effective and outlook solutions focused on the consumption of cheap and affordable resources. In this context, the use of natural zeolites constitutes a premise for use the nonconventional eco-technologies in applications for environmental decontamination and especially for wastewaters cleaning.

The theme is focused on the possibilities for using the Bârsana zeolite tuffs (Maramureş County) in geological and economical context, in wastewater cleaning having as aim the surveillance of the eficiency and the influence of some parameters upon the mechanisms for retaining the heavy metal ions from wastewaters.

The waters from the Baia Mare City and its surroundings are still strong polluted with heavy metals because of the lack of some post-closure effective measures of the inactive mining perimeters, as well as the eviction of the technological waters from the main metallurgical plant, SC Romplumb SA Baia Mare.

The reason for choosing the Bârsana zeolitic tuff in order to get the experimental information is supported by the tuff high quality (high content of zeolites and especially of clinoptilolit) but also by the outcrops near the Sighetu-Marmaţiei city and Baia Mare city, which would constitute a facility for the future usage attempts of these mineral resources in decontamination processes applied at semi-industrial or industrial scale.

Because the classical processes of cleaning the industrial wastewaters like: ion exchange with organic resins, chemical precipitation, ultrafiltration, reverse osmosis, electrodialysis and adsorption are very expensive, the necessity to use the natural zeolites becomes more and more acute both as cost-effectiveness and as factor for environmental protection.

For knowing these tuffs the approach of the research subject under geological aspect is very important so that to be able to outline a well based vision as regards the petrographical and mineralogical features as well as the physic, chemical and structural ones of the used zeolitic tuffs.

Along the reseach direction in the paper will be approach the fundamental fields as: geological-petrographical features of the Maramures Basin (the origin area of the studied zeolitic volcanic tuff), the originating geological environment of the zeolitic tuffs, occurences and the zeolitic tuff abundance in the world and country, petrographical – mineralogical features as well as the physical-chemical proprieties and the usage possibilities of the zeolic tuffs that will culminate with the laboratory part of evaluation the efficiency of the zeolitic tuff usage from the Bârsana area in decontamination of the polluted water with heavy metals.

The geological environment of formation the zeolitic tuffs on the Romanian area corresponds with the neogen paroxistical volcanic activities which have marked the petrographical and mineralogical features of the products. Generally, the volcanic tuffs from Romania have a high content of clinoptilolit which confer them a high value.

In the world the zeolits occurrence knows a widespread, the best known being from: USA, Cuba, Mexic, China, Turkey, Hungary, Russia, Japan, Slovakia, Bulgaria, New Zealand, Greece, Island etc. In Romania the most important zeolitic tuffs occurrences are situated in: NW region of the Transylvanian Basin (near localities: Dej, Beclean, Nimigea de Jos, Nimigea de Jos Cepari, Dumitra, Prundu Bârgăului, Mureşenii Bârgăului, Colibiţa, Tărpiu, Vale, Bobâlna, Aluniş şi Şoimeni, Mirşid, Bocşa - Borla, Chilioara - Coşeiu, Ortelec, Guruslău, V. Pomilor – Mocirla), in Maramures Basin (the Bârsana tuff identify especially in areas of Văleni-Călineşti, Ocna Şugatag, Coştiui şi Sighetu-Marmaţiei), in the inner curvature of the Eastern Carphatians (The Perşani Department) as well as in the Subcarpathians region (The Tarcău Unit from the Slănic Prahova region).

So acclaimed qualities of this „boiling stone" are given by its extraordinary features of making the ion exchange at a very high level without affecting the crystalline network, by its feature of molecular sieve as well as by the easy capacity of hydration – dehydration.

The laboratory research results conjunction with the results gained after the studies concerning the region geology have a high significance in appreciating the importance and the efficiency of the Bârsana zeolitic tuffs and especially of those from the Valea Morii quarry in

wastewater cleaning operations being a starting base for other issues related to the tuffs usage at higher level.

Through these research instruments a comparative analyse for the efficiency of zeolitic tuff usage on the two laboratory direction will be made: batch regime and dynamic regime using ion exchanger columns, which will constitute an informational support very useful for other tries of using this kind of tuffs both in economical sphere and mostly in environmental decontamination and wastewater cleaning processes.

The zeolitic tuff usage generally in Romania and especially of those from Bârsana area in alternative applications for removing the pollutants from environment, there is in a shy development stage. Although, on the our country area very high quality tuffs occurrece abundantly, these are not deeply exploited because of lack of a promoting policy of their turning into account and although there are remarkable laboratory results gained by the romanian experts concerning the usage of the zeolitic tuffs in cleaning technologies of the aquatic environment these were not entirely used in applications on semi-industrial or industrial scale.

The zeolitic tuffs represent an eco-alternative technological source for the future and so that the knowing and dissemination the information regarding the usage efficiency of these tuffs in nonconventional technology for environmental depollution and especially for the wastewaters are very important.

1. GEOLOGICAL –PETROGRAPHICAL FEATURES OF THE MARAMUREŞ BASIN

1.1. Evolution and geology of the Maramureş Basin

Maramureş Basin is a vast mountain depression, surrounded by Maramureş and Rodna Mountains and Ţibleş Oaş-Gutâi-Ţibleş Neogene eruptive chain. Located in the north of Romania, Maramureş Basin belongs to the Carpatho-Pannonian Region, which evolved during the Neogene due to complex subduction processes at the edge of European plate, that have led to the formation of volcanic chains inside the Carpathian arc (Seghedi et al ., 1998) (Fig. 1.1).

Maramureş Basin as a major geological unit consists mainly of Paleogene and Neogene deposits, affected by extensional tectonics. Overlaying the Transylvanian folded flysh deposits, the depression was a result of Ţibleş Oaş-Gutâi volcanic chain generation. Both the tectonic and volcanic processes have an important role in depression formation (Fülöp et al., 2003).
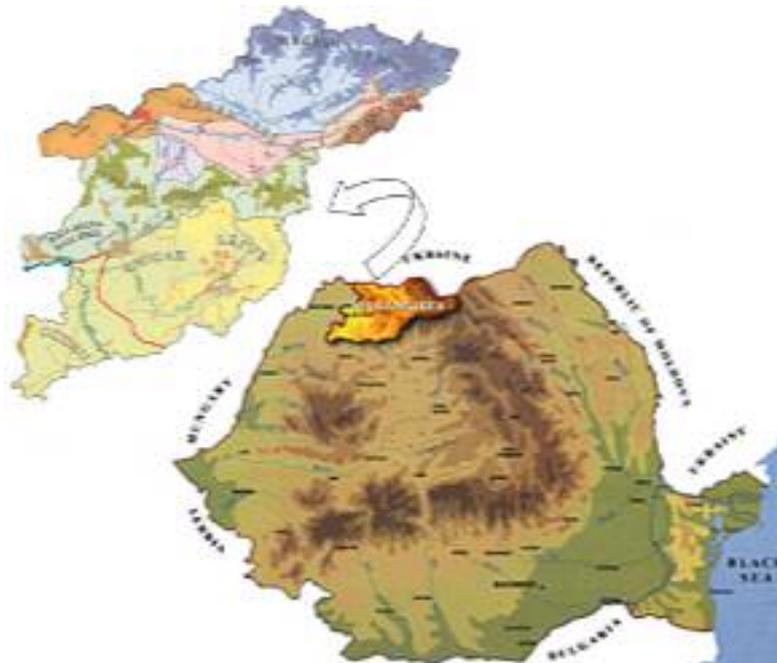
Fig. 1.1. Geographic view of the Maramureş County
(http://www.romanianmonasteries.org/Maramureş)

Volcanic formation investigations conducted by Pécskay et al., (2006) focused on their spatial distribution, relationship to tectonic processes and chemical composition during Neogene-Quaternary period, suggests that the Maramureş Basin area is generally characterized by the

presence of intermediate calc-alkaline formations during the advanced stages of the back-arc extenstion.

The basement belonging to the Oaş-Gutâi and Ţibleş Mountains consists of crystalline foundation, then by pre-volcanic sedimentary formations, Neogene volcanites and sedimentary formations synchronous with the volcanic activity. The basement is composed of Internal Dacides represented by precambrian metamorphic rocks belonging the Bihor and Median Dacide units constituted by an overlapping nappe system, composed of precambrian and/or paleozoic metamorphic rocks as well as the Triassic – lower Cretaceous age sedimentary formations (Săndulescu, 1984; Săndulescu et al., 1993). Over these formations belonging the Internal and/or Median Dacides there are a series of formations belonging Pienides unit (Săndulescu, 1984).
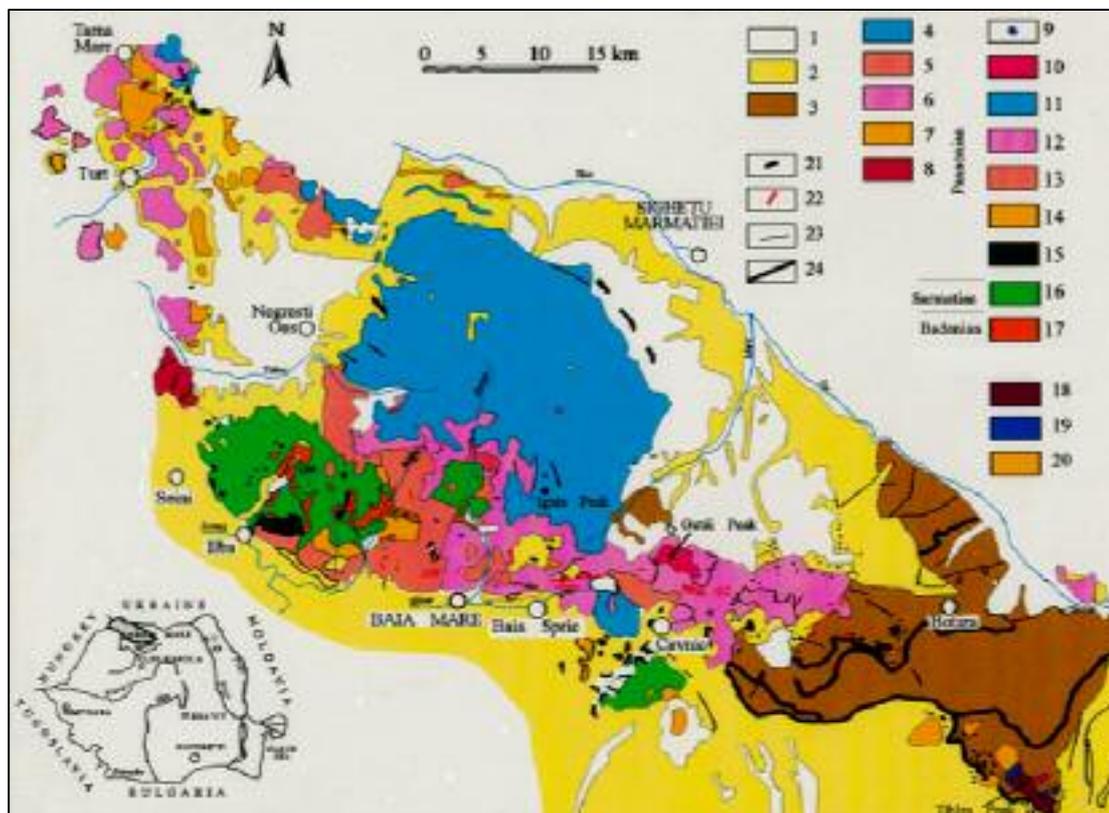
Fig. 1.2. –The geological map of the Oaş- Gutâi –Ţibleş mountains chain. Legend: 1 – Quaternar, 2 – Neogene, 3 – Paleogene; 4 – Upper pyroxenic andesites, 5 – Quarty-andesites, quartz-diorites, 6 – Lower pyroxenic andesites 7 – Dacites, hialodacites, 8 – Riolites, perlites; 9 – Basalts, 10 – Andesites with pyroxens, hornblende, biotite and quartz, 11 – Pyroxenic andesites, Basaltoid andesites with pyroxens, 12 – Basaltoid andesites with pyroxens, pyroxenic andesites, andesites with pyroxens and amphiboles, 13 – Quartz-andesites, 14 – Dacites, hialodacites, 15 – Pyroxenic andesites, 16 – Basaltic andesites with pyroxens, pyroxenic andesites, 17 – Volcanic complex, predominant ignimbrites; 18 – Quartz-monzodiorites, 19 – Andesites, microdiorites, diorites, 20 – Microgranodiorites, dacides; 21 – Intrusions, 22 – Veins, 23 – Fault, 24 – Nappe (after Edelstein et al., 1980).

Upper Cretaceous and Burdigalian tectogenesis led to overlapping Pienniny nappes over the post-tectogenetic coverlet of the Median Dacides (Fig. 1.2) (Săndulescu, 1988, Săndulescu et al., 1993).

Tectonic movement of the Pienniny nappes during Burdigalian was directed by two major transcrustal faults, along which strike-slip movement took place: Dragos Voda fault and North Transylvanian fault. Thus, the presence of Dragoş Voda and Iza fault on the northern edge of the Ţibleş and Rodna Mountains indicates a plunge of the basin along the faults plan. Continuous fronts of the nappes are cut by numerous faults, especially of strike –slipp type, having different orientations. The nappes located south of Dragoş Vodă fault have southern vergence while the nappes located northern of this fault have vergence from NE to SW (Fig. 1.3).

The structure of the pre-volcanic fundament of Oaş-Gurâi region is made by the evolution in time of a two major fractures: Dragoş-Vodă orientated E-W and Gutâi fracture orientated NW-SE.

The Dragoş-Vodă fracture extends from east, from the Bistrita valley basin, to the west in the Pannonian Depression; the Gutâi fracture extends toward northern-west to Virholat area and to south-east up to the Călimani - Harghita volcanic chain (Borcoş et al., 1979). Dragoş-Vodă/Bogdan Vodă fault is part of the faults system with regional character called Mid-Hungarian Line (Fig. 1.3) (Csontos et al., 1992).

According to Gröger et al., (2008), the Pienides consists of non-metamorphic flysch nappes emplaced during lower Burdigalian (20.5 - 18.5 Ma). Between Middle and Upper Miocen (16-10 Ma) tectonic movements led to the elevation of the Rodna horst and the Preluca massive (Tischler et al., 2006). The most important structures belonging to the Middle Miocene up to Upper Miocene are Preluca faults, Greben fault and Bogdan Voda - Dragos Voda fault. To the west, Bogdan Voda fault is hidden by the volcanic Neogene rocks (Fig. 1.3) (Gröger et al., 2008).

The so-called Bucovinian nappes (Fig. 1.3) of the Dacia block belonging to the Precambrian-Paleozoic period are made of metasediments and subordinated by orthognaise (Kräutner, 1991; Vodă et Balintoni, 1994). The Alpine Bucovinian nappes present the following succesion: Infra Bucovinian nappes, Sub Bucovinian nappes and Bucovinian nappes separated sometimes by sediments belonging to Permian up to Lower Cretaceous (Săndulescu, 1984, Gröger et al., 2008).
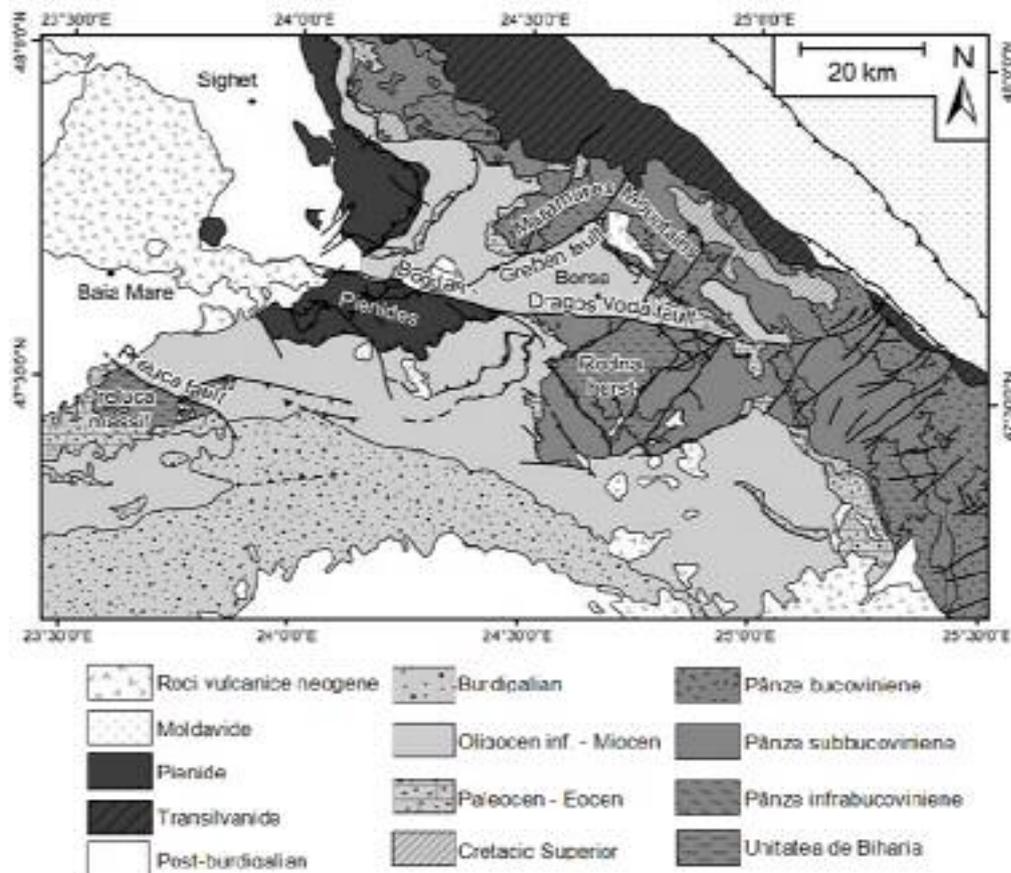
Fig. 1.3. The tectonic map of Maramureş Basin (Gröger et al., 2008)

The volcanic activity in the Maramurs Basin took place in two distinc phases: the first phase, Badenian-Sarmatian (Middle Miocene) is calc-alkaline characterized by explosive eruptions which generated huge ash amounts of acid rocks deposited mainly as fall-out tuffs and the second phase, Sarmatian – Pannonian, representing by paroxistic episodes of the volcanic activities which generated large amounts of andesitic lava (Cochemé et al., 2003; Fülöp şi Kovacs, 1996).

The Maramureş Basin contains Miocene deposits of molase type represented by detritic sedimentary sequences and intercalated volcanic rocks, that overly the Paleogen flysch and the metamorphic rocks basements and in its north - western area consists of Senonian, Eocene, Oligocene, Badenian, Sarmatian and Pliocene age formations (Fig. 1.4) (Cochemé et al., 2003; Fülöp şi Kovacs,1996, Damian et al, 1991). The Paleogene deposits belong to Petrova nappe and are made of Middle Eocen and Upper Eocen flysch deposits (Săndulescu et al, 1993) and the

neogene deposits are represented by Badenian and Sarmatian detritic sedimentary and volcanoclastic (dominant pyroclastic) deposits.
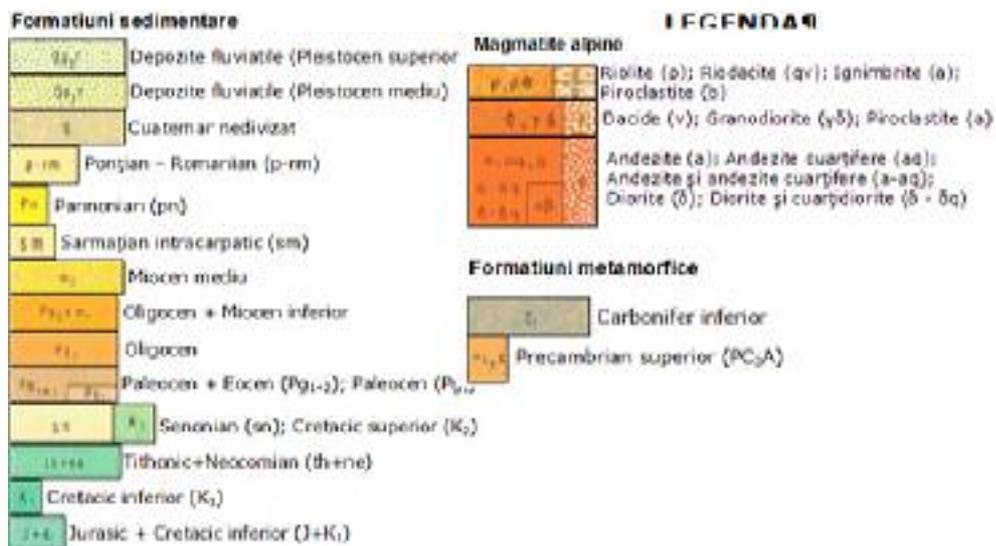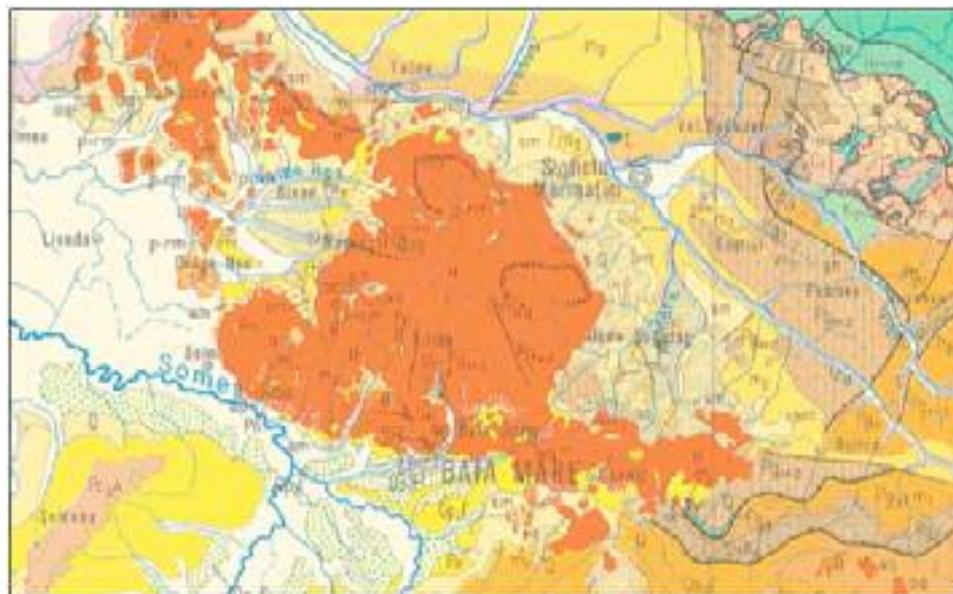
Fig. 1.4. Harta geologică a Bazinului Maramureş (dupa Harta geologică a României, Scara 1:1.000.000)

The Badenian deposits reach approx.1000 m total thick and consist of clay, siltstones and sandstones interbedded with volcanoclastic deposits having a pyroclastic origin (Fig. 1.4). Locally, they contain lenses of salt and gypsum. Although it has not been realized yet a clear stratigraphy of the deposits of Maramureş Basin, preliminary data show the presence both of Lower Badenian and Upper Badenian in a similar facies (Fülöp et al., 2006).

3. GENESIS AND OCCURRENCES OF ZEOLITIC TUFFS IN ROMÂNIA

3.1. Geological conditions for genesis of zeolitic tuffs in România.

Volcanic tuff in România are related to paroxysmal explosive volcanic activities character who delivered sufficient quantities of volcanic ash that had accumulated as thick intercalations or large banks in the Miocene and Pliocene formations, in particular (Cochemé et al. , 2003).

Tuffs were formed as a result of cementation products of explosion of acid and intermediate magmas. Over 90% of volcanic tuff and zeolite has a rhyolitic and dacitic composition. The zeolitization process took place in the marine environment at alkaline pH between 9.5 and 9.8.

Volcanic glass in particular, has been replaced by zeolites, due to its great instability in the marine environment. In addition to volcanic glass, were affected by zeolitization both silicates or micas and the magmatic quartz (Măicăneanu et al., 2008; Anastasiu, 1977).

Figura 3.2. The main occurrence areas of zeolitic tuffs in România (Bedelean et al., 2005).

According to Bărbat et Marton, (1991) and Măicăneanu et al., (2008) volcanic tuffs in our country have known an emphasized development in the Miocene and Pliocene formations being able to mention in this connection the following geological units: intra and extra Carpathian

depressions (Transylvania, Sylvania, Maramureş, Getica), Eastern Carpathians (Perşani Deparment, Tarcău Unit, Carpathian Avanphose) (Table 3.1).

Table 3.1. Occurrences of zeolites in România (Matei, 2004)

No. crt.	Mineral	Magnetic rocks				Metamorphic rocks	Sedimentary rocks
		Prealpine	Alpine				
			Ophiolites	Banatites	Neogene - Quaternare		
1	Natrolite	Central Dobrogea	Metaliferi Mountains	Bihor Mts.	Gutâi Mts. Harghita Mts.		Dep. Maramureş
2	Mesolite		Metaliferi Mountains	Bihor Mts.	Ţibleş Mts.		
3	Scolecite		Perşani Mountains	Banat Mts.	Rodnei Mts.		
4	Thomsonite Gonnardite			Bihor Mts. Vlădeasa Mts.		M. Bihor	
5	Heulandite		Perşani Mountains	Bihor Mts.	Gutâi Mts. Highiş Mts.		Transylvanian Dep.
6							
7	Clinoptilolite Stilbite		Metaliferi			M. Bihor, Dobrogea	Tarcău Unit. Transilvania,
8	Epistilbite		''		Metaliferi		Silvania,
9	Phillipsite		''			M. Bihor	Maramureş
10	Harmotom		''		Ţibleş Mts.		Dep.,
11	Chabazite		''	M. Banat			Tarcău Unit.
12			''		Metaliferi		Transylvanian Dep.
13	Laumontite Gmelinite		''	Banat Mts.	Gutâi Mts.	M. Bihor, Poiana Ruscă	
14	Mordenite		''	Banat Mts.	Gutâi Mts.		Maramureş,
15	Analcime		''	Oaş Mts.	Gutâi Mts. Harghita.		Dep.
16					Oaş Mts. Oaş Mts.		Subcarphatic

According to Mârza et Meszaros (1991), in extension, thickness and content of zeolite, the most important volcanic tuffs belong to the lower Badeniene deposits and the the most important deposit is the "Dej Tuff", which appears in the Transylvanian Basin (and bears that name), but which in Sylvaniei Basin (or Şimleu) was appointed local tuff of Mirşid, being actually the same level (as the Maramureş area). So it is with the Perşani tuff, which is really all the Dej Tuff.

In the same period formed the Slănic tuff, which being across the Carpathians has no connection with the Dej tuff.

The best known geological structures that have stuck are the volcanic tuff of Transylvania Depression and the extra-Carpathian Depression. They may also be mentioned, the intra-mountain depressions (Sylvania, Maramureş, etc.) (Meszaros et Mârza, 1991).

The rhyolitic Complex of "Dej Tuff" of Middle Miocene age consisting of conglomerates and volcanoclastic sandstones, medium and fine grained tuffs and alternations of fine tuffs layers,

tuffits, tufaceous marls record the beginnings of Neogene volcanic activity in România (Szakács, 2003)

The predominant and characteristic zeolite for volcanic tuffs in România is clinoptilolite followed by mordenite, heulandite, phillipsite and analcime (Anastasiu, 1977).

The zeolite rich tuffs containing more than 50% clinoptilolite reaching even to 90% there are in Tarcău Unit, Maramureş Depression, Sylvania and Transylvania, with a thickness from 1.5 m to 40 m (Matei, 2004).

3.2. Genesis and occurrence of zeolitic tuffs in Transylvanian Basin

Transylvanian Depression is a well individualized structural unit, being the largest tertiary molasse basin developed in our country. The form is roughly circular and morphologically limited by the Eastern Carpathians and by the Neogene eruptive chain at east and north, by the Southern Carpathians at south and by the Apuseni Mountains in the west and north-west.

The most important horizons of Badenian-volhynian tuffs there are in NW Transylvanian Basin, in the western area of Someşul Mic, in the norther of Someşul Mare near localities: Dej, Beclean, Nimigea de Jos, continuing to southern of Someşul Mare between the localities Nimigea de Jos Cepari, Dumitra and to the east between localities: Prundu Bârgăului, Mureşenii Bârgăului and Colibiţa (Mârza et Maszaros, 1991). In addition to these, there are volcanic tuff deposits in the Sylvaniei and Maramureş Basin. In the NW of the Transylvanian Basin zeolites occur as alteration products of acidic badenian tuffs predominantly vitric (Middle Miocene). The lithological study of this tuffs complex that occurs anywhere in the Transylvanian Basin indicates a wide range of development of zeolitized rocks (Seghedi et al., 2000).

3.3. Genesis and occurrence of zeolitic tuffs in Maramureş Basin

Tectonic movements during the Miocene resulted in silicic and intermediate volcanism in the inner part of the Eastern Carpathians. Here the explosive events have led to the formation of deposits of pyroclastic flows and ash deposits intercalated with marine sediments. The upper part of the sequence contains detritic lacustrine sediments rich in coal belonging to Pontian (Cochemé et al., 2003).

The central area of Maramureş Basin is characterized by the presence of fine zeolitized tuff deposits occurred in: Bârsana, Onceşti, Nǎneşti, Cǎlineşti, Ocna Şugatag, Sǎlişte, Vadu Izei etc with a stronger emphasis of the outcrops complex in Valea Morii (Fig. 3.2) (Fülöp et Crihan, 2002).

Fig. 3.2. The main occurrences of zeolitic volcanic tuffs in Maramureş County

Also, at the upper Badenian a level of vacuolar spongy tuff was found near Văleni - Coaş - Berchezoaia (Fig. 3.2) in south – western Maramureş Basin (Cochemé et al., 2003).

The Sarmatian deposits are overall similar with the badenian deposits but the volcanoclastics are subordinated to sedimentary clay and sandstone deposits.

▪ **Bârsana zeolitic tuffs in Valea Morii and Ocna Şugatag area**

The „Bârsana Tuff" represents a generic term, which refers to zeolitizated fine tuff, known for its economical valorization potential. It occurs in several areas of the Basin, at: Bârsana, Onceşti, Năneşti, Călineşti, Ocna Şugatag, Sălişte, Vadu Izei etc. The most complex outcrops occur in the central part of Maramureş Basin, in Valea Morii area (Fig. 3.2) where may be highlighted the relations between the spatial relations of the zeolitized tuff and other co-genetic deposits useful in the perspective of establishing the exploitable zeolites reserves (Fülöp et Crihan, 2002).

According to Antonescu et al. (1979) the identified lower Badenian formations belonging to the Valea Morii-Barsana may be parallelized with the Dej tuff. Valea Morii area formations appear as a succession of: green-gray tuffs, cemented medium and fine sandstones showing marl intercalations, coarse and fine tuffs and poorly consolidated sandstones over which a succession of sandstones with intercalations of marls appears.
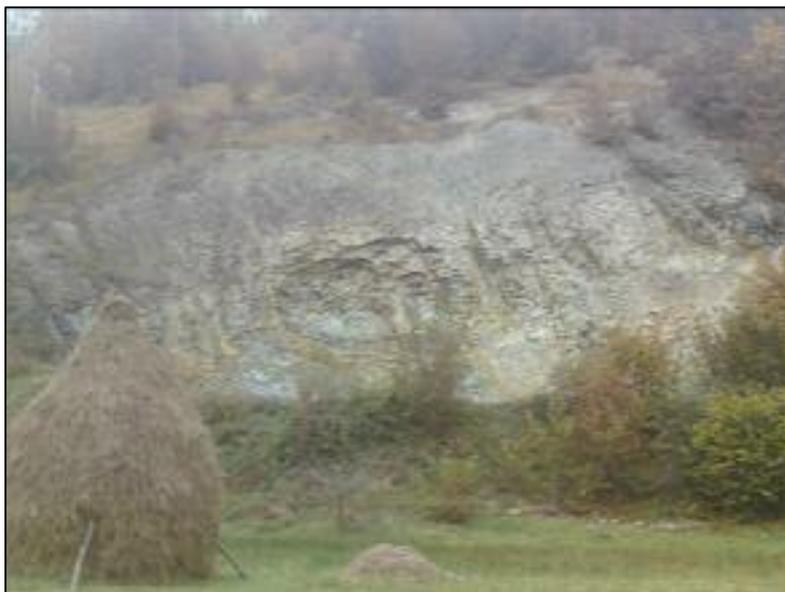
Figura 3.3. Volcanic zeolitic tuff occurrence in Valea Morii –
Bârsana area (photo: Irina Smical)

The volcanic tuffs from Valea Morii area (Călineşti) are zeolitized. Separated by a calcareous sandstone unit, these stratifications appear massive, homogeneous with a thickness between 70 and 100 m. The colour of these tuffs is blue - green (Cochemé et al., 2003).

Tuffs quarry is located in the middle of the intra-Carpathian Basin of Maramureş, in the Basin of Iza Mijlocie between the Pârâul Vălenilor, Valea Morii (affluents of Iza river) brooks and Valea Mijlocie (Fülöp et al., 2006) (Fig. 3.3., Fig.3.4). Tuffs in this area are generally very zeolitizate and have a vitroclastic texture. Pyrogenic crystal fragments include quartz, plagioclase and biotite and lithic fragments are represented in most of the muscovite schist and quartzite. These tuffs commonly contain tabular crystals of clinoptilolite formed by pseudomorphic replacement of vitroclasts (Cochemé et al., 2003).

Tuffs from Valea More are compact zeolitic tuffs, the cracking being more evident only in upper part of the quarry where the limonitic films are more frequent. Locally, in particular to the quarry base, in the tuff appear individualized sporadic bands of 0.5-1 cm thick, where the biotite in submilimetrice sequins, has a notable participation. Zeolitic tuff in this area contain several species: clinoptilolite, mordenite and natrolite and the heulandite proportion is very low. Basic component of these tuffs is made up of vitroclasts (90%) and cristaloclasts and lithoclast being below 10% The structure of these tuffs is mechanical, clastic (Matei, 2004).

Fig. 3.4. Sketch after the geological map of Maramureş Basin – Bârsana area (Fülöp et Crihan, 2002).
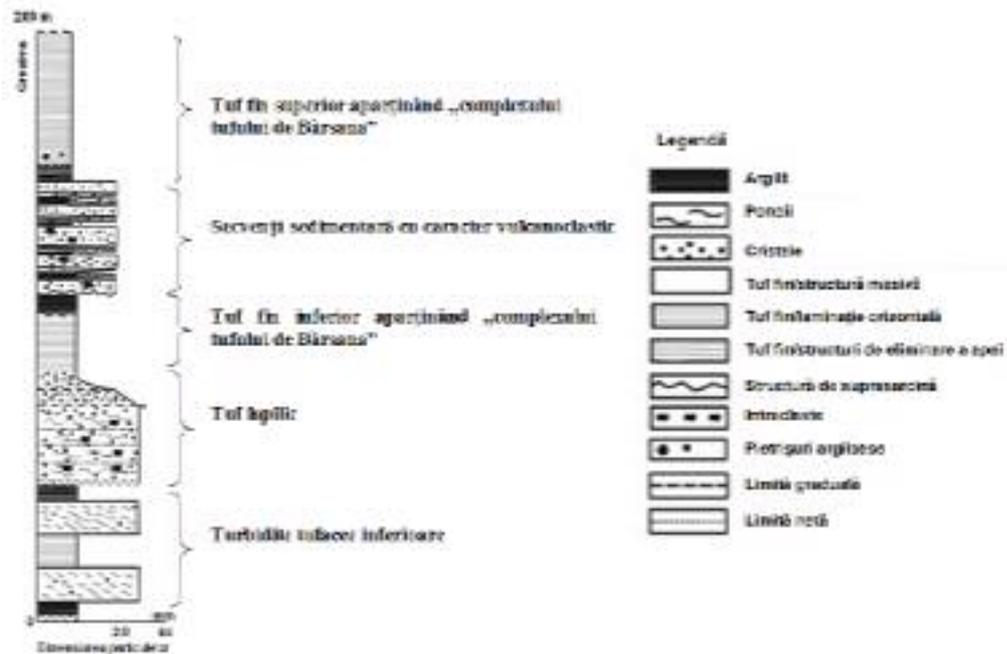
Fig. 3.5.Succesion of volcanocalstic deposits in Maramureş Basin, Bârsana area (după Fulop et Crihan, 2002)

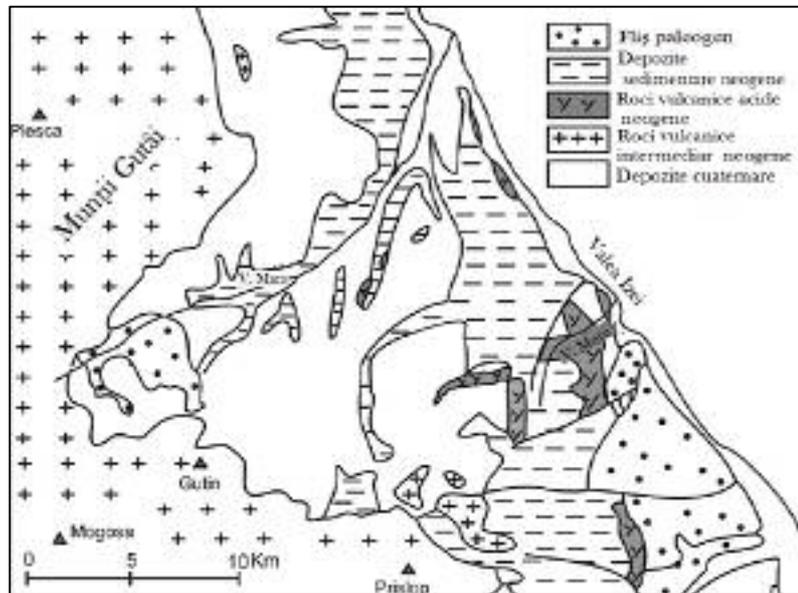Zeolite tuff formations of Bârsana near Ocna Şugatag individualize by the presence of white tuffs, fine-grained. In the vicinity of a sinkholes an spongious tuff unit was identified showing a

pyroclastic flow aspect (Cochemé et al., 2003). Tuffs in this area have an acidic, riodacitic composition and suffered intense alteration processes, including zeolitization, bentonitization, celadonitization, calcitization (Mutihac et al, 2004).

- **Zeolitic deposits in Valea Seneş-Valea Higea area (Coştiui)**

Located in northern Maramureş Basin, the sedimentary basin from Coştiui area constituted by badenien and sarmatien deposits contains dacitic tuffs with a thickness of aprox. 250 m. Sarmatian formations present in this basin consist mainly of: marls, marly sandstone, friable sandstones and sand and tuffs are represented in the basal deposits by lapilic tuff that are overlayed with cristaloclastic and vitroclastic tuffs.

Zeolites were formed by volcanic glass devitrification and most representative of these tuffs are: clinoptilolite, mordenite and heulandite. In a smaller proportion celadonit and cryptocrystalline silica appear (Damian et al., 2007).

3.4. Genesis and occurrences of zeolitic tuffs in Perşani andValea Prahovei area

Zeolitic volcanic tuff from the internal curve of Eastern Carpathians are structurally part of the Perşani Department and shows stratigraphy, mineralogy, petrography and volcanologic similitudines with the volcanic zeolitic tuffs from Transilvanian Basin.

The Dej Tuff outcrops in this region, the most important zeolite tuff deposits being located in the surroundings towns: Şinca-Grind-Perşani, Şinca Veche-Comana de Sus, Racoş. Near the Jibert village the Ghiriş Tuff was identified (Măicăneanu et al., 2008; Brana et al., 1986).

The Slănic Tuff belongs to Lower Badenien geological being represented by tuffs and tuffs with marls intercalation (Mărunţeanu, 1999).

3. PETROGRAPHIC AND MINERALOGIC CHARACTERISTICS OF ZEOLITIC TUFFS IN ROMÂNIA

3.1. General overview on petrography and mineralogy of zeolitc tuffs

Depositing the cinerites in sedimentary basins was held concurrently with sedimentation debris material from the continent, resulting in complex of sedimentary rocks that reach sometimes tens or even hundreds of meters. In these complex multilayered intercalations of tuffs there may exist, well individualized in terms of structural and textural. Sometimes tufaceous intercalations contain more than 10% debris, in which case they are called tuffites. When the pyroclastic materials not exceeds 50% , they are considered sedimentary rocks (Brana et al., 1986).

După Mârza et al., (1991), tufurile propriu-zise conţin între 90-100% material piroclastic. La o participare de 60-90% piroclastite şi 40-10% epiclastite, rocile piroclastice corespunzătoare poartă şi calificativul de „epiclastic".

Granulaţia tufurilor vulcanice definesc tipul de spărtură care poate fi: concoidală la cele pelitice şi pelito-aleuritice, aşchioasă la cele aleurito-psamitice şi neregulată la cele psamitice.

Table 3.1. The main transformation processes take place according to the following possible scheme of alteration of volcanic glass (Ghergari et al., 1989)					
Montmorillonitization	Volcanic glass	$\xrightarrow{\text{-K, Ca}}$	Smectite + SiO_2		
Zeolitization	Volcanic glass (rhyolitic, dacitic)	$\xrightarrow{\text{- Mg, Fe}}$	Clinoptilolite Mordenite	$\xrightarrow{-SiO_2}$	Heulandite Philipsite Chabazit
	Sticla vulcanică (andezitică, andezitică-cuarţiferă)	$\xrightarrow{\text{- Mg, Fe}}$	Heulandite Phillipsite Chabazit	$\xrightarrow{-SiO_2}$	Clinoptilololite Mordenite
Celadonitization	Volcanic glass	$\xrightarrow{\text{- Ca, Na}}$	Celadonite + SiO_2 + Al_2O_3 (4 : 1)		

Among the processes shown in Table 3.1., zeolitization is the most important because it confers to the tuffs a special economic value. The products of this transformation are zeolites, minerals that may exist in a ratio of 20-80% by mass of tuff deposits.

Besides the volcanic glass, tuffs also contain: cristaloclasts of feldspar, quartz, biotite, pyroxene and sometimes hornblende, detritic fragments of quartz, quartzite, calcite, and biotite mica sheets. Sometimes it may contain calcareous organisms, foraminifers (globigerine) (Brana et al., 1986).

Depending on the composition of volcanic tuffs Anastasiu (1977) divided the volcanic tuff in the following categories:

• vitroclastic tuff, with over 50% glass;

• cristaloclastic tuff, with over 50% idiomorfe crystals or crystal fragments;

• litoclastice tuff, with more than 50% lithic fragments.

Also, are defined intermediar categories: vitrocristaloclastic tuffs, vitrolitoclastic tuffs , cristalolitoclastic tuffs, litocristaloclastic tuffs etc (Fig. 3.1.).
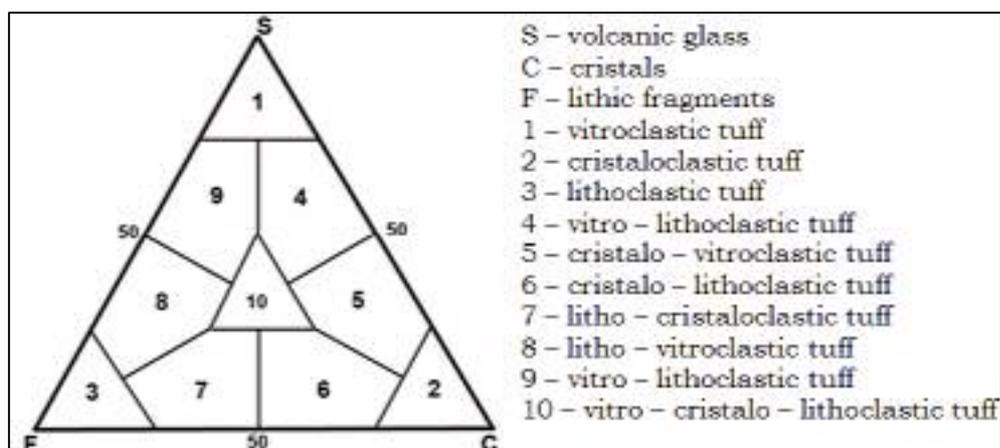
Figura 3.1. Ternary diagram for structural characterization of pyroclastic rocks (Măicăneanu et al., 2008 after Anastasiu, 1977).

In terms of the degree of compaction and cohesion of the rock volcanic tuffs can be friable, consolidated (cemented or welded), porous or compact. The color is different from white gray to greenish, yellowish or violet. Depending on the size clasts, tuffs themselves are classified as: coarse tuffs (0.5-2 mm), medium granular tuffs (0.063 to 0.5 mm), fine tuffs (0.004 to 0.063 mm) (Măicăneanu et al. , 2008).

Depending on the mineralogical and chemical composition, which reflects the type of primary magma, from which they come, they differ in several petrographic types of volcanic tuffs and by petrographic point of view may be: rhyolitic, dacitic, trahitic, andesitic, basaltic and fonolitic as is shown in Table 3.2.

In general, colour is white tuff with shades of green, gray, yellow or brown. These rocks have low compressive strength and do not withstand repeated freeze-thaw sequences (Brana et al., 1986).

Table 3.2. Petrographical types of volcanic tuffs (after Anastasiu, 1977)

Followed element	Determined element	Petrographical types
Salic Minerals - quartz Q - potassic feldspar Fk - plagioclase P(o-xAn) Minerale femice - biotite Bi - hornblende Hb - piroxene Px - olivine Ol	Q, Fk, P 0-20, (+/- Bi)	rhyolitic
	Q, P 0-30, (+/- Bi), (+/-Hb)	dacitic
	P 0-30, Fk (+/-Px)	trahitic
	P 30-70, Hb, Px	andesitic
	P 50-70, Px, Ol, (+/-Hb)	basaltic
	Fk, P0-30, Foide	phonolitic

The name "zeolite" comes from the Greek "zein" that means "to boil" and "lithos" that means "stone" and the specific minerals of this group are named either from Greek or Latin, or by name of persons or locations related to that mineral.

The predominant and characteristic zeolite for the volcanic tuff in Romania is clinoptilolite along with mordenite, analcime and phillipsite. To highlight the zeolitic properties of the volcanic tuff, investigations that may provide relevant information are: optical and electronic microscopy analysis, global chemical analysis, X-ray diffraction analysis, thermal analysis.

To clarify the qualitative differences between parts of a deposit of tuff or between different deposits, (Bărbat et al., 1991) adopted the classification of volcanic tuff quality.

▪ Zeolite – rich tuff (> 50% zeolites)

▪ Medium containing zeolite tuff (20 – 50% zeolites)

▪ Tuff with low zeolites content (< 20% zeolites)

Zeolitic tuffs in Romania are characterized by a high variability of mineralogical constituents (Table 3.3) (Matei, 2004):

▪ Vitreous granoclastes: volcanic glass and glass products of rhyolitic and dacitic glass devitrification like: zeolites, celadonite, montmorillonite;

- Cristaloclasts: feldspars, quartz, biotite, muscovite and accessory minerals like: rutile, apatite, leucoxene, zirconium;

- Metamorphic or endogenous lithoclasts: quartzitics, andesites and dacites.

Table 3.3. Mineralogical composition of zeolitic tuffs in Romania (Măicăneanu et al., 2008; Matei, 2004; Brana et al., 1986)

Geological Unit	Number of analyses	Minerals , %						
		Quartz	Feldspar	Biotite	Muscovite	Calcite	Zeolites	Others
Tarcău	34	0-3	0-8	0-1	0-1	0-15	40-80	0-32
Subcarpathian Depression	29	0-2	0-20	0-2	0-2	0-40	22-60	0-12
Transylvanian Depression	237	1-7	0-20	0-1	0-1	-	35-85	0-37
Sylvanian Depression	48	0-20	0-15	0-1	0-1	0-16	18-90	0-8
Maramures Depression	61	1-10	1-6	0-1	0-1	0-15	45-85	0-33

Percentage of zeolite is generally high, about 50% for most tuff.

SiO_2 and Al_2O_3 content is characteristic for riodacite and dacites, highlighting the compositional correlation between these rocks and volcanic tuff. Some high contents of CaO and K_2O results from the zeolitization of the volcanic glass (Table 3.4) (Mârza et Mirea, 1991).

Table 3.4 Chemical composition of zeolitic tuffs in Romania (Matei, 2004).						
Geological Unit	Main constituents, %					
	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O
Tarcău (Slănic)	62,78 - 67,70	9,30 - 13,10	2,80 - 5,39	0,97 - 1,5	1,37 - 2,89	0,18 -2,85
Subcarpathic Depression	63,78 - 68,05	11,60 -14,56	1,97 - 4,62	0,35 - 2,5	1,17 - 2,84	1,32 - 4,37
Transylvanian Depression	56,94 - 70,70	10,04 - 21,38	1,19 - 3,99	0,3 - 0,96	0,91 - 3,26	0,6 -3,7
Sylvanian Depression	66,25 - 71,10	6,23 - 11,54	1,54 - 4,84	0,78 - 1,74	2,17 - 3,15	0,29 - 1,72
Maramures Depression	63,94 - 68,62	6,98 - 15,96	2,10 - 4,96	0,8 - 1,04	0,36 - 2,35	0,63 -1,45

3.2. Petrographical and mineralogical characteristics of zeolitic tuffs in Transylvanian Basin

The very detalied mineralogical – petrographical research of cinerites in tertiary deposits of Tranylvanian Depression and in some intra-mountainous basins have clarified the mineralogical nature of autigenic zeolities from their composition, being almost exclusivelly represented by clinioptilolite.

The XRD analyses made both on rough tuff samples and submicronic (granulometric separated) show the massive participation of a main mineral from zeolites group namely of clinoptilolite (Bedelean et al., 2005).
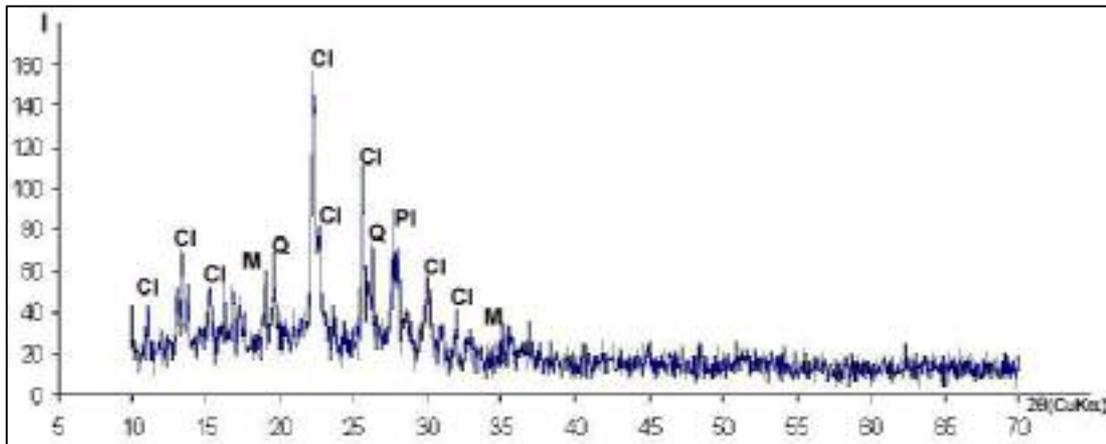
Fig. 3.2. XRD analysis of the volcanic tuff from Măcicaş, (Cluj County) Cl = clinoptilolite, Pl=plalgioclase; Q = quartz; M = montmorillonite (Bedelean et al., 2005)

In terms of microscopic and difractometric analysis made on zeolitic tuffs from outcrops in Cluj County, they highlighted the invariable presence of clinioptilolite in varying proportions of 10-80% (Bedelean et al., 2005).
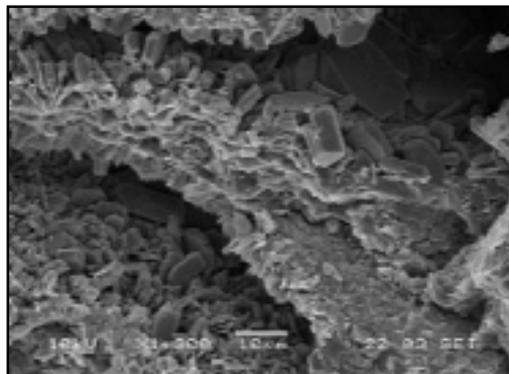
Fig. 3.3. Images by electron microscopy (SEM) of volcanic tuff zeolites from Pâglişa, jud.Cluj (Bedelean et al., 2005).

Analysis by electron microscopy (SEM) showed lamellar prismatic zeolite morphometry associated with xenomorphic volcanic glass fragments or deposits in the rock gaps (Fig. 3.3). (Bedelean et al., 2005).

Research by Bedelean et Stoici (1984), respectively Bedelean et al. (1991) on Mirşid Tuff that looks like the tuff from Maramures Basin, highlighted that this one contains on average 65% clinoptilolite.

3.3. Petrographic and mineralogic characteristics of the zeolitic tuffs from Maramures Basin

In order to determine the petrographic and mineralogic characteristics of the zeolitic tuffs in Maramures Basin several research and investigations were made as results from the speciality literature (Cochemé et al., 2003; Damian et al., 1991; Damian et al., 2002; Damian et al., 2007; Fülöp et al., 2006; Fülöp et Crihan, 2002; Matei, 2004).

Tuffs from Maramures Basin are stongly zeolitized and present in general a vitroclastic texture. Fragments of crystals include: quartz, plagioclases and biotit. Muscovite and small clasts of quartzites and shists with muscovite from the base of the tuffs deposit are dominant along with lithic fragments. Tuffs usually contain tabular crystals of clinoptilolite made by pseudomorphic relocation of vitroclasts. The opal crystals presence and also of celadonites and smectites is obviously (Table 3.5) (Cochemé et al., 2003).

According to reseach made by Cochemé et al., (2003) in tuff from Ocna Şugatag zeolites – clinoptilolite and opal were especially highlighted.

No. crt.	Localisation	Rock description	Mineralogical composition		CEC (meq/ 100g)
			Authigene minerals	Lithic fragments	
1	Sighetu-Marmaţiei	Vitroclastic greenish-gray tuff, heavily compacted	Clay minerals, zeolites, celadonites	Quartz, plagioclase, biotite/muscovite, carbonates, opaque minerals	27
2	Iza-Bârsana Valley	Tuff with coarse yellow-green ponce, fine vitroclastic greenish tuff	Clay minerals, zeolites,	Quartz, plagioclase, biotite/muscovite.	182
3	Morii Valley	Vitroclastic greenish-gray tuffn rich in crystals	Clay minerals, zeolites, calcit	Quartz, plagioclases/muscovit, microfossiles	115
4	Mijlocie Valley	Fine vitroclastic tuff, light green, stratificated relocated tuff	Zeolites, calcite, celadonite	Quartz, plagioclase/muscovite	69
5	Ocna Şugatag	Relocated tuff, white to light green, gray ignimbrites,fine vitroclastic tuff greenish coarse	Clay minerals, zeolites, opal, celadonite,	Quarţ, plagioclazi, muscovite, opac minerals, biotite	99
6	Plopilor Valley	Greenish fine vitroclastic tuff	Zeolites, celadonite	Quartz, plagioclases, biotite/muscovite, microfossile	94
7	Slătioara	White fine vitroclastic tuff	Clay minerals, zeolites, opal	Quartz, plagioclases/muscovite	68
8	Coaş	Coarse tuff, white-yellow, stratificated	Clay minerals	Quartz, plagioclases, biotite	-

Table. 3.5. Petrophysical characteristics of zeolitic tuffs in Maramureş Basin (Cochemé et al., 2003)

Mineralogical and petrographical studies made by Smical, I. et al, 2010a,b regarding the zeolitic tuffs from Bârsana (Morii Valley), foccused on a range of physical-chemical tests which highlighted the type of mineralogical and chemical characteristics of the tuff sampled from the deposit situated at confluence of Mijlocii Valley and Morii Valley on the territory belonging to the Văleni-Călineşti localities.

In order to do these operations the untreated tuff samples were analysed by X- Ray Diffraction method (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), DTA-TG anayses, chemical analyses using X-Ray Fluorescence (XRF) and Flame Spectoscopy.

As is shown in Fig. 3.3 the main zeolitic minerals are respresented by clinoptilolite and in small amount the quartz, albite and cristobalite are noted.
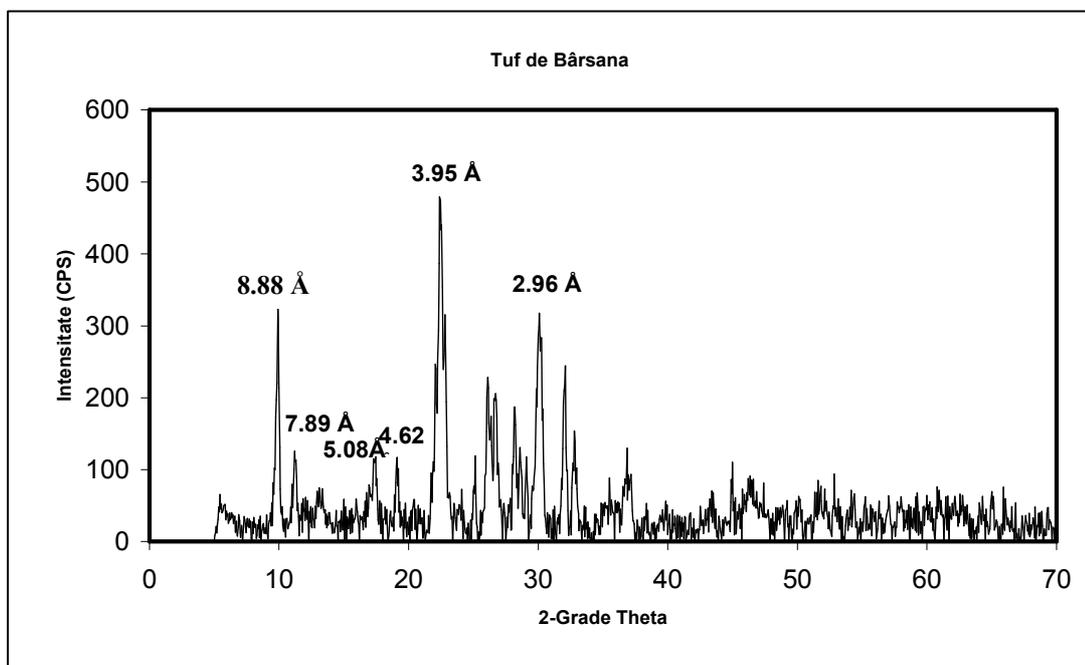

Fig. 3.3. XRD of the Bârsana zeolitic tuff (Smical et al., 2010a)

XRD indicated the presence of very well crystallized clinoptilolite highlighted by the diffraction lines intensity from X-Ray diagram. Along with clinoptilolite in a small amount appear quartz, albite and cristobalite. Their specific diffraction lines are shown on X-Ray diagram (Fig. 3.4).

All X-ray diffraction spectra of diffraction data correspond perfectly with those data presented in the literature for clinoptilolite. Reflexes are well marked by 8,88 Å, 7,89 Å, 5,08 Å,, 3.62 Å,.

If the diffraction spectra of the analysed samples from Bârsana are compared with the standard diffraction model presented by Valiter et al. (1975) for the Zacarpatia clinoptilolitizate tuff, results a higher grade of purity for our samples, as well as a more advanced crystallinity degree of clinoptilolite with the peaks of same more intense and sharp reflexes.

Chemical analysis of Bârsana Zeolitic tuff sample were made using the method of X-Ray Fluorescence (XRF) for major elements and flame spectroscopy for minor elements.

Results of chemical analysis for major elements of the tuff sample are presented in Table 3.6 and the last item in Table 3.7.

Comprehensive chemical analysis results give information on the petrographic nature of volcanic lava Thus the large amount of silica SiO_2 rhyolites indicates the acidic nature and suggests that these minerals have a riolitic, riodacitic or dacitic character. Alumina Al_2O_3 content is normal for a riolitic-dacitic and acidic lava, and is almost entirely retained in the zeolite minerals.

Table 3.6. Chemical composition (mass percent) of the Bârsana zeolitic tuff (Smical et al., 2010a)

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 T (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	P.C.* (%)
72,42	12,22	1,48	0,05	0,20	1,36	2,76	2,80	0,17	0,04	6,51

Specific surface = 43,12 [m^2/g]

CEC**= 2,6 meq/g

* Loss on Ignition

** Cationic exchange capacity

Table 3.7. Chemical composition (ppm) of the Bârsana tuff – minor elements (Smical et al., 2010a)

Ba	Mn	Pb	Zn	Sr	Cu	Rb	Zr	Ce	Ni	La	Cr	Nd
717,5	357,2	306,6	237,1	185,2	115,2	114,7	85,0	51,8	42,4	31,2	23,0	15,6
Y	**Th**	**Ga**	**Sn**	**V**	**Nb**	**Sb**	**Cd**	**Cs**	**U**	**Sc**	**Mo**	
15,5	13,1	11,7	10,6	10,5	7,8	4,4	4,0	3,6	3,2	2,5	1,0	

The content of oxides of alkaline earth elements (Ca and Mg) is subordinated to that of oxides of alkali (K and Na), which may be due to the contribution of the diagenetic environment of deposition of volcanic products and processes of leaching. Loss on ignition (L.O.I.) of 6.51% is inconsistent with the almost subunitary values in case of riolitic-dacitic rocks but this fact can be explain by the zeolitic water presence in the analized sample.

To achieve the determination of Fourier Transform Infrared Spectroscopy (FTIR - Fourier-Transform Infrared) a Bruker Tensor 27 device was used.
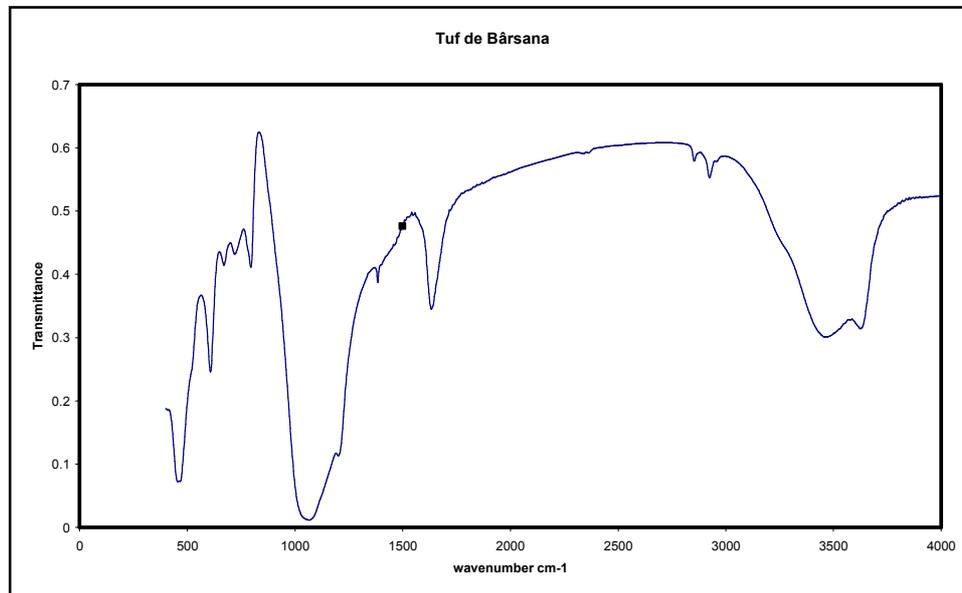

Fig. 3.5 FTIR analysis of the Bârsana zeolitic tuff (Smical et al., 2010b)

Transmission spectrum and IR absorption (Fig. 3.5), indicate by their displayed inflexion the presence of peaks characteristic to zeolites (Stoica et Bedelean, 1984, Castaldi et al., 2005; Iacomi, 2001, Rodriguez-Fuentes et al., 1998; Mozgawa, 2000; Mozgawa et Bajda, 2005). The clinoptilolite separates of heulandit by absorption band at 610 cm^{-1} which is 700 cm^{-1} for heulandit. Spectrum well put out the presence of water by absorption in the domains of 3400 - 3600 cm$^{-1.}$

As can be seen in the DTA-TG plot, at approx. 450 0C a DTA peak appears that expresses a moment of zeolites dehydration, which contain water in various forms, then a landing by the end of the measurement installs.

Findings heulandit and clinoptilolite differentiation of is also based on the dehydration process which is completed at approx. 350 0C for heulandite and at approx. at 700 0C in the case of clinoptilolite (Măicăneanu et al., 2008).

The weight loss of analysed tuff startes from 20 0C and at approx. 180 0C and a shoulder of the representation curve appears. Then continue to lose coordination water and weight loss continues to 450 0C, where DTA peak occurs, then shape is smooth without major changes that would represent a considerable loss of water. An exotherm peak appears at 450 0C on DTA curve indicating a change if crystalline phase of the analyzed tuff.
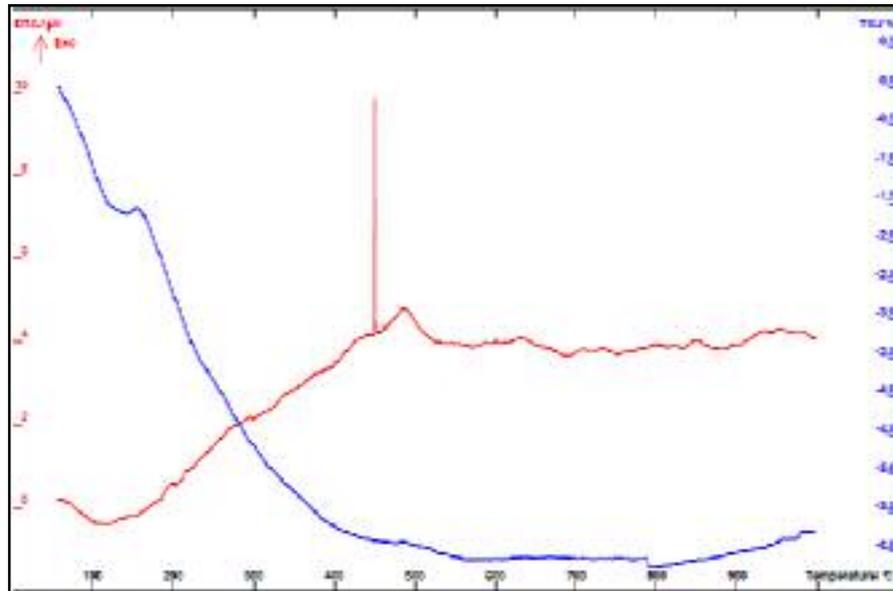
Fig. 3.6. Analiza TG-DTA a tufului zeolitic de Bârsana (Smical et al., 2010b)

Comparing data from TG-DTA chart interpretation with the loss on ignition for determining the chemical composition of Bârsana tuff sample (Table 3.7) can be said that there are similarities of data offered by the two methods of determination.

In order to emphasize mineral constituents of the tuff Zeolitic of Barsana, tests by scanning electron microscopy (SEM) were conducted using a Hitachi-S4100 microscope with dispersive energy spectroscopy (EDS) and a Rontec detector (Fig. 3.7).

a)   b)
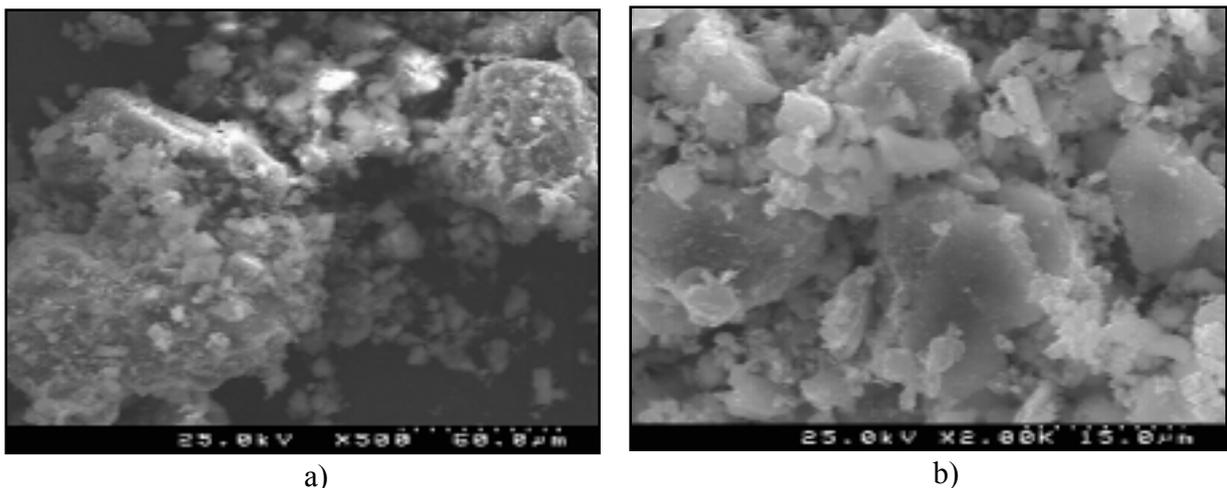
Fig. 3.7. Micrografii SEM (a, b) ale tufului zeolitic de Bârsana (Smical et al., 2010b)

SEM micrographic depictions of figures a, b show the presence of tabular crystals of clinoptilolite as well as feldspars with opal overgrowth.

4. RESEARCH ON THE EFFICIENCY OF USING BÂRSANA ZEOLITIC TUFF IN REMOVING OF $Pb^{2+}Cu^{2+}$ AND Zn^{2+} FROM WASTEWATERS

4.1. The research goal

Industrial waste water due to high content of heavy metals is a growing concern in finding the most efficient high remediation methods. Some ions such as Pb2+, Cu^{2+} and Zn^{2+} where are in high concentrations, represent a danger to the environment and human health because of bioaccumulation in living organisms and bioconcentration (Oros, 2001). Also, these elements in high concentrations in effluents are sources of tributaries and groundwater pollution (Carland et Aplan, 1995; Curkovič et al., 1997; Inglezakis et al., 2003a, b).

Conventional methods of removing heavy metals from wastewater are not efficient anymore when it is desired the purging of these waters below the limits of the standard quality of the surface waters, so that the usage of natural zeolites represents a viable and efficient alternative to the decontamination classical means of wastewaters both as cost-effectiveness and especially as due to their high ion exchange capacity (Alvarez-Ayuso et al., 2003; Vaca Mier et al., 2001; Cerjan-Stefanovici et al., 1996; Inglezakis et al., 2005).

4.2. Mechanisms of heavy metals removal from wastewater

Ion exchange using natural zeolites can be considered one of the most attractive methods, because they are abundant and are low cost.

From literature data (Mozgawa et Bajda, 2005; Trgo et Peric, 2003) emerges that the removal of heavy metal ions from wastewater by natural zeolites is achieved through a series of processes such as:

- ion exchange
- absorption
- surface precipitation
- zeolitic volcanic tuff dissolution

One of the basic mechanisms involved in the absorption of heavy metals is known as ion exchange, which is defined as the equivalent stoichiometric replacement of one ion in the solid phase with the equivalent of another ion in the liquid phase (Petrus et Warchol, 2003; Inglezakis et al ., 2004). Ion exchange reaction takes place between the exchangeable cations (Na+, K+,

Ca2+ and Mg2+) located in the structure of zeolite and cations (Mn+) in solution and can be depicted as follows (Benhammou et al., 2005):

$$Zeolite \equiv n\ (Na, K)^+ + M^{n+} \leftrightarrow zeolit \equiv M^{n+} + n(Na, K)^+ \qquad (1)$$

$$Zeolite \equiv n\ (Ca, Mg)^{2+} + 2M^{n+} \leftrightarrow zeolit \equiv 2M^{n+} + n(Ca, Mg)^{2+} \qquad (2)$$
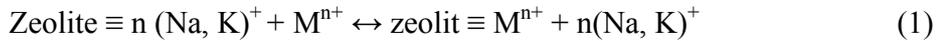
During ion exchange, metal ions must migrate through the pores and channels of zeolite and to replace the exchangeable cations (Na +, K +, Ca2 + and Mg2 +) (Curkovič et al., 1997). Diffusion of metal ions on the surface to intercrystalline spaces is considered stage ion exchange rate control (Helffreich, 1995; Trgo et al., 2006). Diffusion is slow because of delay due to the interaction of metal ions with surface functional group, such as electrostatic attraction, bond formation, etc. (Helfferich, 1995).

Mozgawa et Bajda (2005) stated that for Cd^{2+} and Pb^{2+}, chemisorption predominates while for Ni^{2+} ion exchange predominates. Also, Panayotov Velikov, (2002) conducted experiments of desorption to check how strong were immobilized ions of heavy metals by zeolite and noted that the ions Pb^{2+} are strongly linked with the zeolite, and immobilization of other ions of heavy metals (Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) is relatively weak.

With ion exchange, adsorption and surface precipitation, dissolution of zeolite is a process that helps to remove heavy metals through zeolites. It can be defined as the destruction of the network by peeling central zeolite ions Si^{4+} and Al^{3+}.

4.3. Surce of raw materials. Describing the quarry of zeolitic volcanic tuff from Valea Morii area (Călineşti, Maramureş County)

Zeolitic volcanic tuff used in experimental research was globally sampled (approx. 30 samples) of the upper, basal and center of the quarry located on the village Văleni (Călineşti, Maramures County) (Figure. 4.1). It is located on the right side of the Mijlocie Valley and near its confluence with Valea Morii brook (Fig. 4.2).

Fig. 4.1. Geographic view of the locality Călineşti, Maramureş County (Irina Smical)

Figure 4.2. Area of sampling tuff rocks in theValea Morii quarry (foto
Irina Smical)

Călineşti is located in north-central part of the Maramures County, in Maramures Depression, on the river Cosău and Văleni Valley, approx. 22 km distance from Sighet and approx. 60 km away from Baia Mare.

Geological and petrographic research conducted for the investigation area reveals that the enlarged portion of the site next to Bârsana village, between the valleys of Morii Brook,

Vălenilor brook, Valea Mijlocie brook, and Măgurii hill, is made of sandstones and marls and dacitic – badeniene greenish tuffs (Dej Tuff).

Badeniene formations are composed of volcanoclastic deposits (so called Dej tuff - the tuff here is called Bârsana, the zeolite tuff) stacked transgressive than earlier layers, as a result of effusive volcanic activities. The Dej Tuff of Badenian age, outcrops in openings of the Iza basin and is also intercepted in evaporitic salt level in Ocna Sugatag, Coştiui and oil areas from and coastal areas to oil from Dragomireşti, Săcel, Botiza.

Măgura Hill - Pleşa – Între Stânci, up to Mijlocie Valley brook, starting from Iza (Bârsana Depression), with thick banks of sandstone, then along the Morii Valley stream continues with the zeolite tuff up to Mijlocie Valley brook.

Fig. 4.3. Samples of volcanic zeolitic tuff from quarry of
Valea Morii (sampling and photo: Irina Smical)

The Dacite tuffs from quarry have fine granulation, greenish – gray colour, and sometimes are pigmented with iron oxides. They have vitroclastic structure, compact texture and irregular fracture (Fig. 4.3).

Physical-mechanical analyses indicate that rock is light, absorbent, porous, with average compressive strength, less resistant to shock, with high attrition, poor weather resistant (Brana et al., 1986).

The physical-chemical and mineralogical analyses of the zeolitic tuff sampled from Valea Morii quarry are well detailed in a separate chapter of thesis as well as in Smical et al., 2010 a and 2010 b published papers.

4.4. Preparing of the Bârsana zeolitic tuff samples

The tuff crushing consisted in breaking of volcanic zeolitic tuff samples up to 1 – 3 cm followed by grinding by bar mill and the and separation was made using Retsch A220 basic (Germany) dried sieves obtaining in this way a global sample (Fig. 4.4). Samples were processed in several cycles. After every cycle, fraction of – 2.5 mm was removed using a dried sieve in order to prevent the over grinding.

Fig. 4.4. Technological flux used for getting various Bârsana tuff fractions

Using a much shorter milling time the over-grinding is avoided. In the primary zeolitic tuff, the crystals amount which must be removed is very small. By grinding, the calcite and claying fine material is removed in fraction of – 0,074 mm. After grinding, the sample was classified on sieves + 2 mm, +1 mm, + 0,250 mm, + 0,125 mm and + 0,074 mm. After classifying on sieves

the following fractions were obtained: : 2 – 1 mm – 9,7%; 1 – 0,250 mm, 46,2%; 0,250 - 0,125 mm, 28,3%; and on sieve of 0,074 mm, 7,8% of material (Fig. 4.5, Fig. 4.6).

The average diameter of tuff granules after processing is presented in table 4.1.

No. Crt.	sieve	d min	d max	d med	difference	±%
Tabel 4.1. Diameters of Bârsana zeolitic tuff after grinding and classifying						
1	2	2				
2	1	1	2	1.5	0.5	33.33
3	0.25	0.25	1	0.625	0.375	60.00
4	0.125	0.125	0.25	0.1875	0.0625	33.33
5	0.074	0.074	0.125	0.0995	0.0255	25.63
6	0	0	0.074	0.037	0.037	100.00

Classifying percents of the Bârsana ground volcanic zeolitic tuff are given in figure 4.5.
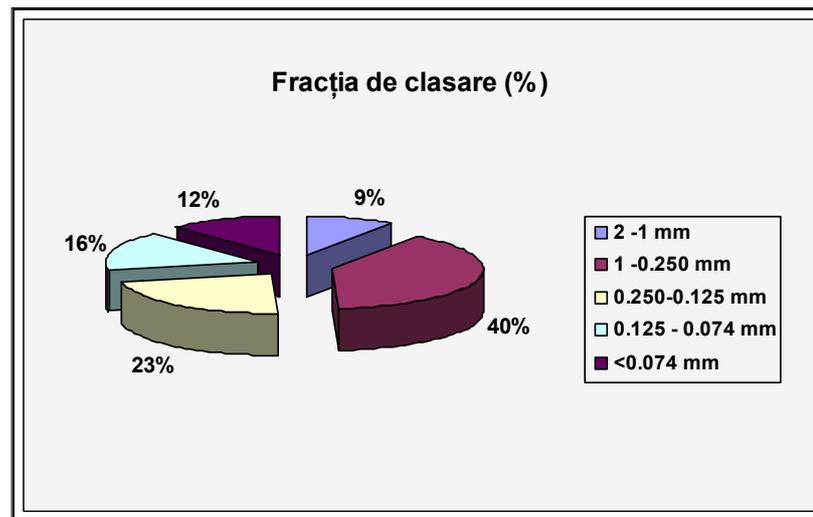

Fig. 4.5. Classifiying fractions of the ground zeolitic tuff (%)

4.5. CONDUCT AND INTERPRETATION OF EXPERIMENT RESULTS

To determine the retention efficiency ions Pb^{2+}, Cu^{2+} and Zn^{2+} by the Bârsana Zeolitic tuff, after the preparation and characterization of the Bârsana zeolitic tuff the experiment conducting started.

Chemical experiments were conducted on two main areas:

BATCH EXPERIMENT

1. Establishing the influence of particle diameter of adsorption ions Pb^{2+}, Cu^{2+} and Zn^{2+} by zeolitic material used.

1. Establishing the influence of pH of the solution to contact the adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} ions with the fitting of experimental data using different models for isotherms of adsorption (Langmuir, Freundlich and Dubinin Radushkevich) as well as determining changes in Gibbs free energy using the coefficient of distribution.

2. Determination of adsorption kinetics by fitting the experimental data using different kinetic models applied in the study of adsorption of heavy metal ion exchange (pseudo-order 1, pseudo-order 2 and Weber Morris).

EXPERIMENT WITH THE ION EXCHANGE COLUMN

1. Following the adsorption efficiency of Pb^{2+}, Cu^{2+} and Zn^{2+} ions, by the Bârsana zeolitic tuff using ion exchange column, characterized by the ratio D/H = 1/10. The effect of vehicular flow of the solution on the breakthrough capacity ion exchange column was also followed.

4.5.1. CONDUCTING THE BATCH EXPERIMENT

4.5.1.1. Influence of diameter of particles and pH of contact solution on retention of the ions Pb^{2+}, Cu^{2+} and Zn^{2+} by Bârsana Zeolitic tuff

4.5.1.1.1. Working method and presentation of experimental data

An amount of 1 gram of each fraction size zeolitic tuff was contacted, stirring continuously for 24 hours (sufficient for equilibration) in thermostatic conditions at 25 ^{0}C, using a Heidolph Unimax 1010 - Germany orbital shaker with a volume of 50 ml of synthetic solutions of Pb^{2+}, Cu^{2+} and Zn^{2+} respectively.

Equilibrium concentrations were determined by atomic absorption spectrometry using a Perkin Elmer AAS800 (Shelton USA) atomic absorption spectrometer.

Using the equilibrium solution concentrations the specific adsorption q (M^{2+} mg/g) calculated (Zuhairi, 2003):

$$q = \frac{(c_0 - c) \cdot V}{1000 \cdot m} \qquad (1)$$

where:

q = amount of metal ion removed from solution (mg/g)

c_0 = initial concentration of the solution (mg M^{2+}/L)

c = concentration of equilibrium (mg M^{2+}/L)

V = volume of contact solution (mL)

m = mass of adsorbant (g).

In the case study of the influence of mean diameter of particles (d = 0.037 mm, d = 0.0995 mm, d = 0.1875 mm, d = 0.625 mm, d = 1.5 mm) on the adsorption ion Pb^{2+}, Cu^{2+} and Zn^{2+} in terms of contacting 1 g of milled Bârsana zeolitic tuff with 50 ml of each solution of Pb^{2+}, Cu^{2+}, respectively Zn^{2+} at pH = 4 to 6 of solution concentrations (100 mg/l, 200 mg/l, 400 mg/l, 600 mg/l, 800 mg/l and 1000 mg/l) different values of equilibrium concentration and specific adsorption were obtained.

To follow the influence of pH on the retention efficiency by the Bârsana Zeolitic tuff of the studied heavy metal ions the working method was the same with that one for the establishing the particle diameter sizes influence but in this case contact solutions were brought to 4 values of pH, namely: pH = 4 pH = 3, pH = 2 and pH = 1 using a solution of H_2SO_4 respectively CH_3COOH. It has also been calculated distribution ratio (K_d) using the following equation (Menhage-Bena et al., 2004):

$$K_d = \frac{C_i - C_f}{C_f} \cdot \frac{V}{m} \quad (L/g)$$

$$Kd = \frac{Q_e}{C_e} \ (L/g)$$

4.5.1.1.2. Results and discussion

In the diagrams below the adsorption isotherms of Pb^{2+}, Cu^{2+} and Zn^{2+} ions by Bârsana zeolitic tuff are presented for the following concentrations of the solution with the studied heavy metals: 100 mg/l, 200 mg/l, 400 mg/l, 600 mg/l, 800 mg/l and 1000 mg/l.
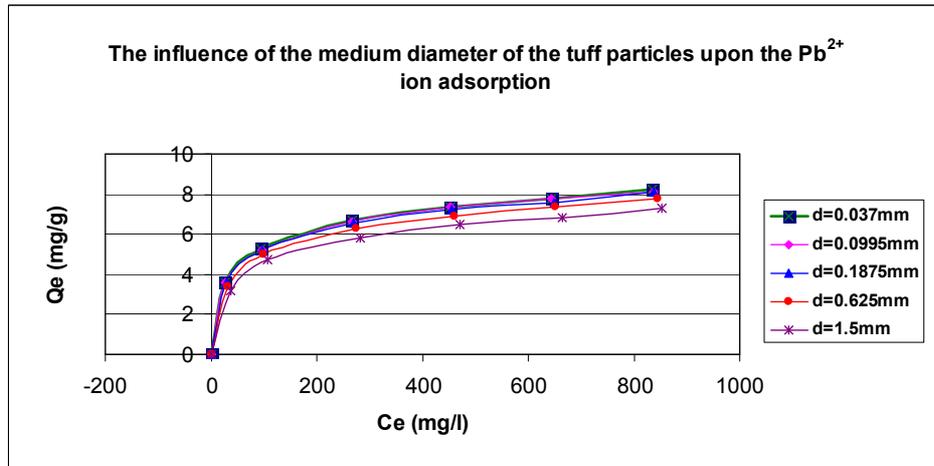
Fig. 4.6 Adsorption isotherm of Pb2+ by Bârsana zeolitic tuff depending on the average diameter of tuff particles
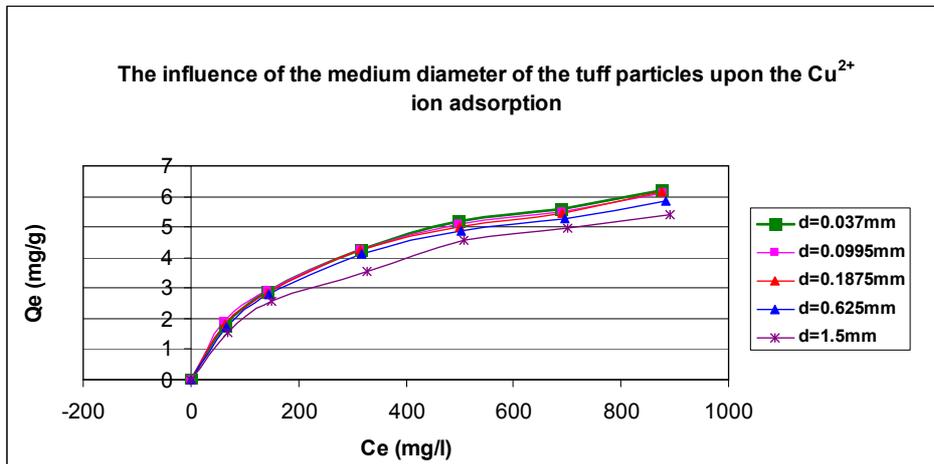

Fig. 4.7 Adsorption isotherm of Cu^{2+} by Bârsana zeolitic tuff depending on the average diameter of tuff particles
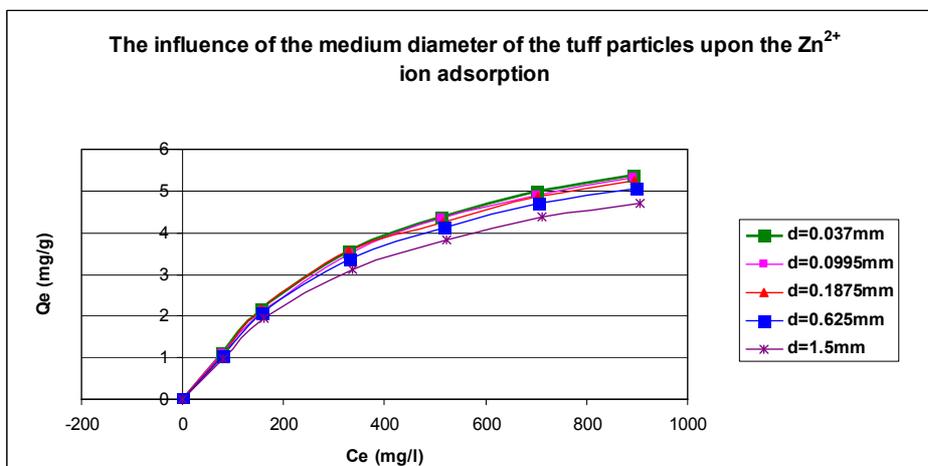

Fig. 4.8 Adsorption isotherm of Zn^{2+} by Bârsana zeolitic tuff depending on the average diameter of tuff particles

In tables 4 and 5 the comparative experimental data resulted from contact of 1 g Bârsana zeolitic tuff having the granule diameters of 0,037 mm, 0,0995 mm, 0,1875 mm, 0,625 mm and1,5 mm with 50 ml solution of Pb^{2+}, Cu^{2+} and Zn^{2+} having 1000 mg/l concentration, pH = 4 and temperature conditions of 25 ^{0}C are shown.

No. Crt.		d (mm)	Q_e (mg/g)		
			Pb^{2+}	Cu^{2+}	Zn^{2+}
1	1000 mg/l	0.037	8.261	6.1855	5.3715
2	pH=4	0.0995	8.102	6.1355	5.3275
3	t=25 ^{0}C	0.1875	8.096	6.16	5.246
4		0.625	7.766	5.8665	5.068
5		1.5	7.2995	5.416	4.7155

Table 4 The specific adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} by Bârsana zeolitic tuff at pH=4 and 25 ^{0}C

It is noted that the highest levels of specific adsorption is recorded for the smallest average diameter of particles of Bârsana zeolitic tuff for all studied heavy metal ions. This is explained by the fact that these particles have the highest specific surface and thus greater places adsorption of heavy metals.

No. Crt.		d (mm)	%		
			Pb^{2+}	Cu^{2+}	Zn^{2+}
1	1000 mg/l	0.037	100	100	100
2	pH=4	0.0995	98.075294	99.1916579	99.18086196
3	t=25 ^{0}C	0.1875	98.002663	99.5877455	97.6635949
4		0.625	94.007989	94.8427775	94.34980918
5		1.5	88.360973	87.5596152	87.78739644

Tabel 5 Percentage retaining of Pb^{2+}, Cu^{2+} and Zn^{2+} at different average diameters of Bârsana zeolitic tuff

From experimental data where 5 average diameters of Bârsana zeolitic tuff were used, a concentration of 1000 mg/l of Pb^{2+}, Cu^{2+} and Zn^{2+}, at pH=4 in thermostatic conditions of 25 ^{0}C, and as results from the graphical illustration of the results presented in diagrams 4.6, 4.7 and 4.8, there is not a too big difference between the influence degree of the heavy metal ions adsorption at small diameters (d=0.037 mm and d=0.0995 mm).

A bigger difference is recorded for the bigger diameter (d=1.5 mm). As can be noticed in graphical representation 4.6 concerning the influence of the average diameter of Bârsana zeolitic tuff on Pb^{2+} adsorption, at equilibrium concentrations of Pb^{2+} afferent to the initial concentrations

of 100 mg/l and 200 mg/l the specific adsorption records high values then the curves allure become flattened gradually. In the case of graphic representations 4.7 and 4.8 referring to the influence of average diameters of the Bârsana zeolitic tuff on retaining of Cu^{2+} and Zn^{2+} it can be noticed that there is a proportionality between the equilibrium concentration increasing and specific adsorption of Cu^{2+} and Zn^{2+}.
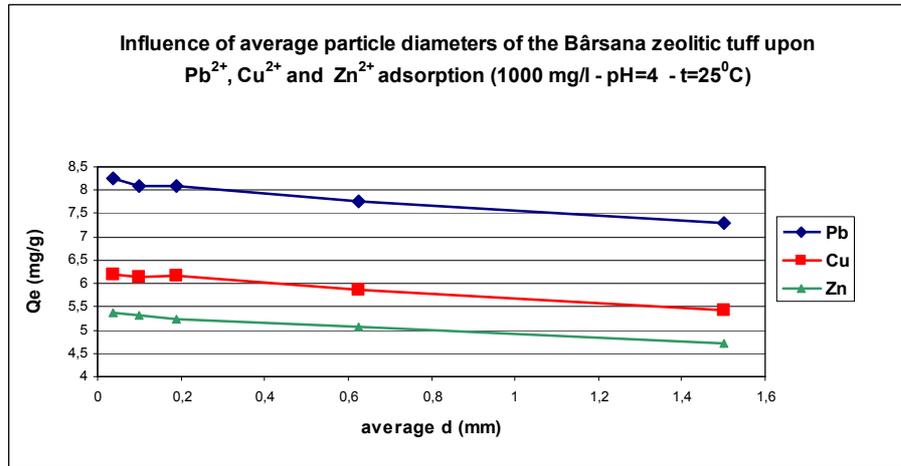

Fig. 4.9 Influence of average diameter of the Bârsana zeolitic tuff particles upon adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+}

In the same experimental conditions for the three studied heavy metals, as it is illustrated in graphic 4.9, the best adsorption is recorded by Pb^{2+} followed by Cu^{2+} and Zn^{2+}. The diagram look expresses a decreasing of the efficiency in retaining the Pb^{2+}, Cu^{2+} and Zn^{2+} as increasing the average diameters of the Bârsana zeolitic tuff particles used in the experiment.

In graphic 4.10 are shown the influence of 4 pH values (pH=4, pH=3, pH=2 and pH=1) on the efficiency of the adsorption of Pb^{2+} by Bârsana zeolitic tuff having the particles diameter of 0.037 mm. The graphic gives the specific adsorption variation of the Bârsana zeolitic tuff depending on the equilibrium concentration gained at the four values of the solution pH.

Fig. 4.10 The influence of pH upon Pb²⁺ adsorption by the Bârsana zeolitic tuff (D = 0.037 mm).

Fig. 4.11. The influence of pH upon Cu²⁺ adsorption by the Bârsana zeolitic tuff (D = 0.037 mm).

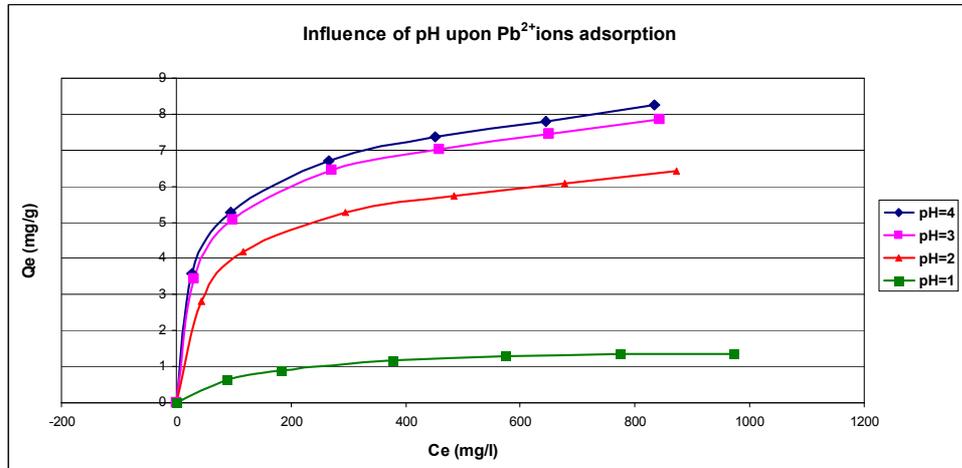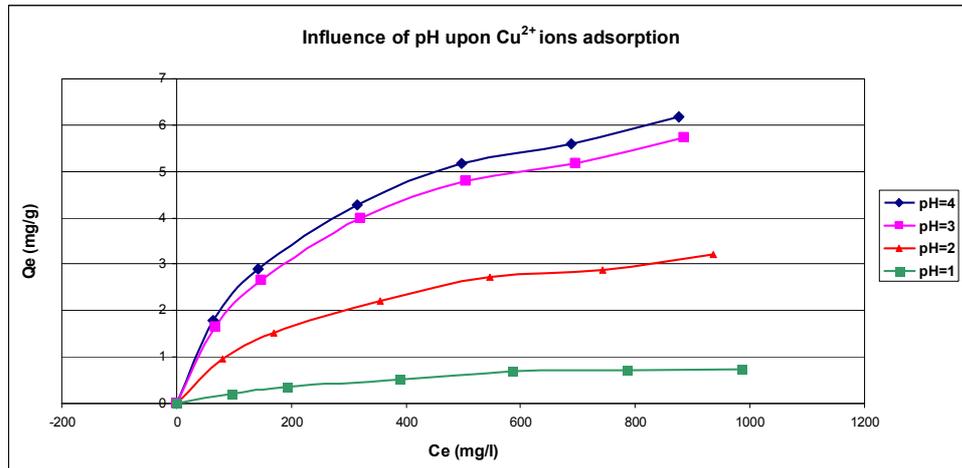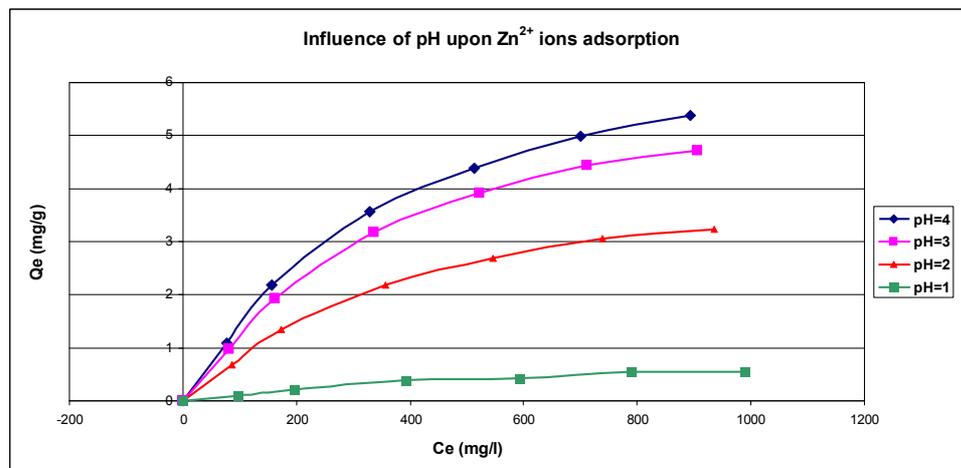
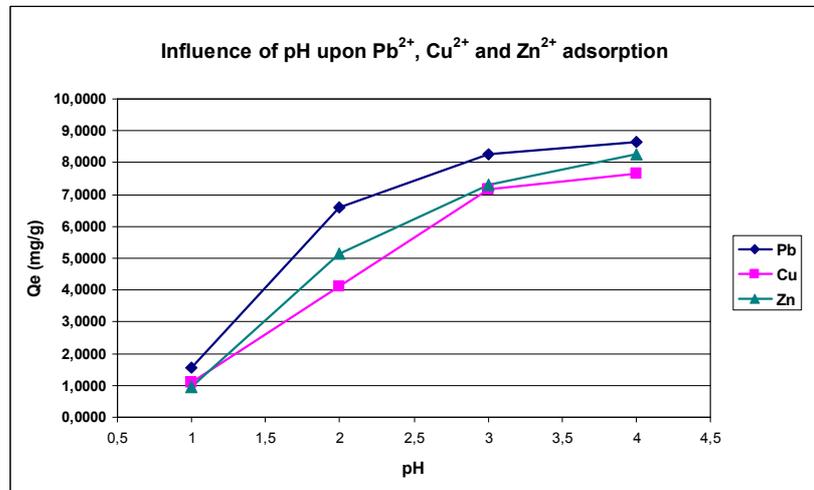Fig. 4.12. The influence of pH upon Zn²⁺ adsorption by the Bârsana zeolitic tuff (D = 0.037 mm).

Fig. 4.13. The influence of pH upon adsorbtion of Pb^{2+}, Cu^{2+} and Zn^{2+} by the Bârsana zeolitic tuff

It is noted an emphasized increasing of the specific adsorption of Pb^{2+} by the Bârsana zeolitic tuff in case of solutions with a higher pH (pH=4, pH=3) and much lower in case of solution with a lower pH (pH=1).

In graphics 4.11, 4.12 and 4.13 there are shown the four pH values (pH=4, pH=3, pH=2 and pH=1) influence on the adsorption efficiency of Pb^{2+}, Cu^{2+} and Zn^{2+} by the Bârsana zeolitic tuff having the particles diameter of 0.037 mm.

Like in case of the experiments where were used solutions with Pb^{2+} and Cu^{2+} it can be noticed a very good adsorption capacity of zeolitic tuff for solutions with higher pH (pH=4, pH=3) and a lower adsorption in the conditions of using a lower pH (pH=1). This can be explained by fact that at lower pH (under 3) an excessive protonation of the active centers created upon the zeolitic material leading to hinder the formation of links between heavy metal ions and active centers. At moderate pH (pH=3, pH=4), H+ is released from on the active centers and the heavy metals amount increases. At higher pH (over 4) though the adsorption is better, there is the possibility to precipitate the heavy metals.

Comparing the diagrams look in case of specific adsorption for the three heavy metals it can be remark a better adsorption of the Pb^{2+} in the same pH conditions like other studied metals (Fig. 4.13). As well, the K_d distribution ratio can be calculated using the following equation (Menhage-Bena et al., 2004):

$$K_d = \frac{C_i - C_f}{C_f} \cdot \frac{V}{m} \quad (L/g)$$

$$Kd = \frac{Qe}{Ce} (L/g)$$

C_i = initial solution concentration (mg M^{2+}/L)

C_f = final solution concentration (mg M^{2+}/L)

V = volume of contact solution (mL)
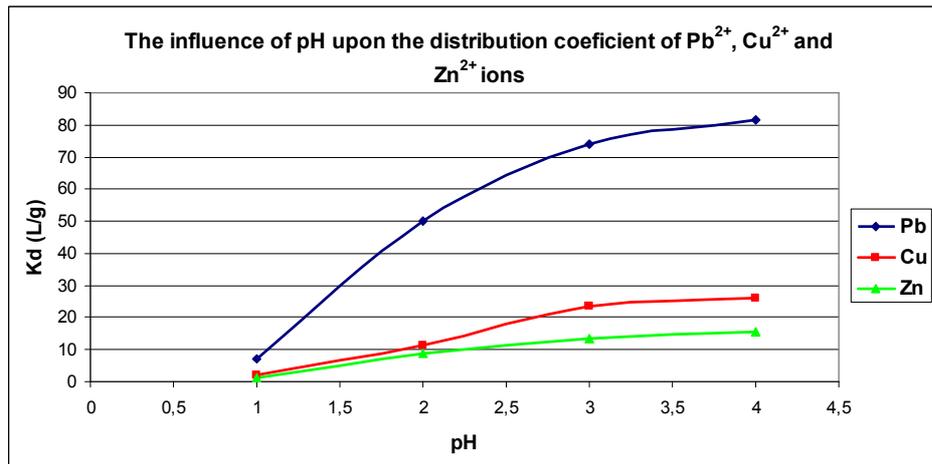
m = adsorbent mass (g).

Fig. 4.13 Kd variation of Pb^{2+}, Cu^{2+} şi Zn^{2+} on the adsorption surface of the Bârsana zeolitic tuff depending on the pH of contact solution

From the graphic representation of the K_d variation with the pH of the contact solution (Fig. 4.13) it can be noted the lower the pH of the contact solution is the lower the K_d distribution coefficient is. This thing may be correlated with the increasing of the adsorption capacity of the zeolitic tuff once with pH of contact solution increasing.

4.5.1.1.3. Fitting the experimental data using different models of adsorption isotherms (Langmuir isotherm, Freundlich isotherm, Dubinin – Radushkevich isotherm)

There is a variety of mathematic models referring to the processes and adsorption isotherm of heavy metals from wastewaters or residual solutions that allow to establish of several parameters and characteristic values of these processes like: adsorption energy and adsorption capacity being known as specific adsorption that correspond to the maximum degree to cover the surfaces (Olmez et al., 2004; Ulmanu et al., 2003; Zuhairi, 2003; Ho et McKay, 2004). The data processing was made using *Curve Expert 1.3*.

Langmuir isotherm was established based on the equilibrium achieved between the simultaneously adsorption and desorption based upon the following principles (Allen et al., 2003, Senthil Kumar et Gayathri, 2009):

$$q = q_m \frac{b \cdot C_e}{b \cdot C_e + 1}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot b} + \frac{C_e}{q_m}$$

where: q = retained adsorbate amount (in this case, mol Pb^{2+}, Cu^{2+}, $Zn^{2+} \cdot g^{-1}$), corresponding equilibrium concentration C_e (mol Pb^{2+}, Cu^{2+}, $Zn^{2+} \cdot L^{-1}$), q_m = the maximum amount of adsorbate retained for the totally cover of the monolayer (mol Pb^{2+}, Cu^{2+}, $Zn^{2+} \cdot g^{-1}$), b = constant (adsorption coefficient) referring the adsorption energy (L·mol^{-1}).

- **Freundlich isotherm (Freundlich van Belemen)** was empirically established and in case of a heterogeneous surface of the adsorbent, it is applied with a better correlation coefficient than Langmuir isotherm (Senthil Kumar. et Gayathri, 2009):

$$q_e = k_F \cdot C_e^{1/n} \tag{6}$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{7}$$

where,

q_e = retained adsorbat amount (in this case, mol Pb^{2+}, Cu^{2+}, $Zn^{2+} \cdot g^{-1}$)

C_e = equilibrium concentration (mol Pb^{2+}, Cu^{2+}, $Zn^{2+} \cdot L^{-1}$)

k_F and n - constant (n is related to the adsorption energy).

- **Izoterma Dubinin-Radushkevici** (Shahwan et Erten, 2004; Atun et Kilislioglu, 2003) was drawn up since assumption theory of Polanyi applied to the volumetric pore filling.

The terms are:

$$\ln q_e = \ln X_m + \beta \cdot F^2 \tag{8}$$

$$\varepsilon = R \cdot T \cdot \ln(1 + \frac{1}{c_e}) \qquad E_s = \frac{1}{\sqrt{-2\beta}} \tag{9}$$

Where, ε= Polanyi potential; E_s – adsorption energy

X_m = maximum adsorption capacity; β – activity coefficient

The resulted adsorption energy indicates a similar variation with the adsorption capacity K_d, ΔG^0 and it can be noted that the decreasing range of E_s is: Pb (72.718) > Cu (25.75) > Zn (18.32) (Kj/g)

4.5.1.1.3.1.1. Results and discussions

In case of experimental data fitting according to Freundlich isotherm results less correlation coefficient (r) versus those resulted from using Langmuir isotherm which denotes a relative energetic uniformity of adsorption centers of zeolitic material (Table 6).

Table 6 Comparative data of the correlation coefficient (r) in case of using the Langmuir and Freundlich isotherms.			
No. Crt.	Metal	Langmuir	Freundlich
1	Pb^{2+}	0,9983	0,9859
2	Cu^{2+}	0,9966	0,9906
3	Zn^{2+}	0,9862	0,9827

Table 7. Comparative values of maximum adsorption capacity based on Langmuir isotherm depending on pH of the contact solution				
No. crt	pH	$q_m(mg/g)$ Pb^{2+}	$q_m(mg/g)$ Cu^{2+}	$q_m(mg/g)$ Zn^{2+}
1	4	8,6532	7,6474	8,2770
2	3	8,2580	7,1467	7,3069
3	2	6,5849	4,1089	5,1518
4	1	1,5489	1,0883	0,9736

Although the Freundlich isotherm has a better concordance with experimental data, it presents deviation of small concentrations range and no limit of adsorption provides in the high concentration range.

D-R isotherm has the advantage that it allows the establishing of adsorption energy Es. Although the correlation coefficient are less than those resulted from Langmuir and Freundlich isotherms it is noted that Es decreases with pH of contact solution decreasing, which denotes that the adsorption conducts the better the pH of contact solution is higher (table 8).

Table 8 Adsorption energy values based on Dubinin-Radushkevici isotherm				
No. crt	pH	E_s (Kj/mg)		
		Pb^{2+}	Cu^{2+}	Zn^{2+}
1	4	0.07271895	0.025753559	0.01832852
2	3	0.065291407	0.02469472	0.017824139
3	2	0.046747774	0.02050359	0.016568442
4	1	0.022943654	0.016062785	0.01425325

The obtained adsorption energy indicates a similar variation with the adsorption capacity, K_d, ΔG^0 and it can be noted that decreasing range of E_s is: Pb (72.718) > Cu (25.75) > Zn (18.32) (Kj/g).

4.5.1.1.4. Thermodynamic aspects of heavy metal adsorption by the Bârsana zeolitic tuff.

The experimental data modeling in order to gain the variation of Gibbs free energy (ΔG^0) was made using the program Curve Expert 1.3.

1. $\Delta G^0 = -R \cdot T \cdot \ln b$

2. $\Delta G^0 = -n \cdot R \cdot T$

3. $K_d = \dfrac{q_e}{C_e}$ $\quad \Delta G^0 = -R \cdot T \cdot \ln K_d$

The values of variation of Gibbs free energy (ΔG^0) may be both determined taking into account the constant b values of the Langmuir isotherm, of constant n from Freundlich isotherm model and distribution constant K_d (Sudha et al., 2007; Hema et Arivoli, 2007).

The values ΔG^0 resulted based on Langmuir isotherm are positive being in inconsistency with the experimental results which indicates a spontaneous adsorption of studied ions by the Bârsana zeolitic tuff.

No. crt	pH	E_s (Kj/mg)		
		Pb^{2+}	Cu^{2+}	Zn^{2+}
1	4	-10.9128813	-8.08744946	-6.81889445
2	3	-10.6672105	-7.81768181	-6.47383639
3	2	-9.6997371	-6.0611673	-5.3792749
4	1	-4.80734689	-1.95637755	-0.56113372

Table 9 Variation of adsorption energy depending on K_d for Pb^{2+}, Cu^{2+} and Zn^{2+}.

As can be noticed in the tables above, the Freundlich isotherm and K_d conduct to negative ΔG^0 values and indicates that the process runs the more spontaneously the more solution pH is higher (table 9).

It is considered appropriate that ΔG^0 determination to be made using K_d which indicates the fact that as the contact solution become acidic, the values of Gibbs free energy increase which shows that the adsorption process runs hardly that is confirmed experimentally by reducing the adsorption capacity once with the pH of contact solution decreasing.

After analysis the influence of solution contact pH upon thermodynamic processes running it can be said that at the value 4 of pH the smallest variations of ΔG^0 are given for Pb^{2+} which denotes the preference of the zeolitic material for it.

The obtained values of ΔG^0 during this experiment of retaining the Pb^{2+}, Cu^{2+} and Zn^{2+} on the Bârsana zeolitic tuff are bigger than -11 kJ/mol which denotes that the physical adsorption is the predominant mechanism in the process of retaining the studied heavy metals onto the zeolitic tuff (Abdel Ghani et Elchaghaby, 2007).

4.5.1.1.5. Studying the adsorption kinetics of Pb^{2+}, Cu^{2+} şi Zn^{2+} onto Bârsana zeolitic tuff by processing the experimental data using Pseudo-order 1, Pseudo-order 2 and Weber Morris models.

By studying the adsorption process the rate and the reaction mechanism are followed. The adsorption rate is in general given by equation (Senthil Kumar et Gayathri, 2009):

$$\frac{da}{dt} = k\left(C - C_E\right) \qquad (1)$$

where,

a= adsorbed amount onto one gram of adsorbent (mol/g); t = time at starting adsorption (min);

k = a rate constant (min^{-1});

C = adsorbent concentration in fluid phase (mol/L);

C_E = adsorbent concentration in fluid phase in equilibrium conditions (mol/L).

In order to do a kinetic study on the adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+}, the following working conditions were assured:

- Temperature of 25 ^{0}C
- Temperature of 50 ^{0}C
- Initial concentration of metal in solution of 100 mg/l
- Initial pH of solutions of 4.0
- Mixing ratio R=S/L=1/50

At different time intervals solution samples were collected, centrifuged and subjected to analysis for determination of the heavy metals concentration using atomic adsorption spectrometry. The obtained experimental data were processed with the main models for adsorption kinetics, namely: kinetics of pseudo-order 1, kinetics of pseudo-order 2 and kinetic model Weber-Morris kinetic model.

The kinetic equations used for Pb^{2+}, Cu^{2+} și Zn^{2+} adsorption onto zeolitic tuff can be write in the following integrated forms:

- **For kinetics of pseudo-order 1** (Namasivayam et Holl, 2004; Acemioglu et Alma, 2004):

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

$$\ln(q_e - q_t) = \ln q_e - k \cdot t \qquad (2)$$

where:

q_t = adsorbed amount of Pb^{2+}, Cu^{2+} and Zn^{2+} (mol Pb^{2+}/g, mol Cu^{2+}/g, mol Zn^{2+}/g)

q_e = adsorbed amount of Pb^{2+}, Cu^{2+} and Zn^{2+} in equilibrium conditions (mol Pb^{2+}/g, mol Cu^{2+}/g, mol Zn^{2+}/g)

t = time (min)

k = adsorption constant which involves the activation energy (g·mol^{-1} min^{-1})

- **For kinetics of pseudo-order 2** (Ho et McKay, 2004; Namasivayam et Holl, 2004):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

$$\frac{t}{q_t} = \frac{1}{k \cdot q_e^2} + \frac{t}{q_e} \qquad (3)$$

where:

q_t = adsorbed amount of Pb^{2+}, Cu^{2+} și Zn^{2+} (mol Pb^{2+}/g, mol Cu^{2+}/g, mol Zn^{2+}/g)

q_e = adsorbed amount of de Pb^{2+}, Cu^{2+} și Zn^{2+} in equilibrium conditions (mol Pb^{2+}/g, mol Cu^{2+}/g, mol Zn^{2+}/g)

t = time (min)

k = adsorption constant which involves the activation energy (g·mol^{-1} min^{-1})

- **For Weber Morris kinetic model (intraparticle diffusion) (**Mckay et Poots, 1980**):**

$$q_t = I_0 + k_p \cdot t^{0.5} \qquad (4)$$

$$q_t = k_i \cdot t^{0.5} \qquad (5)$$

$$D_e = \pi\left[\frac{d_p \cdot k_p}{12 \cdot q_e}\right]^2 \text{ - effective diffusion coefficient} \qquad (6)$$

The best processing was made using the kinetic model of pseudo-order 1. This shows that the interaction between the metallic ions with the adsorbent surface is made on only one adsorption site.

Using the Weber-Morris kinetic model the following values were obtained: $1.42 \cdot 10^{-13}$ for Pb^{2+}, $1.02 \cdot 10^{-13}$ for Cu^{2+} and $1.11 \cdot 10^{-13}$ for Zn^{2+}, respectively. This size orders show that the adsorption mechanism is diffusive in the adsorbent pores that is confirmed by the speciality literature.

4.5.2. CONDUCTING EXPERIMENT IN DYNAMIC REGIME

4.5.2.1. The influence of the passing flow in column on the ion exchange capacity of the Bârsana zeolitic tuff

4.5.2.1.1. Method and presentation of the laboratory installation.

In experiments synthetic solutions of Pb^{2+}, Cu^{2+} and Zn^{2+} were used in concentration of 100 mg/L and an initial pH of 4.0. In figure 4.14 the laboratory installation is presented.
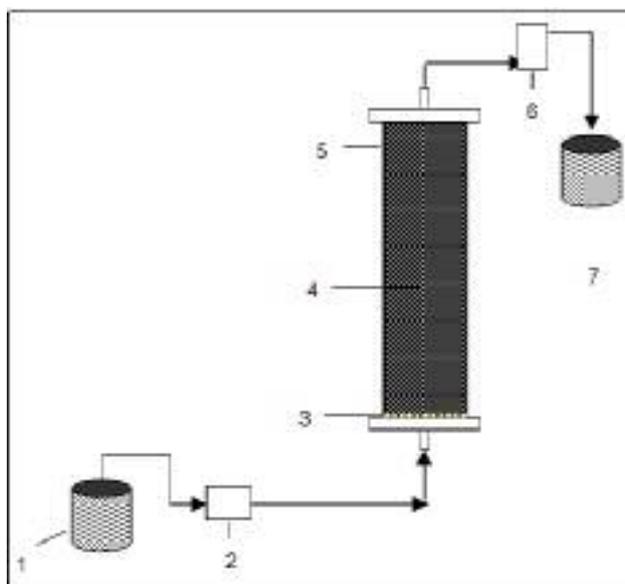
Fig. 4.14. Schematic presentation of the adsorption installation in fixed bed column: 1 – solution storage vessel, 2 – peristaltic pump, 3 – plastic sieve, 4 – natural zeolite layer, 5 plexiglass column, 6 – samples collector, 7 – collector vessel of resulted solution

The used installation is made of a column with an inner diameter D=2 cm, the zeolite bed height H=20 cm. A volume of zeolitic tuff of 62.8 ml was used which correspond to a zeolite amount of 60.28 g (the zeolitic tuff bulk density of 0.9598 g/ml was considered).

The corresponding solution volume of the bed zeolite was BV=30.14 ml. The passing flows were: 8, 10, 12 BV/h which correspond to flows of 4.02, 5.02 and 6.03 ml/min, respectively. The adjustment of flows was made with a peristaltic pump.

4.5.2.1.2. Results and discussions.

În figures 4.35. – 4.37 the variations of experimental data are graphically shown.
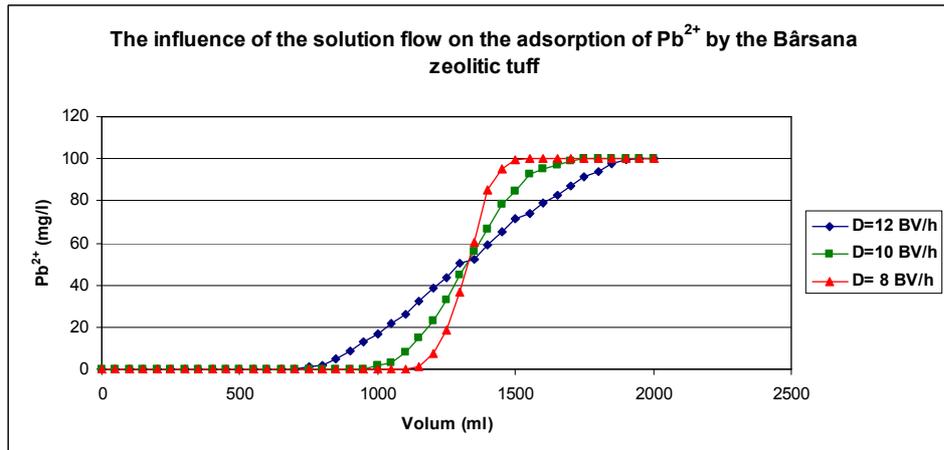

Fig. 4.15. The influence of the flow of solution with Pb^{2+} through the Bârsana zeolitic tuff column
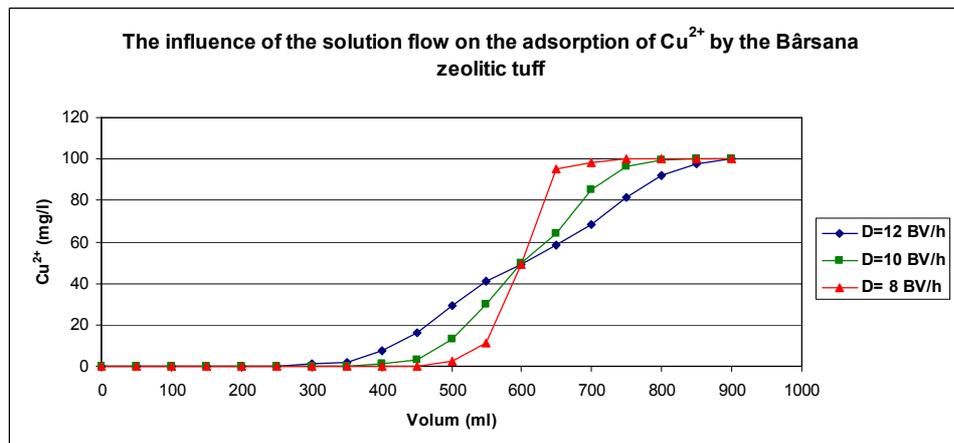

Fig. 4.16. The influence of the flow of solution with Cu^{2+} through the Bârsana zeolitic tuff column
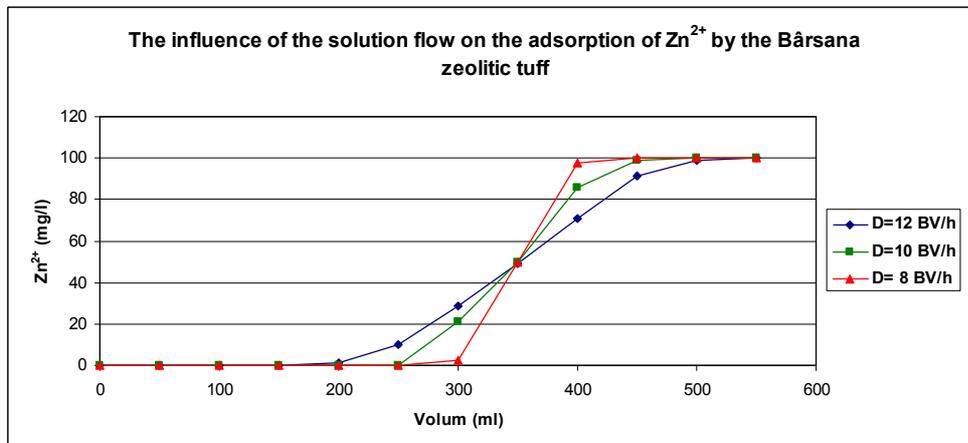
Fig. 4.17. The influence of the flow of solution with Zn^{2+} through the Bârsana zeolitic tuff column

In tables from 4.58 to 4.60 the breakthrough ion exchange capacities depending on the solutions flow are presented and these variations are graphically shown in figure 4.38.

As it can be seen, the flow increasing from 8 to 12 BV/h, generates for the three analyzed metallic ions a decreasing of the breakthrough ion exchange capacity by 36.37% for Pb^{2+}, 39.99% for Cu^{2+} and 33.34% for Zn^{2+}, respectively.
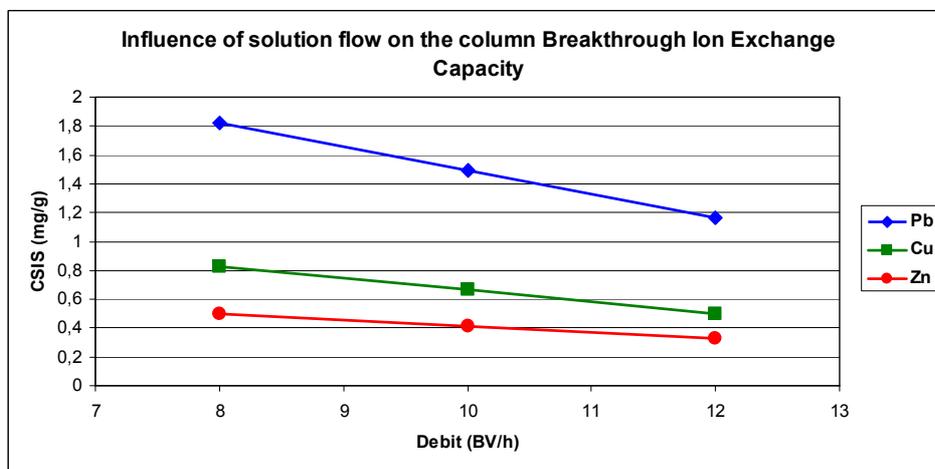
Fig. 4.18. The influence of solution flow on the breakthrough ion exchange capacity of the Bârsana zeolite tuff

In dynamic regime (in column) lower values of the total ion exchange capacity were recorded than the values of ion exchange capacity in batch regime.

In dynamic mode, total ion exchange capacity (obtained for exhausted zeolite column) represented 68.22% for Pb2+, 67.55% for Zn2+ and 61.81% for Cu2+ versus the ion exchange capacity obtained in batch mode.

5. CONCLUSIONS AND RECOMMENDATIONS

Thematic scope of this paper on the use of zeolitic tuff in wastewater remediation process involves a comprehensive approach conducted on two main research focused first on the knowledge used tuff geological aspect and on the other hand the pursuit of efficiency of use their experimental applications.

There are discussed and developed areas that cover: geological and petrographic characterization of the Maramures Basin, geological environments of formation of zeolitic tuff in the world and national area, occurrences of zeolite tuffs in Romania with a focus on the area of origin of the tuff used in experimental applications, mineralogical and petrographic features and physical-chemical and structural characteristics, presentation of the problem risen by the environmental high pollution, assess the effectiveness of removal of heavy metal ions (Cu^{2+}, Pb^{2+} and Zn^{2+}) from contaminated water and fields and perspective of zeolitic tuff usage both economically and especially as regards environmental protection.

Formation of zeolitic tuff in Romania takes place consistent with the paroxysmal volcanic activity with explosive character that generated huge quantities of volcanic ash that has accumulated in Miocene formations in particular in association with deposits and Pliocene sedimentary basins located within the Carpathian arc but also in several adjacent. The volcanic activity took place in two phases: the first phase belongs to Badenian-Sarmatian and the second one, to Sarmatian-Pannonian generating huge amounts of andesitic lava. Zeolitic volcanic tuff occurrence is due to cementation products of explosion of acid and intermediate magmas that have impregnated them a riodacitic and riolitic composition.

Compositionally, tuffs identified on national region are part of the category of vitroclastic and sometimes vitrocristaloclastic fine zeolitized tuffs, cristaloclasts of quartz, plagioclase, biotite and rarely xenolite of metamorphic and andesitic rocks as well as bioclaste.

The results of physical-chemical and mineralogical analyses indicate that volcanic tuffs from Romania are strongly zeolitized and have in general a vitroclastic texture. Clinoptilolite is the

predominant zeolite along with appear: mordenite, phillipsite, analcime followed by secondary ones, like: quartz, calcite, feldspars, muscovite, biotite, plagioclases so on.

The chemical analyses made of numerous Romanian zeolitic tuff samples indicate a composition from riodacitic to dacitic one of the volcanic glass subjected to changes during sedimentation and diagenesis. Te zeolitization process of the volcanic glass is very important because it confers to high mineralogical proprieties and implicit a high economical value to the volcanic tuffs.

The zeolites from the volcanic tuffs are hydrated aluminosilicates mostly of calcium and magnesium from tectosilicates group. These are characterized by a crystalline structure made of tridimensional networks represented by: tetrahedral of aluminium, silicon and oxygen having large hollow like channels which are commonly occupied with water molecules that can be gradually easy eliminated by heating and which can be absorbed again and replaced by the molecules of other substances.

The exceptional qualities attributed to natural zeolites, surnamed the "boiling stone" are based on their remarkable properties which provide an extensive utility in various applications: ion exchange and molecular sieve adsorption, catalysis, high hydration and easily dehydration, low density and a large pore volume when dehydrated, lattice stability after drying, molecular-sized channels in the dehydrated crystals. These properties of natural zeolites can be influenced by some parameters such as: pH, temperature, presence of impurities in solution, the characteristics of heavy metal cations as a "solution-specific factors", conditioning applied to zeolites, pore clogging, particle size, mineral properties as" solid-specific factors".

Focused on these considerations, natural zeolites are considered viable and effective depollution solutions which in recent years have known an increase in the concentrations of contaminants and in particular heavy metals and organic compounds coming with predilection from industrial activities , especially metallurgical and mining, as well as applications of herbicides and chemical fertilizers in agriculture.

Studies and research presented in this paper concern the analysis of the zeolitic volcanic tuff Bârsana, located at confluence of the Morii Valley and Mijlocie Valley area situated at the border of Văleni - Călineşti locality and Bârsana village territory.

Tuffs belonging to the MoriiValley quarry, have been analyzed by the physical-chemical and mineralogical methods XRD, FTIR, DTA-TG, SEM, FRX, in a collaborative partnership

between the Babes- Bolyai University of Cluj-Napoca, Faculty of Science and Environmental Engineering and the University of Porto, Faculty of Science.

The experimental research following the effectiveness of retaining by Bârsana zeolitic tuff the heavy metal ions (Pb^{2+}, Cu^{2+} and Zn^{2+}) from wastewater were carried out on two basic directions: Experiments in Batch and Experiment under dynamic ion exchange columns.

Prin experimentul desfăşurat în regim batch s-au urmărit: influenţa pe care o exercită diametrul mediu al particulelor de tuf de Bârsana asupra adsorbţiei ionilor de Pb^{2+}, Cu^{2+} şi Zn^{2+} din soluţiile cu conţinut de metale grele; influenţa pe care o are pH-ul soluţiei de contact asupra eficienţei de reţinere de către tuful zeolitic de Bârsana a ionilor de metale grele studiate , fitarea datelor experimentale în vederea obţinerii izotermelor de adsorbţie (Langmuir, Freundlich şi Dubinin Radushkevich) şi a energiei libere Gibbs prin utilizarea coeficientului de distribuţie Kd precum şi stabilirea cineticii de adsorbţie prin fitarea datelor experimentale folosind diferite modele aplicate în studiul cinetic al adsorbţiei metalelor grele pe schimbători de ioni (pseudo-ordinul 1, pseudo-ordinul 2 şi Weber Morris).

The experiment was conducted in dynamic conditions to consider the effectiveness of retention ions Pb2+, Cu2+ and Zn2+ by the Bârsana zeolitic tuff using ion exchange column, characterized by the ratio D/H = 1/10. The effect of solution flow on ion exchange column breakthrough was followed.

Data resulted from the batch experiment shows that the efficiency of retention of the studied heavy metal ions (Pb^{2+}, Cu^{2+} and Zn^{2+}) is higher for smaller average diameters of zeolitic tuff particles and the best affinity is recorded for Pb^{2+}. Regarding the influence of pH of the contact solution on the retaining of Pb^{2+}, Cu^{2+} and Zn^{2+} by the Bârsana zeolitic tuff, it was found that the best retention of these occurred for higher values of the solution pH (pH = 4), which is graphically shown by curve variation of pH contact solution versus K_d.

Values ΔG^0 obtained in this experiment of retaining Pb^{2+}, Cu^{2+} and Zn^{2+} on the Bârsana zeolitic tuff are higher than -11 kJ/mol, which shows that the physical adsorption is the predominant mechanism in retaining the studied heavy metal ions on the natural tuff. Also, it can be said that at pH = 4, the smallest changes of ΔG^0 are obtained for Pb^{2+} which shows the preference of the used zeolitic tuff for it.

Following experimental data processing using Freundlich isotherm model correlation lower coefficients (r) were obtained compared with those obtained using Langmuir's isotherm which

shows a relative uniformity of the adsorption energy of the centers on zeolitic tuff. Dubinin-Radushkevich isotherm has the advantage that allows Es energy absorption determining. Although correlation coefficients are inferior to those obtained using Langmuir and Freundlich isotherm models it can observe that Es decreases with pH of the contact solution decreasing, which suggests that the higher is the contact solution pH the better is the adsorption process.

Of the three used adsorption kinetic models (Pseudo - Order 1, Pseudo - Order 2 and Weber Morris) the best fitting of the experimental data was achieved with Pseudo - Order 1. This shows that the interaction between metal ions and the adsorbent surface is done on every single adsorption site. The results obtained after using Morris Weber model indicates that the adsorption mechanism is the diffusion type in the adsorbent pores, as is confirmed by the literature.

For application in dynamic conditions, it was found that increasing the flow from 8 to 12 BV/h, conducts for the three metal ions, a decrease of breakthrough ion exchange capacity by 36.37% for Pb^{2+}, 39.99% for Cu^{2+}, respectively 33.34% for Zn^{2+} compared with data obtained in batch experiment. In the case of the dynamic regime the total ion exchange capacities (obtained for exhausted tuff column) were 68.22% for Pb^{2+}, 67.55% for Zn^{2+} and 61.81% for Cu^{2+} versus the exchange capacities obtained in batch regime which confirms data from literature that indicate the lower adsorption effectiveness of heavy metal ions by zeolite tuff in the case of the dynamic state versus batch regime.

Zeolitic tuffs, with predilection the ones in clinoptilolite rich, called "stones of the future" attracted a growing interest in studying the properties of their occurrence and their application to future remediation technologies and processes of aquatic systems in particular and the whole environment, in general.

Although there are many zeolite volcanic tuff deposits in the territory of our country, however, their exploitation and valorization are not made at the very high level. This may be due to insufficient or ineffective marketing policies that are not able to achieve a connection between the possibilities of exploitation and the final product usage. Currently the largest use of zeolitic tuff in our country takes place in the building sector where they are used as monolithic blocks of tuff and in various preparations and products of zeolitic volcanic tuffs. Unfortunately, zeolitic tuff in the territory of our country are poorly promoted despite the fact that many impressive scientific research results have been obtained that highlight the exceptional qualities of these mineral resources.

Since the literature provides very little or no data on the possible uses of zeolite volcanic tuff from Barsana area in technology for treatment of heavy metals contaminated wastewater, the results of studies and experiments presented in this work could be a starting point for future studies and research in the area of zeolite volcanic tuff Barsana and for finding new means and possibilities of use them both in economy and environmental applications. A big advantage of these ion exchangers is that they can be reused and recycled (30 cycles) and waste resulting from their application are less harmful pollutants for the environment. In addition, exhausted tuff can be used as component material in construction materials, pavements, slags as well as filling material of the abandoned mine galleries.

The experimental results obtained combined with geological and geographical aspects of the area where the Morii Valley quarry with zeolitic volcanic tuffs is located it can say that there are favorable conditions for tuff quarrying. Considering the relatively small distance between quarry and the city Sighetu Marmatiei (approx. 22 km) and Baia Mare (approx. 60 km) as well as that there are access roads to the quarry, it can say that the exploiting of tuff in this area would involve relatively low costs.

Physical-chemical properties and exceptional high retention capacity of heavy metal ions by these zeolite tuffs recommend them as cheap and effective solution for nonconventional technologies for wastewater treatment in the Maramures County and other areas.

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