USE OF ZEOLITES IN THE PROCESS OF CLEANING WASTE INDUSTRIAL WATER WITH HEAVY METALS CONTENTS

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Abstract: *The paper presents laboratory tests for the purification of mine waters with the help of zeolites, using as zeolite clinoptinolite, this being a natural zeolite, with a large capacity to remove metal ions from mine waters. The combination of different wastewater cleaning processes results in wastewater treatment technologies. The technological flow must ensure the reduction of pollutant concentrations below the limit allowed by the legislation in force. Mainly, the purification of mine waters requires pH adjustments, ensuring the conditions for producing redox reactions and stabilizing the residues resulting from the treatment. The main processes for wastewater treatment, classified according to the mechanism that leads to the reduction of the pollutant are: physical, chemical and biological processes. Their combination allows for advanced purification.*

Key words: *industrial waste water, heavy metals, chemical processes, physical processes, biological processes, zeolites*

1. Introduction

The waste water from the mining industry does not comply with the quality conditions required by the legislation in force regarding: pH, total suspensions, sulphate content, heavy metals, fixed residue, etc.

As pollutants, heavy metals are among the most toxic because of their long persistence in solutions and the difficulty of being transformed into insoluble compounds in surface waters. The danger of heavy metal contamination is increased in the presence of complexing agents, which strongly bind these metals into soluble compounds, which cannot be removed during water treatment.

Pollution of industrial wastewater is the most massive and harmful category of pollution. The causes of the pollution of industrial wastewater emissions originate from the „gaps" in the conception about the production process, the summary examination of the secondary phenomena that influence the results of the basic process, the elimination of waste and by-products without special concerns regarding the consequences that may have on the environment.

In heavy metal pollution of industrial waste water, the largest contributions have the activity of the mining industry, the mineral processing industry, the metallurgical industry, the chemical industry.

Due to their special properties (adsorption, desorption, ion exchange, catalytic), zeolites have become successfully used in the field of control and steering of polluting processes.

Cleaning treatment with zeolites can be said to be a natural and clean method. In addition, the retained substances can be recovered, which represents an economic advantage or an internalization of environmental costs. Worldwide, the first place in terms of consumption of zeolites is occupied by Western Europe, followed by North America and Asia; at the end of the ranking - Central and Eastern Europe (Male A., A. Marton, 1989).

Romania, especially Transylvania, has deposits of zeolites which, however, are not sufficiently utilized. Currently there are only a few companies that deal with the exploitation of zeolite volcanic bushes.

2. Procedures of industrial wastewater cleaning

The choice of one of the processes is based on: the quantity of effluent, the content in pollutants, the quality conditions imposed by the legislation in force, the financial means of the economic agent.

Physical procedures for wastewater treatment

In these processes, pollutants do not undergo transformations into other substances. These processes include: sedimentation, flotation, centrifugation, filtration, membrane separation, phase transfer.

Sedimentation involves the gravitational separation of coarse particles, not dissolved in water, under the influence of the gravitational field; this process can be intensified by coagulation and flocculation (R. Sarbu, 2008).

Flotation is the separation process based on the differences between the surface properties of the solid particles. At the base of this process is the adhesion of solid particles to the gas bubbles with the formation of bubble-particle aggregates to be transported to the surface of the water, forming a foam that is removed by different processes (S. Krausz, P. Ilie, 2001).

Centrifugation is the process of separating the suspensions from the water in centrifugal field.

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Sedimentation rates are high, which results in a greater mass separation of mineral suspensions in the unit of time.

Filtration - is the process of passing water through a porous environment, on which the retention, through predominantly physical phenomena, of some of the constituents of waste water takes place.

Membrane separation. The membrane is defined as a phase that acts as a barrier for the molecular or ionic species in the water, through which the membrane can only pass water molecules. Of the processes that use membrane separation, the largest use is: direct and reverse osmosis, ultrafiltration and electro-dialysis.

Chemical procedures for wastewater treatment

Through chemical purification processes, the pollutants are transformed into other substances more easily separated such as: insoluble precipitates, gases, which have a lower harmful activity or are more likely to be removed. The chemical procedures applied for wastewater treatment are: neutralization, oxidation and reduction, precipitation, coagulation and flocculation, ion exchange on resins.

Neutralization is a process by which the pH of a water is regulated by the addition of acids or bases. This process also has the effect of reducing the corrosive properties of the water.

Oxidation and reduction - the purpose of this process is to convert undesirable chemical compounds into less harmful ones.

Precipitation realizes the transformation of pollutants from wastewater into insoluble products that can be subsequently separated from water. Cyanides, salts of alkali metals, sulphides, ortho-phosphates, proteins, aromatic amines can be removed by precipitation.

Coagulation and flocculation. The term coagulation is used to describe the destabilization process produced by the compression of the two electrical coatings that surround the colloidal particles, which makes it possible to aggregate them and thereby decrease the specific surface of the system. The term flocculation refers to destabilization by adsorption of large polymer molecules that form bridges between particles.

Treatment by ion exchange is based on the property of some materials, which come into contact with mineralized water (containing ionized salts), replacing the ions in the water with the ions coming from the material itself.

Processes for biological treatment of waste water

By biological purification is meant the complex of operations and technological phases through which the organic matter existing in the waste water is transformed, with the help of cultures of microorganisms, into products of harmless degradation and a new cell mass (biomass), harmless.

Biological treatment of wastewater containing metal ions can be done by two methods:

1.Reduction of metals and their precipitation in the form of sulfides by means of sulfate-reducing bacteria; Sulphate-reducing bacteria have the ability to reduce the sulphate ion by several steps, until the formation of hydrogen sulphide, which reacts with metal ions from wastewater and transforms them into precipitating sulfides and thus can be separated and removed by decantation and filtration.

2. Extraction of metals from water through their sorption on biological materials, process known as bio-sorption of metals. (C. Badulescu, 2010). The process uses living or dead biomass to hold impurities, especially rare metals and radioactive metals, from waste water.

3. Research on the use of zeolites in treatment of waters loaded with metal ions

General considerations

Zeolites are minerals that have hydrated aluminosilicates in their composition and have a high porosity structure having large areas of internal and external surface for ion exchange.

Zeolites have a significant importance in the efficiency of water treatment processes with concentrations of silicon dioxide, aluminum oxide, as well as the exchangeable cations K^+, Ca^{2+}, Mg^{2+} and other elements present in lower concentrations. Depending on the proportion of exchangeable cations, the type of zeolite can be characterized.

The selectivity is the characteristic of the ion exchange material to have affinity for the particular ions and is closely interrelated with the intensity of the fields in the zeolite pores.

Zeolites with high intensity fields, with higher Al content, are more selective than metal cations with a high charge density (Li^+, Na^+).If the solution contains different ions having the same charge, the selectivity increases, in proportion to the increase in the atomic number. ($Li^+ > Na^+ > NH^{4+} > K^+$).

The exchangeable cations in the volcanic tuffs of zeolites, such as (Na^+, K^+, Ca^{2+}, Ba^{2+}) are located in a network of channels being surrounded by water molecules, which gives them high mobility, being able to exchange metal ions.

Zeolites have a negative electrical charge due to isomorphic substitution of cations in mineral structures. They have a high affinity for metal cations and a low affinity for anions (T. Rusu, A. Rusu-2009). The heavy metals in the form of dissolved ions will move through the channels of the zeolite materials replacing their exchangeable cations: (Na^+, K^+, Ca^{2+}, Mg^{2+}) (T. Cătuneau, et all, 2010).

The adsorption efficiency of metal ions is determined by the relation:

$$\eta(\%) = \frac{Ci-Cf}{Cf}.100$$

where:
Ci–ions concentration before adsorbtion;
Cf –ions concentration after adsorbtion.

Natural zeolites have multiple advantages over cation exchange resins, as they have a low cost price, having a very high selectivity for different metal cations. For the definition and identification of the different types of natural zeolites, chemical and instrumental analyzes of great importance are used, for the development of research on water treatment (Szollosi-Moța A, et all, 2017).

A general technological scheme for treatment with zeolites of waste water with metal ions, with zeolites, is shown in Figure 1.

The technological flow involves the removal of coarse materials with the help of a grate, the settling of mineral suspensions with the help of the decanters, after which, the waters charged with metal ions, will pass through the sludge decanter and will be treated in three steps passing through filters with zeolites, in order to efficiently remove them. of heavy metals (Semsettin A, Gul Huseyin, 2007).

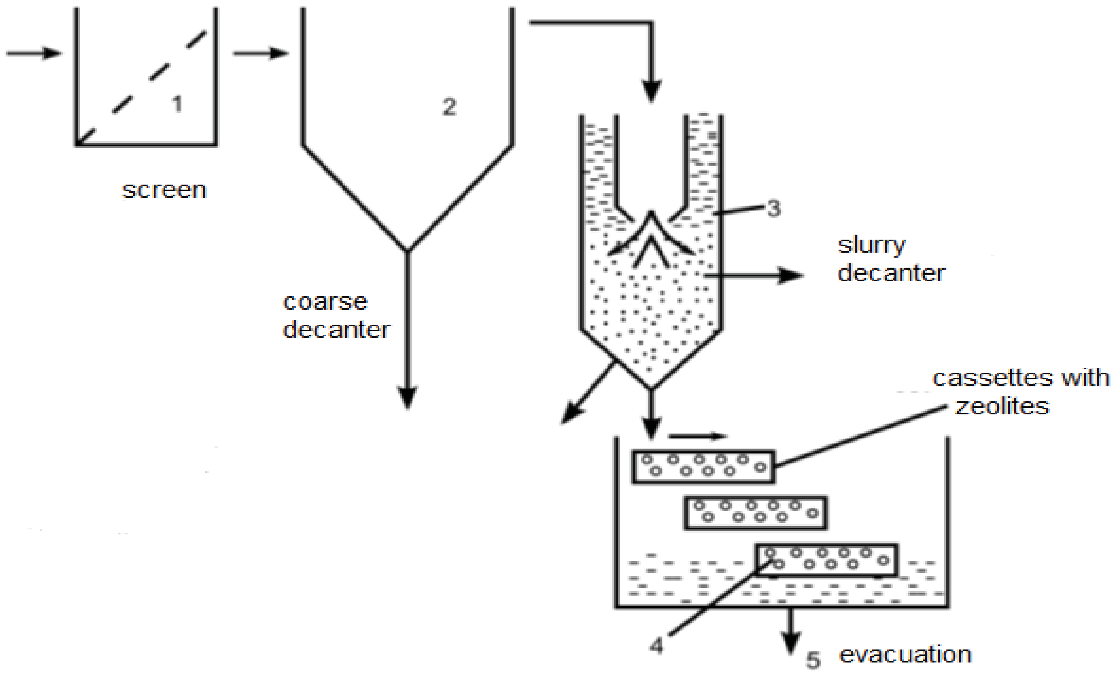

Fig.1 *The technological scheme for treatment with zeolites of waste water with metal ions*

The research has focused on purifying mine waters, charged with heavy metal ions, using zeolite as clinoptinolite because it has a very good adsorption capacity, being a natural zeolite, applicable because it has a very good removal efficiency of metal ions. Clinoptilolite is part of the stability group and is one of the most representative exponents of volcanic bushes in our country.

In the table no. 1 presents the chemical and mineralogical composition of the volcanic tuff - clinoptinolite. (T.Rusu , A. Rusu, 2009).

Table 1. *The chemical and mineralogical composition of the volcanic tuff*

Chemical compound	*%*	***Mineralogic compound***	*%*
SiO_2	11,7- 12,62	Clinoptilolite + heulandite	20-80
Al_2O_3	68,12- 70,06	Volcanic glass	10-64
Fe_2O_3	0,67-1,06	Quartz	2-5
CaO	3,36-4,82	Biotite	2-3
MgO	0,55-0,82	Limonite, goethite	0,5
K_2O	2,20-3,5	Celadonite, chlorite	1,2
Na_2O	20,40-20,60		
TiO_2	0,18-0,24		
P.C.	8,40- 10,61		

Photo zeolite

Zeolite volcanic tuff requires a succession of preparatory operations (physical treatment, chemical treatment) in order to be used in ion exchange processes. The physical treatment consists of grinding the volcanic tuff in the ball mill, followed by its sorting on granulometric classes (<0.2 mm, 0.2-0.4 mm, 0.4-0.6 mm and 0.6-1, 0 mm) with the help of a vibrating site.

The physical treatment is completed with the washing step of the zeolite volcanic tuff with distilled water until the complete removal of very fine powder that could clog the pores, followed by drying in the oven at 105 ° C for 6 hours.

The chemical treatment consists of bringing the natural zeolite into the form - Na, which has proven to be the most efficient in ion exchange processes. The treatment involves the introduction of the zeolite resulting from the physical process together with the sodium chloride solution, in a stirrer, the solid ratio: liquid used being 1:10, the conditioning time being one hour. After decanting the solution, the solid is washed with distilled water until the pH of the water reaches 7. The zeolite in the form - Na (Z - Na) is thus obtained.

Laboratory research has focused on removing from the analyzed mine waters heavy metals: cadmium, copper, zinc, iron, manganese. The metal concentrations in the analyzed water sample are shown in table no.2 (NTPA001 / 2005)

Table 2. *Concentrations of metals in the analyzed water sample*

Metal	*Metal concentration (mg/l)*	*Admissible concentration for evacuation (mg/l)*
Cadmium	0,077	0,2
Copper	0,249	0,1
Iron	0,870	5
Manganese	9,61	1
Zincum	17,90	0,5

The highest concentration is zinc and manganese with significant exceedance of the maximum permissible concentrations. In order to determine the physic-chemical properties of the waters, the pH and the conductivity of the samples collected from the discharged waters from the analyzed mining areas were determined.

The samples collected from the waters of the mining perimeters have pH values between 3.09 and 5.8, the value admitted by NTPA 001/2005 being 6.5-8.5. The experimental tests aimed at obtaining the highest purification yields.

In the table no. 3 shows the pH and conductivity values for the water samples from mining perimeters, the settling time on the zeolite columns being 1 hour, 2 hours and 72 hours.

In order to study the degree of purification, under static regime, experiments were performed on the purification efficiency of the samples, the residual water samples being kept on the columns with zeolites for one hour, two hours, respectively 72 hours. (table 3)

Table 3. *pH values and electrical conductivity of waste water after settling on columns with volcanic tuff*

Column	***pH ,unit.pH***			***Conductivity, µS/cm***		
	Settling time 1hour	***Settling time 2 hours***	***Settling time 72 hours***	***Settling time 1hour***	***Settling time 2hours***	***Settling time 72 hours***
Column 1	6,89	7,25	6,89	921	1163	1153
Column 2	7,39	7,29	7,39	1036	1203	1244
Column 3	7,57	7,45	7,57	1117	1244	1276

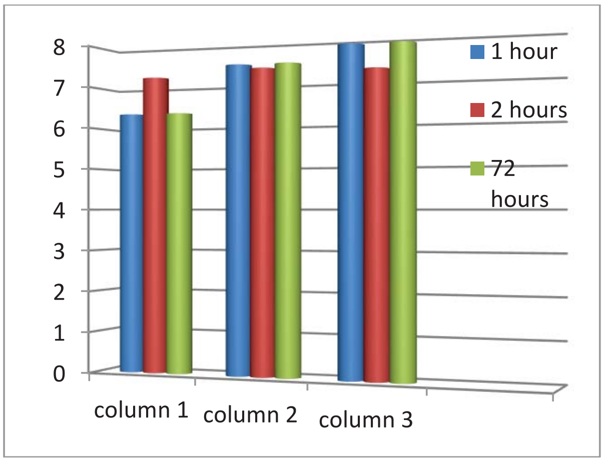

Fig. 2. *pH variation in correlation with the settling time in columns with zeolites*

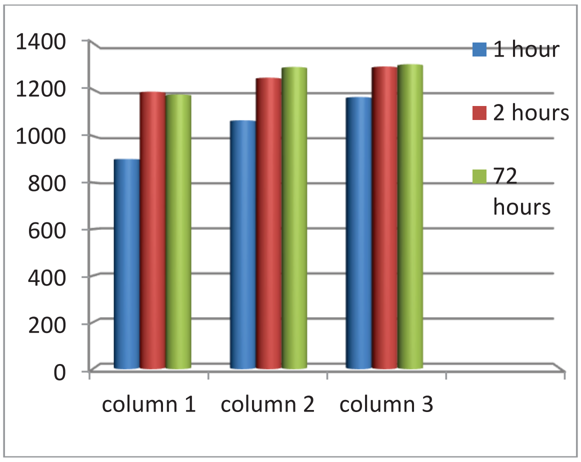

Fig. 3. *Conductivity variation (µS/cm) in correlation with the settling time in columns with zeolites*

In order to determine the degree of purification of the water samples charged with metal ions, the initial concentration of the metals and the concentration following the purification were determined using the purification columns. (table 4).

Figure 4 shows the degree of purification achieved, on the three columns with zeolites, depending on the time of settling the waste water on columns, respectively 1 hour, 2 hours, 72 hours.

Table 4. *The degree of purification on columns according to the time of the stand*

Metal	***The degree of purification, % 1 hour***	***The degree of purification, % 2 hours***	***The degree of purification, % 72 hours***
Cadmium	93,22	94,92	99,00
Copper	22,10	57,20	76,38
Iron	91,16	92,07	96,09
Manganese	85,10	97,22	96,70
Zincum	99,60	99,00	97,04

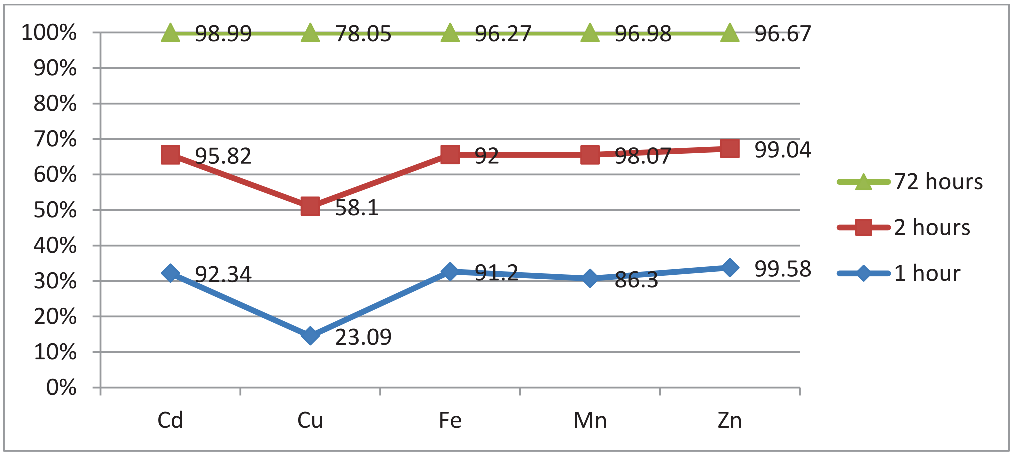

Fig. 4. *Degree of purification (%) on columns with zeolites, depending on the time of waste water stationing*

4. Conclusions

Experimentation of new efficient and lower cost methods, compared to other methods, for removing metallic pollutants from mine waters is one of the priorities in the field of water purification from mining areas.

Industrial waste waters are characterized by a high concentration of heavy metals whose elimination or reduction implies the application of physical, chemical or biological processes. By combining different processes, wastewater treatment technologies are born whose flow must ensure the reduction of pollutant concentrations below the limits imposed by the legislation in the field.

In order to choose the most suitable method of treatment of wastewater containing heavy metals, a comparative study is required, depending on the composition of the waste water to be treated, the level of neutralization that can be achieved and the concrete conditions existing in the respective locations.

Volcanic tuff is abundant, is environmentally friendly and cheap to exploit, having efficiency similar to the synthetic resins used today, but very expensive.

The most important benefits of using zeolites for the manufacture of filter cartridges required for industrial wastewater treatment are: light and durable; environmentally friendly and recyclable; resistant to temperature variations; resistant to atmospheric agents, acids, corrosions and immune to mold and lichens; easy to install; easy to move.

The use of the natural ion exchanger - the clinoptinolite volcanic tuff - for the retention of copper, zinc, cadmium, manganese, iron ions has the following advantages:

- high natural availability
- accessible exploitation
- rich resources
- low price
- recycling possibilities.

The ion exchange between the zeolites and the metal ions analyzed is a process of adsorption - chemical reaction - desorption, and through experimental research it was concluded that, from a kinetic point of view, ion transfer through the pores of the zeolites is the stage that conditions the process.

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