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The Detention of the Heavy Metal Ions by the Zeolitic Volcanic Tuffs (A Case Study of Cluj County, Romania)

KEYWORDS: volcanic tuffs, polluted mine water, IR spectroscopy

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ABSTRACT *This work presents a case study of the main zeolites volcanic tuffs from Cluj county. The results of experimental research have a high significance in assessing the importance and efficiency of using zeolite tuff from Cluj area and especially from Cornesti, Tiocu, Paglisa and Macicasu careers regarding the water remediation processes as water mine depollution. We studied the samples of these quarries which are not exploited to establish the mineralogical and chemical constituents, untreated tuff samples were analyzed by infrared spectroscopy (IR). We analyzed the samples of zeolite volcanic tuffs, before and after the contact with mine water from Larga de Sus mine (Alba county). This reseach can be a basis for launching other concerns of the zeolitical volcanic tuffs use more efficient at pilot or industrial stage.*

INTRODUCTION

Zeolites, besides in construction and other areas of interest and found the widest application in purification and industrial wastewater. In our experiments were also done in recent years and where volcanic tuffs were used as coagulant in Mirsid of different types of water to help eliminate pollutants and microorganisms compounds as has been shown (Bedelean & Stoici , 1984).

The names of these minerals comes from Greek and means "boiling stone", making reference to their property that removes water by heating, increasing its volume. First, zeolites have a high capacity for adsorption, desorption, respectively, thus fulfilling the function of "molecular sieves" pore size are inherent in each type of zeolite as (Bedelean & Stoici , 1984) said. Another category are the catalytic properties of zeolites. Because of these properties, zeolites have come to be used in pollution control and stewardship processes as Agnes Keri (2010) did.

RESEARCH OF VOLCANIC TUFF ZEOLITES IN CLUJ COUNTY AREA

Experimental research on the topic has been studied zeolite volcanic tuffs from Cluj county area namely samples were collected from the tuff quarries Cornesti, Tiocu, Paglisa and Macicasu.

Zeolite volcanic tuff was taken globally (approximately 5 samples) at the top, basal and the center of career located in the village Corrnesti,Tiocu, Paglisa and Macicasu (Cluj county).

THE PREPARATION OF TUFFS SAMPLES

Zeolite volcanic tuffs were washed with distilled water and dried at 350 ^{0}C. In order to analyze these samples, they were crushed and classified into three classes of grain via the web, as follows: 5-2 mm, 2-1 mm and 1 to 0.125 mm, as can be seen in Figure 1.

Figure 1: The prepared samples of the Paglisa quarries (prepared and photo: Corina Adriana Dobocan)

The IR Spectrometry is considered a fast and simple method of zeolites identification from tuffs volcanic samples. The measurements were done at room temperature (22^{0}C) in region of 1400-400 cm^{-1}, the resolution of 4 cm^{-1} with FT/IR-6200typeA spectrometer, from Technical University of Cluj-Napoca. The IR specters are presented in Figure 2.

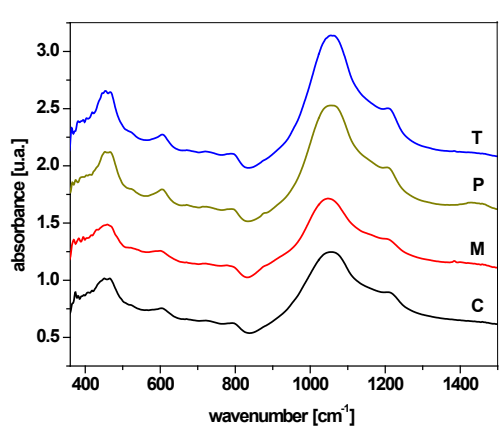

Figure 2: The IR analysis of volcanic tuffs BEFORE the mine water contact (C- Cornesti, T – Tiocu, P- Paglisa and M-Macicasu)

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It can be observed that the fourth tests have absorption bands. The picks which characterize the absorption from 453-608 cm^{-1} band represents the combined absorption and aluminum and silico- compounds. The strongest absorption band (1213 cm^{-1}) appear at Cornesti test and is due to (Al-Si)-O vibration compounds.

Also, the IR spectra show the clinoptilolite presence as a main phase in all four tests corresponding the absorption bands [1058 cm^{-1}, 836-1062 cm^{-1}, 792 cm^{-1}, 600-608 cm^{-1}]. The cristobalite is present in all tests also and can be identified by the following bands: 1209-1213 cm^{-1} and the quartz by 371-457 cm^{-1} band.

These samples were analyzed for metals removal from mine water from the mine Larga de Sus (Alba County) because the water flow is low; it permits the access to the mouth of the gallery and shows a specific metal content.

We collected the mine water from a wide and it has a sulphurous odor and reddish color due to the high concentration of metals. The samples were taken for analysis at The Environment Analyses Laboratory from Cluj-Napoca in February 2013. Due to this analysis the mine water contains the following metals: Al (16,9 mg/l), Fe (47,8 mg/l), Mg (23,9 mg/l), Co (72,5 µg/l), Cu (233 µg/l), Ni (164 µg/l) and another metals.

THE EXPERIMENTAL MEASUREMENTS IN STATIC

The experiments carried out by the method required reaction vessels in which we introduced the materials investigated. This method involves putting in contact mode the inert material between its desired ion exchanging. By the "batch" method was realized a set of experiments used 40 g of volcanic tuffs of 1-2 mm grain, 1000 ml of acid mine water by working at room temperature (about 20 - 22 °C), taking as reaction time 24 h. After this time, the samples were removed from the acid mine water and dried at 106^{0}C.

To determine how the polluting metals are retained of the mine water after being in contact with it, we considering the samples again by IR spectrometry.

The samples were pulverized before analyzing them. As can be seen in Figure 3, the IR spectra are visibly altered.

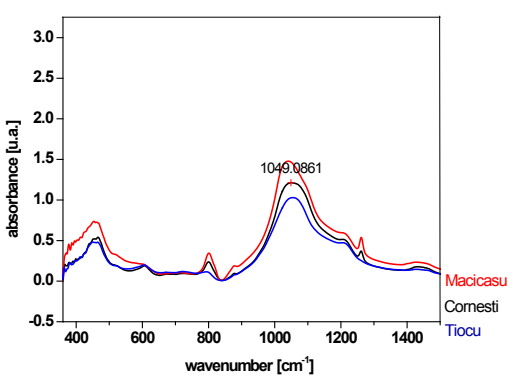

Figure 3: The IR analysis of the samples AFTER the mine water contact (24h)

These studied samples contain cristobalit and clinoptilolit relieved by the main band in the region 1000-1100 cm^{-1} (1049 cm^{-1}. This band is determined by the Al content of the clinoptilolit zeolite. The intensity of this band is proportional with the Si/Al content. The decreasing of the number of Al atoms in tetrahedral structure determines bands with more pronounced number of peaks. Al^{+3} is retained in the studied samples by the increasing of peaks number. In this way, the three samples analyzed confirm by the initial bands the fact that metal ions from water polluting mine were detained due to combined vibration and deformation of aluminum and silicon compounds, which highlighted the band 453-608 cm^{-1}.

CONCLUSIONS

From this case study we can certainly affirm that from IR analysis of studied samples after the mine water contact (in field 600-800 cm^{-1}), the bands are assigned to interchangeable cations and these bands are due to pseudo-crystalline vibrations.

In untreated zeolites these bands are clear, but in zeolites put in contact with mine water appear new and more numerous peaks because the loss of crystallinity due decationization networks. This is because of quartz and cristobalite.

Due to these properties, the 795-800 cm^{-1} band shows a significant decrease after this treatment, that retention of metal ions from polluted water. This leads to the conclusion that the evidence of the careers studies can be used in remediation of mine water, respectively, the retention of metal ions from polluted water. This leads to the conclusion that the evidence of the samples studied can be used in remediation of mine water.

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