

## **EFFECT OF A ROMANIAN ZEOLITE ON HEAVY METALS TRANSFER FROM POLLUTED SOIL TO CORN, MUSTARD AND OAT**

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*Obiectivul acestui studiu a fost evaluarea abilității unui zeolit natural românesc de a imobiliza o serie de metale grele din solul poluat datorită activității industriale desfășurată de o întreprindere metalurgică românească și a influenței acestui material asupra disponibilității metalelor din solul poluat față de plantele de porumb, muștar și ovăz.*

*Rezultatele obținute arată că zeolitul studiat poate fi utilizat ca amendament pentru imobilizarea plumbului, cuprului, zincului, cadmiului și manganului din solul poluat, prezența zeolitului în solul poluat conducând la diminuarea transferului acestor metale din solul poluat în plantele de porumb, muștar și ovăz.*

*Eficiența zeolitului este direct proporțională cu concentrația zeolitului în solul poluat și depinde de speciile de plante studiate.*

*The objective of this study was to evaluate the ability of a natural Romanian zeolite to immobilize the heavy metals from polluted soil in the vicinity of a Romanian metallurgical plant and the influence of this material on the pick up of lead, copper, zinc, cadmium and manganese from polluted soil, by corn, mustard and oat.*

*Natural Romanian zeolite appears to be an effective amendment to stabilize soil polluted with lead, copper, zinc, cadmium and manganese and have reduced the transfer of these metals from polluted soil into corn, mustard and oat plants, the efficiency in reducing the availability being in direct proportionality relation with the concentration of zeolite in polluted soil and depending of the species*

**Keywords:** Immobilization, zeolite, soil depollution, lead, copper, zinc, cadmium, manganese

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## Introduction

The contamination of soil with heavy metals due to the industrial activity has increased considerably nowadays, adverse effects of contamination being reported in several habitats in the world [1] - [4].

Romania has not paid enough attention to protect the environment and consequently today there are many sites polluted with heavy metals. Because metals in soil are not biodegraded by natural processes and remain in the ecosystem, the remediation of these soils is one of the stringent problems in the field of environment protection, for quality of life improving and to ensure a sustainable development in Romania.

Among the contaminant metals, lead is almost always present in contaminated soils together with copper, zinc and other heavy metals.

The mobility of the cations of these metals is quite different and there exists the risk of leaching into groundwater and of accumulation in crops and human diet [4].

Lead is considered the least mobile heavy metal especially under reducing or non – acidic conditions, complexation with organic materials, chemisorption on different siliceous materials and precipitation as insoluble salt or hydroxide being the mechanisms responsible for its immobilization.

The behavior of copper is similar, copper cations being sorbed on oxides, silicate materials etc.

Zinc and cadmium are one of the most soluble and mobile of heavy metals cations, being uptaken in siliceous materials and organic matter, [4]. Manganese is not so dangerous and its presence in soil does not constitute usually a problem.

The natural capacity of soils to reduce the bioavailability of metals is not able to avoid environmental risks due to the high concentration of these metals in many of contaminated sites, this situation requiring immediate action.

Chemical stabilization with different appropriate materials was evaluated as one of the most cost – effective remediation techniques for heavy metals contaminated sites [5].

For chemical immobilization ‘in – situ’ of lead, zinc, cadmium or copper have been investigated the efficiency of soil amendments [6], phosphate rocks [7- 11].

Phosphate rocks are efficient in remediation of soils polluted with zinc, cadmium or copper [9], [11], [12].

In general, these treatments lessen the risk of polluted soils by limiting metal leach ability and reducing metal bioavailability.

The main objective of our study was to evaluate the effectiveness of a Romanian zeolite to reduce the mobility of lead, copper zinc, cadmium and manganese in a polluted soil from the vicinity of a metallurgical plant. This was

done by evaluating the reduction of the availability of these metals to corn, mustard and oat plants.

## 1. Materials and methods

### *The natural zeolite*

The natural zeolite used in this study came from Baia Mare district quarry, Romania. Some characteristics of this material are presented in table 1

The mineralogical composition by X – ray diffraction measurements and the specific surface area was determined using BET N<sub>2</sub> adsorption method.

*Table 1*  
**Physical, mineralogical and chemical characteristics of a Romanian zeolite**

Parameter	Value
Main component – clinoptilolite	about 80%
Quarz	4 – 5%
Feldspar	3 – 4%
Mordenite	1- 2%
Ratio SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	5.6
B.E.T surface area, m <sup>2</sup> /g	52.0165 ± 0.2833
External surface area, m <sup>2</sup> /g	45.7051
Micro-pore area, m <sup>2</sup> /g	6.3115
Micro – pore volume, cm <sup>3</sup> /g	0.002466
Pore diameter (mean), Å	101.8246
CEC, meq/g	1.5105
SiO <sub>2</sub> , %	64.58
Al <sub>2</sub> O <sub>3</sub> , %	11.49
CaO, %	1.19
MgO, %	0.33
Na <sub>2</sub> O, %	2.50
K <sub>2</sub> O, %	2.55
Fe <sub>2</sub> O <sub>3</sub> , %	1.31
H <sub>2</sub> O, %	12.92
Other, %	3.13

### *Polluted soil*

The samples of polluted soil were collected from 3 points from polluted area existing around the metallurgical plant situated in the vicinity of Baia Mare, from the depth 0 – 20 cm. These samples were sieved to remove non soil impurities, are dried at room temperature and ground to pass through a 2-mm screen.

Fractions smaller than 2 mm from each sample were mixed, homogenized and the resulted average sample was analyzed for physical and chemical characteristics determination.

The pH was measured in the clean aliquot above the soil, in agreement with Romanian Standard ISO 10390 – 1999.

The water content was analyzed using Romanian Standard ISO 11405 – 1997.

The heavy metal content of soil sample was determined in the clean aliquot above soil, in agreement with the recommendation of Romanian Standard ISO 11047 – 1999, by atomic absorption spectrometry.

Some characteristics of polluted soil are presented in table 2.

Table 2

**Some characteristics of polluted soil sample smaller than 2mm**

pH	N <sub>total</sub> , %	Humus %	Humidity, %	Heavy metal content, mg/kg dried soil				
				Pb	Cu	Zn	Cd	Mn
7.72	0.387	7.2	5.53	3138	610	585	8.9	1850

#### *Soil treatment with zeolite*

Soil samples were mixed with different quantities of zeolite, to obtain mixtures containing 1, 2.5, 5 and 7% zeolite, after homogenization 2 hours in a vertical rotary shaker. The particle size of zeolite was less than 0.2mm.

The mixtures of polluted soil – zeolite was subjected to the Static Leaching Test [13], which predicts the following leaching conditions:

- leaching agent – distilled water and aqueous nitric acid solutions 0,1N to obtain the desired pH values;
- contact time: 2 hours;
- solid : liquid ratio 1:100;
- room temperature;
- continuous mixing

After the solid – liquid separation, the concentration of metals in the solution was determined by mass absorption spectroscopy and the final pH was measured.

The results are illustrated in Figs. 1, 2 and 3.

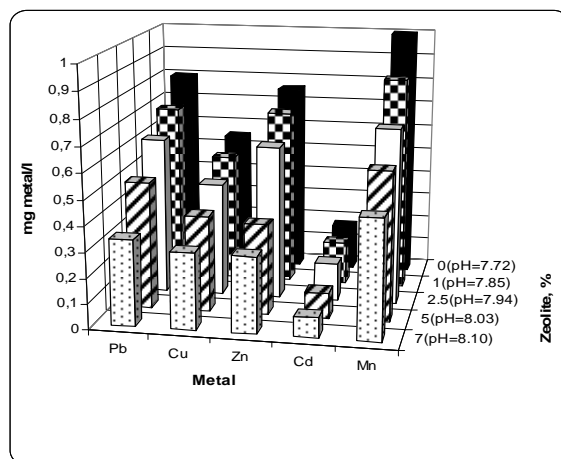


Fig 1. Leaching test (using distilled water as leaching agent) results for the mixtures polluted soil: zeolite; the pH of the polluted soil without zeolite is 7.7

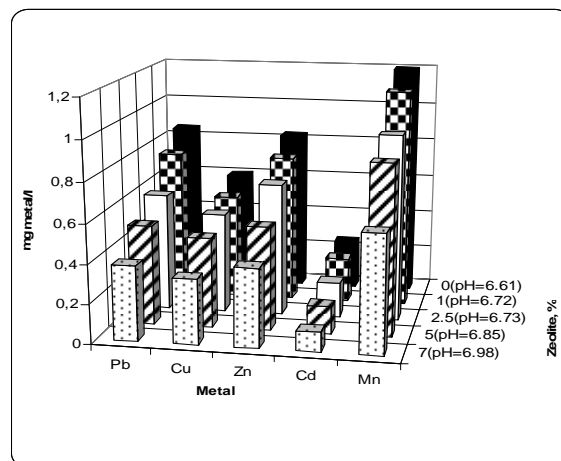


Fig.2 Leaching test (using diluted aqueous nitric acid solution as leaching agent) results for the mixtures polluted soil: zeolite; the pH of the polluted soil sample without zeolite is 6.6

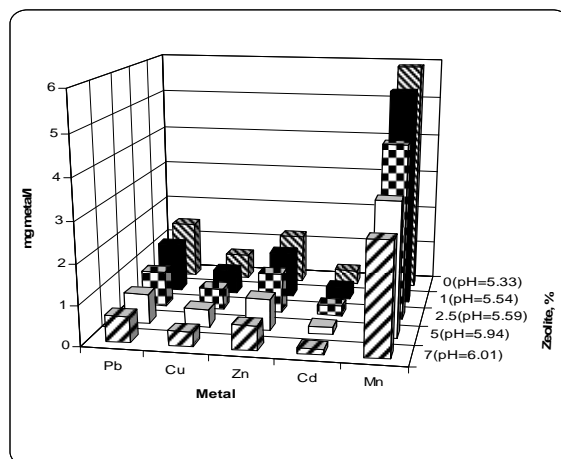


Fig. 3 Leaching test (using diluted aqueous nitric acid solution as leaching agent) results for the mixtures polluted soil: zeolite; the pH of the polluted soil sample without zeolite is 5.33

#### *Uptake of heavy metals by corn, mustard and oat*

Pot experiments were performed in green house in 5 variants with three replicates. The variants were:

- V<sub>1</sub> – polluted soil without zeolite;
- V<sub>2</sub> – polluted soil treated with 1% zeolite;
- V<sub>3</sub> – polluted soil treated with 2.5% zeolite;
- V<sub>4</sub> – polluted soil treated with 5% zeolite;
- V<sub>5</sub> – polluted soil treated with 7% zeolite.

Each treated soil was incubated with 60% water holding capacity at room temperature (22°C) for 45 days, [3]. Then the corn, mustard and oat were planted. The plants are grown for 70 days at room temperature at a relative air humidity of 60%.

The plants were sampled, washed with water and dried at 60°C for 48 hours, ground to pass a 40 µm sieve.

1 g of dried weight of each plant powder was digested with 14 M HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub> at a solid : liquid ratio of 1:15, heated at 120°C for 2 hours [8].

The digested solutions were filtered with a Whatman paper no 42 and analyzed for lead, copper zinc, cadmium and manganese concentration, by atomic absorption spectroscopy and for pH.

## 2. Results and discussion

### *Soil pollution*

In agreement with UNESCO classification the soil from the industrial area is Chernozem having characteristics presented in tables 2.

The evolution of soil content in lead, copper, zinc, cadmium and manganese is presented in table 3, in comparison with the values for non – polluted soil sample collected from 6 km north distance from the plant. For a correct estimation of the soil pollution, in table 4 are presented the limits of concentration for lead, copper, zinc, cadmium and manganese, predicted by Romanian Environment Protection Law.

Table 3

**Range of metal concentration in polluted soil samples, comparatively with the data for non- polluted soil sample, mg metal/ kg dried soil.**

Metal	Lead	Copper	Zinc	Cadmium	Manganese
The range of the metal concentration in polluted soil	34 - 3037	16 – 721	83 – 732	0.1– 9.1	152 – 1815
Metal concentration in non- polluted soil	22	16	27	0.1	100

Table 4

**Limit values for metal concentration in soil predicted by Romanian Environment Protection Law, in mg metal/ kg dried soil**

Metal	Normal values	Limit of alert		Limit of intervention	
		Sensible areas	Less sensible areas	Sensible areas	Less sensible areas
Cadmium	1	3	5	5	10
Copper	20	100	250	200	500
Manganese	900	1500	2000	2500	4000
Lead	20	50	250	100	1000
Zinc	100	300	700	600	1500

\*Authorities has to be informed about the pollution to take supplementary monitoring measure

\*\* The evaluation of risk is obligatory and measures must be taken to reduce the concentration of pollutant substances

\*\*\*Sensible area means agricultural areas, domestic farms etc.

\*\*\*\*Less sensible area means industrial area

From the data presented in tables 3 and 4 is obvious that the main pollutant in this industrial area is lead, followed by copper, zinc and cadmium. Manganese concentration in soil is not dangerous, according with the data from table 4.

#### *Soil treatment with zeolite*

From Figs. 1,2 and 3 it is evident that the metal concentration in the leaching solution is strongly influenced by the pH, the concentration of metals increasing with pH decreasing (increasing of the acidity).

The concentration of the zeolite in soil for an efficient immobilization of metals is also depending on the pH; for pH 7.72 the concentration of zeolite is 2.5%, for 6.61 is 5% and for 5.33 is 7%.

#### *Uptake of heavy metals by plants*

The results obtained in pot experiments, in green house concerning the influence of the concentration of zeolite in polluted soil on the transfer of lead, copper, zinc, cadmium and manganese from soil to corn, mustard and oat plants are illustrated in Figs. 4, 5, 6, 7 and 8.

(0%) zeolite from the Figs. 4, 5, 6,7 and 8 corresponds to the data resulted from the variant symbolized  $V_1$ , polluted soil without zeolite, which gives the background level of heavy metals in corn, mustard and oat.

(1%) zeolite in all Figs. corresponds to the data resulted from the variant symbolized  $V_2$ ;

(2.5%) zeolite in all Figs. corresponds to the data resulted from the variant symbolized  $V_3$ ;

(5%) zeolite in all figures corresponds to the data resulted from the variant symbolized  $V_4$ ;

(7%) zeolite in all figures corresponds to the data resulted from the variant symbolized  $V_5$ .

From the figures it is evident that the concentrations of Pb, Cu, Zn, Cd and Mn in biomass of all three species decreases significantly as the rate of zeolite application is increased.

The concentration of Pb, Cu, Zn, Ca and Mn in biomass was affected by the species too, being higher in mustard grown in untreated and treated soil.

The lines in Figs. 4,5,6,7 symbolize the accepted limit concentration for the lead, copper, zinc, cadmium and manganese in plants, according to the Romanian legislation.



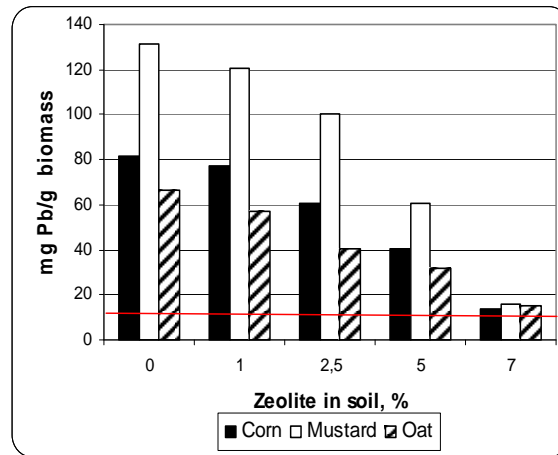


Fig 4. Influence of zeolite concentration in polluted soil on the availability of lead from soil to corn, mustard and oat plants

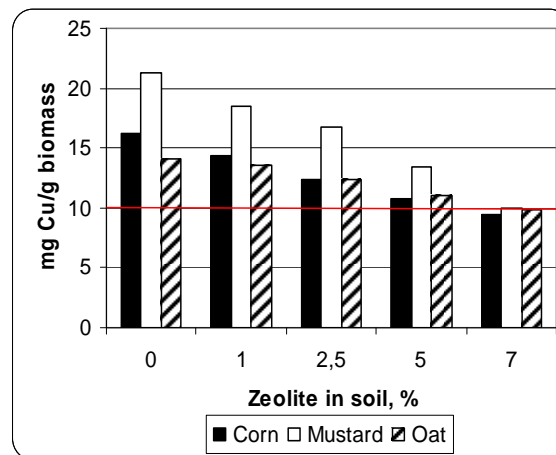


Fig 5. Influence of zeolite concentration in polluted soil on the availability of copper from soil to corn, mustard and oat plants

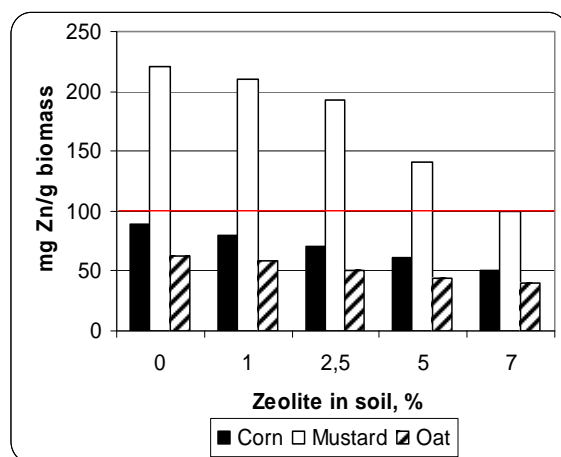


Fig 6. Influence of zeolite concentration in polluted soil on the availability of zinc from soil to corn, mustard and oat plants

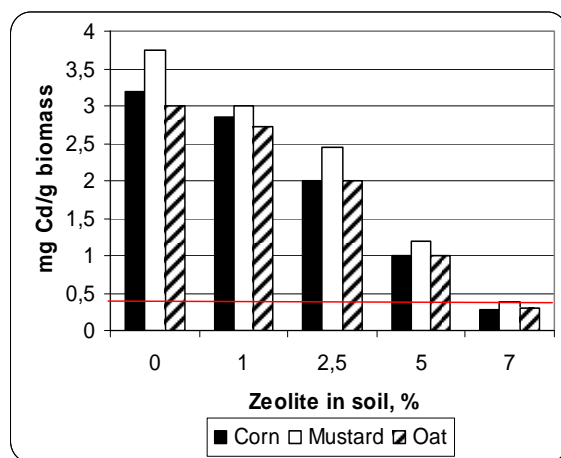


Fig 7. Influence of zeolite concentration in polluted soil on the availability of cadmium from soil to corn, mustard and oat plants

The concentration of metals in biomass of all species followed the series:  
 $Mn > Pb > Zn > Cu > Cd$

## Conclusions

The soil from the vicinity of the metallurgical plant is polluted with lead, copper, zinc, cadmium and manganese.

For the heavy metal immobilization from polluted soil a Romanian natural zeolite was used.

The results show that this material is able to immobilize lead, copper, zinc, cadmium and manganese from polluted soil.

The treatment of polluted soil using zeolite has reduced the transfer of lead, copper, zinc, cadmium and manganese from polluted soil into corn, mustard and oat plants, the efficiency in reducing the transfer of these metals from soil into plants being in direct proportionality relation with the concentration of zeolite in polluted soil.

Romanian zeolite appears to be an effective amendment to stabilize soil polluted with lead, copper, zinc, cadmium and manganese.

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