



**AgroSym**  
2019

**BOOK OF**

**PROCEEDINGS**



*X International Scientific Agriculture Symposium  
"AGROSYM 2019"  
Jahorina, October 03-06, 2019*

# **BOOK OF PROCEEDINGS**

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“AGROSYM 2019”**



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## FOREWORD

### *A Word from the Editor-in-Chief*

Dear colleagues,

In your hands is the Book of Proceedings of the X International Scientific Agricultural Symposium "AGROSYM 2019", which I hope you will find useful in your work. As many as 900 contributions, from 82 countries, have been accepted for oral or poster presentations. Symposium themes cover all branches of agriculture and are divided into 7 sessions: 1) Plant production, 2) Plant protection and food safety, 3) Organic agriculture, 4) Environmental protection and natural resources management, 5) Animal husbandry, 6) Rural development and agro-economy, 7) Forestry and agroforestry. Papers dealing with agricultural engineering and technology were included into one of the seven sessions depending on their focus.

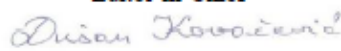
In the plenary lectures were addressed interesting topics; one keynote was on biotechnology and two others dealt with organic farming in Australia and Europe. This confirms the role of AGROSYM as a forum for open discussions and exchanges on agriculture, food, the environment and rural development in the Balkans and beyond. Many of the papers identify a number of approaches and market-based incentives to encourage producers to achieve higher levels of performance (from both economic and environmental points of view) and as a result to meet the expectations of governments and consumers.

The successful management of agricultural resources to satisfy changing human needs, while maintaining or enhancing the quality of the environment and conserving natural resources, indicate a long-term agricultural development imperative. Advances in productivity, profitability and stability of modern cropping, animal and forestry systems will have to be achieved globally on an ecologically sustainable basis. Today, it is obvious that conventional methods of agricultural production, while providing sufficient food and various products to humanity, have led to a number of negative impacts, including the transgression of many planetary boundaries. These negative impacts raise serious questions about the long-term sustainability of high-input agriculture and call for a genuine transition towards sustainable agro-food systems, which achieve food and nutrition security for present and future generations within the safe operating space for humanity.

Full texts of the submitted communications will be available on the website of AGROSYM (<http://agrosym.ues.rs.ba>). Each paper included in the present Book of Proceedings was positively reviewed.

Much appreciation is due to the authors of all papers submitted and presented at the symposium as well as to all symposium participants whose ideas and contributions allowed rich and lively discussions during the various sessions. Many thanks to all reviewers, session moderators and colleagues for their help in editing the Book of Proceedings. Special thanks go to all co-organizers, partners and sponsors for their unselfish collaboration and comprehensive support.

Editor-in-Chief



Dusan Kovacevic, PhD

East Sarajevo, 12 October 2019



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**EFFICIENCY AND THE POSSIBILITY OF USING ZEOLITE AND APATITE IN PURIFYING WATER FOR IRRIGATION AND REMEDIATION OF CONTAMINATED SOIL**

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**Abstract**

Knowledge of the mobility of heavy metals and radionuclides, such as Pb, Cd, Zn and U, represents one of the goals of protection, regulation, rational use and irrigation of agricultural soils from the aspect of safe food production. The aim of this work was investigation of efficiency of natural mineral materials based on zeolite and apatite from domestic deposits in the mobility of heavy metals and radionuclides in the waters and soils of the different physico-chemical characteristics (pseudogley and chernozem). The affinity, efficiency, zeolite adsorption mechanisms and apatite adsorption precipitation were determined in a constant-pressure column system at 300 mg l<sup>-1</sup> for different pH values (5.00 and 7.00) of the basic contaminated solution (Pb, Cd, Zn, U) at time intervals of 30, 60, 90, 120, 180 minutes. In all experiments, significant changes in the pH of the filtrate occurred. The most significant changes in the pH of the filtrate, minimal fluctuations in the time interval, at pH = 5.00, recorded the basic solutions of Pb (7.69-7.87) and U (7.77-7.93) during leakage through the column with apatite, while slightly lower changes for Cd and Zn were observed. Changes also occurred in the column with the zeolite, but with a much lower intensity compared to the column of apatite, and with the trend of changes U > Pb > Cd > Zn. The trend of changes between apatite and zeolite also occurred in the basic contaminated solution with initial pH=7.00. Zeolite and apatite adsorption/precipitation processes successfully immobilized Pb at both tested pH values of stock solution. Our investigation showed that in colonies, apatite better immobilized U, zeolite is better for immobilization of the Cd, while for the Zn both materials showed a very similar affinity. Zeolite and apatite were added in amount of 20 g kg<sup>-1</sup> soil to reduce the content of water-soluble and easily accessible forms of Pb, Cd and Zn in uncontaminated and contaminated soil.

**Keywords:** *soils, water for irrigation, zeolite, apatite, heavy metals*

**Introduction**

The partial damage and destruction of land and water are a major problem for many countries in the world today, especially in food production. Land and water are the main natural resource not only in food production but as an environment with which human are in constant contact. According to that, it is a very serious problem for both: professional and socio-political organizations how to protect these irreplaceable natural resources. Increasingly stringent conditions and rules to produce health food are provided from "HACCP" and "GAP" concepts. It is predicted that Serbia will not be able to export any agricultural product without a certificate of land quality as a "critical place" in primary agricultural production after 2020 (Grubišić, 2017). Usage of nonmetallic mineral materials is important "in-situ" technology for remediation of toxic metals and radionuclides. The materials used for this purpose must be efficient, inexpensive, available in tonnes, and applicable in different mediums (water, soil). The most commonly used materials are iron oxides, zeolites, apatites, MgO, carbonates, compost, peat, cottonseed flour and lime (Conca, 1997, Brown *et al.*, 1996).

"In situ" technology is a successful and efficient passive method for the sanitation of contaminated groundwater and surface water as well as soil. It involves in some way control-management combining chemical, biological and physical remediation processes. The use of "in situ" technology has advantages in comparison to the conventional technologies for remediation due to it requires no maintenance and minimal operation (Knox *et al.*, 2000, NATO/CCMS U.S. EPA, 2002).

It is known that zeolites (from the clinoptilolite group) can be successfully used for immobilization of Cs, Sr, Cu, Cd, Pb, and Zn in soil and water (Alther, 2005, Ming & Mumpton, 1989). Ma *et al.*, 1993 showed that metal stabilization is efficient in combination with apatite especially for Pb, Zn, Cu, Cd, Ni, U, Ba, Cs, Sr, Pt, Th and other elements.

The usage of minerals for adsorption and precipitation processes in soils and waters is highly dependent on the pH of the medium, the presence of carbonate, organic matter, Fe-Mn oxides as well as the mechanical composition and type of soil mineral clay (Mission *et al.*, 2009). Prior to the in-situ remediation procedure and the use of mineral raw materials, it is necessary to carry out the procedure under laboratory conditions in order to determine the fillers (adsorbents, precipitators), the amount of material, the shelf life, the methods efficiency, etc. Based on experimental results and equations it can be calculated efficiency (K) and capability (Cap) of the various additives for immobilization and outdoor application in field conditions (Jang *et al.*, 1998).

The aim of the study is to investigate the efficiency and possibility for application of zeolites and apatites for remediation of contaminated groundwater, irrigation water and soil.

#### Material and Methods

Efficiency of mineral raw materials (zeolites and apatites) in a mobility of toxic metals and radionuclides are investigated in Institute for Technology of Nuclear and other Mineral Raw Materials. Experiment was carried out in glass columns (diameter 4 cm), with controlled constant flow. The mass of the clinoptilolite zeolite in the column was 30 g, granulation of 0.8-2.0 mm. The weight of the second mineral supplement-apatite was 30 g, granulation <100 microns. Due to the low filtration coefficient of micronized material, the apatite was mixed with 300 g of purified and calcined quartz sand (ratio 1:10). In this way, a complete control of the constant-pressure filtration coefficient of 200 ml/h for both mineral adsorbents was performed (Figure 1a).

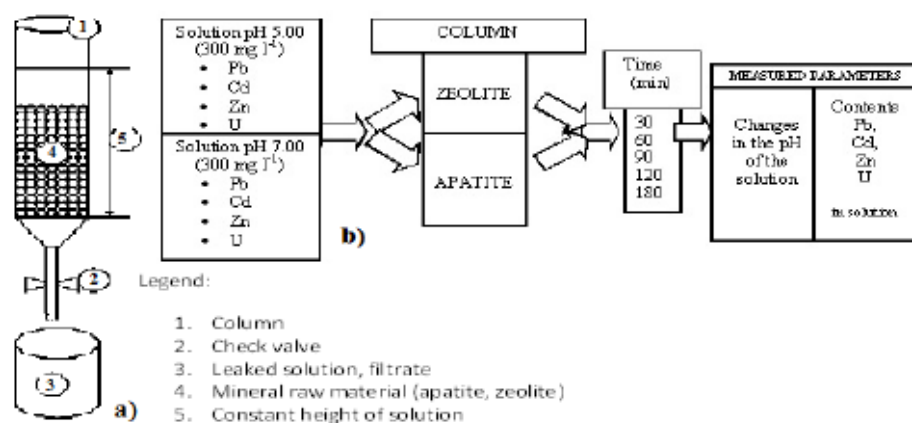


Figure 1 – Schematic view of: column a), column experiment b)



The concentration of toxic metals (Pb, Cd, Zn) and radionuclides (U) used for column experiments was 300 mg/l. Toxic metals solutions were prepared from acetates and radionuclide solution Uran-a was prepared using uranyl nitrate. The pH value of prepared solutions were adjusted at pH 5.00 and pH 7.00. Prepared solutions were passed through a system of columns filled with mineral additives (zeolite, apatite). The samples are collected at different period times: 30, 60, 90, 120, and 180 min. In this way, 4 x 100 ml and 1 x 200 ml solutions for chemical analysis at the 5 different intervals based on the filtration coefficient were collected (Figure 1b). The second part of experiments involved adding of 20 g kg<sup>-1</sup> zeolites and apatites in the soil (pseudogley pH=5.55, sand chernozem pH=7.05). In prepared soils the portion of 50 mL solution with 2 mL Pb-Zn-Cd synthetic solution were added. The concentration of synthetic solution was: Pb=50 mg cm<sup>-3</sup>, Zn=30 mg cm<sup>-3</sup>, Cd=1 mg cm<sup>-3</sup>. After first and thirtieth days, water-soluble and accessible forms of added toxic metals (Pb, Zn, Cd) as well as their total content in prepared soil samples were determined.

### Results and Discussion

The affinity of mineral adsorbents in reducing the mobility of toxic (Pb, Cd, Zn) metals and radionuclides (U) at different pH values (pH 5 and pH 7) of the solution was determined at the first part of experiments.

The change of pH value of a basic toxic solution at pH 5 in a column system with apatite and zeolite after passing through column are shown in Table 1. As can be seen from Table 1, the filtrates with the highest pH value at pH 5 have the basic solutions of Pb and U which passed through apatite column at all investigated intervals (t1-t5). Also, the differences in pH value between investigated solutions are minimal: Pb (7.75-7.80) and U (7.77-7.93) (Figure 1).

Slightly lower intensity of pH value change was detected in the basic solution at pH 5 contaminated with Zn and Cd.

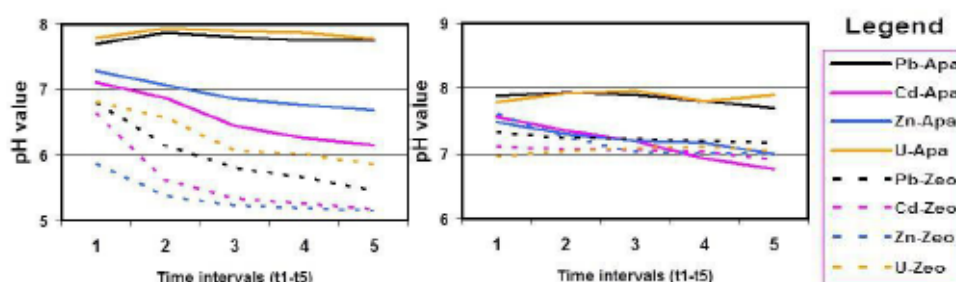


Figure 1. The change of pH value of basic solution (pH 5, left), (pH 7, right) with toxic metals after passing through column with apatite and zeolite

That solutions of Cd and Zn (pH 5) which passed through the apatite column, have lower pH of the filtrate and record a linear, slight decrease in the pH of the filtrate in Zn basic solution (7.28-6.68) and slightly faster in Cd basic solution (7.11-6.15) Knox *et al.* (2003).

The change of pH value of a basic toxic solution (Pb, Zn, Cd, U), pH 5, are also detected in a column system with zeolite. As can be seen, the lower pH change intensity but with same distribution of contaminant (U, Pb, Cd, Zn) in comparison with experimental results from apatite column was observed.

Also, the pH value change was detected after passing of basic contaminated solution (Pb, Zn, Cd i U), pH 7, through apatite-zeolite column (Figure 1, right).

The pH value changes at pH 7 are significantly less than the basic solution pH 5, and the variations range is in interval from 6.77 to 7.96. The same trend with the pH 7 solution (the largest pH changes) occurred in the Pb and U filtrate obtained through an apatite column. The

pH of the filtrate is quite uniform for the apatite column for contaminated solutions with Pb (7.70-7.94) and U (7.79-7.96). The obtained filtrate from the apatite column for Cd and Zn have linear decrease in pH over all investigated intervals t1-t5: from 7.56 to 6.77 and from 7.49 to 7.00 for Cd and Zn, respectively (Matusik *et al.*, 2012).

Zeolite adsorbent, as a filter in the columns, influenced the pH changes of the basic contaminated solutions (Pb, Zn, Cd, U), pH 7, but with a much smaller effect compared to the same conditions where the filter was apatite. Zeolite had a greater influence on the filtrates when the initial contaminated solution with toxic metals (Pb, Zn, Cd, U) was acidic.

Zeolite and apatite can successfully mobilize Pb at pH 5, stock solution through adsorption/precipitation processes (Figure 2). The U-ion is better immobilized by apatite than by zeolite, while Cd is better immobilized by zeolite and has a very similar affinity for immobilization of Zn over a 180-min in the acidic medium of stock solution, pH 5.

Zeolite and apatite, at the pH = 7.00 are very efficient in reducing the mobility of Pb, at all investigated intervals (t1-t5).

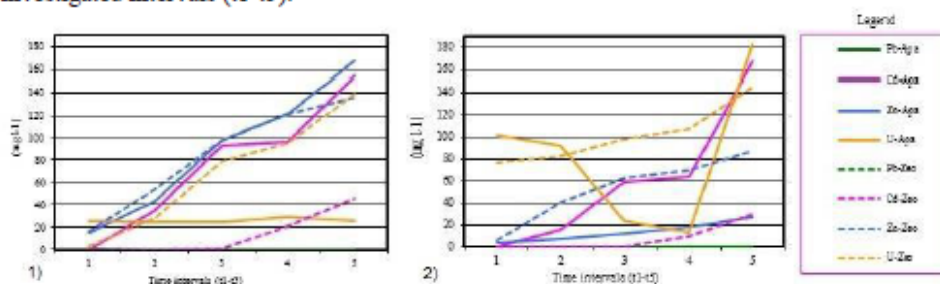


Figure 2. Dynamics of adsorption-precipitation of toxic metals and radionuclides in time, concentration of contaminants in stock solution was 300 ppm, pH 5 (1) pH 7 (2)

Zeolite is very efficient adsorbent for Cd, especially in the first three time intervals (Figure 2). Compared to zeolite, the efficiency of apatite is significantly lower for Cd immobilization. Zn stock solution (pH 7) after passing through apatite and zeolite columns was well immobilized. The Zn content in filtrate is lower than in the acidic stock solution.

The efficiency of zeolite and apatite for U immobilization in neutral stock solution (pH 7) is significantly reduced compared to the acidic stock solution (pH 5)

Immobilization, the process of precipitation of U ions was very slow under neutral reaction conditions, it took 60 minutes (t2) to initiate Ca ions from apatite and create stable complexes. The efficiency of zeolites in the immobilization of uranium ions in the neutral pH medium is weak, the U content in the filtrate increase linearly during the investigated time from 76.66 (t1) to 145.33 mg l<sup>-1</sup> (t5).

The efficiency of adsorbent/precipitator mineral resources in the soil-toxic element system in two soil types (Table 1) was investigated in the second part of experiment.

The same amount of added toxic elements (Pb, Cd, Zn) in pseudogley and sand chernozem had a different influence on the content of readily available forms of the same elements, so the content of readily available Pb is 146.0 mg kg<sup>-1</sup> in sand chernozem, while Pb content in pseudogley is 195.0 mg kg<sup>-1</sup>. The content of readily available Cd in contaminated soil depends on the pH value, on th pseudogley Cd content is higher (2.70 mg kg<sup>-1</sup>), while on sand chernozem is lower (1.12 mg kg<sup>-1</sup>). The similar results were obtained for the content of readily available Zn: in pseudoglej the content was 121.0 mg kg<sup>-1</sup> while in sand chernozem was 47.7 mg kg<sup>-1</sup>, as well as for the readily available form Pb (in pseudogley the content was 195.0 mg kg<sup>-1</sup> while in sand chernozem 146.0 mg kg<sup>-1</sup>).

Table 1. Content of water-soluble and easily accessible forms of toxic metals in soil, 24 hours after contamination with Pb, Cd, Zn

Soil type	Variant	Toxic element, (TE), (mg kg <sup>-1</sup> )					
		Pb		Cd		Zn	
		H <sub>2</sub> O	DTPA	H <sub>2</sub> O	DTPA	H <sub>2</sub> O	DTPA
Sand Chernozem	Control (K)	0.2	1.2	0.07	0.44	0.16	0.60
	K+Apatite	0.2	0.6	0.08	0.22	0.14	0.38
	K+Zeolite	0.2	0.9	0.08	0.24	0.08	0.33
	K+Toxic Element	1.5	146	0.20	1.12	0.87	47.7
	K+Apatite+TE	1.4	110	0.18	0.95	0.12	29.5
	K+Zeolite+TE	1.2	96	0.14	0.95	0.24	32.1
Pseudogley	Control (K)	0.1	2.2	0.08	0.26	0.10	1.24
	K+Apatite	0.05	1.8	0.08	0.22	0.08	0.98
	K+Zeolite	0.1	2.1	0.06	0.21	0.08	0.94
	K+ Toxic Element	1.0	195.0	0.16	2.70	0.82	121.0
	K+Apatite+TE	0.4	69.7	0.15	1.40	0.36	59.8
	K+Zeolite+TE	0.8	79.2	0.15	2.10	0.56	85.8

The content of readily available forms of toxic metals Pb, Cd, Zn is much higher in the acidic pH of the pseudogley soil (pH in H<sub>2</sub>O, 5.55) than in the soil of neutral pH (pH in H<sub>2</sub>O, 7.05) in sand chernozem. According to experimental results it can be concluded that zeolite and apatite are efficient as reductants of the content of water-soluble and easily accessible forms of Pb, Cd and Zn in uncontaminated and contaminated soil, regardless of soil conditions (pH, mechanical composition, mineralogical composition, chemical composition), which is of great importance for the remediation of agricultural land. Also, a small difference between the forms of toxic metals for the 720 hour duration of the experiment is statistically insignificant. This indicates that there was no increase in the water-soluble and readily available forms of toxic metals, suggesting strong adsorption/precipitation process performed by zeolite and apatite.

#### Conclusions

The mineral raw materials (zeolite and apatite) from the territory of Serbia can be successfully used in groundwater and soil remediation technologies by using them as fillers for semi-permeable reactive barriers (PRB). These adsorbent precipitators are efficient in the column system in reducing the mobility of Pb, Zn, Cd and U at different pH values (pH 5.00 and 7.00). In this way, the wide use of non-metallic mineral raw materials from the territory of Serbia was once again confirmed. Zeolite and apatite can be successfully used as minerals for reducing the mobility of Pb, Cd, Zn and U in pseudogley and sand chernozem soils as well as surface irrigation waters. Short equilibrium time, efficiency, high sorption capacity, degree of stabilization are the main advantage for application of these materials from domestic raw material in the technology of immobilization of harmful elements in soil in a simple, inexpensive and successful procedure.

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