

**IN-VITRO  $^{137}\text{Cs}$  SORPTION BY NATURAL AND MONOIONIC FORMS OF CLINOPTILOLITE**

MLADENOVIĆ VERICA\*, VITOROVIĆ GORDANA\*\*, SLAVATA BRANISLAVA\*\*\*, D. VITOROVIĆ\*\*\*,  
S. IVKOVIĆ\* and VUKOVIĆ DUBRAVKA \*\*\*\*

*\*Military Technical Institute, Vojvode Stepe 445/06, 11000 Belgrade, \*\*Faculty of Veterinary Medicine, Bul. JNA 18, 11000, Belgrade \*\*\*Faculty of Agriculture, Nemanjina 8, 11080 Zemun; \*\*\*\*Veterinary Institute of Serbia, Vojvode Toze 14, 11070 Belgrade*

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*The objective of the present study was to evaluate the  $^{137}\text{Cs}$  binding capacity of natural and different monocationic forms of clinoptilolite in vitro, in a highly acid solution prepared to be similar to that within the stomach of swine. With the lower clinoptilolite concentration (100 mg) half of the initial  $^{137}\text{Cs}$  activity was sorbed during first 6 hours of incubation (48,9 %). Prolongation of the time of contact did not decrease solution activity. Using higher clinoptilolite concentrations (300 mg and 500 mg) the equilibrium of  $^{137}\text{Cs}$  ions was also established after 6 hours, but 75 % and 84 % of the initial  $^{137}\text{Cs}$  activity was sorbed. The similar efficiencies (84-85 %) found for natural and prepared forms of clinoptilolite indicated that there is no need to prepare mono-ionic forms ( $\text{Na-}$  and  $\text{NH}_4$  - clinoptilolite).*

*Key word: clinoptilolite,  $^{137}\text{Cs}$ , sorption, radiation protection*

**INTRODUCTION**

The history of protection of animals and humans from internal radioactive contamination is as old as knowledge of the harmful influence of radiation on live organisms. Radioactive contamination of the environment, as a consequence of the Chernobyl nuclear accident in 1986., made this aspect of protection very relevant. Special attention was paid to animal and human protection from internal contamination with long lived fission products, such as  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ . It is possible to prevent contamination of people, through the food chain (consuming animals products), by application of effective radioactive protection measures in domestic animals (Vitorović and Draganović, 1995). Cesium isotopes  $^{137}\text{Cs}$  and  $^{134}\text{Cs}$  are of major importance and have radiation safety implications, because they can accumulate in muscular tissue of animals.

One way to protect domestic animals from radiation is to use cesium binders which are able to keep cesium in the digestive tract and reduce transfer into body tissues. There are many investigations on the effects of different Cs-binding

compounds, such as bentonite (Iben et al., 1987.; Beresford et al., 1989; Unsworth et al., 1989.) and ammonium-ferric-cyanoferrate (Arnaud et al., 1988.; Giese, 1988.; Hove and Ekern, 1988.; Vitorović, 1993.). Clinoptilolite binding efficiency in experiments with animals was investigated by Pethes et al. (1988) in rabbits, Phillippo et al. (1988) in sheep and Mladenović et al. (1997) in broiler chickens.

The objective of the present study was to evaluate the  $^{137}\text{Cs}$  binding capacity of natural and different monoionic forms ( $\text{Na-}$  and  $\text{NH}_4\text{-}$ ) of clinoptilolite in vitro, in highly acid solutions prepared to be similar to that within the stomach of swine.

#### MATERIALS AND METHODS

Clinoptilolite is a zeolite with a high silica content, and has great stability in ionizing radiation, at elevated temperatures and extreme pH levels. The  $\text{Na(I)}$  and  $\text{K(I)}$  ions in the framework channel may be replaced by  $\text{Ca(II)}$  and  $\text{Mg(II)}$  ions.

Clinoptilolite from Zlatokop mine is mainly in the  $\text{Ca(II)}$  form. An average sample of the deposit, of particle size 1,0-0,3 mm was used for our investigation. A fraction with particle size 0,090-0,063 mm was separated by grinding and sieving, without removing the ingredients. The adhering dust was washed away with distilled water. The sample was dried at 105 °C and hydrated in a dessicator over saturated  $\text{NH}_4\text{Cl}$  solution. The  $^{137}\text{Cs}$  binding capacity of clinoptilolite was determined in-vitro in two experiments.

In the first experiment, 100 mg and 300 mg samples of natural clinoptilolite were treated with 100 ml electrolytic solution containing  $\text{HCl}$ ,  $\text{NaCl}$  and  $\text{KCl}$ , doped with 1440 Bq  $^{137}\text{Cs}$ . The acidity of the solution was adjusted to  $\text{pH} = 2\text{-}3$ , with  $\text{NaOH}$ , which resembles the conditions within the stomach of swine. Sorption was performed in a water bath at 37 °C with slow shaking. Contact times were 2, 4, 6 and 8 hours and there were three samples for each period of time. After sorption, the liquid fraction was separated by centrifugation and remaining activity measured. A 50 ml aliquot of the bulk solution was put in a marinelli beaker, water added to the volume of 0,5 l and  $^{137}\text{Cs}$  content determined by gamma ray spectrometry. The activity of each solution was determined using a high purity germanium (HPGe) detector with the resolution of 1,95 keV for the energy level 1,33 MeV and a relative efficiency of 10 % in the multichannel analyzer (Canberra 90). The measurement time was 40 000 s and the statistical error 10 %. The activities of the solutions before and after sorption in all experiments were measured in the same way.

In the second experiment, the  $^{137}\text{Cs}$  binding capacities of natural and monoionic  $\text{Na-}$  and  $\text{NH}_4\text{-}$  forms of clinoptilolite were compared. Hydrated samples of natural clinoptilolite were treated with 3 M  $\text{NH}_4\text{Cl}$  and 3 M  $\text{NaCl}$  solutions to prepare monoionic  $\text{NH}_4\text{-}$  and  $\text{Na-}$  forms of clinoptilolite. In order to achieve maximum exchange, equilibration was consecutively repeated with fresh solution. The obtained samples of  $\text{NH}_4\text{-}$  and  $\text{Na-}$  clinoptilolite were washed with distilled water until the reaction for  $\text{Cl (I)}$  ions was negative and rehydrated over saturated  $\text{NH}_4\text{Cl}$  solution. For the investigation of the efficiency  $\text{Cs(I)}$  ions, 500 mg of the

sample was equilibrated with 50 ml electrolytic solution doped with 1440 Bq  $^{137}\text{Cs}$  with the same composition and acidity as in the first experiment. After 6 hours at 37 °C, the remaining activity of  $^{137}\text{Cs}$  in solution was measured.

The results obtained were statistically analysed, and differences between treatments were tested using Student's t-test.

## RESULTS AND DISCUSSION

The activities of the solution after sorption for different contact times and with different amounts of clinoptilolite are given in Table 1. as mean values for three samples.

Table 1.  $^{137}\text{Cs}$  sorption by different concentrations (100 mg and 300 mg) of clinoptilolite ( $^{137}\text{Cs}$  activity in solution before sorption was 1440 Bq)

Time of incubation (hours)	$^{137}\text{Cs}$ activity in solution (Bq)		Sorbed activity (%)	
	100 mg clinoptilolite	300 mg clinoptilolite	100 mg clinoptilolite	300 mg clinoptilolite
2	1001±15.0	466±10.0**	30.4	67.6
4	894±4.0	383±8.0**	37.8	73.4
6	748.0±15.0	364±11.0**	48.0	74.7
8	739.0±12.0	371±10.0**	48.6	74.2

Means ± Standard deviation;

Statistical significance of differences between solutions with different clinoptilolite concentrations:

\*\* -  $p < 0.01$

With the lower clinoptilolite concentration (100 mg) half of the initial  $^{137}\text{Cs}$  activity was sorbed during first 6 hours of incubation (48 %). Prolongation of the time of contact to 8 hours did not decrease solution activity further. Equilibrium of  $^{137}\text{Cs}$  ions was also established after 6 hours, with a higher clinoptilolite concentration (300 mg), but 75 % of initial  $^{137}\text{Cs}$  activity was sorbed. The finding of  $^{137}\text{Cs}$  binding by natural clinoptilolite *in vitro*, confirms results obtained *in vivo* (Phillippo et al., 1988; Pethes et al., 1988; Mladenović et al. 1997). The higher clinoptilolite concentration had a higher sorbent efficiency (68-75 %) than the lower clinoptilolite concentration (30-48 %).

The effects of two mono-ionic forms (Na- and  $\text{NH}_4$ - clinoptilolite) forms of clinoptilolite on  $^{137}\text{Cs}$  sorption are shown in Table 2.

Both natural and prepared forms of clinoptilolite showed significant  $^{137}\text{Cs}$  sorption (84-85 % of initial activity). The high efficiency of the zeolite in the sorption of  $^{137}\text{Cs}$  is in accordance with the selectivity series for this zeolite and its high affinity for Cs (I) ions. The similar efficiencies of the natural and prepared forms suggest that there is no need to prepare monoionic forms. The higher  $^{137}\text{Cs}$  sorption efficiency (84-85 %) of clinoptilolite in this experiment compared to that

in the first experiment, was probably the result of using a higher clinoptilolite concentration (500 mg/50 ml solution).

Table 2. Activities of  $^{137}\text{Cs}$  in solution after sorption for 6 hours with different forms of clinoptilolite ( $^{137}\text{Cs}$  activity in solution before sorption was 1440 Bq)

Forms of clinoptilolite	Activity after sorption (Bq)	Activity sorbed (%)
Natural	230±11.0	84.0
Na -	215±11.0	85.1
NH <sub>4</sub>	215±7.00	85.3

Means±Standard deviation

## CONCLUSIONS

In vitro experiments, in high acidity solution (pH=2-3), showed that natural clinoptilolite had a definite sorption capacity for  $^{137}\text{Cs}$ , which increased with clinoptilolite concentration. Equilibrium of the sorption process is reached within 6 hours of contact. The similar efficiencies of natural and prepared forms suggest that there is no need to prepare mono-ionic forms.

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#### **IN VITRO SORPCIJA $^{137}\text{Cs}$ PRIRODNIM I MONOJONSKIM OBLICIMA KLINOPTILOLITA**

MLADENOVIĆ VERICA, VITOROVIĆ GORDANA, SLAVATA BRANISLAVA, VITOROVIĆ D., IVKOVIĆ S. I VUKOVIĆ DUBRAVKA

#### **SADRŽAJ**

Cilj rada je bio da se ispita kapacitet vezivanja prirodnog i jonski izmenjenog oblika klinoptilolita za  $^{137}\text{Cs}$  u rastvoru visoke kiselosti ( $\text{pH}=2-3$ ), pripremljenom tako da elektrolitički bude sličan sadržaju u želudcu svinja. Ispitivanje sa manjom koncentracijom klinoptilolita (100 mg) je pokazalo da se polovina od početne aktivnosti  $^{137}\text{Cs}$  sorbuje za 6 sati (48 %). Produžavanjem vremena kontakta ne dolazi do smanjivanja aktivnosti rastvora. Korišćenjem veće koncentracije sorbenta (300 mg) ravnotežni odnos jona  $^{137}\text{Cs}$  u čvrstoj i tečnoj fazi se takođe uspostavlja posle 6 sati, pri čemu se sorbuje 75 % početne aktivnosti. U drugom eksperimentu je izvršeno poređenje efikasnosti prirodnog klinoptilolita i pripremljenih monojonskih formi natrijum ( $\text{Na}^-$ ) i amonijum ( $\text{NH}_4^-$ ) klinoptilolita. Količina sorbenta je povećana na 500 mg a zadržano je optimalno vreme kontakta od 6 sati. Dobijeni rezultati su pokazali da je njihova efikasnost u vezivanju  $^{137}\text{Cs}$  veoma bliska (84-85 %) i ukazuju da u cilju izrade protektora, nije neophodno prevođenje prirodnog klinoptilolita u monojonske oblike.

