



PHYSICAL CHEMISTRY 2008

Proceedings

*of the 9th International Conference on Fundamental
and Applied Aspects of Physical Chemistry*

Volume II

The Conference is dedicated to the 200th Anniversary of the University in Belgrade



UNIVERSITY OF
BELGRADE
1808 • 2008

September 24-26, 2008,
Belgrade, Serbia



PHYSICAL CHEMISTRY 2008

Proceedings

*of the 9th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry*

Volume II

ISBN 978-86-82475-13-2
Title: Physical Chemistry 2008. (Proceedings)
Editor: Prof. dr A. Antić-Jovanović
Published by: The Society of Physical Chemists of Serbia, Studentski trg 12-16, P.O.Box 137, 11001 Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For publisher: Prof. dr S. Anić, president of the Society of Physical Chemists of Serbia
Printed by: "Jovan" Printing and Published Comp;
250 Copies; Number of Pages: x + 301 (469-770);
Format B5; Printing finished in September 2008.
Text and Layout: Aleksandar Nikolić
250 – copy printing

THE EVALUATION OF RADIONUCLIDES REMOVAL USING CLINOPTILOLITE, HYDROXYAPATITE AND THEIR MIXTURES

I. Smičiklas, S. Dimović, M. Šljivić and I. Plečaš

The Vinča Institute of Nuclear Sciences, P.O.Box 522, 11001 Belgrade, Serbia

Abstract

The sorption properties of clinoptilolite and hydroxyapatite towards Cs^{1+} , Co^{2+} , and Sr^{2+} ions were compared, under the same experimental conditions. Cs^{1+} was preferably sorbed by natural clinoptilolite. Conversely, synthetic hydroxyapatite exhibited higher sorption capacities for Co^{2+} and Sr^{2+} , while the sorption of Cs^{1+} was negligible. It was shown that, as a consequence of different affinity towards investigated cations, application of mixed clinoptilolite/hydroxyapatite sorbent represents a good strategy for the purification of effluents containing a mixture of Cs^{1+} , Co^{2+} and Sr^{2+} .

Introduction

Sorption technologies in liquid radioactive waste management, based on the use of selective sorbents, have been developed rapidly due to simplicity of the technology and necessary equipment and possibility of obtaining good liquid/solid radioactive waste ratio [1].

The sorption studies are generally focused on an individual sorbent, and single metal solution, while little effort has been done to perform the studies with the combinations of different sorbents and/or sorbates. The objective of the present work was to compare the effectiveness of local clinoptilolite (Serbia), synthetic hydroxyapatite (HAP) and their mixtures in decontamination of mixed metal solutions ($^{60}\text{Co}^{2+}$, $^{90}\text{Sr}^{2+}$ and $^{137}\text{Cs}^{1+}$).

Materials and Methods

Zeolite sample was obtained from the Zlatokop mine near Vranjska Banja, Serbia. XRD analysis of the sample have shown that it consists mainly of clinoptilolite (>90%), with quartz and albite as impurities [2]. A fraction of particles 200 - 250 μm in size was used. Low-crystalline hydroxyapatite (HAP) sample was synthesized at room temperature, by neutralization method [3].

Sorption experiments were conducted using inactive forms of metal cations. As most real wastes consist of mixtures of various contaminants, a solution containing 100 mg/dm^3 of each contaminant (Co^{2+} , Cs^{1+} and Sr^{2+}) was prepared. This solution was shaken with HAP, clinoptilolite or their mixtures prepared at different HAP/clinoptilolite ratios, at initial pH 5, solid to solution ratio of 1: 200, for 24 hours, at room temperature ($20 \pm 1^\circ\text{C}$). The suspensions were filtrated, and the metal concentrations were determined using Perkin Elmer Analyst 200 Atomic Absorption Spectrometer.

Experimental Results

Table 1. presents the mass ratios of sorbents, as well as the percentages of metal cations removed and final solution pH values.

Table 1. Mass ratio of HAP and clinoptilolite and the amounts of metal ions removed from the mixed metal solution.

| HAP/Clin. ratio | Cation sorbed (%) | | | |
|--------------------|-------------------|------------------|------------------|-------|
| | Cs ¹⁺ | Sr ²⁺ | Co ²⁺ | Total |
| 1 : 0 | 0.0 | 53.6 | 51.3 | 35.9 |
| 5 : 1 | 31.9 | 49.1 | 43.2 | 41.6 |
| 3 : 1 | 47.3 | 48.0 | 43.5 | 46.2 |
| 2 : 1 | 65.9 | 45.8 | 41.8 | 50.8 |
| 1 : 1 | 78.5 | 41.7 | 35.1 | 51.0 |
| 1 : 2 | 89.6 | 35.8 | 25.8 | 49.2 |
| 1 : 3 | 91.9 | 33.3 | 16.7 | 45.9 |
| 1 : 5 | 93.6 | 31.0 | 18.0 | 46.1 |
| 0 : 1 | 95.6 | 20.8 | 5.6 | 39.0 |

Synthetic HAP powder, applied as an individual sorbent, retained 53.6 and 51.3 % of Sr²⁺ and Co²⁺, whereas the sorption of Cs¹⁺ was in the range of experimental error. The previously determined HAP selectivity towards Sr²⁺ and Co²⁺ from their single metal solutions was the same, while the calculated maximum sorption capacities were 26 mg/g and 20 mg/g, respectively [3, 4]. HAP selectivity towards divalent metal cations is a result of the ion-exchange process with Ca²⁺ ions [5]. Crystal radii of strontium (1.13 Å) and cobalt (0.72 Å) slightly differ from Ca²⁺ crystal radius (0.99 Å); therefore these cations can substitute Ca²⁺ in the HAP crystal lattice. On the other hand, the crystal radius of Cs¹⁺ (1.69 Å) is much larger, which explains why it cannot be effectively sorbed. Similar results were reported by Krajzler and Narbutt [6], for biogenic apatite. This sorbent was efficient for the removal of radionuclides of strontium, as well as europium and trivalent actinides, but not of cesium due to its large ionic radius and low charge.

In the case of clinoptilolite, although various cations are available for ion exchange (Ca²⁺, Mg²⁺, Na⁺, K⁺), the hydrated ionic radii of sorbates were found to be the most influential concerning removal efficiency. Monovalent cations, contrary to divalent ones, have larger ionic but smaller hydrated ionic radii, and with fewer and weakly bonded water molecules they move more freely into and out of the clinoptilolite channels [7]. The sequence of hydrated ionic radii of Cs¹⁺, Sr²⁺ and Co²⁺ (3.29, 4.12, 4.23 Å, respectively) follows the sequence of experimentally determined clinoptilolite capacities: Cs¹⁺ (48.4 mg/g) > Sr²⁺ (9.8 mg/g) > Co²⁺ (2.8 mg/g) [2]. From the results of this study, it can be concluded that clinoptilolite selectivity towards examined cations from their mixture, followed the same trend (95.6 % of Cs¹⁺, 20.8 % of Sr²⁺ and 5.6 % of Co²⁺).

HAP sorption capacity towards Co^{2+} ions from mixed metal solution is ten times higher than the value obtained for clinoptilolite. Furthermore, although among various investigated divalent cations (Pb, Cd, Zn, Sr) HAP exhibit lowest sorption capacity for Sr^{2+} [3], it is still about three times better sorbent of Sr^{2+} than clinoptilolite.

Considering removal efficiency of various HAP/clinoptilolite mixtures, as the fraction of clinoptilolite phase increased, the sorption of Cs^{1+} increased, while the sorption of divalent cations decreased. The highest total percentage of metal ions removed from the solution (51%) was obtained at a HAP/clinoptilolite mass ratio of 1:1.

Conclusion

HAP is more selective towards divalent Sr and Co ions, while clinoptilolite towards monovalent Cs. Sorption of Cs^+ on hydroxyapatite is negligible. If the mixed wastes, containing all three metal cations, have to be treated, the mixture of HAP and clinoptilolite will give better results than each of the sorbents alone. For the wastes containing equivalent concentrations of Cs^{1+} , Co^{2+} and Sr^{2+} , the best total removal efficiency was achieved at HAP/ clinoptilolite =1:1 ratio.

References

- [1] N. V. Elizondo, E. Ballesteros, B. I. Kharisov, *Appl. Radiat. Isotopes*, 2000, **52**, 27-30.
- [2] I. Smičiklas, S. Dimović, I. Plečaš, *Appl. Clay Sci.*, 2007, **35**, 139-144.
- [3] I. Smičiklas, A. Onjia, S. Raičević, Đ. Janačković, M. Mitrić, *J. Hazard. Mater.*, 2008, **152**, 876-884.
- [4] I. Smičiklas, S. Dimović, I. Plečaš, M. Mitrić, *Wat. Res.*, 2006, **40**, 2267 – 2274.
- [5] F. Monteil-Rivera, M. Fedoroff, in: *Encyclopedia of Surface and Colloid Science*, Marcel Dekker. Inc., New York, 2002, p.1-26.
- [6] J. [Krejzler](#), J. [Narbutt](#), *Nukleonika* 2003, **48**, 171-175.
- [7] R. M. Woods, M. E. Gunter, *Am.Mineral.* 2001, **86**, 424–430.