SORPTION AND KINETICS OF Eu(III) ON BENTONITE/PHYLLITE BARRIERS

Joanna KYZIOŁ-KOMOSIŃSKA[1], Monika FABIAŃSKA[2], Janusz JANECZEK[2]

[1]*Institute of Environmental Engineering, Polish Academy of Sciences, ul. Skłodowskiej-Curie 34, 41-819 Zabrze, Poland; joanna.kyziol-komosinska@ipis.zabrze.pl*
[2]*University of Silesia, Faculty of Earth Sciences, ul. Będzińska 60, 41-200 Sosnowiec, Poland*

Introduction

The key function of a nuclear waste repository is to isolate radionuclides from the biosphere by preventing their migration via groundwater to the surrounding environment (IAEA 2011). Since the distribution, mobility, and bioavailability of radionuclides are controlled by the sorption properties of barrier materials, it is vital to find efficient and mechanically and thermally stable, high capacity sorbents (Itälä 2009, Yang et al. 2014). Currently, bentonite or bentonite mixed with quartz sand is used in the majority of programs for radioactive-waste disposal. However, bentonites undergo dehydration, mechanical degradation, and structural transformation decreasing their sorption capacity at a temperature above 100°C expected at the contact with waste containers. Previous studies show that phyllites, while less efficient sorbents than bentonites, have high sorption capacity for actinides and some nuclear fission products. Moreover, they are thermally stable up to 400°C. Therefore, they can be considered as a component of a mixture with bentonite instead of sand to take advantage of phyllite sorption.

The main goal of the research is to determine the removal efficacy of Eu(III) ions - an analog of nuclear fission-originated isotopes of rare earth elements and analog of Am - by bentonite/phyllite (B/Ph) mixtures compared to bentonite as potential repository buffer and/or backfill materials for engineered barriers in a radioactive waste repository. Moreover, the research allowed for choice the Ph/B mixture of the best removal efficacy of Eu(III) ions at with high content of phyllite.

Samples and methods

Sorbents

Mixtures of B/Ph at ratios 75%/25%, 50%/50% and 25%/75% (wt.) were prepared. Bentonite was from the Miocene Kopernica deposit in Slovakia and phyllite from the Dewon–Pokrzywna phyllite deposit from the northern base of the Opava Mountains in Eastern Polish Sudetes. The main properties which decide on the sorption properties are shown in Table 1.

Table 1. *Physico-chemical properties of Ph/B mixtures.*

	B	B/Ph=75/25	B/Ph=50/50	B/Ph=25/75	Ph
Specific surface area, m^2/g	58.24	44.82	31.24	18.55	3.64
Cation exchange capacity, $cmol_+/kg$	79.55	60.44	42.11	21.61	3.55
pH	7.41	7.15	6.97	6.87	6.85
pH_{PZC}	5.95	6.01	6.08	6.14	6.21

Methods of sorption/desorption

Sorption experiments were performed with the batch equilibration method under atmospheric pressure and at room temperature from Eu(III) initial concentration ranging from 0.005 mg/L to 205 mg/L at pH of 4.5 and 7.0 and solid (S):solution (L) ratio of 1:100. The initial (C_0) and equilibrium (C_{eq}) concentrations of Eu(III) were measured either by the ICP-OES or by the ICP-MS spectrometry depending on the Eu(III) concentration.

The results allow to calculate removal efficacy (RE) of Eu(III) ions, $RE=(C_0-C_{eq})/C_0 \cdot 100$ (%) and determine of initial concentration ranges for which Eu(III) ions were sorbed completely, i.e. RE=99.9% and $C_{eq} \leq 0.005$ mg/L. Sorption rate constants were determined for C_0 of 10 mg/L and 205

mg/L during time ranging from 1 to 1440 min and were estimated from the pseudo-first order (PFO) and pseudo-second order (PSO) equations using the non-linear method.

Results

Percentage of bentonite in B/Ph mixture strongly affected the surface area and cation exchange capacity of them while pH and pH_{PZC} have similar values as bentonite (Tab. 1).

The results of Eu(III) ions bonding on B/Ph mixture show that full sorption ranged from 0.001–18.51 mg/L (B/Ph=75/25) to C_0=0.001–4.5 (B/Ph=25/75) at pH 4.5 and from 0.001–38.95 mg/L (B/Ph=75/25) to C_0=0.001–10.1 mg/L (B/Ph=25/75) at pH 7.0. Compared to B very good results have been found for B/Ph mixture of 75/25 and 50/50 at both pHs.

Effect of pH was also observed for Eu(III) removal efficacy by the B/Ph mixture. At C_0 of 50 mg/L and pH 4.5 removal efficacy ranging from 99.8% to 81.76% along to reduction of bentonite in the mixture while at pH 7.0 removal efficiency was at a similar level as bentonite (99.5–99.9%). On the other hand at C_0 of 205 mg/L removal efficacy has ranged from 84.25% (B/Ph=75/25) to 33.8% (B/Ph=25%/75%) at pH of 4.5 and from 98.23% to 58.54% at pH of 7.0 (Fig.1A). The results indicated that very good sorption properties were obtained at 50% B in the B/Ph mixture.

The kinetic study shows that experimental data are described by PFO and by the PSO model at C_0 of 10 mg/L and only by the PSO model at C_0 of 205 m/L. The PSO model is in agreement with chemisorption being the rate controlling step. The rate constant is strongly dependent on the C_0 and it decreases with the increasing C_0 but it is B/Ph mixture composition-independent.

A

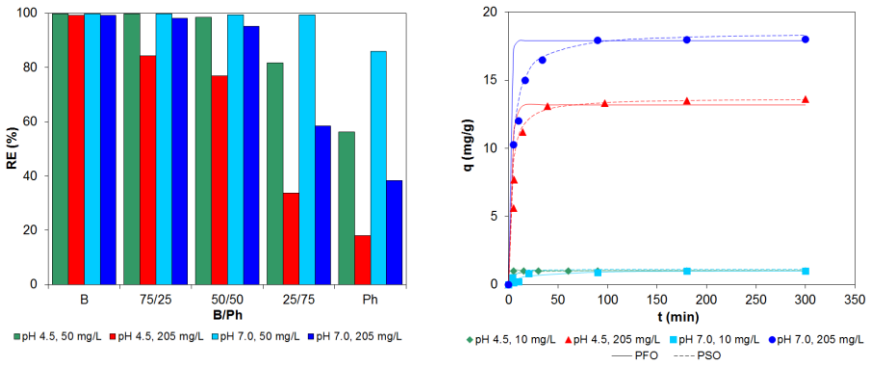

Figure 1. *Removal efficacy (RE) of Eu(III) by B/Ph mixture (A) and the PFO and PSO kinetic sorption models to Eu sorption data by B/Ph=50/50 (B).*

Conclusions

The results of removal efficacy of Eu(III) by B/Ph mixture and sorption process rate indicated that percentage of B of 50% in the B/Ph mixture is enough and ensures sufficient reduction and delay of the Eu(III) migration from the radioactive waste.

Acknowledgments

The National Science Center (Poland) financial support, grant 2014/15/B/ST10/02281 is acknowledged.

References

IAEA Safety Standards 2011. Disposal of radioactive waste. Specific Safety Requirements No. SSR-5, Vienna.

Itälä, A. 2009. Chemical evolution of bentonite buffer in a final repository of spent nuclear fuel during the thermal phase. VTT Publications 721. 78p. + app. 16p. Espoo.

Yang, T., Pusch, R., Knutsson, S. Xiaodong, L. 2014. The assessment of clay buffers for isolating highly radioactive waste. WIT Transactions on Ecology and The Environment, 180, 404-413.