Immobilization of U and Th by Pb-activated zeolite

The objective of this project is experimental investigation of U and Th immobilization through co-precipitation with lead apatite induced on Pb-activated zeolite. This will provide a theoretical basis for future development of new reactive geochemical barrier for use in radioactive element repositories or as container fillers.

It is hypothesized that:

- by appropriate selection of zeolite and activation methodology, it is possible to produce Pb-activated zeolite that is environmentally safe (no Pb release to the environment) while reactive under contamination conditions of U and Th;
- the precipitation of lead apatite (pyromorphite Pb_5PO_4Cl) induced on Pb-activated zeolite, from solutions containing U(VI) and Th, will effectively immobilize these elements through encapsulation in the lead phosphate structure;
- it is possible to produce an environmentally safe reactive geochemical barrier from a mineral mixture of hydroxylapatite (as a source of phosphate) and Pb-activated zeolite (as a source of lead) for effective immobilization of U(VI) and Th from aqueous solutions by co-precipitation with pyromorphite on zeolite.

Research on fillers for containers used in geological repositories for radioactive waste as well as research on fillers for storage spaces is continuously a hot topic. The main rationale for this research is the recently discovered fact that UO_2 & Th can be effectively and efficiently removed from aqueous solutions by co-precipitation with Pb phosphates in the form of Pb-apatite. The fact that Pb-apatite is a relatively mechanically and thermally resistant mineral, exhibiting very low solubility and, in addition, containing lead, makes it an excellent material for encapsulation of radioactive elements. The relatively strong sorption of Pb on zeolites makes Pb-activated zeolite likely to be an environmentally safe reservoir of Pb available for U & Th immobilization reactions in environmental emergencies. Meanwhile, published results on hydroxylapatite $Ca_5(PO_4)_3OH$ indicate that it may be a good source of PO_4^{3-} ions for this reaction. All these observations, so far disconnected from each other, prompt us to study the mechanisms of U & Th removal from solutions by crystallization of Pym triggered by reaction of phosphates with Pb-activated zeolite.

This project is within the discipline of experimental mineralogy and geochemistry. It involves experimental study of mineral-water interactions, including model laboratory experiments, using synthetic Pym precipitated from aqueous solutions at ambient temperatures, carefully controlled conditions and using pure chemicals. The PI is aware of the concerns and special safety requirements associated with the use of U. In all cases, non-radioactive Th and depleted U at low concentrations will be used for safety. Prior to the experiments with UO_2, each experimental setup will be tested by experiments using Th. This approach will allow potential technical problems associated with experiments to be solved in advance. The experiments with Th will be run at the laboratories of the Department of Mineralogy, Petrography and Geochemistry, AGH University of Kraków (Poland), under the direct supervision of the PI. Experiments with U will be run at the Energy Frontier Research Center, Materials Science of Actinides (University of Notre Dame, Indiana, USA) under the joint supervision of the PI and Dr. Peter Burns. All planned experimental setups and analytical techniques for solutions and crystalline phases have been previously used and tested in both laboratories on similar setups and systems, including earlier collaboration on experiments with U.

The novelty of the proposed research on potential future technological solutions is contained in the following contributions:

- A novel method for removal of Th and UO_2 from water is proposed by heterogeneous precipitation of solid, crystalline and sparingly soluble compound of apatite structure: pyromorphite $Pb_5(PO_4)_3Cl$ partially substituted by Th and UO_2, when Pb-sorbed zeolite is a well-controlled, environmentally safe reservoir and source of Pb.
- The construction of a reactive filler composed of a mineral mixture of hydroxylapatite and Pb-activated zeolite is proposed and will be tested with potential future applications for reactive barriers or container fillers in mind.