Retardation of rare earth metals in clay barriers – innovative application of centrifuge modeling and laser ablation ICP-MS

Wendy Timms[a,b], M. Jim Hendry[b], Jason Muise[b], and Robert Kerrich[b] and R. Ian Acworth[a]

[a] National Centre for Groundwater Research and Training, Water Research Laboratory, School of Civil and Environmental Engineering, University of New South Wales, Manly Vale, NSW 2015, AUSTRALIA (* corresponding author: w.timms@wrl.unsw.edu.au)

[b] Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK, S7N 5E2, CANADA

Quantifying the retardation (R_d) of reactive solutes as they migrate through low permeabilty clay-rich media is difficult, thus motivating this study to assess the viability of combining centrifuge modeling and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) techniques. The transport of rare earth metals (eg Th) has implications on the predictability of trace elements and long-lived radioisotopes in subsurface environments, providing an analogue for trivalent actinides and fission products of U and Pu. The use of natural and engineered clay barriers in the subsurface can retard migration of these species.

This work demonstrates an innovative application of centrifuge techniques that will be possible in the new National Centre for Groundwater Research and Training (NCGRT). A geotechnical centrifuge facility (r_{max} = 0.7 m, N_{max} = 300 x gravity) with a core permeameter module will be commissioned during 2010 at the UNSW Water Research Laboratory.

This experiment used a small scale UFA centrifuge (r = 0.087 m) based at the University of Saskatchewan. An influent solution containing Cl^-, trace metals and lanthanide species flowed at 1.0 $mL.h^{-1}$ through an undisturbed clay-rich core sample (33 mm dia. × 50 mm long) mounted in a UFA Beckman centrifuge operating at 3000 rpm (N = 876 × gravity). During the 87 day experiment, the hydraulic conductivity of the core was 3.4 × 10-10 $m{\cdot}s^{-1}$. Effluent breakthrough data indicate the R_d of Tl to be 10; incomplete breakthrough data for ^{145}Nd and ^{171}Yb suggest R_d values of >>75 and >>85, respectively. At the completion of the transport experiment, longitudinal sections of the core solid were analyzed for ^{145}Nd and ^{171}Yb using a Cetac Laser Ablation System coupled with an ICP-MS. The longitudinal core sections yielded R_d values of >10,000 for ^{145}Nd and ^{171}Yb.

Centrifuge modelling can overcome limitations of traditional batch tests in clay-rich media as follows: the flow through column testing removes desorbed species from reaction sites; S:L is maintained at *in situ* values such that surface areas are not artificially increased; and phase separation is not necessary because effluent samples can be sampled directly and laser ablation occurs directly on the solid phase. The chemical properties of the system occur in real time during centrifugation and are not scaled. It was demonstrated that the solute residence time during the experiment was significantly greater than the time required for chemical reaction, based on available kinetic data.

The value of coupling these techniques to obtain R_d values for a wide range of reactive solutes was evident with relatively rapid testing of small scale, low hydraulic conductivity core samples. Highly retarded migration of ^{145}Nd and ^{171}Yb suggest this aquitard and similar deposits could be used to control the long-term migration of reactive solutes and may be a viable media for high-level waste, provided identification of flow and sorption mechanisms can account for varying R_d values.

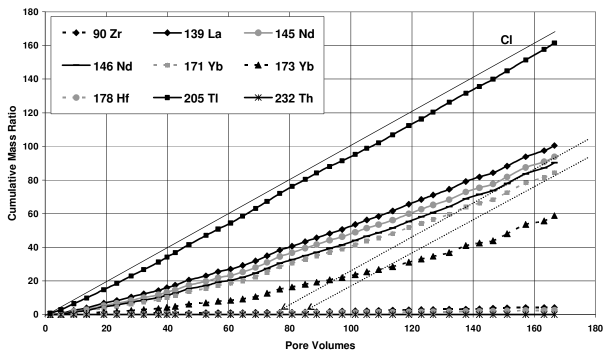

Fig. 1. Effluent plotted as CMR (cumulative mass ratio). Cl and reactive solute Tl exhibit complete breakthrough, with R_d values of 5 and 12, respectively. Transport of Zr, Hf, and Th are highly retarded. Various lanthanide species exhibit partial breakthrough. The estimation of minimum R_d values for partial breakthrough of ^{145}Nd and ^{171}Yb are shown with a 1:1 line extended from the last effluent point to the X axis.

References

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