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Mobility of Ni in carbonate aquifersC. KJØLLER^{1,2}, F. LARSEN¹, S. JESSEN¹ AND D. POSTMA¹¹Environment & Resources DTU, Technical University of Denmark (clk@er.dtu.dk; fl@er.dtu.dk; soj@er.dtu.dk; djp@er.dtu.dk)²RAMBØLL, Virum, Denmark (clak@ramboll.dk)**Introduction**

High Ni concentrations in groundwater are a problem in the carbonate aquifers that are part of the Copenhagen water supply. The aim of the present study is to investigate the mobility of Ni in these carbonate aquifers.

Laboratory studies

Batch sorption experiments were carried out at constant P_{CO_2} and Ca activity in order to construct sorption isotherms describing the sorption of ^{63}Ni on natural glauconitic Selandian Greensand, Danian Limestone and Maastrichtian Chalk sediment samples. Sorption experiments were also carried out on pure samples of clay and calcite. The results show that the sorption density (per m^2 BET surface area) is higher on carbonate samples (>98% $CaCO_3$) compared to clay-rich samples (>15% clay). However, on a mass-by-mass basis, the clay-rich samples were capable of binding more Ni due to the generally greater BET surface area of these samples.

Under varying Ca activity, Ni sorption to the carbonate samples was found to be a function of the Ca activity. Modelling with PHREEQC 2.0 showed that the Ca dependency could be approximated by a simple Ca-Ni exchange reaction and fitting of a single exchange coefficient for the carbonate samples.

Field implications

Distribution coefficients (K_d) for the natural sediments were calculated to vary between 7-20 L/kg for the Limestone sediments and up to 28-92 L/kg for the Greensand sediments. Using average values for the bulk density (1.75 kg/L) and porosity (0.34) of the aquifer matrix, this corresponds to an average retardation coefficient (R) of ca. 50 for transport of Ni in the Limestone aquifer matrix.

The studied aquifers are, however, double permeable media in which preferential flow takes place in fractures of the rock. In order to evaluate the mobility of Ni in such double permeable aquifers, conceptual numerical modeling was carried out with FRAC3DVS. In the numerical models, physical properties of the aquifers, such as distance between fractures and fracture aperture, were estimated on the basis of geophysical borehole logs and pumping tests.

The results of the numerical modeling show that the mobility of Ni in the carbonate aquifers is not only dependent on the sorption to the aquifer sediments, but also dependent highly on the physical properties of the rock, such as distance between fractures and fracture aperture.

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Bridging the gap in metal ion sorption studies with planar oxidesC.F. CONRAD¹ AND M.J. KELLEY^{2,3}¹Virginia Institute of Marine Science, College of William & Mary, Gloucester Point, VA, USA (cfconrad@vims.edu)²College of William & Mary, Department of Applied Science, Williamsburg, VA, USA³Thomas Jefferson National Lab, Applied Research Center, Newport News, VA, USA (mkkelley@jlab.org)

We have developed a novel technique for investigating metal-ion sorption through the use of planar oxides. Planar oxides are thin, flat oxide coatings of uniform thickness (<10⁴ cm) prepared on an underlying metal substrate. Because planar oxides are formed as thin layers on a support, they offer several advantages over the often used bulk oxides for metal-ion sorption studies. They can be characterized by a variety of spectroscopic and microscopic techniques, and because the oxide layer is present as a coating, they are more similar to natural oxide coatings found on sediment surfaces. The major advantage in using planar oxides is that because the oxide is bound to a substrate, they can be emplaced directly in natural sediments, allowed to react, and subsequently returned to the lab where the metal complexes formed on them can be thoroughly characterized. These complexes can then be directly compared to complexes formed on identical materials under controlled laboratory conditions, thus bridging the gap between laboratory and field studies.

Previously, we have demonstrated the usefulness of planar oxides in laboratory studies by comparing Pb(II) sorption to planar and bulk $\gamma-Al_2O_3$ [1]. The objectives of this work is to build upon those results and develop the planar oxides as a field deployable method for investigating metal-sediment interactions in natural aquatic systems. Planar oxides were placed in a series of solutions and solids designed to systematically vary the natural complexity of the solid and solution phases. Mesocosm experiments were also designed to simulate field emplacement of the planar oxides. Metal sorption complexes, specifically Pb(II), formed on the planar oxides under each set of conditions were characterized using ToF-SIMS, XPS, and AFM and/or SEM. Variations in Pb(II) sorption due to changes in the solid and solution phases, specifically the organic content, were observed. This work demonstrates the unique capability of using planar oxides for sorption studies in both laboratory and natural environments and to provide new information that will aid in strengthening the connection between molecular level observations and field scale phenomenon.

References

- [1] Conrad, C.F., Chisholm-Bruase, C. J., and Kelley, M. J. (2002) *JCIS* **248**, 275-282.