

Heavy metal sequestration in nanoporous minerals

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Introduction

The nanoporous minerals sitinakite (sodium titanium silicate hydrate) and umbite (potassium zirconium silicate hydrate) are a pair of highly selective, fast ion conductor that are being tested for targeted removal of cesium and strontium from high level waste solutions [1]. In addition to their environmental applications, titanium silicates, and similar zirconium and yttrium silicates, have many technological uses including battery materials, hydrogen storage, and rare earth and transition element catalysts for gasses and petrochemicals [2]. Sitinakite and umbite are stable under a wide range of pressure, temperature, and chemical conditions making them potential host materials to perform selective chemistries in extreme environments. We are determining the fundamental structural properties governing ion selectivity in these unique minerals with emphasis toward understanding their energy related applications.

Results and Discussion

The studied materials exhibit multiple ion exchange steps that serve to enhance ion selectivity, and these steps are controlled by the host crystalline framework as well as the chemistry and hydration state of the native and ion exchanged compounds. To determine the exchange mechanisms, we collected high resolution in situ Raman spectroscopy, X-ray diffraction and computational data to capture the ion exchange processes from the natural forms, to the enhanced hydrogen form, and finally to the heavy metal exchanged structure.

The results from these ion exchange studies (using Y, Eu, Gd, Cu, Ni, Cs, Sr) indicates that a range of exchange dynamics exist within a single host mineral. Specifically in sitinakite the exchange dynamics are significantly different for each REE tested (Y, Gd, Eu). This was somewhat surprising as all three elements possess the same valence charge, similar ionic radii ($\pm 0.05 \text{ \AA}$), and similar hydration states in aqueous solutions (CN=8-9). TGA/DSC curves for before and after exchange states showed significant variation in nanopore H₂O capacities, indicating that the hydration states of the element and valence electron conduction have an effect on the sequestration mechanisms and pathways through the porous host structure. The selectivity hypothesis concerning the effects of internal hydration and valence electron conduction has been previously proposed [3,4], however the mechanisms of framework conformational changes, presence of intermediate structural states, and diffusion pathways have only been reported for a handful of materials and is the main area of focus for this study.

- [1] Wilmarth (2011) *Solvent Extraction and Ion Exchange* **29**, 1-48.
 [2] Rocha (2000) *European Journal of Inorganic Chemistry* **5**, 801-818.
 [3] Clearfield (2006) *Journal of Materials Science* **41**, 1325-1333.
 [4] Celestian (2008) *Journal of the American Chemical Society* **130**, 11689-11694.

Implementing Stable Isotope Fractionation of Two Elements in Reactive Transport Models to Validate Novel Assessment Methods for Biodegradation in Aquifers

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Compound-specific stable isotope analysis has been established as a viable method to detect and quantify *in situ* biodegradation. Even the identification of dominant degradation pathways is possible if stable isotope data of two elements are combined in the so-called two-dimensional isotope analysis. These assessment methods can be applied at field sites where degradation occurs via a single dominating pathway that does not change qualitatively over space. If spatially varying redox conditions lead to multiple degradation pathways, each associated with a different zone along a groundwater flow path, the application of current stable isotope based methods is not straight forward. For such conditions, novel analytically derived concepts are presented which allow the use of two-dimensional isotope analysis for estimating the share of two competing degradation pathways on overall degradation at a specific location as well as along a given flow path interval. In order to test these novel estimates, reactive transport simulations implementing a generic benzene plume/degradation scenario with aerobic and anaerobic degradation as exemplary degradation pathways were performed using the numerical model GeoSysBRNS [1]. Simulations considered besides biochemical reactions also the associated concurrent fractionation of both carbon and hydrogen isotopes. Resulting isotope signatures were used to estimate pathway contributions which were then compared to actual contributions calculated from simulated reaction rates. Estimates were very accurate for one-dimensional plume scenarios. For two-dimensional plume scenarios, estimates for pathway specific contributions to overall biodegradation were most accurate along the center of the plume, but lost accuracy towards the fringe, where transversal mixing processes were shown not only to affect contaminant concentration but also associated stable isotope signatures [2]. Total estimates could be significantly improved if additional observation points were taken into account along the flow path. Reactive transport models that incorporate the concurrent fractionation of two elements are helpful in validating and testing novel assessment methods based on two-dimensional stable isotope data and can also be applied to field sites where two-dimensional isotope data are available, improving the expressive power of the model by considering the concurrent fractionation of two elements as an additional process parameter.

- [1] Centler (2010) *Computers & Geosciences* **36**, 397-405.
 [2] Thullner (2012) *Organic Geochemistry* **42**, 1440-1460.