



Iodide uptake by negatively charged clay interlayers?



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ABSTRACT

Understanding iodide interactions with clay minerals is critical to quantifying risk associated with nuclear waste disposal. Current thought assumes that iodide does not interact directly with clay minerals due to electrical repulsion between the iodide and the negatively charged clay layers. However, a growing body of work indicates a weak interaction between iodide and clays. The goal of this contribution is to report a conceptual model for iodide interaction with clays by considering clay mineral structures and emergent behaviors of chemical species in confined spaces. To approach the problem, a suite of clay minerals was used with varying degrees of isomorphic substitution, chemical composition, and mineral structure. Iodide uptake experiments were completed with each of these minerals in a range of swamping electrolyte identities (NaCl, NaBr, KCl) and concentrations. Iodide uptake behaviors form distinct trends with cation exchange capacity and mineral structure. These trends change substantially with electrolyte composition and concentration, but do not appear to be affected by solution pH. The experimental results suggest that iodide may directly interact with clays by forming ion-pairs (e.g., $\text{NaI}_{(\text{aq})}$) which may concentrate within the interlayer space as well as the thin areas surrounding the clay particle where water behavior is more structured relative to bulk water. Ion pairing and iodide concentration in these zones is probably driven by the reduced dielectric constant of water in confined space and by the relatively high polarizability of the iodide species.

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1. Introduction

Subsurface clay formations are one of the major rock types being considered by several countries for geologic disposal of nuclear waste. Even when clays will not be used as host rock, engineered barrier materials often include a compacted bentonite buffer surrounding a waste package for chemical and structural stabilization. Clays are an ideal material as they possess low permeabilities where ion transport is dominated by diffusion. Clays also possess high sorption capacities for many cations present in nuclear waste. The high cationic sorption capacities are caused by the simultaneous presence of negatively charged cation exchange sites on the planar surfaces of clay layers, and amphoteric surface complexation sites on the edge of the layer. However, the negative structural charge minimizes anion interactions with clays. Iodine is expected to be present as iodide under the reducing conditions of waste disposal in clay (Whitehead, 1984). The assumed lack of interaction

between iodide and clays causes iodine-129 to have earlier breakthrough times and make a larger contribution to predicted dose from a deep geological repository compared to other radionuclides (Altmann, 2008; Mallants et al., 2001). Performance assessment calculations show that even a small retention capability of clay materials for iodide can make a substantial difference in total dose predictions (Altmann, 2008).

A growing body of work points to the potential presence of a weak interaction between iodide and clays (Bazer-Bachi et al., 2006; Jansson and Eriksen, 2004; Van Loon et al., 2003) (Descostes et al., 2008; Wittebroodt et al., 2008; Savoye et al., 2012). The weakness of the interaction has made experimental measurements somewhat contradictory. Several major hypotheses exist to explain observed interactions, including: isotopic dilution with native iodine (Tournassat et al., 2007; Gaucher et al., 2004), co-precipitation or uptake into carbonates (Claret et al., 2010; Montavon et al., 2014), the presence of organic matter (Fuge and Johnson, 1986; Hu and Moran, 2005; Kaplan, 2003; Li et al., 2014), uptake to ancillary minerals (Couture and Seitz, 1983; Fuhrmann et al., 1998), and impure radiotracers or unconsidered alterations to iodide redox state (Glaus et al., 2008; Tournassat

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et al., 2007; Hu et al., 2005). All of these explanations rely on the premise that iodide does not interact with clays in any meaningful way, and the observed iodide uptake and retardation are caused by other components or processes occurring in natural clay samples.

Attempts to gain a mechanistic understanding of iodide interaction with clays and clay bearing soils are rare. In two separate studies iodide uptake tends to increase with decreasing pH both for pure illite and a natural soil sample (Kaplan, 2003; Kaplan et al., 2000). This is consistent with an outer sphere interaction with highly protonated, positively charged metal oxides and clay edge sites. However, most diffusion studies and porewater analysis from clay mineral systems have pH values >7 (Gaucher et al., 2006) limiting this mechanism in natural systems. As pointed out by others (Tournassat et al., 2007), if edge complexation was controlling iodide behaviors similar responses would be expected between clays with similar edge charge behavior such as illite and montmorillonite. But illite has been shown to have much higher uptake than montmorillonite (Kaplan et al., 2000).

The goal of this study is to consider interactions between iodide and clays beyond those described in classical interpretations of clay surface chemistry (Bradbury and Baeyens, 1997; Baeyens and Bradbury, 1997). This new view requires a different experimental approach. Most studies examining iodide interactions with clay minerals use clay samples from a specific formation of interest to a national nuclear waste disposal program, or on purified clay minerals generically relevant to waste disposal, most commonly montmorillonite and illite. The focus on these clays and clay minerals is pragmatic and directly useful; however, it limits data interpretation within the confines of classical clay surface chemistry models and/or with K_D values. Single clay studies remove the ability to compare uptake as a function of other key clay characteristics, including: structural charge variability, different layer structures, and variable nanopore scale chemistry caused by constrained space within the clay mineral (Miller and Wang, 2012). In this study, we focus on a series of clay minerals, and measure iodide uptake under several swamping electrolyte strengths and compositions. Iodide uptake is reported as a function of lattice substitution (represented by the cation exchange capacity value, CEC) and as a function of clay structure. Two classes of clay structure are used in these experiments, layered and fibrous clays. The results imply a mechanism including ion-pair formation and the concentration of iodide within the interlayers and other confined pore spaces.

2. Materials and methods

2.1. CEC and surface area determinations

The surface areas and CEC of the clay minerals were measured using N_2 BET (Brunauer et al., 1938), methylene blue exchange, and $BaCl_2$ exchange. Nitrogen (N_2 gas) is generally considered unable to enter the interlayer porosity and only represents the external surface area of clays. Methylene blue adsorption takes place in aqueous solution where the clays can de-laminate giving both a total surface area. The methylene blue (MB) procedure requires sodium exchanged clays (Kahr and Madsen, 1995). The clays were converted to the sodium form using a method similar to the gentle purification method in (Bergaya et al., 2006). The clays were mixed with a 1.0M NaCl solution overnight. For all of the clays except montmorillonite, a single centrifugation for 60 min at 4400 g was sufficient to separate the clay from the solution. The montmorillonite often required several centrifuge cycles (6–7 h). Once a pellet was formed, the solution was decanted and discarded, and fresh NaCl solution was added. The mixing and centrifugation processes were repeated three times. The entire process was repeated three times with DI water instead of 1.0M NaCl. Once the clays were

washed they were dried in a 100 °C oven for several days before the MB determination was completed. The MB surface area determination uses a fixed solid:liquid ratio (20 g/L) and an increasing concentration of MB. Sorption isotherms are plotted, and the surface is assumed to be saturated at the point where the isotherm shifts from being linear (Kahr and Madsen, 1995). The total amount of MB exchanged can then be calculated. Barium exchange also takes place in aqueous solution. Barium is added in excess (0.1M solution) to a clay slurry (solid:solution = 6.25 g/L) thereby displacing all of the native cations. Major cations (Na, Ca, K, Mg, Fe) can then be measured and the exchange capacity determined (Gillman, 1979). The major cations were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

2.2. Clay minerals and purification

The clays used all originate from the Clay Mineral Society source clays project at Purdue University. Seven total clays were used including: kaolinite, ripidolite, illite, montmorillonite, palygorskite, sepiolite, and a 70/30 illite/smectite mixed layer (ID numbers: KGa-1b, CCa-2, IMt-1, SWy-2, PFI-1, SepNev-1, and ISCz-1, respectively). The layered clays are kaolinite, ripidolite, illite, montmorillonite and the illite/smectite mixed layer. The fibrous clays are palygorskite and sepiolite. All of the clay minerals were subjected to dry sieving at 75 microns. The <75 micron fraction was used in all the experiments presented here. Each clay was examined by X-ray diffraction (XRD) analysis for impurities. The kaolinite, sepiolite, and ripidolite did not have any measurable impurity minerals. All of the other clays had measurable amounts of quartz. There were no other clearly identifiable oxides or carbonates. The best match to the illite spectrum was muscovite, although due to the small degree of crystallinity, the spectra peaks were small. The XRD spectra for the illite/smectite mixed layer clay most closely resembled pure illite, although the match was not exact. Initial surface titrations showed significant pH buffering around pH 8.3, suggesting a calcite impurity in the illite and montmorillonite samples that was not detectable using XRD. The buffering capacity was non-existent in samples subjected to the Na-exchange procedure described above. For the iodide uptake experiments, the <75 micron fraction was used without further purification.

2.3. Iodide sorption experiments

Batch iodide sorption experiments were completed in at least triplicate for all of the clay minerals. For each set of experiments, the ionic composition and concentration of the swamping electrolyte was held constant. The electrolytes and concentrations used are shown in Table 1. A constant solid:solution ratio of 100 g/L was used in all of the experiments.

The batch reactors were 50 mL centrifuge tubes. Blanks (electrolyte and iodide spike without clay) confirmed the absence of wall sorption or iodide loss to volatilization. Clay blanks (electrolyte and clay without iodide) confirmed the lack of leachable iodide from the clays. To each tube the clay and electrolyte solution was added, and the suspensions were equilibrated overnight. An iodide spike was added after equilibration. A constant iodide

Table 1

Summary of electrolytes and concentrations for batch uptake experiments. An × denotes which were used in these experiments.

Concentration (M)	NaCl	NaBr	KCl
1.0	×		
0.1	×	×	×
0.01	×		

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