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.

Keywords: nuclear waste, radioiodine, ion pairing, clay minerals

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 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 minutes at 4400 g was sufficient to separate the clay from the solution. The montmorillonite often required several centrifuge cycles (6-7 hours). 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 (20g/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 = 6.25g/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.

Table 1- Summary of electrolytes and concentrations for batch uptake experiments. An x denotes which were used in these experiments.

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

The batch reactors were 50mL 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 concentration of $3.94\text{E-}4$ M (50 mg/L) was used for all of the batch reactors. The spike was an ion chromatography (IC) iodide standard with no detectable iodate. The batch reactors were mixed in the dark at room temperature for 7 days in a horizontal position on a shaker table. After 7 days, the samples were centrifuged for 1 hour at 4400g. The supernatant was removed with a pipette and refrigerated for analysis. The pH was measured immediately before the iodide spike was added, and again at the end of the 7 day mixing period both before and after centrifuging. No attempt was made to keep the pH constant or at a specific level. As mentioned above, the pH in the illite and montmorillonite reactors was controlled both by the clay and potentially through some amount of calcite dissolution. For all of the other clays, the pH was controlled only through clay buffering. The pH reported is the equilibrium pH for the given clay minerals in the specified electrolyte. After the uptake sample had been removed, an equal amount of DI water was added to the vial. The slurry was mixed for four days. At the end of four days the sample was centrifuged as above, and a sample was removed for analysis. This sample represents a reversal of the uptake process, and gives information regarding the oxidation state of the iodine species after uptake.

The samples were analyzed using a Dionex 1100 ion chromatograph (IC) with an AS23 guard and analytical column, and a bicarbonate/carbonate eluent. For the eluent and column used both iodate and iodide were observable.

3. Results

3.1 CEC and surface area

Table 2 shows the results of the CEC and surface area determinations. CEC values are generally in good agreement, approximately within a factor of 2 to published values for the source clays (Borden and Giese, 2001). Methylene blue sorption allows for the calculation of surface area assuming monolayer sorption and a molecular area of $130 \text{ \AA}^2$. Generally methylene blue surface areas are higher than BET surface area determinations. The BET surface area is interpreted as representing only the

external surface area of the clay particles; the methylene blue surface area is more representative of the total surface area. The difference between them is the interlayer area. Sepiolite is the one exception to the general behavior. The BET surface area was larger than the methylene blue surface area, possibly due to N₂ condensation within the nanochannels of the material (Cases et al., 1991). This leads to the physically meaningless negative internal surface area shown in Table 2.

Table 2- CEC and surface area values for the clays used. Surface area determination methods are explained in the text.

	BaCl ₂ CEC (meq/100 g)	BET S.A. (m ² /g)	MB S.A. (m ² /g)	Internal S.A. (m ² /g)
Kaolinite	4.61	11.3	11.8	0.45
Ripidolite	6.03	8.02	23.5	15.5
Illite	27.6	31.5	117	85.8
Illite/Smectite	30.4	29.8	193	163
Montmorillonite	152	28.3	857	829
Sepiolite	8.98	201	136	-65.2
Palygorskite	29.2	142	625	484

3.2 Iodide batch uptake experiments

Table 3 shows the initial and final pH values in the experiments. In general the values are somewhat bimodal being centered around pH 4 or pH 8. During the course of mixing, the pH changed only slightly, typically decreasing within ~0.2 pH units. Centrifuging caused larger shifts in pH, the largest being 0.98 pH units for the KCl electrolyte experiments with ripidolite (data not shown). Differences between equimolar electrolytes are fairly small suggesting similar Na⁺/H⁺ and K⁺/H⁺ exchange constants. With increasing sodium concentration, the pH decreases consistent with Na⁺ exchange for H⁺ on the basal surfaces of the clays.

Solid:liquid partitioning coefficients (K_D values, mL/g) were calculated using equation 1,

$$K_D = \frac{(C_I - C_F)}{C_F * S} \quad (1)$$

where C_I is the initial aqueous iodide concentration (mg/L), C_F is the final aqueous iodide concentration (mg/L), and S is the solid:solution ratio (g/mL). Table 4 shows iodide K_D values as a function of electrolyte identity, and Table 5 shows iodide K_D values as a function of NaCl concentration. Negative values are generally interpreted to be anion exclusion due to the fixed negative charge of the clay interface. The correction of iodide uptake for this anion exclusion effect is difficult due to the inability to quantify the liquid volume affected by anion exclusion. The K_D values presented here can thus be viewed as a lower bound for iodide uptake. As with other studies, the error (standard deviation of at least three replicates)

is often the same magnitude or larger than the K_D value. In this case, the arithmetic standard deviation is used only to gauge experimental variability. Instead of considering the values themselves, trends between the clays under the different electrolyte conditions are of interest. For the layered clays, K_D values are correlated with the total surface area of the clay minerals for both NaCl and KCl electrolytes (Figure 1). Since the total surface area is dominated by the internal surface area, similar relationships are found with internal surface area or CEC. No obvious trends are found when uptake is plotted as a function of external surface area (see Supporting Information). The nature of the trends is influenced by swamping electrolyte compositions, but they are essentially independent of pH (Table 3). For example, the iodide uptake trend with NaCl declines with increasing total surface area, while the uptake trend with NaBr is quite flat. In both the NaCl and NaBr experiments the pH values are similar. For experiments with variable concentrations of NaCl, the uptake trends are similar in nature for both the 0.01M and 0.1M NaCl; uptake decreases with increasing total surface area (Figure 2). Also, the uptake is larger with 0.1M NaCl concentrations than with 0.01M. At the 1.0M NaCl concentration, the trend is dramatically different with positive K_D values for all of the layered clays, and a very slight increase with increasing surface area. The fibrous clays (palygorskite and sepiolite) act substantially different than the layered clays. For four out of the five electrolyte identities and concentrations, the K_D value increases with CEC; the one exception is at 0.01M NaCl.

While iodide was quantified using the IC technique, iodate quantitation was hampered by an impurity present in many of the clays which could not be resolved from iodate. However, the unresolved peak areas in the iodide uptake samples were no larger than peak areas from the clay blanks suggesting no conversion of iodide to iodate. Further, in the water rinses performed after the iodide uptake experiments, iodide was present and quantifiable. The impurity peak areas were again no larger than those from clay blanks treated in an identical manner. The amount of iodide associated with the clays was an insignificant fraction of the total mass added, invalidating attempts to use mass balance calculations to determine iodide to iodate conversions. These results suggest that all of the uptake behaviors presented are iodide interactions with clay minerals, and there was little to no conversion to iodate.

4. Discussion

In developing a conceptual model for iodide uptake in these experiments two major factors need to be considered. The first is the K_D relationship as a function of electrolyte composition. If an anion exchange type of mechanism were controlling iodide behavior, similar results would be expected for equimolar Cl^- concentrations. Since the NaCl and KCl experiment showed very different results anion exchange can be ruled out, corroborating the mathematical analysis rejecting non-specific anion exchange in (Tournassat et al., 2007). If the interaction were based solely on surface charge properties and the nature of the electrical double layer, similar results would be expected between the NaCl and NaBr experiments. With the Na^+ ion being present in equimolar concentrations, the interlayer spacing for a given clay should be identical as should the surface charge distribution into solution. However, the

Table 3- Initial (before the iodide spike was added) and final (after the centrifugation) pH values for the various electrolytes and electrolyte concentrations used.

	0.1M Electrolyte						NaCl Electrolyte			
	NaCl		NaBr		KCl		0.01M		1.0M	
	Initial pH	Final pH	Initial pH	Final pH	Initial pH	Final pH	Initial pH	Final pH	Initial pH	Final pH
Kaolinite	4.23	4.39	4.43	4.28	4.18	4.07	4.70	4.73	4.27	4.19
Ripidolite	8.73	8.10	8.76	8.20	8.79	7.81	8.79	8.15	8.59	8.37
Illite	8.45	8.16	8.48	7.95	8.28	8.01	8.68	8.30	8.22	7.87
Illite/Smectite	4.00	4.24	4.22	4.03	3.91	3.82	4.38	4.40	3.65	3.74
Montmorillonite	8.15	8.05	8.19	8.05	8.09	7.90	8.65	8.50	7.77	7.73
Sepiolite	7.89	7.83	7.98	7.75	7.92	7.80	7.92	7.83	7.50	7.71
Palygorskite	7.98	7.90	8.05	7.82	7.84	7.87	8.17	7.99	7.75	7.75

Table 4- K_D values for iodide in the different swamping electrolytes used. Standard deviation is presented in parentheses.

0.1M Electrolyte				
	BaCl ₂ CEC	K_D [mL/g] (Std. Dev.)		
	meq/100g	NaCl	NaBr	KCl
Kaolinite	4.61	1.61 (0.28)	0.02 (0.63)	-0.01 (0.22)
Ripidolite	6.03	1.13 (0.38)	-0.16 (0.72)	-0.31 (0.17)
Illite	27.6	0.54 (0.12)	0.13 (0.002)	-0.50 (0.24)
Illite.Smectite	30.4	0.38 (0.08)	-0.01 (0.11)	-0.49 (0.11)
Montmorillonite	152	-0.32 (0.35)	-0.58 (0.07)	-1.69 (0.90)
Sepiolite	8.98	0.01 (0.28)	0.79 (0.14)	0.11 (0.30)
Palygorskite	29.2	0.24 (0.30)	1.26 (0.05)	0.99 (0.17)

Table 5- K_D values for iodide in variable concentrations of NaCl electrolyte. Standard deviation is presented in parentheses.

NaCl Electrolyte				
	BaCl ₂ CEC	K_D [mL/g] (Std. Dev)		
	meq/100g	0.01M	0.1M	1.0M
Kaolinite	4.61	0.48 (0.26)	1.61 (0.28)	0.11 (0.29)
Ripidolite	6.03	0.14 (0.21)	1.13 (0.38)	0.44 (0.17)
Illite	27.6	-0.46 (0.41)	0.54 (0.12)	0.27 (0.21)
Illite.Smectite	30.4	-0.16 (0.25)	0.38 (0.08)	0.30 (0.08)
Montmorillonite	152	-1.35 (0.54)	-0.32 (0.35)	0.60 (0.09)
Sepiolite	8.98	1.38 (4.03)	0.01 (0.28)	-0.01 (0.30)
Palygorskite	29.2	-0.23 (0.54)	0.24 (0.30)	0.70 (0.26)

Figure 1- K_D values for the layered clays as a function of the total surface area for the three electrolytes considered.

Figure 2- K_D values for the layered clays as a function of total surface area for each of the NaCl concentrations used.

iodide did not behave similarly in these two systems either. The underlying mechanism is dependent both on the cation and anion present in the swamping electrolyte. The second major consideration is the physical location of iodide. The trend between K_D and CEC with total surface area (Figures 1 and 2) and lack of trend with BET surface area (Supporting Information) suggest iodide interactions with negatively charged sites in the clay interlayers. This is supported by the facts that the observed trend is not related to solution pH (Table 3) and that there is no obvious trend between K_d and external surface area (Supporting Information), both indicating that external surface sites (i.e., edge sites) do not play a significant role in iodide uptake by clay materials for the conditions considered here. Using classical clay models, iodide cannot approach areas of negative charge due to electrical repulsion. This suggests the iodide is not present as free iodide, but instead as a neutral or positively charged species. Ion-pairing and subsequent interaction with the clays is a potential mechanism consistent with the data. It has also been suggested as a possible mechanism in clay diffusion studies (Appelo et al., 2010) (Kozaki et al., 2001) and has been studied as a process for a significant period of time (Sposito, 1991, Mattigod et al., 1985, Sposito et al., 1983) (Charlet and Tournassat, 2005). Previous work predominantly focuses on a monovalent anion association with a polyvalent cation yielding an aqueous species with an overall positive charge (e.g., CaCl^+ and $\text{CaB}(\text{OH})_4^+$). However, in this case the expected ion-pairs are neutral (e.g., $\text{NaI}_{(\text{aq})}$), which removes the thermodynamic driving force of positively charged ion-pair association with the negatively charged clay surface.

To gain a driving force for the neutral ion-pair to concentrate in the zone of negative charge on the clay surfaces, relative hydration energies and polarizability of the anions may need to be invoked. Within 1-2 water layers surrounding a mineral phase, water properties are heavily affected by the mineral surface and are distinctly different from those in bulk solution (Hiemstra and Van Riemsdijk, 1991). For most minerals in dilute systems this effect is negligible. However for clays, the large specific surface area and interlayer environments may create a significant amount of confined volume where water properties are different from bulk solution. Most notably, the confined structure decreases the dielectric constant in both charged and uncharged pores (Senapati and Chandra, 2001, Yeh and Berkowitz, 1999). Ion pair formation is increasingly favored as the dielectric constant decreases (Fuoss, 1980, Shock and Helgeson, 1988). Thus within the confined spaces of the clay interlayer, free iodide is less likely than in bulk solution. Furthermore, at air-water and hydrophobic surface-water interfaces, a similar change to water structure and dielectric is expected. Within about 2nm of the interface, halogen concentrations follow the Hofmeister series, $\text{F} < \text{Cl} < \text{Br} < \text{I}$. Bromide and iodide concentrations are larger at the interface than in bulk, chloride is approximately equally distributed, and fluoride concentrations are smaller at the interface than in bulk solution (Figure 3a) (Jungwirth and Tobias, 2001, Lima et al., 2008, Manciu and Ruckenstein, 2005). This trend is explained by comparing the relative polarizability of the anions. It is more thermodynamically favored for the highly polarizable iodide to be present in areas where water is more structured. In equimolar halogen solutions, the relative concentrations are also a function of surface charge (Lima et al., 2008). The data presented here are generally consistent with the work completed for other types of surfaces. Bromide and iodide have more similar polarizabilities than chloride and iodide. When shifting from a NaCl to a NaBr electrolyte, the Br competes more directly with iodide uptake mechanisms, and the relatively higher concentration of Br can displace iodide leading to smaller iodide K_D values. Chloride is less likely to displace iodide as it is significantly less polarizable than iodide, and the iodide K_D values are higher. This conceptual model is also consistent with (Kaplan et al.,

2000) who found increased iodide desorption efficiency when mixed with equimolar salt solutions in the order $F < Cl < Br < I$. Also, the larger iodide uptake in Na dominated systems compared to the K systems for the layered clays is consistent with the trend in ion pair formation constants (Fuoss, 1980). Considering the role of structured water in a confined space favorably compares with the data as the electrolyte identity changes, and it may also explain the difference in iodide behavior between the clay structures. The channel structure of the fibrous clays is considerably different from the platy structure of the layered clays and so is iodide uptake. Palygorskite and illite have similar CEC values, and yet the iodide uptake as a function of electrolyte concentration and identity is significantly different. When moving from the NaCl to either the NaBr or KCl electrolyte uptake decreases in illite while increasing with palygorskite. Furthermore, comparing uptake between palygorskite and sepiolite, the expectation based on charge exclusion is less iodide uptake for the more highly negatively charged palygorskite. And yet uptake is almost always higher with palygorskite than it is with sepiolite. This conformational difference between the fibrous and layered clays and the different sizes of the pore channels between the fibrous clays may lead to variable water properties leading to increased uptake despite the higher structural charge (Ockwig et al., 2009, Galan, 1996).

Current mathematical interpretations of the changing dielectric constant describe the dielectric as a function of distance away from the interface (Manciu and Ruckenstein, 2005) (Lima et al., 2008). These models use interconnected partial differential equations, which may or may not be informed/simplified by molecular dynamics calculations. Clays are simpler in that a 2-box model may be sufficient; one box represents the bulk water and the other box represents the confined water (Figure 3B). However, calculating the dielectric constant in the interlayer is not trivial. The exact interlayer spacing depends on the structural charge of the clay as well as the exchanging ion (Laird, 2006). The dielectric constant will depend on both the spacing and the geometry of the interlayer (layered vs. fibrous). The 2-box model would be similar in concept to previously developed Na/Cs exchange models (Teppen and Miller, 2006, Van Loon and Glaus, 2008). In those cases, hydration energy alone was sufficient to suggest why Cs uptake is favored over Na uptake as a function of increasing compaction. In

Figure 3- A- Conceptual model of the dielectric constant change near the air-water interface, **B-** 2-box model proposed here for clay minerals. T = tetrahedral layer, O = octahedral layer.

this case, a similar conceptual model may still hold, but the variables of interest need to include: the polarizability of the anion, the formation constant of the ion pair, changes to the dielectric constant based on geometry and clay charge, as well as the hydration energies of the ions involved. Molecular simulations would be required to understand the ultimate driving force for iodide concentration near the clay surfaces.

It is difficult to extrapolate such results to more disposal relevant systems. Generally the ionic strength of clay pore waters is on the order of 0.1M, and tend to be dominated by NaCl, although Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-} , and HCO_3^- are also generally present. Given the variability between the iodide uptake in the different swamping electrolytes it is unclear if the behaviors observed would still occur in mixtures of those electrolytes. Also the aqueous iodide concentrations used here are likely much higher than what will be seen in the far field of a waste repository. It is not clear whether these interactions would still be observable at more relevant concentrations. Finally, if the proposed interpretation is correct, iodide uptake should be exacerbated in compacted systems where a larger proportion of the pore water is affected by the clay surfaces. The proposed interpretation may also help to explain the diffusion of anions at large dry densities ($> \sim 1600 \text{ kg/m}^3$). At these very high densities there is a theoretical point where the clay double layers overlap, filling the pore space and excluding anions from diffusing. One hypothesis to explain anion diffusion above that critical dry density is non-uniform pore structure (Tournassat and Appelo, 2011). An alternative version is that some anions are diffusing as neutral ion-pairs, and thus would not be affected by the charge domain in solution.

Iodide interactions with clay minerals are so weak experimental attempts at understanding them are hampered by the fact that the error is generally larger than the K_D value. The same was true here. Furthermore, the physical model described was arrived at by excluding other processes based on the data. Thus the model is proposed and not unambiguously confirmed. However, in this case, using a broad study of several clay minerals allowed for the observation of trends as a function of lattice substitution and clay structure. This in turn gave insight into a possible, generally unconsidered mechanism for direct iodide interaction with clays that does not violate current surface complexation/ion exchange models for clays. This relationship appears valid despite the variability in pH values for the different electrolyte systems, the chemical variability between the clays used and the general lack of clay purification. The iodide uptake mechanism appeared as an emergent property heavily related to structural charge and clay texture alone. However, the thermodynamic driver of iodide accumulation near clay surfaces is still vague. And, although the experimental data indicate that iodide can directly interact with clay minerals despite the negative charge, it also remains unclear what ultimately controls the slope of iodide uptake as a function of CEC. One possible explanation is that given the affinity of iodide for interlayer sites created by nanopore confinement (through ion pairing) and molecular polarization effects, the increase in the negative structural charge of clay plates tends to reduce the overall affinity for iodide uptake. Finally, the proposed mechanism does not invalidate any of the other potential mechanisms for iodide interaction with clays discussed in the Introduction. Several weak mechanisms may be needed to describe iodide interaction with various clay minerals in various geologic environments.

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Supporting Information Available

Plots showing the K_D values as a function of BET surface area for all of the electrolyte compositions and concentrations are available in the supporting information.

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