

**Iodide Sorption to Clays and the Relationship to Surface Charge and Clay Texture
– 12356**

Andrew Miller*, Jessica Kruichiak*, Hernesto Tellez*, and Yifeng Wang*

Sandia National Laboratories, Albuquerque, NM 87185

ABSTRACT

Iodine is assumed to behave conservatively in clay barriers around nuclear waste repositories and in natural sediments. Batch experiments tend to show little to no sorption, while in column experiments iodine is often retarded relative to tritiated water. Current surface complexation theory cannot account for negatively charged ion sorption to a negatively charged clay particle.

Surface protonation and iodide sorption to clay minerals were examined using surface titrations and batch sorption experiments with a suite of clay minerals. Surface titrations were completed spanning a range of both pH values and ionic strengths. For reference, similar titrations were performed on pure forms of an Al-O powder. The titration curves were deconvoluted to attain the pK_a distribution for each material at each ionic strength. The pK_a distribution for the Al-O shows two distinct peaks at 4.8 and 7.5, which are invariant with ionic strength. The pK_a distribution of clays was highly variable between the different minerals and as a function of ionic strength. Iodide sorption experiments were completed at high solid:solution ratios to exacerbate sorption properties. Palygorskite and kaolinite had the highest amount of iodide sorption and montmorillonite had the least.

INTRODUCTION

Despite the final location and conceptual design of a nuclear waste repository, clays will play an important role in waste isolation. Clay minerals will be used as a backfill or sealant material and may be the host rock surrounding the engineered zone. The major advantages of clays are their low permeability and high sorption capacities. Much of the sorption capacity stems from the fixed negative charge present on the basal surface of clay minerals. The fixed negative charge presents a large number of sorption sites for cations, but they repel anions. In performance assessments the repellent behavior has led to treating anions as non-reactive. This assumption translates into anions being the largest dose contributors at times >10,000 years. However, there is data available in the literature showing that many anions are retarded in clays relative to tritiated water. It is assumed that the retardation occurs due to sorption, which is often quantified with a K_D value. These values are small; iodide K_D values have been reported from ~0.001-2.9mL/g. While small, the assumption that the iodide will behave conservatively overestimates iodine dose in a performance assessment. Despite the experimental

evidence, little headway has been made with respect to the understanding of how a negatively charged ion sorbs to a negatively charged surface.

While other possibilities exist, three main hypotheses are considered here. These three hypotheses are based on charge arguments, redox arguments and the presence of ancillary minerals. The charge hypothesis is related to the relatively unique charge environment surrounding clays. Clays can be conceived as small plates, with a large basal surface and an edge. The fixed negative charge is located on the basal plane, and is caused by isomorphous substitution of lower valence ions for higher valence ions in the mineral lattice. The edge of the clay mineral is dominated by aluminum and silicon oxide sites which exhibit amphoteric behavior based on the pH and ionic strength in solution. The electric double layer (EDL) developed at both site types extends out into solution, and can overlap. Thus, unlike simple metal oxides such as Al-O, the EDL is spatially heterogeneous at the scale of the clay mineral particle. The heterogeneous charge distribution has not been captured in current geochemical models. This heterogeneous charge environment is exacerbated when clay minerals are heavily compacted where the charge from an individual particle not only interferes with itself, but also with the charge distributions of other clay particles. It is unclear how this variable charge distribution would affect anion sorption.

The second major hypothesis to explain the aberrant sorption behavior is that sorption behavior is different for different oxidation states of the same element. For iodine, there is an increasing body of knowledge that oxidation state is critical to describing sorption properties, and that the oxidation state may be alterable by the clay mineral itself. In [1], the two oxidation states were separated using an anion exchange column so that the oxidation state being injected into a diffusive column was irrefutably known. With this careful control of oxidation state, it was found that iodate was reduced to iodide upon contact with Opalinus Clay from Haute-Marne, France. The iodide, once formed, behaved similarly to chloride. From deduction this would mean that small K_D values are probably not attributable to iodide, but some other form of iodine, either iodate or elemental iodine. If the sorbing ion is iodate, a sorption mechanism to clays remains unclear as iodate is also a monovalent anion. However, in other studies, iodide and iodate were shown to have significantly different sorption properties when exposed to various minerals [2, 3].

The third hypothesis to explain iodine migration behavior is that the sorbing ion is not interacting with a clay mineral, but it is interacting with either an ancillary mineral or a weathering product of the clay minerals. In [1], the iodate was reduced to iodide upon contact with the Opalinus clay. The authors attribute this to an unidentified reducing agent in the clay. In [2], the author rules out the likelihood of reduced iron or sulfide playing a role in iodide reduction, but comments that the presence of these ions in the mineral lattice may play a role in sorption. In many clay-rock systems, there are several mineral species present. Any of these minerals may be responsible for the observed iodine retention.

While determining a specific mechanism for anion sorption to clay minerals is beyond the scope of the current work, the three hypotheses considered above are tested to various degrees. Protonation state distributions are studied on a range of clay minerals

and are related to the physical structure of the clay minerals. Batch experimentation is used to probe iodide sorption to the same clay minerals. The solution phase redox state of iodide is monitored in these experiments with ion chromatography.

EXPERIMENTAL METHODS

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 clays used were relatively pure; however, for several of the clays purification steps were required to remove certain impurities. The main purification step used in this study was mechanical separation at 75 microns. The <75 microns size fraction was used in all the experiments presented here. Each clay was examined by XRD for impurities. The kaolinite, sepiolite, and ripidolite did not have any measurable impurity minerals. All of the other clays had measurable amounts of quartz. The best match to the illite sample 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.

In initial titration experiments, described below, the illite and montmorillonite samples showed a large buffer capacity around pH 8.3. It was assumed that this was a calcite impurity, as the initial titration curves were significantly different from other published sources. To remove the calcite, these two clays were washed and converted to the sodium form with ion exchange and centrifugation. Both clays were mixed with a 0.1M NaCl solution overnight. For illite, a single centrifugation for 60 minutes at 4400g was sufficient to pelletize the clay. The montmorillonite often required several centrifuge cycles. Once a pellet was formed, the solution was decanted and discarded, and fresh NaCl solution was added. The mixing and centrifugation processes were repeated. The entire process was repeated two more times with DI water. Once the clays were washed they were dried in a 100°C oven for several days.

Titration experiments

The surface titration of the clays was completed with a Mettler Toledo DL55. For each analysis 1g of clay mineral was added to 50mls of the swamping electrolyte. Electrolytes used were 0.01, 0.1, and 0.5M NaCl solutions. The solution was constantly sparged with nitrogen to exclude atmospheric carbon dioxide. Upon addition of the clay, the solution was stirred and sparged until the pH stabilized. This generally took 10-30 minutes. Titrations were separated at the natural pH of the clay in the electrolyte. For each ionic strength, one clay sample was titrated up to pH 10.5 (base leg) while a

separate sample was titrated down to pH 2.5 (acid leg). The titrants were 0.1M HCl or 0.1M NaOH. The NaOH solution was always made immediately before use to minimize CO₂ dissolution. The titrants were added in 0.1mL increments. Between additions, the rate of pH change was <0.02 pH unit/second for seven seconds. The results from the two legs were combined in a spreadsheet to create the entire titration curve. Blank titrations and titrations of a commercial AIO powder were also completed. Because of the smaller surface area of the AIO powder, 5 grams of material had to be used instead of 1g. The longest titrations required about 20 hours to complete, while the shortest required only 10-20 minutes.

Iodide sorption experiments

Batch iodide sorption experiments were completed with all of the clay minerals. A total of 42 batch reactors were used to cover the parameter space. The variables of interest were the clay mineral, the solid:solution ratio as well as the initial concentration of iodide. For each of the clays, 6 reactors were needed as two different solid:solution ratios were used, and three different iodide concentrations. Because of the low degree of expected sorption, the solid:solution ratio was kept quite high, 66 and 100g/L. The initial iodide spikes were: 1.269mg/L, 10.152mg/L, and 50mg/L (10^{-5} , 8×10^{-5} , and 3.9×10^{-4} M, respectively).

The batch reactors were 50mL centrifuge tubes. To each tube 1g of clay was added, as well as an appropriate amount of 0.1M NaCl solution. These suspensions were mixed overnight to allow for equilibration of the clay with the solution. To each vial a measured amount of an iodide parent solution was added to get the initial iodide concentrations noted above. The batch reactors were mixed in the dark at room temperature for 7 days in a horizontal position on a shaker table. The pH was monitored periodically over the 7 days, but no attempt was made to keep it constant or at a specific level. The pH reported is the 'natural' pH for the given clay minerals. After 7 days, the samples were centrifuged for 1 hour at 4400g. The supernatant was removed with a pipette and refrigerated for analysis.

The samples were analyzed using a Dionex 1100 ion chromatograph (IC) with an AS23 guard and analytical column, and a bicarbonate/carbonate eluent. Methods were developed to simultaneously measure iodide and iodate.

RESULTS

pK_a distributions

Surface charge of clay minerals can be calculated from the titration curves using equation 1[4],

$$= \frac{C_A [OH^-] - C_B [H^+]}{F S_a} \quad (\text{Eq. 1})$$

where C_A and C_B are the concentrations of acid and base needed to attain a specific pH on the titration curve, $[OH^-]$ and $[H^+]$ are the OH^- and H^+ concentrations, F is the Faraday constant (96,490 C/mol) and S_a is the surface area of the clay mineral. For surface area we use the measured BET surface area. In the case of clays, this method does not give total surface charge as it does not take into account the fixed charge of the clay surfaces. More accurately, this method quantifies the total amount of proton sorption to the clay, and converts this to sorbed proton charge. Assuming that the protons exhibit Langmuirian behavior, the protonation state of clays (Q) can be calculated and related to the binding site distribution ($f(pK)$), and the acidity constants (pK) by equation 2,

$$Q = \int \frac{f(pK)}{1 + 10^{pK - pH}} dpK \quad (\text{Eq. 2})$$

Q is calculated from the titration curves, and the distribution of acidity constants is calculated from de-convolution of Eq. 2 with the condensation approximation (equation 3),

$$f(pK) \approx \frac{dQ}{dpK} \quad (\text{Eq. 3})$$

The calculated distribution of sites is presented using a five-point smoothing window. The individual distributions are shown in Figures 1 and 2.

For many of the clays and for the AIO material, the behavior of the pK distributions is erratic at $pH < 4$ and > 10 . It is suspected that dissolution of the minerals was occurring which interferes with the titration process. The results and discussion here are restricted to pH values between 4 and 10. The pK values are read directly from the plots; pK values correspond to the peaks in the curves. For example, the AIO plot has two distinct peaks at pH 4.7 and 7.5 for both 0.01M and 0.1M NaCl concentrations. When the ionic strength is at 0.5M, other peaks may be present. A major point from these curves, which is elaborated below, is that for changing ionic strengths, the AIO peaks are largely invariant. For nearly all of the clay minerals, there are significant changes as a function of ionic strength. For some clays it appears that the increase in ionic strength diminishes surface proton activity by suppressing the peaks (e.g., ripidolite). In others it appears that more peaks are present with increasing ionic strength (e.g., palygorskite). And in others the number of peaks is similar but the pK value is shifted (e.g., illite/smectite mixed layer).

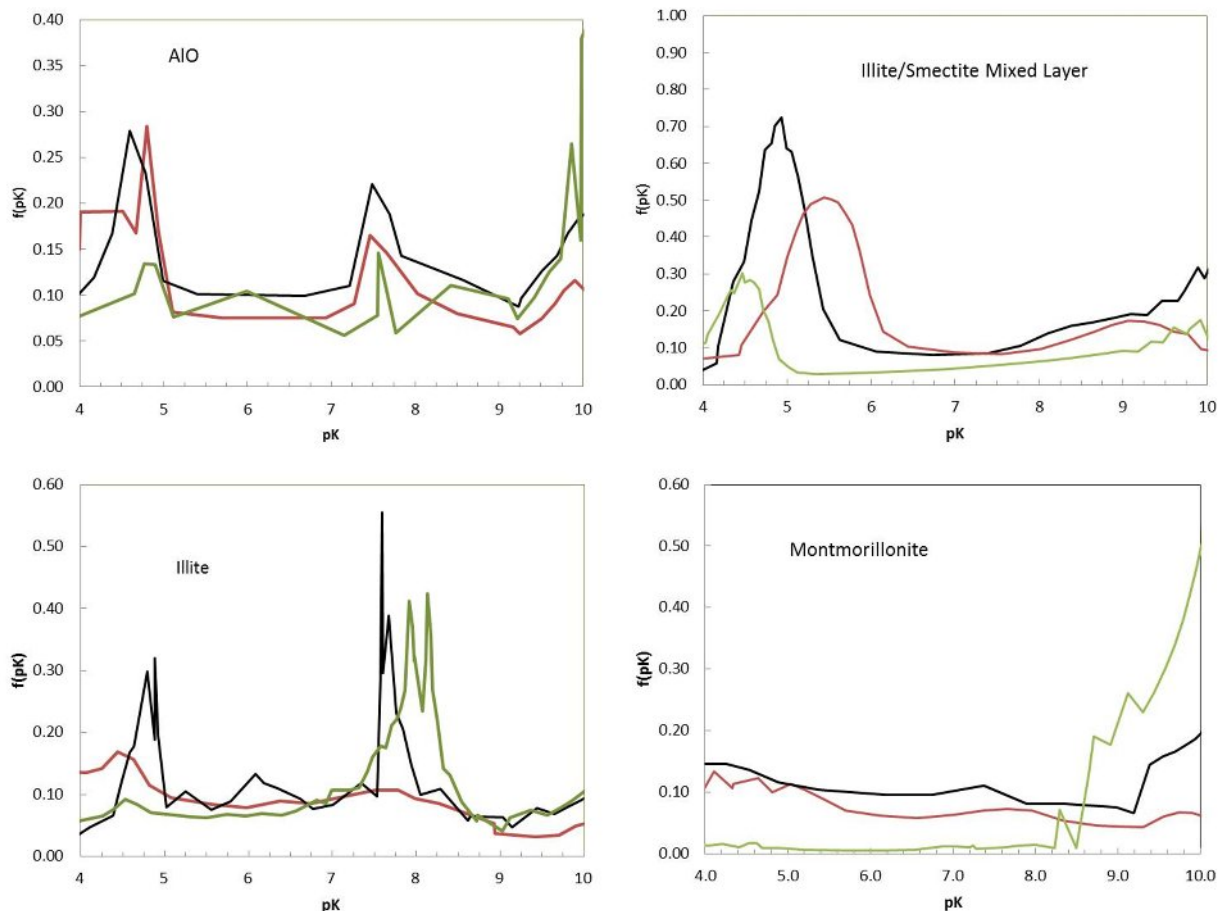


Figure 1 pK_a distributions for AIO, illite, illite/smectite mixed layer, and montmorillonite. The red, black and green lines represent 0.01M, 0.1M, and 0.5M NaCl, respectively.

Iodide sorption

The iodide sorption results to the various clay minerals are shown in Table 1. For simplicity, only the results for the higher solid:solution ratio are shown. Overall trends were similar between the two solid:solution ratios. The lower solid:solution ratios had slightly smaller percent sorbed values, but similar sorption densities were observed. Also shown are the final measured pH values, BET surface areas, and ideal chemical structures for each clay mineral. Illite/smectite does not have a chemical structure, but by definition it could be represented by a mixture of the illite and montmorillonite endmembers.

Palygorskite had the largest and most consistent iodide removals; however, the sorption densities were highest on kaolinite and ripidolite. Thus the chemical affinity was the highest between iodide and kaolinite and ripidolite. Montmorillonite had the lowest values, and even showed evidence of negative sorption (anion exclusion).

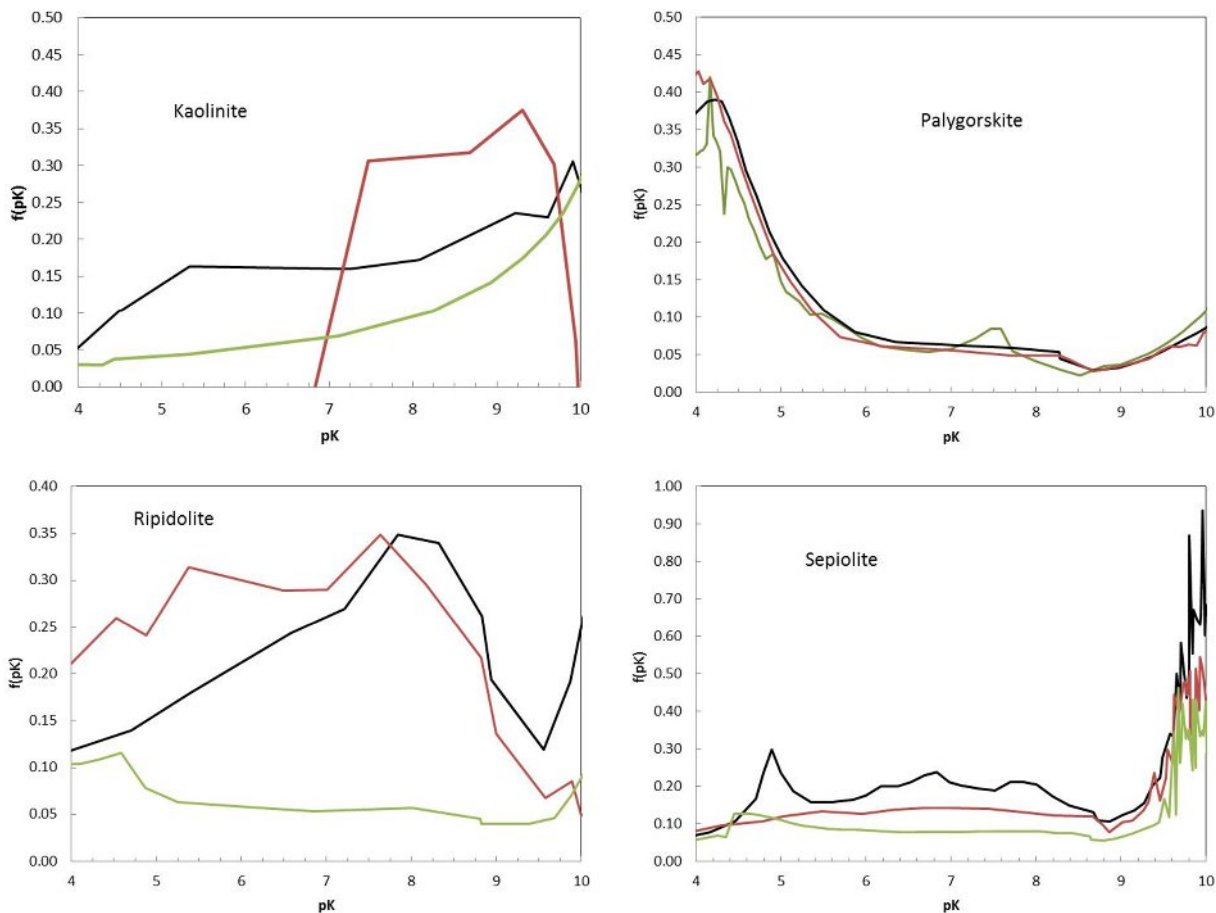


Figure 2 pK_a distributions for kaolinite, ripidolite, palygorskite, and sepiolite. The red, black and green lines represent 0.01, 0.1 and 0.5M NaCl concentrations, respectively.

The pH values are fairly bimodal, centered around either pH 8 or pH 4. The illite and montmorillonite samples were washed for the titrations, but not for the sorption experiments. Thus it is expected that calcite is buffering the pH. For the other clay minerals, the only buffer is the clay itself. In general pH values did not change dramatically over the seven day mixing period. Both illite and ripidolite dropped by almost 0.5 pH units, for the rest the final values were typically within about 0.1 pH units. No discernible relationship between pH and iodide was observed. The range in behavior between clay minerals was broader than that related to pH.

DISCUSSION

Aluminum oxide is acting as a simple model system in this series of experiments; it both confirms the methodological process and acts as a frame of reference for understanding the clay behaviors. As expected from surface complexation theory as well as other experiments and models, the pK_a values are largely invariant as a function of ionic

Table 1 Iodide sorption results. The solid:solution ratio for the data shown is 100g/L. The number in the clay mineral column refers to the initial iodide spike concentration: 1 = 1.269mg/L, 2 = 10.152mg/L, and 3 = 50mg/L.

Clay Mineral/Sample	% Sorbed	Sorption Density (mol/m ²)	pH-Initial	pH-7 days	BET Surface Area (m ² /g)	Ideal Formula ^a
Illite A-1	39.97	1.27E-09	8.515	8.178	31.457	$K_{0.6}(H_3O)_{0.4}Al_{1.3}Mg_{0.3}Fe^{2+}_{0.1}Si_{3.5}O_{10}(OH)_2 \cdot (H_2O)$
Illite A-2	6.39	1.62E-09	8.516	8.188		
Illite A-3	5.64	7.06E-09	8.517	8.190		
Illite/Smectite A-1	23.80	7.98E-10	3.992	4.049	29.822	
Illite/Smectite A-2	3.83	1.03E-09	3.988	4.073		
Illite/Smectite A-3	4.44	5.87E-09	3.994	4.091		
Montmorillonite A-1	11.32	4.00E-10	8.146	8.027	28.290	$Na_{0.2}Ca_{0.1}Al_2Si_4O_{10}(OH)_2(H_2O)_{10}$
Montmorillonite A-2	-5.17	-1.46E-09	8.134	8.079		
Montmorillonite A-3	0.75	1.04E-09	8.143	8.103		
Palygorskite A-1	35.75	3.83E-10	7.957	7.855	141.521	$Mg_{1.5}Al_{0.5}Si_4O_{10}(OH) \cdot 4(H_2O)$
Palygorskite A-2	27.70	2.37E-09	7.971	7.877		
Palygorskite A-3	25.24	1.06E-08	7.971	7.900		
Sepiolite A-1	16.95	1.28E-10	7.934	7.716	201.431	$Mg_4Si_6O_{15} \cdot 6(H_2O)$
Sepiolite A-2	12.60	7.58E-10	7.928	7.696		
Sepiolite A-3	14.09	4.18E-09	7.933	7.731		
Kaolinite A-1	38.15	5.11E-09	4.449	4.564	11.308	$Al_2Si_2O_5(OH)_4$
Kaolinite A-2	12.97	1.39E-08	4.438	4.565		
Kaolinite A-3	16.08	8.49E-08	4.434	4.548		
Ripidolite A-1	26.54	5.02E-09	8.755	8.303	8.017	$Mg_5Al(Si, Al)_4O_{10}(OH)_8$
Ripidolite A-2	9.94	1.50E-08	8.768	8.303		
Ripidolite A-3	13.54	1.01E-07	8.782	8.340		

^aIdeal formulas from www.webmineral.com

strength. Small shifts may be attributable to changes in chemical potential as a function of ionic strength. This affect is not taken into account with the titration curve inversion method. It does appear that there may be other peaks starting to appear at the highest ionic strength studied, although there is no ready explanation for this behavior.

The clays have a much broader range of behaviors. Illite, illite/smectite mixed layer, and montmorillonite set up a continuum of minerals (smectite and montmorillonite are synonymous in this case). These three clays represent two mineral endmembers with an intermediate that is a mixed composition. The major pK_a values for illite are centered at a pH of about 8 with smaller peaks at pH ~4.6. There also appears to be more pK_a

peaks at 0.1M NaCl than at either 0.5 or 0.01M NaCl. The illite/smectite mixed layer has some of the most consistent behavior across the range of ionic strength. The major pK_a peak is ionic strength dependent. At low ionic strength it is centered at pH 5.5, at 0.1M ionic strength the peak is centered at pH 5, and at the highest ionic strength the peak is centered at pH 4.5. This peak shifting is far more extreme than was seen for the AIO material, so it can be surmised that the shift is caused by something other than changing EDL potential. Since the change in ionic strength corresponds with a change in the sodium concentration, this peak may be representative of the Na^+/H^+ exchange reaction. If this is the case, it is unclear why a similar reaction was not seen in the montmorillonite sample where Na^+/H^+ exchange would also be common. For montmorillonite the pK_a distribution is not particularly remarkable. The surface appears proton neutral independent of ionic strength. At the highest ionic strength there appears to be a broad peak starting at pH 8 which does not return to 'baseline' in the experimental range; this may be attributable to the same mechanisms which cause similar noise at pH >10. Despite the continuum of mineralogy, there is no consistency between the pK_a distributions of these three minerals. From the observable scale, the clay minerals seem to act independently; the illite/smectite behavior is not dominated by the contribution of either of the endmembers.

Kaolinite is proton neutral at both 0.5M and 0.1M NaCl values. At the 0.01M NaCl values, there is a broad peak ranging from pH 7 to 10. Ripidolite becomes progressively more proton neutral with increasing ionic strength. At the lowest ionic strength there are three potential peaks. At the intermediate ionic strength there is a single broad peak centered at pH 8.2, while at the highest ionic strength there is only a single discernible peak at pH 4.5. This type of behavior is consistent with a 'masking' of surface effects as a function of increasing ionic strength. The increased sodium may be dampening the effect of proton sorption.

Sepiolite and palygorskite are structurally similar minerals. Both are fibrous in nature but have differently sized pore spaces which allow for different amounts of associated water. They are also chemically distinct as palygorskite has structural aluminum, and sepiolite is a pure magnesium silicate. Unsurprisingly their titration data is also quite distinct. Sepiolite appears proton neutral, except for a peak at pH 5 at 0.1M ionic strength. The noise at pH >9.5 continues as pH increases, and this is attributed to dissolution. Palygorskite has similar behaviors independent of ionic strength. There is a large single peak at 4.2, and a smaller peak at pH 7.5 when ionic strength is 0.5M. The pK_a values of palygorskite are similar to those of the pure AIO. This was the anticipated result from all of the clays expect for sepiolite. All of the other clay minerals used have edge aluminol sites that may have similar behavior to the surface sites of AIO. The lack of pK_a peaks for the clay minerals either means that the overall differences between AIO and clay alters the acidity of the edge aluminol sites so that they are no longer comparable [5], or some other process besides surface protonation is dominating behavior (i.e., Na^+/H^+ exchange).

Much of the iodide sorption data is also attributable to surface charge. The smallest amount of sorption was on montmorillonite. Montmorillonite also has the most negative structural charge. Thus the larger negative charge of the surface means that the

negatively charged iodide cannot approach the surface due to charge repulsion. There is even evidence of negative sorption (anion exclusion). The highest amount of sorption was observed with palygorskite. Due to structural considerations, the charge domain of palygorskite is more highly heterogeneous than that of many other clays. Locally there is the possibility of both positive and negative charges. It would appear that the localized positive charges are favorable for iodide removal. Kaolinite and ripidolite have the highest sorption densities. Kaolinite is not typically highly substituted, leading to a small fixed charge. Thus it is not surprising that surface concentrations are higher. It is suspected, but unconfirmed, that the isomorphous substitution of this ripidolite is also low. Generally the highest percent removal occurred at the lowest concentration of iodide, while smaller percent removals were seen at higher iodide concentrations. It is difficult to discern with only three data points and a limited iodide concentration range, but all the sorption isotherms except for montmorillonite appear linear for the range studied (Figure 3).

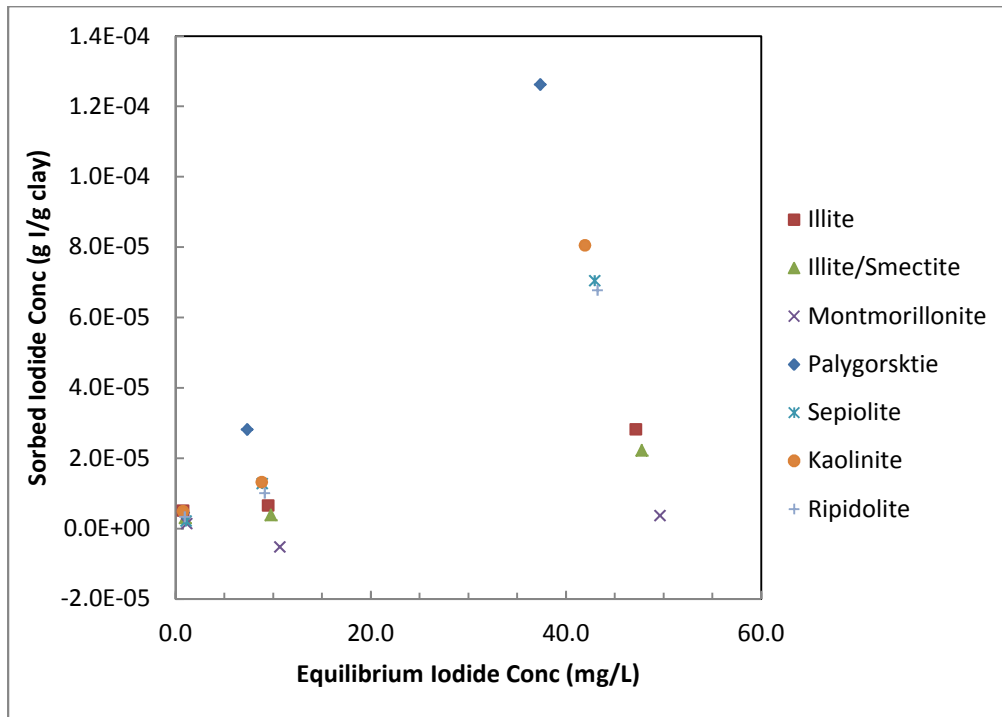


Figure 3 Iodide sorption isotherms for each individual clay mineral studied.

Initially it was conjectured that three different hypotheses could possibly explain anion sorption to negatively charged clay minerals. Those hypotheses were based on surface charge, the presence of ancillary minerals, and iodide redox speciation. From these experiments, the protonation state of the surface was determined using surface titrations. The change in the determined pK_a distribution as a function of ionic strength was unexpected. One physical interpretation of this behavior is that different sites or site

types are more or less accessible as a function of ionic strength. The pK distribution curves give some information about the activity of protons near the surface of the clay mineral, but does not allow for direct determination of the fixed charge component of surface charge. Future experiments are planned to determine the cation exchange capacity, which is directly associated with fixed charge. Nevertheless, based on prior knowledge of clay minerals, it can be said that the lower fixed surface charge correlates with higher anion sorption. Quartz and calcite were initially present in some of the clay samples, but many were quite pure. Thus much of the data here represents interactions with the pure mineral alone. However, further work is needed to determine if any clay weathering or alteration products were produced during the sorption experiments. And finally, there was no measurable iodate in the aqueous phase of any samples. However, this does not give any concrete information with respect to the species that is sorbing to the clay mineral. In other words, the experimental design does not allow for determining the ion that is actually interacting with the clay minerals.

REFERENCES

1. Glaus, M.A., W. Muller, and L.R. Van Loon, *Diffusion of iodide and iodate through Opalinus Clay: Monitoring of the redox state using an anion chromatographic technique*. Applied Geochemistry, 2008. 23: p. 3612-3619.
2. Fuhrmann, M., S. Bajt, and M.A.A. Schoonen, *Sorption of iodine on minerals investigated by X-ray absorption near edge structure (XANES) and I-125 tracer sorption experiments*. Applied Geochemistry, 1998. 13(2): p. 127-141.
3. Couture, R.A. and M.G. Seitz, *Sorption of anions of iodine by iron oxides and kaolinite*. Nuclear and Chemical Waste Management, 1983. 4: p. 301-306.
4. Wang, Y.F., et al., *Control of pertechnetate sorption on activated carbon by surface functional groups*. Journal of Colloid and Interface Science, 2007. 305(2): p. 209-217.
5. Brady, P.V., R.T. Cygan, and K.L. Nagy, *Molecular Controls on Kaolinite Surface Charge*. Journal of Colloid and Interface Science, 1996. 183: p. 356-364.

ACKNOWLEDGEMENTS

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract

WM2012 Conference, February 26 – March 1, 2012, Phoenix, Arizona, USA

DE-AC04-94AL85000. This work is supported by DOE Sandia Laboratory-Directed R&D Program and DOE Used Fuel Disposition Program.