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Natural Clays with an Inherent Uranium Component that Nevertheless Sequester Uranium from Contaminated Water

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Abstract

Clays present a cost effective and sustainable method for removing uranium and heavy metals from drinking water because of their cation exchange capabilities. However, managing muddy suspensions is problematic; therefore, clay pellets as presented in this paper are a promising alternative. Three standard clays and two regional clays were evaluated for sorption, both in powder form and in pellet structure for comparison. The objective was to evaluate individual sorption processes and assess the effect on uranium sorption due to the process of altering the clay powder to produce pellets. The sorption capacity of the pellets is sufficiently large to not only sorb the intrinsic non-bonded uranium but to continue to sorb uranium from contaminated water. Furthermore, the uranyl cation was also removed preferentially in the presence of Pb^{2+} and Cd^{2+} heavy metal cations, hydronium ions, and more importantly the naturally occurring cations, Na^{1+} , Ca^{2+} , and Mg^{2+} that occur in abundant concentrations. Clay pellets as well as powders reduced uranium concentrations, and in extreme cases from 450 ppb, 15 times the Environmental Protection Agency maximum contaminant level to non-detectable limits. Clay pellets are excellent candidates for the safe and manageable removal of uranium and heavy metals to produce potable water

Keywords

clay ceramics; sorption; uranium; intrinsic geologic uranium; water

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Introduction

Uranium contamination of groundwater increasingly concerns rural residents depending on home wells for their drinking water in communities with a legacy of mining. ^[1] Naturally occurring uranium is also a source of contamination. ^[2-4] In the United States, elevated concentration levels of natural uranium in groundwater are widespread in the West and in scattered locations in the eastern states. ^[2, 5] Also significant problems stemming from the legacy of uranium development since WWII still exist today in the Four Corners area. ^[6] The Four Corners is a relatively large area in the U.S. that incorporates corners from the states of New Mexico, Arizona, Utah, and Colorado. This activity led to uranium leaching into the ground water used for consumption and adversely impacting the health of many Navajo people in particular. ^[7-11] Because they have very limited economic resources and a severe lack of infrastructure, a simple, robust, and inexpensive technology is paramount. A technology to remove uranium from their scarce water sources that are highly contaminated must be explored, designed, and primed for implementation. This is important not only in the Navajo Nation but for economically limited people worldwide.

Uranium in ground water is most commonly found in its hexavalent oxidation state U(VI) as the uranyl cation (UO_2^{2+}). ^[12] The aqueous solubility of some uranyl salts makes it difficult to physically remove them from water. For simplicity, the term uranium for the duration will imply the soluble uranyl cation in aqueous settings. Established technologies that produce potable water are not always the best option for applications in economically limited situations. For example, reverse osmosis and distillation are more suitable in large communities that can dissipate the cost and provide the necessary infrastructure. ^[13-16] Moreover, an important consideration for these technologies is the highly concentrated fraction of the water that must be discarded, stored, or transported. In the case of uranium and heavy metals this aspect cannot be ignored because the contaminants are highly toxic. Commercial solid state sorption methods are available for removing uranium from water; however, they are cost prohibitive and inapplicable in remote and isolated areas. ^[17]

Natural montmorillonite clays are ideal candidates for uranium sorption that meet the stringent application requirements above. ^[18-20] However, the drawback for using clays in their unadulterated state as sorbents in aqueous applications is that they suspend in water thus making the complete removal of the muddy suspension problematic. Consequently, the clays were transformed into insoluble pellets to make the uranium sorption and subsequent safe disposal processes manageable. ^[21] The purpose of the present study is to investigate the applicability of clay ceramic pellets as sorbents for the treatment of uranium-contaminated water. In addition, intrinsic geologic uranium in clay materials needs attention to make clay pellets a viable technology. Because each clay is unique in its composition, specifically uranium composition, we will investigate the uranium sorption distinctions for the different clays. This will include the effect of pelletization on uranium sorption. Uranium sorption by pulverized clay versus pelletized clay was the measure of efficacy and potential of clay pellets to be utilized in the field for water purification.

The essence of sorption onto clays is the cation exchange capacity, CEC, of these solid-state sorbents. The charged sites on the clay structures are negative and the uranyl cation, UO_2^{2+} , binds to the negative clay sites by an ion exchange mechanism. [22, 23] The numerical value of the CEC represents the total negative charge density that a particular clay possesses, meq(q)/100 g clay. Because the negative charges are neutralized by exchangeable cations, the CEC is also equivalent to the total number of monovalent, exchangeable cations that bond to the clay. [22] Due to the exchange, uranium is now sequestered and removed to subsequently produce potable water. The core of this investigation was to confirm that sorption via ion-exchange was maintained for the clays once they were converted to pellets and to what extent the sorption occurred due to the transformation. Furthermore, the clays were deliberately used in a chemically unadulterated state to assume conditions that would be used in the field. The only clay treatment was to grind and pulverize them for control purposes and to facilitate pellet fabrication, especially for simple, sustainable use in the field.

Inductively coupled plasma-mass spectrometry, ICP-MS, was used to measure uranium at ppb concentration levels. [24] Uranium was removed to and below the Environmental Protection Agency - maximum contaminant level, EPA-MCL, for uranium, 30 ppb. These low ppb measurements made the present approach useful for potential implementation of the technology in the field. For example, trace concentrations of uranium below 10 ppb allowed us to formulate a uranium sorption model with regional clays. Some clays and pellets leached uranium when placed in ddiH_2O due to the non-bonded uranium that was already present in the clay. There was a need to evaluate this phenomenon to assess the overall efficacy for water purification in the presence of natural uranium that pre-existed in the clay. To differentiate between the uranium that was spiked into the solution for sorption analysis and the non-bonded uranium that was already present in the clay, all samples were initially pre-soaked in ddiH_2O . The water was decanted daily to ensure that the naturally occurring uranium not interfere with the uranium-clay interactions investigated under controlled conditions. As the predominant interaction between uranium ions and the clay is electrostatic, competing ions may interfere. For example, other cations of the unadulterated clay can behave as the competitors for the binding sites as well as affect uranium solubility. [25] Thus, hydronium ions, H_3O^+ , were added to probe the effect of sorption competitors because they are not present in solution at high concentrations nor are they released by the clay. [26] Cadmium and lead competitor ions were also tested in conjunction with uranium to probe this sorption possibility.

Materials and methods

Three standard montmorillonite clays, Arizona (SAz-2), Texas (STx-1B), Wyoming (SWy-2) and two regional clays, Berino (Lat-32.3°55'33" N Long-106.37°53.84"W) and Gallup (Lat-35.31°41.97" N Long-108.40°19.84"W) were investigated because they encompass a large range of CECs. The first three are standard clays that are used internationally. The last two are regional clays from soils in the state of New Mexico. The reason for the choice of the latter two is because they are close to the uranium affected

regions in New Mexico; Gallup is adjacent to the Navajo Nation. If their utility proves beneficial, they are in proximity. Furthermore, the latter two are rich in clay, but they are not recognized clay deposits. The only treatment to all clays was pulverization to pass through a 150 μm sieve. That the clays were not chemically adulterated was deliberate to assess sorption under conditions that would prevail in the field. A first step to fabricate pellets is the addition of water to create a plastic body. The plastic mixture is then shaped into cylindrical pellets and thermally treated. A furnace, set to 650 $\pm$ 25°C, was used to sinter the pellets for 4 hours. For elemental composition analysis, the clays were digested to completion with the U.S. EPA Method 3050B Microwave Assisted Acid Digestion. This method was applied twice to each sample.

Uranium abatement - static column test

The potential to abate uranium with clay pellets was probed first with Arizona and Gallup clays. These two clays were used for reasons above and because their CECs are the most extreme. Acrylic tubes, 25.4 cm height and 2.5 cm internal diameter, were fitted with Mininert valves for sampling. One tube was filled with Arizona pellets whereas another was filled with Gallup pellets. In both cases 151 g of pellets were used, each pellet approximately 0.5 g. The uranium solution for testing was prepared by dissolving uranyl nitrate hexahydrate in ddiH_2O to 375 ppb. 80 ml of the uranyl solution were added to the tubes with the pellets; these portions filled the tubes. This action also started the sorption clock. Small aliquot samples for uranium analysis were withdrawn at times 0, 1, 2, 3, 4, 6, 8, and 10 hours for both clays. The Gallup clay was further analyzed at 24 and 36 hours. The analyses were performed on an Agilent ICP-MS, Model 7500 instrument.

Solutions containing 5% PVA powder were prepared with distilled water and autoclaved at 90°C for 30 min. The pH of each PVA solution was then adjusted to 4.2 with 0.1N HCl.

12 hour pre-soak / static exposure, clays and pellets

The different initial behaviors of the Arizona clay versus the Gallup clay (Fig. 1 and Table 1) prompted the pre-treatment of the clays. Suspect introduction or leaching of uranium into the aqueous fraction occurred. The intent was to remove soluble and easily extracted impurities that could potentially interfere with the uranium sorption study. To this end, a 12-hour pre-soak was conducted in two stages for the five clays and their pellet analogues. For the clay powders, 0.5 g was placed in a 15 ml plastic Falcon conical centrifuge tube, and 10 ml of ddiH_2O were added. After 6 hours, the tubes were placed in a centrifuge and subjected to greater than 4699 gauss for 30 minutes. The water was decanted and fresh ddiH_2O added for the second stage of the pre-soak. The clays were agitated in the fresh water until they were suspended and left to pre-soak a second time for another 6 hours without agitation. Again, the suspension was centrifuged and the supernatant decanted for analysis. This portion is called the “pre-soak”. Then 10 ml of the 25 ppb uranyl solution were added to the clay and resuspended with agitation. This low concentration below the 30 ppb EPA-MCL was deliberate to potentially discern the various sources of uranium in the samples. The clays were exposed to the uranyl solution for 24 hours without agitation. The solution was removed as above for analysis. For the pellets (0.5 g is approximately 1 pellet), the procedure

was similar. The exceptions were that the solution was simply decanted because the pellets did not suspend and there was no need to agitate. After the final 24 hour uranium exposure and separation of the aqueous phase, all solutions were filtered through a 0.45 μm nylon syringe filter. Small 6 ml aliquots were acidified with 2 μl of concentrated HNO_3 in preparation for ICP-MS analysis.

7-day pellet desorption with acid exposure / static exposure, clays and pellets

This experimental section is to verify uranium presence in the clays and the effect that acidic conditions might have on sorption of external uranium. The clays were subjected to fresh water every day for seven days at 3 different pHs before they were exposed to a uranyl solution. For this 7-day experiment, all samples were treated as previously described in the 12-hour pre-soak with the following two exceptions. Each clay and pellet sample was tested at 3 different pHs, and the clays and pellets were exposed to an enhanced concentration of uranyl solution, 123 ppb, to explore efficacy in the field. For the various acidities, ddiH_2O was adjusted to pH 2, 4, and 6 with HCl. Initially, the pellets were exposed to the three acidified water solution, and the solutions were completely removed and analyzed every 24 hours. This process was repeated for 7 days, and this entire period is the “presoak” phase. The final acidified water supernatant was separated and collected. Then the 123 ppb uranyl nitrate solution was added and exposed to the clays and pellets for another 24 hours. Centrifugation, decantation, resuspension, filtration, and elemental analyses were executed identically as in the previous 12-hour experiment, and all points were performed in triplicate.

Lyotropic series test

A test to assess the binding of the uranyl cation in the presence of competitor ions was performed. The Texas clay was used for this purpose. The first task was to produce a sodium homo-ionic clay. Dialysis tubing was used to permit easy ion migration in either direction while restricting clay passage. The clay was exposed to NaCl at three times the CEC in a dialysis tube (MWCO 12-14 kD). This stoichiometry was equivalent to 15 g of STx-1B exposed to 637.5 mL of 0.1 M NaCl. Because the clay was difficult to exfoliate in dialysis tubing, a slurry was first created outside of the dialysis tube with a portion of the 0.1 M solution and then poured into the tubing. The tubing was then transferred to a container such that the net solution remained at 637.5 mL. Ion exchange was expected so the NaCl solution was refreshed every 24 hours for 3 days to remove the exchanged cations and thus drive the equilibrium to a sodium homo-ionic clay. The sample was subsequently dialyzed using 5 L of ddiH_2O and stirred for 24 hours with water exchanged after 12 hours. Conductivity measurements confirmed that excess sodium had been removed to the limits of the technique. Moreover, x-ray diffraction verified the saturation of the sodium ions onto the clay surface.

The sodium saturated Texas clay powder was then used to conduct, in triplicate, a lyotropic series study using $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, and $\text{UO}_2(\text{NO}_3)_2$, all at 500 ppb. All nitrate salts were dissolved together in 50 mL ddiH_2O , to which 0.5 g sodium saturated clay powder was added and exposed for one month (31 days). Additionally,

controls of pure ddiH₂O and 0.5 g clay powder in 50 mL ddiH₂O with no additional ions were included in the set. Finally, samples were centrifuged, decanted and the supernatant analyzed with the Agilent ICP-MS, Model 7500 instrument.

Dynamic flow to probe capacity

This dynamic study was prepared in the same fashion as above in the static column test. However, the solution was 425 ppb and now fed through the bottom of the vertical column at a rate of 5.75 ml/hr. The effluent from the top of the column was directed back into the column with a peristaltic pump. This flow was continuous for 24 hours at which time a small aliquot was drawn for analysis with the same instrument as above. Next, the uranium solution was removed, and this cycle was replaced with a 12-hour rinse and flush cycle with clean ddiH₂O. This combined 24-hour uranium cycle followed by a 12-hour rinse cycle sequence was repeated 4 times for a total of 144 hours or 6 days.

Results

Uranium abatement - static column test

The potential of clay pellets for uranium abatement was probed with a static batch study. The uranium concentration versus time exposure to the clay pellets is shown in Fig. 1. Arizona clay pellets removed the uranium from a heavily concentrated uranium solution. This abatement reduced uranium to potable concentration levels, 30 ppb EPA-MCL, rather quickly (31 ppb after less than 10 hours). In contrast, the Gallup clay took at least 36 hours to accomplish the same feat to 23 ppb. Of significance in Fig. 1 is the upsurge of uranium after the Gallup clay was exposed to water. Ultimately, the Gallup clay reduced the uranium concentration to potable levels under these static conditions.

12-hour pre-soak / static exposure, clays and pellets

Because the Gallup and Arizona clays exhibited different sorption behaviors (Fig. 1), this phenomenon was probed further with all five clays. An additional pre-treatment was introduced to remove soluble components, especially uranium, so that they not interfere with the uranium sorption study. The uranium concentration levels in the pre-soak and post uranium exposure are shown for the clay powders and pellets in Fig. 2 and Table 2. For the first 6-hour phase, only the Wyoming and Gallup powders exhibited discernible concentrations of uranium in the pre-soak, 23 and 2.8 ppb respectively, yet statistically below the 30 ppb EPA-MCL. The solutions for the remaining 8 clays and pellets were at or below the 10 ppb limit of quantitation, LOQ. For the second 6-hour pre-soak phase, only the Wyoming clay powder persisted and demonstrated any uranium, and it had dropped to 7.7 ppb. All others were statistically below the LOQ. After the 24-hour exposure to the 25 ppb uranyl nitrate, uranium concentrations increased above the 25 ppb spike concentration for only four samples: Wyoming powder, Wyoming pellets, Gallup pellets, and Berino pellets, 41.1, 33.3, 87.1, and 40.0 ppb, respectively. The Gallup pellets in Fig. 2 verify the results in Fig. 1 where there is an initial slight upsurge of uranium in the initial 12 hours. The remaining clays all reduced the uranium levels below the 25 ppb spike concentration.

Clay digestion to probe natural uranium presence

Figures 1 and 2 indicate the presence of uranium in the pre-soak solutions; this is before uranium spikes were added to the solutions. The supposition was that uranium is already present in some form in the clays that were investigated. To verify this hypothesis, the unadulterated clays were digested and the uranium content measured. Uranium concentrations in the soil are listed in Table 3. Most notably, uranium was present in all clays. The digestion process does not distinguish between the states of uranium in the samples. Specifically, uranium can be bound to the clay, exist as a soluble salt, be present in an insoluble form, or any combination of these. This measured uranium presence verifies the hypothesis that uranium leaches from some clay sources.

7-day pellet desorption with acid exposure / static exposure, clays and pellets

The phenomenon of increased uranium in solution ^[27] during the pre-soak phase was examined further by increasing the pre-soak to 7 days under different pH conditions. Results for the 24-hour exposures of the various aqueous solutions are shown in Figs. 3 and 4 for the clay powders and the pellets, respectively. Because the clays were tested at various acidic conditions, a relevant observation was the evidence of clay platelet hydrolysis to a visible siliceous precipitate, a slight tinge of cloudiness. ^[28] For the clay powder samples at pH 2, clay platelets were hydrolyzed to some extent. ^[29] At pH 4 and pH 6 the clay powders remained in complete suspension after agitation, an inherent physical property of integral clays. In contrast, the pellets remained entirely intact at pH 6; however, partial hydrolysis occurred at pH 2 and pH 4.

For the pre-soak span, again the Wyoming powder at pH 2 released a significant amount of uranium only on the first day. Uranium was not detected for the remaining clay powders except for the Texas clay at the three pHs. The only pellet to release uranium in the pre-soak was the Texas pellet at pH 2. Wyoming clay has the largest amount of inherent uranium and leaches the greatest amount. Texas clay with the second largest amount of inherent uranium also released uranium, especially in the most acidic solutions. After introduction of 123 ppb uranium, approximately 5 times the concentration in Fig. 2, and a 24-hour exposure time, all clay powder samples at the 3 pHs abated uranium below the 30 ppb EPA-MCL. For the pellet counterparts, all pellets except the Berino and Texas pellets at pH 2 reduced the uranium concentrations to levels below the 30 ppb EPA-MCL. The two exceptions reduced the concentration levels to 60 ppb and 45 ppb, respectively. Under appropriate conditions, clays abate uranium; moreover, clays in pellet form are equally viable and have the added advantage of application in the field.

Lyotropic series test

All previous experiments involved only uranium; however, for applications in the field, aqueous solutions will have a variety of ions and an elevated ionic strength. Therefore, this experiment was designed to evaluate uranium sorption in competition with other ions. Two other heavy metals, lead and cadmium, were added. In addition to uranium, two other toxic heavy metals, lead and cadmium, were added. Naturally abundant sodium, calcium and magnesium ions were also added in the same overwhelming amounts as uranium. The

solution was 500 ppb for all ions. The large concentration was chosen to assure the sorption chemical potential would be in effect. Thus chemical sorption pressure would be identical for all ions. Moreover, except for sodium, uranium and all the ions have a +2 charge. Because the concentrations and charges were identical, the relative binding strengths for the sorption onto the clays could be assessed readily. Uranium was abated from 500 ppb to 79 ppb while cadmium and lead were reduced to 97 and 126 ppb, respectively. Conversely, the magnesium concentration rose to 129 ppm; the calcium increased to 9.3 ppm; and sodium was too concentrated to measure quantitatively. Uranium was the most sorbed ion in this very complex matrix of competing ions; the lyotropic series was $\text{UO}_2^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} \gg \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^{1+}$. This is assurance of uranium abatement applicability in the field.

Dynamic flow to probe capacity

Another facet to consider for pellet application is capacity, see Fig. 5. For both the Arizona and Gallup clays, the same pellets significantly abated uranium four times from extremely concentrated 425 ppb uranium solutions. The Arizona pellets removed approximately 80 percent of the uranium in each of the four trials and the Gallup pellets removed a bit more than half of the uranium. The first trial for the Arizona pellets produced the most efficient abatement, and the uranium abatement reached equilibrium in the last two trials. That the uranium abatement equilibrated for the last two trials was also true for the Gallup clay. Again, this is a verification that the Gallup clay leaches naturally occurring uranium (Fig. 1) before the uptake of uranium from a contaminated source.

Discussion

Clay powders sorbed uranium, and the pellet structures were as efficient as powders (Figs. 1-4). With appropriate design, uranium abatement achieved the 30 ppb EPA-MCL with all the clay pellets, albeit some pellets decreased the uranium concentration more quickly than others (Figs. 1-4). Absolute adsorption rates and measurements were not in the scope of this study. All references to rates are strictly relative. For example, various conditions and parameters affected the immediate uranium sorption, and one of them was the inherent presence of uranium in the unadulterated natural clays. Figs. 2 and 3 indicate that the Wyoming clay powder and pellets initially introduce uranyl ions into solution at a rate faster than the sorption rate; this is more apparent when compared to the sorption plot for the Arizona clay in an identical time frame, Fig. 1. On digestion, the Wyoming clay had the largest concentration of uranium as compared to the other four clays, three times that of Texas and an order of magnitude more than the Gallup clay. More notably, this uranium is in a soluble, unbound state, so the uranyl ions leached immediately into solution. The uranium was nonetheless quickly sorbed by the Wyoming clay as shown in Figs. 2 and 3 and Tables 2 and 4.

In the same manner, the Gallup clay pellets always had an initial upsurge before all uranium was sorbed and removed, regardless of the source. This is most evident in Fig. 1. In Fig. 2b, the Gallup clay was still contributing to trace amounts of uranium at 36 hours. More subtly in Fig. 5, the sorption trend at the end of the 24-hour exposures was different for the Gallup

pellets relative to the Arizona pellets. The Arizona pellets were immediately more efficient in the first trial and equilibrated continuously with the subsequent trials. Conversely, the first trial for the Gallup pellets was not the most efficient, and this phenomenon is additionally revealed in Fig. 2 and especially Fig. 1. The model suggests that there was a presence of a uranium salt in the natural Gallup clay that was slightly soluble. This contributed to the increase of uranium concentrations after the external addition of uranium to the solution. Figs. 2 and 4 and especially Fig. 1 also suggest that a kinetic parameter for the dissolution and subsequent binding of intrinsic uranium was involved and centered about 36 hours. Kinetically, some clays outperform others; i.e., in the same time frame they abate uranium to potable levels more quickly than others, Fig. 1. In addition, some clays will seemingly sorb more pollutants on per mass basis. Thermodynamic modeling and capacity studies were not the scope of this investigation. However, the Arizona clay sorbed 25 percent more uranium than the Gallup clay, Fig. 5. This is most likely due to the fact that the Arizona CEC is approximately three times that of the Gallup clay.

Another trend was observed in Fig. 2 for the Gallup and Berino pellets that was not observed with their powders; pellets released uranium whereas the powders did not. The only difference was that the pellets were exposed to elevated temperatures, possibly consistent with carbonate decomposition. Uranyl carbonates are relatively insoluble (K_{sp} : CaCO_3 , ~6-8; UO_2CO_3 , ~14), thus uranium was not detected in the pre-soak phase for these two clays. However, thermal decomposition produced soluble uranyl ions that were detected for the Berino pellets and especially for the Gallup pellets. Two parameters should be noted for these two clays: Berino and Gallup clays have the smallest CECs and the smallest natural inherent uranium concentrations from the group of five clays.

The Texas clay had its unique narrative, Figs. 3 and 4 and Tables 4 and 5. It was the only clay, aside from the very abundant soluble uranium in the Wyoming clay, that had a slightly measurable uranium concentration in the acidic pre-soak solutions. The concentration was above the LOQ, yet still potable, below the 30 ppb EPA-MCL. After the initial “bump”, characteristic of soluble uranium salts as evidenced by the Wyoming clay, the Texas clay exhibited a relatively constant concentration of uranium for days. Support for this hypothesis is that the most acidic solution dissolved the insoluble uranium to a greater extent. This was not observed in the solutions without acid. The uranium was present as an insoluble salt that released the uranyl cation on acidification.

Finally, at the other extreme, the Arizona clay powders and pellets provided another model. The Arizona clays and pellets never exhibited the presence of uranium in the aqueous pre-soak solutions under any conditions. If there was uranium, its concentrations were always below the detection limit, 10 ppb. Yet on digestion there was a significant amount of uranium in the Arizona clay. Arizona clay has an inherent uranium component that is strongly bound to the clay. This ionic bond to the Arizona clay was favored, and consequently the uranium was never in any aqueous fraction. Nonetheless, 375 ppb uranium was abated to potable levels in less than 5 hours with Arizona pellets, Fig. 1; this is the consequence of Arizona clay having the largest CEC. Furthermore, the strong ionic bond

between the uranyl cation and clay was evident for all the clays because all clays eventually abated uranium to the EPA-MCL, Figs. 1-4.

All clays had a natural uranium component; however, the chemical state varied from one clay to another. The different clays provided a variety of uranium sorption pathways, each with its unique kinetic timeframe. The strongest bond is the ionic bond to the clay, and this was the only pathway for the Arizona clay. Uranium in the aqueous phase was observed for some clays only when they were exposed to elevated temperatures and for some when exposed to acidic solutions. Completely soluble uranyl salts dissolve, but they are subsequently sorbed onto the clays. Complete abatement took longer to achieve in the latter cases. In all trials, ionic bonding is the final stage. The capacity to sorb was large enough for all clays to abate uranium to potable levels.

When insoluble uranium salts were not present, it appeared that kinetically a 24-hour time frame was sufficient to obtain uranium concentrations that were 13 ppb, Fig. 2. Dissolution of uranyl salts took longer for complete abatement because clay binding did not occur until the uranyl cations were solvated. A typical timeframe in these trials was approximately 36 hours. The data demonstrated the capability for clay pellets to sorb excessive levels of uranium from drinking water to below the EPA MCL. Regardless of whether there is naturally occurring uranium in the clays, given enough time, quantity of pellets, or both, uranium can be abated to the EPA MCL. Many pellets in proximity and in flow conditions, Fig. 5, will capture both the soluble and insoluble forms of uranium that are introduced by the clay source itself.

Again capacity studies were not conducted; however, several of our experiments imply a large sorption capacity, and three examples follow. In the lyotropic series test, three heavy metal ions in large concentrations, 500 ppb each were reduced to levels below 100 ppb with 0.5 g of clay. This occurred in the presence of sodium, calcium, and magnesium, also at 500 ppb. Next, despite the fact that some pellets were partially hydrolyzed, the sorption levels nonetheless approached potable levels. For the Arizona pellets in Fig. 5, the uranium was 6-10 times more concentrated than the highest levels observed in the Four Corners area. Uranium at these huge concentrations was abated 4 times in succession to extremely reduced levels. More cycles were possible. Further experimentation will verify this hypothesis.

The hydronium ion did not interfere with uranium sorption; the uranium was abated to potable levels even under very acidic conditions. The uranyl ion bonding to clays is much stronger than the hydronium ion bond. The uranyl ion is much higher on the lyotropic series than is the hydronium ion. Furthermore, prolonged exposure to extreme acidity, pH 2, did partially hydrolyze clays, but these conditions do not exist naturally, so this is not problematic.

The toxic heavy metals were sorbed extremely well in the presence of highly abundant natural cations such as sodium, magnesium, and calcium. This is an important consideration for producing potable water because it is difficult to accomplish this separation when non-heavy metal competitors of the same charge abound. This is possibly a charge density phenomenon due to charges, hydrated radii, and the influence of the ionic strength which

will have a large impact, especially with contaminated water sources that are anticipated. Indeed, the heavy metals exhibited preferential binding. For example, cadmium is considered a mobile ion. ^[30] Yet in our study, it was sorbed in amounts quite similar to uranium when exposed for 31 days. Cadmium ions were potentially transforming from outer sphere to inner sphere configurations; the outer sphere ions are more mobile whereas the inner sphere ions would bind more efficiently. ^[31] This would suggest that kinetic and thermodynamic processes are both affecting the uranium and heavy metal sorption model. A more thorough understanding of this type of information is crucial for eventual applications in the field. Thermodynamic sorption studies with Langmuir, Freundlich, and Horvath-Kawazoe modeling will ensue. Kinetic studies were not in the scope of this study. Nonetheless, Fig. 1 suggests a first order reaction. For example, the enhanced uranium concentration provided by the Gallup clay did not enhance the sorption rate; it was actually slower. Furthermore, it is not the amount of clay that is central to the reaction rate, but rather the ion exchange sites, and the Arizona CEC is approximately three times that of the Gallup clay. The same arguments hold in Fig. 5.

Conclusion

Given enough time and the appropriate amount of pellets, uranium was abated to potable levels for all clays. The hypothesis would be to extrapolate this statement to all clays worldwide. Clay pellets can help alleviate a pressing environmental and health problem. It is important to note that any field implementation of clays must use ceramic pellets. Otherwise, proper disposal of the clay after uranium abatement cannot take place safely and efficiently using non-pelletized clays that swell and produce unmanageable slurries. Non-pelletized clay utilization also has the potential of accidental consumption. Future experiments will include isotherms to study the effects of, pH, pE, ionic strength, clay platelet size, and elemental composition. This will allow for the improvement of the uranium abatement model with ion exchange as well as accounting for the release of naturally occurring uranium.

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Figure 1.

Pellets were exposed to 375 ppb uranium in a static environment and samples taken at various times.

Figure 2.

Uranium concentration after pre-soak for a) clay powders and b) pellets. Pellets were soaked in ddiH₂O for 12 hours. Samples were decanted at the mid-point (6 hours) and replenished with fresh ddiH₂O. Sample was decanted again at 12 hours and 25 ppb UO₂ was then added. A final measurement taken at 36 hours

Figure 3.

Clay powder soaked for 7 days with samples decanted every 24 hours and fresh water added. After the day 7 sample was decanted, 123 ppb uranium was added and the final sample was taken 24 hours later.

Figure 4. Clay pellet soaked for 7 days with samples decanted every 24 hours and fresh water added. After the day7 sample was decanted, 123 ppb uranium was added and the final sample was taken 24 hours later.

Figure 5.

Pellets were exposed to 425 ppb uranium with the solution continuously flowing. Samples were taken every 24 hours with a 12- hour intermediate flushing period. The cycle would begin again with 425 ppb uranium.

Table 1.

Pellets exposed to 425 ppb uranium with the solution continuously flowing

Time (Hr.)	Gal (ng/mL)	Az (ng/mL)
0	369.8	369.8
1	113.44	43.37
2	121.66	36.83
3	119.41	34.89
4	121.9	32.92
6	101.34	32.54
8	93.53	31.89
10	79.56	31.01
12	71.07	
24	35.08	
36	22.75	

Table 2a.

Uranium concentration after pre-soak for clay powders

Time (Hrs)	Wyoming	Texas	Arizona	Gallup	Berino
0	0	0	0	0	0
6	23.66	0.33	0.15	2.84	0.61
12	7.75	0.52	0.082	0.79	0.54
Add 25 ppb uranium	25.0	25.0	25.0	25.0	25.0
36	41.058	4.194	0.611	7.627	12.498

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Table 2b.

Uranium concentration after pre-soak for clay pellets

Time (Hrs)	Wyoming	Texas	Arizona	Gallup	Berino
0	0	0	0	0	0
6	0.783	0.224	0.081	0.265	0.096
12	0.145	0.064	0.005	0.078	0.083
Add 25 ppb uranium	25.0	25.0	25.0	25.0	25.0
36	33.325	8.259	12.703	87.077	33.977

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Table 3.

Uranium Concentrations (ppm – g/g) for the Five Clays

Wyoming	Texas	Arizona	Berino	Gallup
1.485	0.496	0.276	0.189	0.138

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Table 4.

Clay powder sample soaked for 7 days with samples decanted every 24 hours and fresh water added

Day	pH 2		pH 4		pH 6	
	Tx	Wy	Tx	Wy	Tx	Wy
0	6.52	0.44	6.52	0.44	6.52	0.44
1	22.33	73.52	9.69	4.44	7.44	0.91
2	25.40	3.81	18.05	2.03	14.63	0.86
3	23.70	3.97	16.67	1.14	11.07	0.65
4	23.60	3.45	8.14	1.03	8.04	0.58
5	22.10	1.70	7.26	0.47	7.13	0.47
6	23.20	3.52	7.26	0.88	7.47	0.55
7	24.53	3.30	7.36	0.70	7.24	0.56

Table 5.

Clay pellet sample soaked for 7 days with samples decanted every 24 hours and fresh water added

Day	pH 2		pH 4		pH 6	
	Tx	Wy	Tx	Wy	Tx	Wy
0	6.52	0.44	6.52	0.44	6.52	0.44
1	24.93	2.39	7.05	0.48	8.41	0.48
2	11.40	1.88	6.86	0.47	7.16	0.50
3	17.00	1.62	6.62	0.47	6.98	0.49
4	15.09	1.41	6.56	0.47	6.73	0.48
5	12.56	1.65	6.58	0.47	6.79	0.48
6	12.77	1.43	6.57	0.47	6.91	0.47
7	12.47	1.82	6.58	0.47	7.06	0.48