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RADIUM REMOVAL FROM UNCONVENTIONAL GAS WASTEWATER  
VIA SORPTION TO PROPPANTS

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## ABSTRACT

A major concern in the field of high volume hydraulic fracturing (HVHF) for unconventional gas development is the treatment of flowback waters containing radium, a hazardous radioactive element. This research seeks to remove radium through sorption to specialty proppants so that it is retained in the subsurface. Experiments were first conducted using barium as an analog of radium. Batch sorption tests were conducted with sand, ceramic, manganese dioxide, and magnetite proppants in order to construct sorption isotherms with solutions of  $\text{BaCl}_2$ . Analysis of the solutions by inductively coupled plasma optical emission spectrometry (ICP-OES) indicated that magnetite and manganese dioxide proppants sorbed 10 and 5 times more barium per gram, respectively, than conventional fracking sand. The sorption tests were repeated with competing ion solutions of up to 400 meq/L Na-Ca-Cl electrolyte, which resulted in a 75.3% reduction in barium sorption. Tests were then conducted with  $\text{RaCl}_2$  and competing ion solutions of up to 1200 meq/L Na-Ca-Cl. Analysis by liquid scintillation counting (LSC) and gamma spectroscopy showed that radium sorbed to magnetite with a greater selectivity than barium, but the sorption was reduced by up to 97.1% in the presence of competing ions. Additional testing is needed to verify these results and investigate the performance of magnetite at concentrations typical for proppant application. Although magnetite proppants may be a promising solution for in-situ radium removal, their effectiveness in the high salinity conditions of an actual gas well remains unclear.

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## Chapter 1

### Introduction and Literature Review

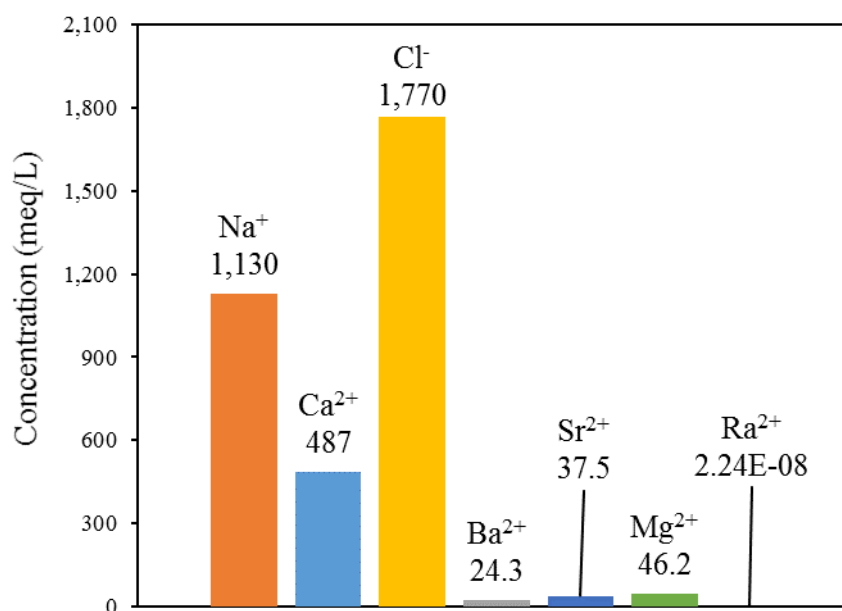
Hydraulic fracturing has existed for decades within the oil and gas industry. With advances in technology over the last 15 years, fracturing of horizontally-drilled wells has become a widespread and lucrative method of extracting petroleum resources that were previously inaccessible.

Current industry practice uses a total about 9 million gallons of water to fracture a single well over a 10-year lifetime (Abdalla and Drohan, 2010). Solid grains known as proppants are pumped with the water and serve to hold open fractures in formation rock so that gas can flow out of the well. Most wells contain about 1.4 million kg of proppant, a concentration of approximately 40 g/L of fluid. By volume, water and proppant constitute roughly 90% and 9.9% of the total fracturing fluid pumped into a well. The remaining 0.1% consists of a variety of chemical additives intended to optimize well performance. Among these chemicals are acid to clear debris, thickener to disperse proppant, friction reducer to aid fluid flow, scale inhibitor to prevent carbonate and sulfate deposits, corrosion inhibitor to protect steel casings, and biocide to guard against microbial fouling. These chemicals are useful in improving well performance but can often cause serious environmental harm in the event of accidental surface water or groundwater contamination (Ritter, 2014).

After fracking fluid is pumped into a well, it gradually returns to the surface as flowback. Most flowback returns within the first few days after fracking, while some is produced gradually over the lifetime of the well. Flowback water from the Marcellus Shale formation is primarily a

Na-Ca-Cl brine but also contains Ba, Sr, Mg, and Ra in smaller quantities (Stewart et al., 2015).

Figure 1 displays the typical ionic composition of Marcellus Shale flowback water, based on the averages of sample data published in several papers (Hayes, 2009; Chapman et al., 2012; Osborn et al., 2012; Haluszczak et al., 2013). Although the exact source of the brine is unknown, studies suggest that it arises from trapped formation water that has been released by fracking (Stewart et al., 2015). Even though acid is a typical component of fracking fluid, flowback water generally returns with a near neutral pH due to carbonate buffering (Wang et al., 2015).



**Figure 1. Typical ionic composition of Marcellus Shale flowback water (Hayes, 2009; Chapman et al., 2012; Osborn et al., 2012; Haluszczak et al., 2013).**

The majority of the Ra found in flowback water is Ra-226, which has a half-life of 1600 years (Gonneea et al., 2008). Ra-226 is formed from the decay of U-238 and exists naturally in the Earth's crust. The median concentration of Ra-226 in Marcellus Shale flowback water is approximately 2,500 pCi/L but can range from several hundred to over 10,000 pCi/L (Zhang et



al., 2015). Because of its high radiotoxicity, Ra-226 must be removed from wastewater, presenting a serious treatment issue for the industry (Sajih et al., 2014).

Chemical precipitation is currently the most cost-effective treatment method for Ra. Ra can be removed through co-precipitation with barite,  $\text{BaSO}_4$  ( $K_{\text{sp}} = 1.08 \times 10^{-10}$ ) (Solubility Product Constants). Since Ba and Ra are both alkaline earth metals,  $\text{Ra}^{2+}$  ions can replace  $\text{Ba}^{2+}$  ions within a  $\text{BaSO}_4$  crystal lattice through a process known as inclusion (Zhang et al., 2015). Ra can also be removed through the addition of sulfate to form the highly insoluble species  $\text{RaSO}_4$  ( $K_{\text{sp}} = 3.66 \times 10^{-11}$ ) (Solubility Product Constants).

This current research project focuses on the possibility of removing Ra from flowback before it reaches the surface, thus decreasing treatment costs and reducing the potential for surface water or groundwater contamination. The sorption of Ra to proppants will be tested as a potential solution to this problem.

A study of estuary sediments indicated that Ra has a high affinity for iron oxides and an even higher affinity for manganese oxides. Ra adsorption to sediments occurs rather quickly and generally goes to completion within a few hours. It was also found that increasing salinity causes Ra desorption, likely due to competitive sorption by other cations (Gonneea et al., 2008). A separate study of Ra sorption to manganese dioxide ( $\text{MnO}_2$ ) indicated that Ra sorption is pH-dependent and mostly occurs at  $\text{pH} > 3.6$  (Koulouris, 1995).

Experiments with goethite ( $\alpha\text{-FeO(OH)}$ ) and ferrihydrite ( $(\text{Fe}^{3+})_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ ) showed that Ra readily adsorbs to these minerals via surface complexation. In this endothermic process, Ra binds to the outer surface of the sorbent as an outer sphere complex. The sorption is pH-dependent, with greater sorption occurring at  $\text{pH} > 7$ . Ba and Ca were both found to compete with Ra for sorption to ferrihydrite (Sajih et al., 2014).

Ra sorption is also influenced by temperature, with higher temperatures resulting in increased Ra solubility in salt marsh sediments (Rama and Moore, 1996). This notion is supported by thermodynamic data on a variety of sulfate and carbonate minerals, which also suggest that Ra solubility is greater at higher temperatures (Langmuir and Riese, 1985).

As a result of these studies, it was decided to test magnetite ( $\text{Fe}_3\text{O}_4$ ) and  $\text{MnO}_2$  as potential proppants for Ra sorption.<sup>1</sup> Saint-Gobain's Titan ceramic proppant (0-15% aluminum silicate, 60-80% aluminum oxide, 15-30% ferric oxide, and 0-5% titanium dioxide) was also tested due to its iron oxide content (*Titan*<sup>TM</sup> SDS). Additionally, Unimin frac sand (87-99.9% silica), a conventional proppant material, was tested as a standard of comparison (Unifrac Hydraulic). The effects of pH, temperature, and reaction time were considered in the design of sorption experiments.

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<sup>1</sup> Although the magnetite and  $\text{MnO}_2$  were technically particles of varying size ( $d < 150 \mu\text{m}$ ) and not proppants, all four materials will be referred to as proppants in this text for the sake of simplicity.

## Chapter 2

### Methods

A series of seven experiments were conducted in this research project. Batch sorption tests were first conducted using Ba, an element that has similar chemical properties to Ra but is less hazardous to test. In Experiment 1, 20 mL of  $6.58 \times 10^{-5}$  M BaCl<sub>2</sub> electrolyte (about 1/100<sup>th</sup> the Marcellus Shale formation concentration) was added to 50 mL polypropylene centrifuge tubes along with the following four proppants: Unimin frac sand, Titan ceramic, MnO<sub>2</sub>, and magnetite. The proppant concentration in each tube was varied from 0-500 g/L. The tubes were agitated in an incubator shaker to promote sorption of the electrolyte to the proppant. The samples were then filtered, checked for pH, acidified, and analyzed by ICP-OES to determine the concentration of Ba<sup>2+</sup> remaining in solution. The difference between initial and final concentrations of Ba<sup>2+</sup> was assumed to be due to sorption to the proppant. These tests were conducted at room temperature and at 60°C for periods of 6 hours and 48 hours in order to determine the effects of temperature and time on sorption. The temperature of 60°C was chosen in order to approximately match the average temperature of Marcellus Shale (Kargbo et al., 2010).

In all subsequent tests, 10 mM 3-morpholinopropane-1-sulfonic acid (MOPS) buffer was added to the background electrolyte in order to maintain a constant pH during sorption. The pH was set to 7.0 through the addition of NaOH.

Experiment 2 was conducted using only magnetite and  $\text{MnO}_2$  proppants, which were the most effective sorbents from Experiment 1. Unimin frac sand was also tested for the purpose of comparison. The three proppants were pulverized in a ball mill and passed through a  $150\ \mu\text{m}$  sieve. All particles smaller than  $150\ \mu\text{m}$  were rinsed with ultrapure water and dried. The resulting rinsed proppant was used for Experiments 2-5.

In Experiment 2, batch sorption tests were conducted at  $60^\circ\text{C}$  using a similar method as before. Because the reaction time in Experiment 1 was not found to have a noticeable effect on sorption, the time was reduced to 40 hours for convenience. All tubes in Experiment 2 contained 10 mL of 1 mM  $\text{BaCl}_2$  with 10 mM MOPS, and the concentration of proppant in each tube was varied from 0-64 g/L. Approximately 4 meq/L of NaOH was added to adjust the pH to 7.0. The tube caps were wrapped with Teflon tape on the inside and duct tape on the outside in order to prevent evaporation when heated. The results of this experiment were used to generate sorption isotherms for each proppant.

Experiment 3 tested the effect of competing ions on Ba sorption. Background electrolyte solutions were prepared containing 10 times and 100 times the concentration of Na used in Experiment 2, or approximately 40 and 400 meq/L, respectively. Electrolyte solutions of  $\text{CaCl}_2$  were also prepared at the same meq/L concentrations as the NaCl. In addition to a competing ion, each solution contained the same concentration of  $\text{BaCl}_2$  and MOPS as in Experiment 2 (1 mM and 10 mM, respectively). Batch sorption tests were then conducted with these solutions with 64 g/L of magnetite or 64 g/L of  $\text{MnO}_2$  proppant. The tests were run for 40 hours at  $60^\circ\text{C}$  as before.

Experiment 4 was conducted to generate a preliminary Ra sorption isotherm for magnetite. Teflon centrifuge tubes were used in order to minimize sorption of Ra to the tubes

themselves. Each tube contained a background electrolyte of 20,000 pCi/L RaCl<sub>2</sub> with 10 mM MOPS. In order to adjust the pH to 7.0, approximately 12 meq/L NaOH was added. The proppant concentration was varied from 0.01-100 g/L. The tubes were agitated for 40 hours at 60°C as before. After completion of the experiment, the tubes were filtered but not acidified.

Vials were prepared for analysis by liquid scintillation counting (LSC) by adding 2 mL of each sample to 18 mL of EcoLume scintillation fluid. The results from LSC were then analyzed to determine the amount of Ra sorption under these experimental conditions.

Experiment 5 was conducted to determine whether sulfate impurities were leaching from the surface of the magnetite proppant and potentially removing Ba or Ra through precipitation. Centrifuge tubes were filled with 10 mL ultrapure water and 64 g/L magnetite. The tubes were then placed in the incubator shaker at 60°C for 40 hours. Afterward, the samples were tested for sulfate via ion chromatography (IC). Following this test, the magnetite proppant to be used in Experiments 6 and 7 was rinsed with ultrapure water and dried in an attempt to remove most residual sulfate from the proppant surface. Subsequently, the rinsate was retested for sulfate via IC.

Experiment 6 was conducted with the same methods as Experiment 4 using NaCl and CaCl<sub>2</sub> solutions of approximately 12, 40, 400, and 1200 meq/L. The solutions with 12 meq/L Na only contained Na from pH adjustment with NaOH. The highest concentration tested (1200 meq/L) was chosen to approximately match the average Na concentration in Marcellus Shale flowback waters. This experiment used different Teflon tubes with fewer interior scratches in order to prevent any possible sorption to the tube walls, which may have occurred in Experiment 4. Each tube contained 35 mL of 20,000 pCi/L RaCl<sub>2</sub> with 10 mM MOPS at pH 7.0 along with 0.5 g/L magnetite. The tubes were agitated for 40 hours at 60°C as before. Rather

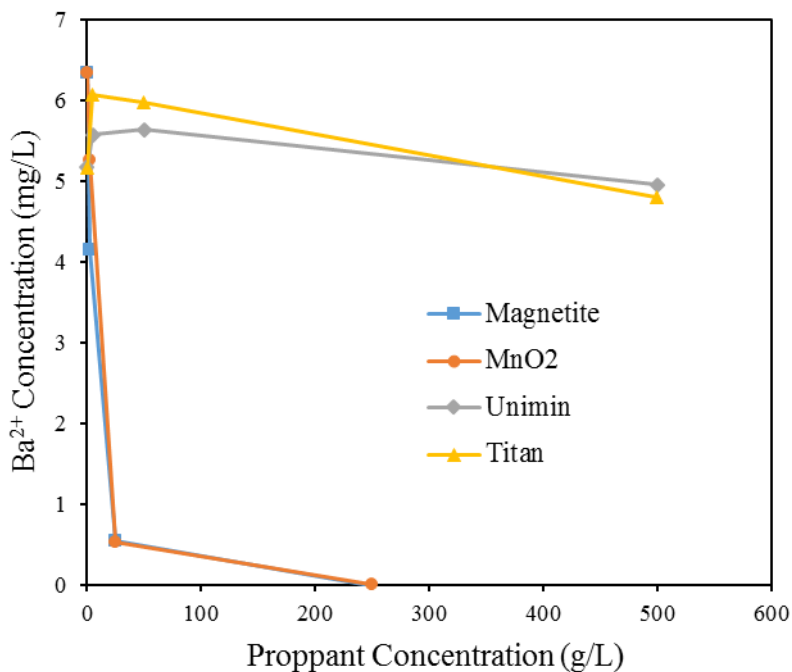
than filtering, the tubes were centrifuged and decanted into scintillation vials. The vial caps were sealed with electrical tape to prevent evaporation. The samples were then analyzed by gamma spectroscopy to demonstrate the effect of competing ions on Ra sorption.

Experiment 7 was conducted to quantify the amount of Ra removal potentially caused by  $\text{RaSO}_4$  precipitation. This test used a background electrolyte of 20,000 pCi/L Ra, 1200 meq/L Ca, and 10 mM MOPS. The pH was set at 7.0 through the addition of 7.4 meq/L NaOH. Two Teflon centrifuge tubes were then each filled with 25 mL of background electrolyte and a small quantity of  $\text{Na}_2\text{SO}_4$ . Enough  $\text{Na}_2\text{SO}_4$  was added to the first tube to produce a  $\text{SO}_4^{2-}$  concentration of 17 mg/L, the concentration found in the samples of Experiment 5 prior to rinsing. Five times this amount of  $\text{SO}_4^{2-}$ , or 85 mg/L, was added to the second tube. The tubes were then placed in the incubator shaker at 60°C for 40 hours. Upon removal from the shaker, the samples were centrifuged and decanted into scintillation vials. The vial caps were sealed with electrical tape to prevent evaporation. The sample activities were then measured by gamma spectroscopy to determine whether  $\text{RaSO}_4$  precipitation lowered the activity of Ra in solution.

## Chapter 3

### Results and Discussion

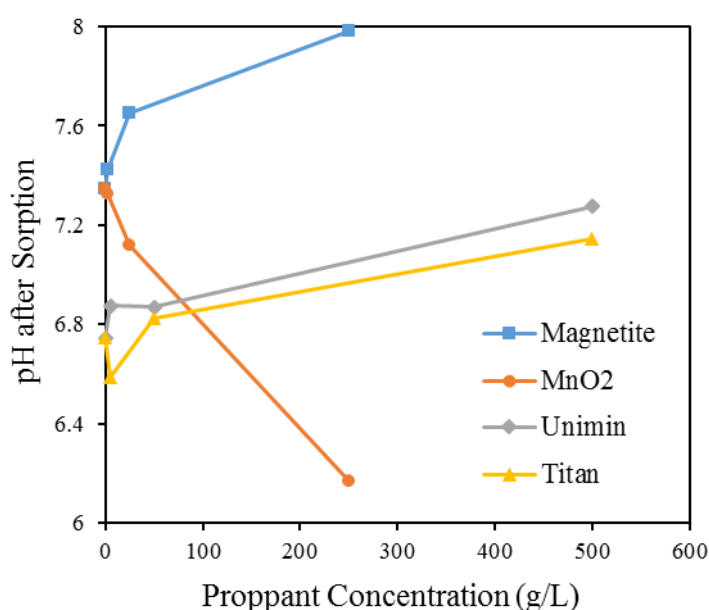
In Experiment 1, batch sorption tests were conducted with Unimin frac sand, Titan ceramic,  $\text{MnO}_2$ , and magnetite proppants. As shown in Figure 2, magnetite and  $\text{MnO}_2$  sorbed essentially all  $\text{Ba}^{2+}$  from solution.<sup>2</sup> However, sand and ceramic proppants did not sorb a significant amount of  $\text{Ba}^{2+}$ . Since magnetite and  $\text{MnO}_2$  were shown to be the most effective sorbents, these two proppants were analyzed further in subsequent tests.



**Figure 2.  $\text{Ba}^{2+}$  concentration measured by ICP-OES after 48-hr batch sorption tests at 60°C for four proppants (Experiment 1).**

<sup>2</sup> Error bars do not appear in Figures 2-5 because they are too small to be visible.

The pH of each sample was also measured after sorption. As shown in Figure 3, sorption caused a pH change of up to ~1.2 pH units, with a greater change occurring in solutions containing MnO<sub>2</sub> or magnetite. In order to eliminate the effect of pH change on sorption, all subsequent experiments were conducted with a 10mM MOPS buffer added to the background electrolyte.



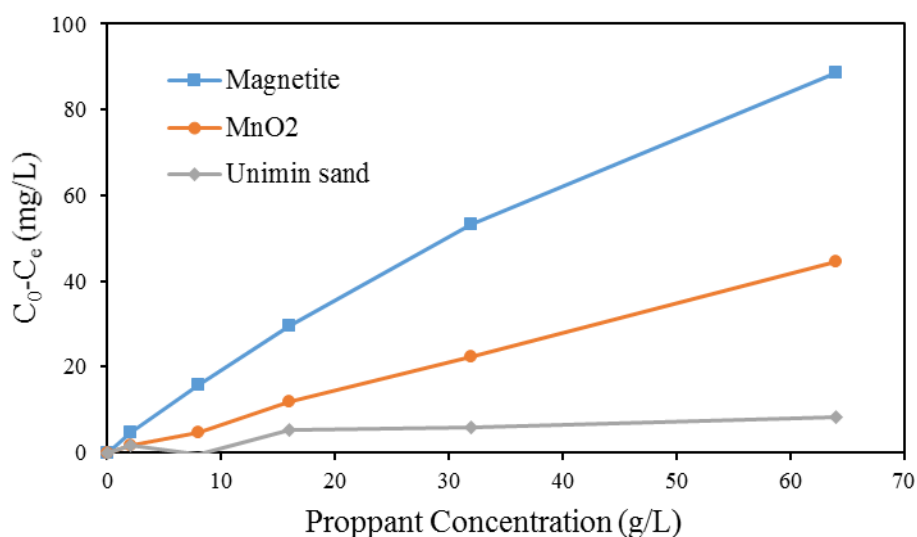
**Figure 3. Solution pH after 48-hr batch sorption tests at 60°C for four proppants (Experiment 1).**

Experiment 1 also measured the effect of sorption time and temperature on the amount of Ba sorption. Samples were agitated at 25°C and at 60°C for time periods of 6 hours and 48 hours. For all four proppants, the variables of time and temperature did not have a significant effect on the degree of sorption. Therefore, all subsequent tests were conducted at the formation temperature of 60°C for a period of approximately 40 hours for testing convenience.



The ICP-OES data from Experiment 1 also indicated that detectable quantities of Al, B, Ca, Fe, K, Mg, and Mn were released from the proppants during sorption. Many of these same metals were also released in controls containing only proppant and ultrapure water. Therefore, the proppant was rinsed with ultrapure water in order to remove these elements prior to completing Experiments 2-5.

In Experiment 2, batch sorption tests were conducted at 60°C for 40 hours using magnetite, MnO<sub>2</sub>, and Unimin frac sand proppants. The test generated isotherms for each proppant, displayed in Figure 4. As seen below, Unimin sand at a concentration of 64 g/L sorbed 8.2 mg/L of Ba. The same concentration of MnO<sub>2</sub> sorbed 44 mg/L of Ba, or about 5 times that of Unimin. Magnetite sorbed the largest amount of Ba at 88 mg/L, or about 10 times that of Unimin and twice that of MnO<sub>2</sub>.



**Figure 4. Ba<sup>2+</sup> removal in 40-hr batch sorption tests at 60°C for three proppants, as measured by ICP-OES (Experiment 2).**

The average partition coefficient  $K_d$  was also calculated for each proppant according to Equation 1,

$$(1) \quad K_d = \frac{\frac{\text{Mass of Ba}^{2+} \text{ or Ra}^{2+} \text{ sorbed (mg)}}{\text{Mass of proppant (g)}}}{[\text{Ba}^{2+} \text{ or Ra}^{2+}] \text{ in solution at equilibrium } (\frac{\text{mg}}{\text{L}})}$$

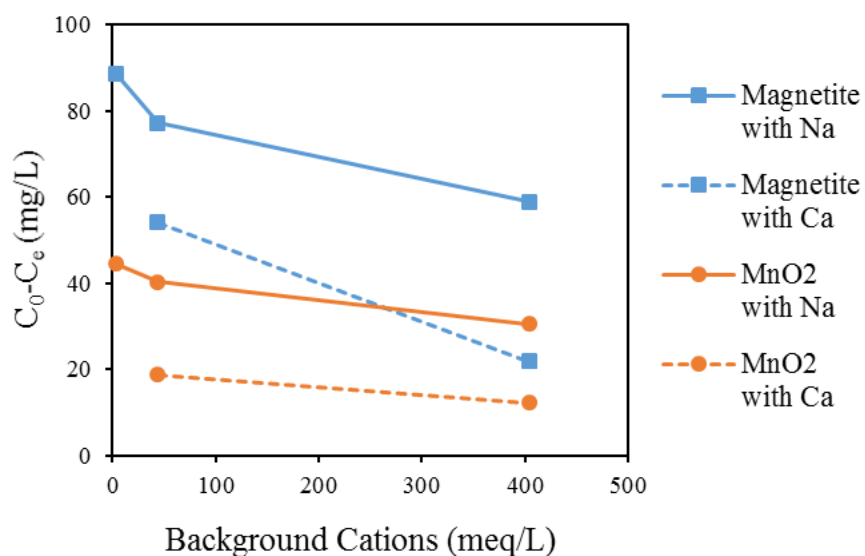
where  $K_d$  has units of L/g proppant (Sheppard et al., 2009). The  $K_d$  of Ba sorption to each proppant is shown in Table 1. The relative order of  $K_d$  values followed that of Ba sorption, with  $K_{d,\text{Mag}} > K_{d,\text{MnO}_2} > K_{d,\text{Unimin}}$ . This ranking supports the conclusion that magnetite and  $\text{MnO}_2$  are the most effective sorbents of Ba.

**Table 1. Average  $K_d$  values for  $\text{Ba}^{2+}$  sorption to three proppants (Experiment 2)**

<b>Proppant</b>	<b>Average <math>K_d</math> (L/g proppant)</b>
Magnetite	$2.36 \cdot 10^{-2}$
$\text{MnO}_2$	$6.59 \cdot 10^{-3}$
Unimin	$2.45 \cdot 10^{-3}$

In Experiment 3, batch sorption tests of magnetite and  $\text{MnO}_2$  were again conducted for 40 hours at  $60^\circ\text{C}$ , this time with competing ion electrolytes of NaCl and  $\text{CaCl}_2$ . Figure 5 displays Ba sorption as a function of background cation concentration, including both data from this experiment and the data points from Experiment 2 with the same concentration of proppant (64 g/L). The data points from Experiment 2 contained 4 meq/L Na. It is apparent from the figure that Ba sorption decreased for both proppants as the concentration of background cations increased. Ca caused a greater effect than Na, likely because it is a divalent cation that can better

compete with Ba. Table 2 displays the maximum percent reduction in Ba sorption to each proppant when compared to the 4 meq/L Na samples from Experiment 2. As indicated in the table, magnetite and MnO<sub>2</sub> samples with 404 meq/L CaCl<sub>2</sub> exhibited a 75.3% and 72.5% decrease in the value of C<sub>0</sub>-C<sub>e</sub>, respectively. It is worth noting that even in the magnetite sample with the least sorption, approximately 22 mg/L of Ba still sorbed, with a K<sub>d</sub> of 3.67\*10<sup>-3</sup> L/g proppant. As before, magnetite sorbed a greater quantity of Ba than MnO<sub>2</sub>.

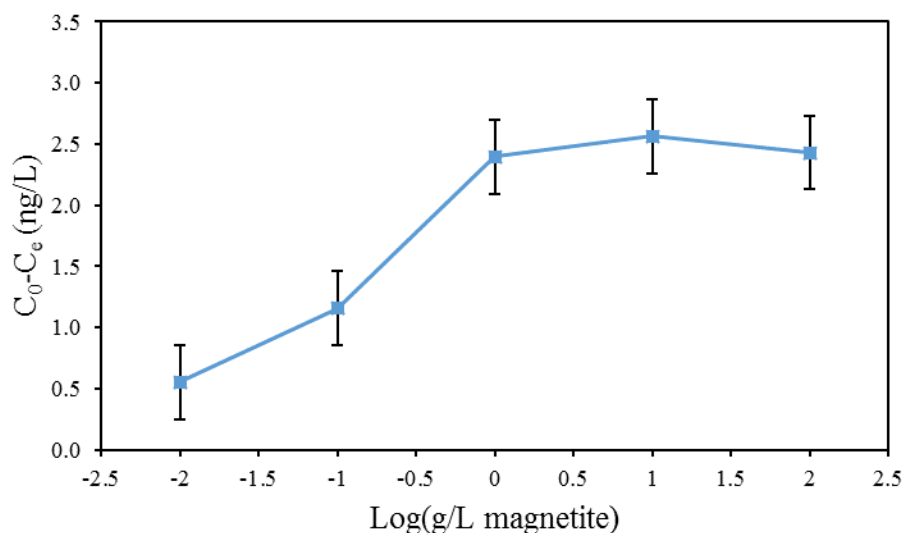


**Figure 5. Ba<sup>2+</sup> removal in 40-hr batch sorption tests at 60°C with varying concentrations of background cations, as measured by ICP-OES (Experiments 2, 3).**

**Table 2. Maximum percent reduction in Ba<sup>2+</sup> sorption to each proppant when compared to background electrolyte of 4 meq/L Na (Experiments 2, 3).**

<b>Proppant</b>	<b>Background Cation</b>	<b>Cation Concentration (meq/L)</b>	<b>% Reduction in C<sub>0</sub>-C<sub>e</sub></b>	<b>K<sub>d</sub> (L/g proppant)</b>
Magnetite	Ca	404	75.3	3.67*10 <sup>-3</sup>
MnO <sub>2</sub>	Ca	404	72.5	1.85*10 <sup>-3</sup>

In Experiment 4, batch sorption tests with magnetite were conducted using a 20,000 pCi/L RaCl<sub>2</sub> background electrolyte containing 10 mM MOPS. The total activity of each sample was measured by LSC (in cpm) and converted to a Ra concentration (in ng/L) under the assumption that all measured activity was due to Ra-226, which has a specific activity of 0.99 Ci/g (Radium MSDS). These activity concentrations were then plotted as an isotherm (Figure 6). As seen in the figure, maximum Ra sorption of 2.56 ng/L occurred when the proppant concentration was at the second highest value tested, or 10 g/L. Adding additional proppant beyond this value did not noticeably increase Ra removal, suggesting that essentially all Ra was sorbed with 10 g/L of proppant. The four samples with the lowest proppant concentrations had an average K<sub>d</sub> of 14.1 L/g proppant, nearly three orders of magnitude greater than the value calculated in Experiment 2 for Ba sorption to magnetite (2.36\*10<sup>-2</sup> L/g proppant). This result seems to suggest that Ra sorbs to magnetite with much greater selectivity than Ba. Therefore, in a typical formation brine containing both Ra and Ba, Ra should preferentially sorb to magnetite.



**Figure 6.  $Ra^{2+}$  removal in 40-hr batch sorption test at 60°C with magnetite, as measured by LSC (Experiment 4).**

For some reason, all of the Ra activities measured in Experiment 4 were 2500 pCi/L or lower, significantly below the initial activity 20,000 pCi/L. Even the sample blank, which contained no proppant and should not have shown any Ra loss, had a measured activity of only 2565 pCi/L. This discrepancy may indicate that the LSC was improperly calibrated. It is also possible that some Ra in each sample sorbed to the tube walls, which were somewhat scratched from previous use. Since there is no proof that the same quantity of Ra sorbed to each tube, it is impossible to report this data with a high level of confidence. Additional testing is needed to better understand this Ra loss and to verify the results of this experiment.

Experiment 5 was conducted to determine whether the magnetite surface leached any sulfate into the samples. Because both  $BaSO_4$  and  $RaSO_4$  are highly insoluble, the presence of sulfate could potentially remove Ba and Ra through precipitation (Solubility Product Constants). To prove this, batch sorption tests were conducted with ultrapure water and 64 g/L magnetite. After agitation, the samples were tested for dissolved sulfate via IC.

As seen in Table 3, the samples were found to contain an average sulfate concentration of  $1.78 \times 10^{-4}$  M, or about 17 mg/L. This value, along with the molar concentrations of  $Ba^{2+}$  and  $Ra^{2+}$  added to samples in the other experiments, was used to calculate the reaction quotient  $Q$ , as shown in Equation 2:

$$(2) \quad Q = [Ba^{2+} \text{ or } Ra^{2+} (M)] * [SO_4^{2-} (M)]$$

The reaction quotient of  $RaSO_4$  was less than its solubility product, indicating that the quantity of sulfate present in the samples should not be enough to precipitate  $RaSO_4$  at equilibrium.

However, the reaction quotient of  $BaSO_4$  was greater than its solubility product, suggesting that the samples were supersaturated with respect to  $BaSO_4$ . This indicated that  $BaSO_4$  precipitation was a possible contributor to the Ba removal observed in Experiments 1-3.

**Table 3. Sulfate concentration and equilibrium saturation state of magnetite samples before rinse, as measured by IC (Experiment 5).**

Cation	[Cation] (M)	$[SO_4^{2-}]_{avg}$ (M) from IC	Q	$K_{sp}$	Saturation State
$Ba^{2+}$	$1.00 \times 10^{-3}$	$1.78 \times 10^{-4}$	$1.78 \times 10^{-7}$	$1.08 \times 10^{-10}$	Supersaturated
$Ra^{2+}$	$8.94 \times 10^{-11}$	$1.78 \times 10^{-4}$	$1.59 \times 10^{-14}$	$3.66 \times 10^{-11}$	Unsaturated

Following this IC test, the magnetite proppant to be used in Experiments 6 and 7 was rinsed with ultrapure water and dried in an attempt to remove sulfate impurities from the proppant surface. The rinsate was then retested for sulfate via IC.

As seen in Table 4, the rinse reduced sulfate levels in the samples to  $4.45 \times 10^{-5}$  M (4.3 mg/L), a 74.9% decrease. As before, the samples were unsaturated with respect to  $\text{RaSO}_4$ , indicating that sulfate precipitation should not have a noticeable contribution to Ra removal in Experiments 4 and 6. However, the samples remained supersaturated with respect to  $\text{BaSO}_4$ , implying that sulfate precipitation may contribute to Ba removal. Additional testing (similar to that performed with Ra in Experiment 7 below) is needed to determine if proper conditions exist to allow for noticeable  $\text{BaSO}_4$  precipitation to occur in the other experiments. Without this testing, it is reasonable to conclude that some of the Ba removal observed in Experiments 1-3 may have been due to sulfate precipitation instead of sorption.

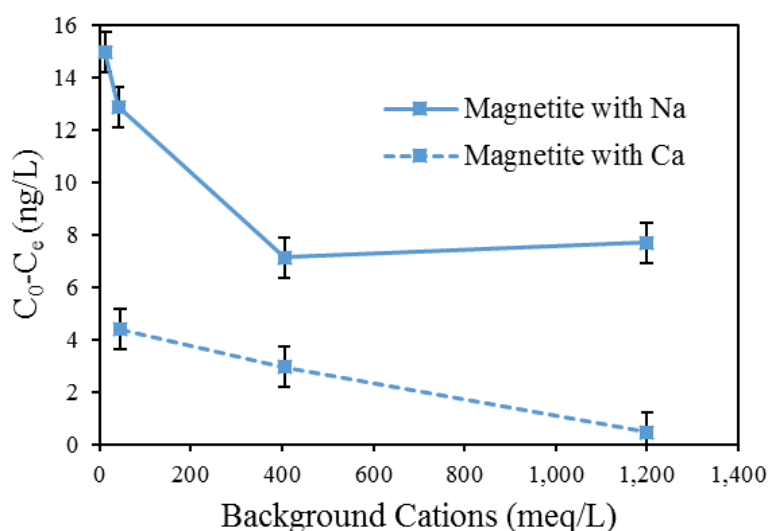
**Table 4. Sulfate concentration and equilibrium saturation state of magnetite samples after rinse, as measured by IC (Experiment 5).**

<b>Cation</b>	<b>[Cation] (M)</b>	<b><math>[\text{SO}_4^{2-}]_{\text{avg}}</math> (M) from IC</b>	<b>Q</b>	<b><math>K_{\text{sp}}</math></b>	<b>Saturation State</b>
$\text{Ba}^{2+}$	$1.00 \times 10^{-3}$	$4.45 \times 10^{-5}$	$4.45 \times 10^{-8}$	$1.08 \times 10^{-10}$	Supersaturated
$\text{Ra}^{2+}$	$8.94 \times 10^{-11}$	$4.45 \times 10^{-5}$	$3.98 \times 10^{-15}$	$3.66 \times 10^{-11}$	Unsaturated

Experiment 6 was conducted to determine the effect of competing ion solutions on Ra sorption. Batch sorption tests were conducted with 20,000 pCi/L  $\text{RaCl}_2$  and 0.5 g/L magnetite. NaCl and  $\text{CaCl}_2$  background electrolytes were used with concentrations varying from 12-1200 meq/L. The activity concentration of Ra (in pCi/L) was measured for each sample via gamma spectroscopy. As shown in Figure 7, maximum Ra sorption of 14.99 ng/L occurred in the sample with 12 meq/L Na. This sorption value is about 6 times greater than the largest sorption measured in Experiment 4 by LSC, suggesting a possible discrepancy between the two analytical methods. This result may be due to the difference in centrifuge tubes between the two

experiments. Experiment 6 used tubes with fewer scratches, which may have resulted in less Ra sorption to the walls, leaving more Ra available to sorb to proppant.

Ra sorption generally decreased with increasing cation concentration, following the same trend as Ba sorption. However, the results show slightly greater sorption for the 1200 meq/L Na solution than for the 400 meq/L Na solution. This result seems to contradict the expectation that background cations will better compete with radium as their concentration increases. This surprising finding is likely due to some form of measurement error and necessitates further testing.



**Figure 7. Ra<sup>2+</sup> removal in 40-hr batch sorption tests at 60°C with magnetite and varying concentrations of background cations, as measured by gamma spectroscopy (Experiment 6).**

The sample with approximately 1200 meq/L Ca exhibited the maximum decrease in sorption when compared to the sample with 12 meq/L Na, with a 97.1% reduction in the value of C<sub>0</sub>-C<sub>e</sub>. Only 0.44 ng/L of Ra sorbed in this sample, a concentration low enough to be considered insignificant. However, it is worth noting that the typical proppant concentration in a well is



~40 g/L, a value 80 times larger than the concentration used in this test (Ritter, 2014). If this experiment were repeated with 40 g/L magnetite, it is possible that  $80 \times 0.44 = 35$  ng/L Ra could be sorbed, enough to remove the average concentration of Ra from typical Marcellus Shale flowback water (2.53 ng/L). Further tests would be needed to determine if this amount of sorption would in fact occur. It would also be helpful to test the performance of magnetite in solutions with the actual composition of flowback water (~1130 meq/L Na, ~487 meq/L Ca) (Hayes, 2009; Chapman et al., 2012; Osborn et al., 2012; Haluszczak et al., 2013).

Additionally, the sample with approximately 1200 meq/L Ca had a  $K_d$  of  $6.36 \times 10^{-2}$  L/g proppant. This value is about 3 times the  $K_d$  of Ba sorption to magnetite with minimal competing cations ( $2.36 \times 10^{-2}$  L/g proppant). This suggests that Ra remains more selective than Ba, even under the most adverse conditions tested in terms of competing cations.

Interestingly, the measured activity concentrations of both blanks with 12 meq/L Na and no proppant were less than half the expected 20,000 pCi/L. However, the activities of all other blanks were reasonably close to 20,000 pCi/L. It would be helpful to retest the 12 meq/L Na sample blank in order to better validate the results of this experiment.

Experiment 7 was conducted to verify the assumption that  $\text{RaSO}_4$  precipitation did not occur to any measurable extent in the previous Ra tests.  $\text{Na}_2\text{SO}_4$  was added to a background electrolyte of 20,000 pCi/L Ra and 1200 meq/L Ca, yielding sulfate concentrations similar to those found in Experiment 5. After the samples were agitated, they were analyzed by gamma spectroscopy to determine whether the presence of sulfate lowered the activity of Ra in solution.

The results, as seen in Table 5, indicate that the addition of sulfate did not significantly decrease the concentration of Ra. The sample with 85 mg/L sulfate exhibited only a 2.29% decrease in Ra concentration, a value small enough to be considered insignificant. For some

reason, the sample with 17 mg/L sulfate actually showed an 11.3% increase in Ra activity over the control with no sulfate. This result is likely due to measurement error and could be resolved through the testing of additional trials. Nevertheless, this experiment offered some confirmation that, as predicted in Experiment 5, the sulfate levels found in the samples are not high enough to result in measurable  $\text{RaSO}_4$  precipitation.

**Table 5. Decrease in Ra concentration in samples due to addition of sulfate, as measured by gamma spectroscopy (Experiment 7).**

<b>Sulfate Concentration</b> (mg/L)	<b>Ra Concentration</b> (ng/L)	<b>% Decrease in [Ra]</b> <b>from Control</b>
0 (control)	14.2	--
17	15.9	-11.3
85	13.9	2.29

## Chapter 4

### Conclusions

The results of the initial experiments indicated that magnetite and MnO<sub>2</sub> proppants are more effective sorbents of Ba than Unimin frac sand or Titan ceramic proppants. Magnetite was the most effective and sorbed 10 times as much Ba as compared to Unimin frac sand. These experiments gave no indication that varying temperature from 25-60°C and reaction time from 6-48 hours had any noticeable effect on Ba sorption.

The addition of background cations was found to decrease, but not completely inhibit, Ba sorption to magnetite and MnO<sub>2</sub>. Ca caused a greater decrease in sorption than Na, likely because it is a divalent cation that can better compete with Ba. The maximum decrease in the value of  $C_0-C_e$  for the magnetite samples was 75.3% and occurred in the sample with 404 meq/L Ca.

Sorption tests with Ra and magnetite yielded a  $K_d$  nearly three orders of magnitude greater than that for Ba sorption. This suggests that Ra has a greater selectivity than Ba for magnetite proppant. Consequently, Ra should preferentially sorb to magnetite in formation waters containing both Ra and Ba.

The addition of background cations was found to generally decrease Ra sorption to magnetite, as seen previously with Ba sorption. As before, Ca had a greater effect than Na. The maximum decrease in the value of  $C_0-C_e$  was 97.1% and occurred in the sample with

1200 meq/L Ca. Notably, the  $K_d$  of this sample ( $6.36 \times 10^{-2}$  L/g proppant) remained about 3 times greater than the highest measured  $K_d$  for Ba sorption to magnetite ( $2.36 \times 10^{-2}$  L/g proppant). This offers further evidence that Ra has a greater selectivity than Ba, even under the most adverse conditions tested in terms of competing cations.

Despite this, the results of the Ra tests are somewhat uncertain due to unexplained Ra loss in some of the sample blanks, possibly due to sorption to the Teflon centrifuge tubes. Additional testing is needed in order to correct this issue and obtain more reliable results.

A test with samples containing only magnetite and ultrapure water revealed that the proppant can leach up to 17 mg/L sulfate into the samples. This value is large enough to make the samples supersaturated with respect to  $BaSO_4$  but unsaturated with respect to  $RaSO_4$ . A later test confirmed that the addition of five times this level of sulfate does not significantly reduce dissolved Ra levels in a sample with 20,000 pCi/L Ra. However, in the absence of a similar test for the Ba samples, it is plausible that some of the Ba removal observed in the first three experiments may have been due to  $BaSO_4$  precipitation.

Based on this research, magnetite appears to be an excellent material for sorbing dissolved  $Ra^{2+}$ . However, it is unclear if magnetite remains an effective sorbent under the high salinity conditions of a fractured well. Experiments with 0.5 g/L magnetite indicated that almost zero sorption (0.44 ng/L) occurred in a competing cation solution of 1200 meq/L Ca. However, it is possible that the use of magnetite in typical quantities for proppant application (~40 g/L) would sorb up to 35 ng/L, enough to remove essentially all Ra from the actual formation flowback (Ritter, 2014). Additional experimentation is needed to determine if this is true. Nevertheless, magnetite proppants are a promising possible solution to the problem of Ra in fracturing flowback waters.

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<b>EDUCATION</b>	<b>The Pennsylvania State University, Schreyer Honors College</b>	University Park, PA <i>August 2013- May 2017</i>
	<ul style="list-style-type: none"><li>• Bachelor of Science in Chemical Engineering</li><li>• Minors in Environmental Engineering and Spanish</li></ul>	
	<b>CIEE Seville: Summer Language and Culture</b>	Seville, Spain <i>May 2015- June 2015</i>
	<ul style="list-style-type: none"><li>• Completed Spanish-taught course on Camino de Santiago</li></ul>	
<b>EMPLOYMENT</b>	<b>Langan Engineering &amp; Environmental Services, Inc.</b>	Warrington, PA <i>June 2016- August 2016</i>
	<i>Environmental Intern</i>	
	<ul style="list-style-type: none"><li>• Collected field samples to characterize contaminated sites</li><li>• Organized sample data for inclusion in reports</li><li>• Estimated office power consumption to support energy audit</li><li>• Prepared presentation on regulation of emerging contaminants</li></ul>	
	<b>Coatings For Industry, Inc.</b>	Souderton, PA <i>July 2015- August 2015</i>
	<i>Chemical Lab Technician</i>	
	<ul style="list-style-type: none"><li>• Conducted and analyzed experiment involving preparation of 48 samples to enhance quality of chromium-free binder</li><li>• Prepared samples of chromium-based binder in lab at various temperatures to solve production problem</li><li>• Designed and conducted experiment to measure corrosion-resistance added by trivalent chromium topcoat</li></ul>	
	<i>Lab Technician Intern</i>	<i>July 2014- August 2014</i>
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<b>LEADERSHIP</b>	<b>Reformed University Fellowship (RUF)</b>	University Park, PA <i>August 2016- May 2017</i>
	<i>Vice President</i>	
	<ul style="list-style-type: none"><li>• Collaborated with campus minister and student leaders to oversee activities and implement changes</li></ul>	
	<i>Freshman Small Group Leader</i>	<i>August 2015- May 2016</i>
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<b>SKILLS</b>	40-hour HAZWOPER safety training	<i>June 2016</i>
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