Remediation of Hydraulic Fracturing Flowback Fluids by Trace Element Extraction

Susan A Welch, Julia M Sheets, David R Cole
School of Earth Sciences, The Ohio State University (SES, OSU)

Collaborators
John Olesik SES, OSU
Anthony Lutton SES, OSU
Chandler Adamaitis SES, OSU
Neil Sturchio, Geological Sciences, University of Delaware

Abstract
Experiments were conducted with hydraulic fracturing flowback/produced fluids (FP fluids) to determine the extent to which different species would be partitioned into secondary mineral phases, either by allowing the solutions to age and oxidize, or by adding different amendments to induce mineralization. Naturally aged FP fluids precipitate akaganeite (β-FeO(OH,Cl)) that forms as micron sized precipitates that appear fibrous and hollow or bulbous when viewed in the SEM. Most trace metals measured (Rb, Cs, Ni, Cu, Zn, Pb) were not co-precipitated with this phase, however Si, U and Th were scavenged from solution. FP fluids were amended with solutions of dilute HCl (control), sodium carbonate (pH increase) and phosphate and sulfate rich solutions to induce precipitation. Carbonate addition removed Ca as calcium carbonate, as well as other trace metals, but only small amounts (~ 10s %) of Sr and Ba were removed. Acid addition, either as phosphoric or hydrochloric, did not induce mineralization. Addition of sulfuric acid resulted in the formation of barite-celestite and gypsum phases, and removal of Ba, Sr and Ca from solution; however, mineralogy depended on the concentration of sulfate added. Low levels of sulfate resulted in the formation of small barite roses without significant Sr removal from solution. Intermediate levels of sulfate resulted in the precipitation of euhedral Sr-bearing barite crystals, as well as celestite with elongate crystal habit. The highest level of sulfate addition resulted in the precipitation of abundant gypsum interspersed with elongate celestite; and although barite was not observed in the precipitates, barium was removed from solution. EDX analysis of minerals precipitated with high sulfate addition showed Ba in gypsum and celestite in trace quantities. Radium was co-precipitated in the sulfate addition experiments.

Problem and Research Objectives
Hydraulic fracturing of lateral wells to extract unconventional hydrocarbon resources is generating enormous quantities of natural gas, with approximately 744 billion cubic feet produced from 2011 through the 1st quarter of 2015 in Ohio alone (Riley, 2015). As gas is produced, the water recovered from these wells is in the form of saline brines, typically with total dissolved solids (TDS) in the range 10s to
100s g/L. These brines also contain organic compounds, as well as elevated levels of trace elements such as barium, strontium, radium, transition metals and rare earth elements (Kondash et al., 2014; Nelson et al., 2015; Vengosh et al., 2014; Welch, Sheets and Cole in prep). The fluids are hazardous waste, they contribute to mineral scale that builds up in hydraulic fracturing equipment, and their compositions reflect pore waters derived from the rock formations with which they have interacted. From a hazardous waste standpoint, they are complicated by containing naturally occurring radioactive materials (NORM) derived from the rocks, that may then be concentrated, or technologically enhanced (TENORM). Understanding the nature of precipitates that form and settle out of the fluids in holding tanks is important for their safe handling and disposal. For example, radium has been identified in flowback fluids in water storage impoundments (Zhang et al., 2015). Microorganisms also are present that were either inserted along with input fluids or were indigenous to the subsurface environment and able to thrive in the fracking environment (Daly et al., 2016; Booker et al., 2018a,b; Evans et al., 2018). Although hydraulic stimulation operations increasingly re-use these recovered brines, proper disposal of the fluids remains a problem because of their complex chemistry and potential toxicity. Deep injection of waste brines is prevalent in Ohio, and minimizing this activity is of interest to the general public.

Another view of these hydraulic fracturing flowback fluids is that the trace metals they contain also are a potential resource, given the opportunity to concentrate them so that they become economically viable. For example, it has been demonstrated that Fe, which is the most abundant transition metal element in Earth (and also abundant in these brines) can adsorb trace metals onto the surfaces of Fe oxyhydroxides as they precipitate from natural waters (Webster et al., 1998; Smith, 1999; Bau, 1999), however, the sorption-coprecipitation behavior is complex, and depends on the properties of the solid phase formed (including surface area, mineralogy, and zero point of charge), solution properties (including acidity, salinity, and the concentrations of competing constituents), and the geochemical properties of the selected element. In general, experiments with hydrous ferric oxide phases, and studies of natural waters where Fe has oxidized, show that many trace elements, particularly transition and rare earth elements, are effectively sorbed onto FeOOH phases, however, there are fewer studies conducted on trace element sorption-coprecipitation in brines, where the elevated salinity can impact both element and mineral surface speciation, thus affecting sorptive properties. It would be advantageous to conduct laboratory experiments to determine conditions for the formation of secondary Fe- precipitates (or other phases) that could sequester and concentrate valuable metals from hypersaline FP fluids. If results of such experiments could eventually be scaled up and applied to FP fluid storage facilities (holding tanks or storage ponds), then operators could potentially recover economically valuable metals from this waste product.

This research focused on three key goals:

1) To understand the evolution of the major and trace element composition of FP fluids as they age and secondary mineral phases precipitate, thereby potentially removing trace metals by sorption/co-precipitation reactions.

2) To investigate strategies to actively remove potentially toxic or economically important elements. These include inducing oxidation, addition of different chemical amendments to induce mineralization and concentrate metals in the solid phase, or biologically mediated sorption-precipitation reactions.
3) To determine the feasibility of adding sulfate-rich acid mine drainage (AMD) waste to induce precipitation of sulfate minerals (barite, celestite) or jarosite group minerals, thereby removing both major and trace metals from solution.

**Experimental Methods**

Experiments were conducted on hydraulic fracturing FP fluids collected from several unconventional hydrocarbon wells. Two sites were in the Utica-Point Pleasant Formation in eastern Ohio. The UPP-W4 well was in the wet gas zone in Harrison County, Ohio, and the UPP-S1-4 samples were collected from four wells on the same pad in Monroe County, Ohio that are in the dry gas zone. In addition, FP fluids were sampled from two wells from a dry gas target in the Marcellus Shale from the Marcellus Shale Energy and Environment Laboratory (MSEEL) site in Morgantown, West Virginia. Major and trace constituents and biological properties of these fluids have been analyzed as part of several other studies (Welch, Sheets and Cole in prep, Daly et al., 2016; Borton et al., 2018a,b). FP fluids were stored in large plastic carboys or in large Nalgene bottles and were allowed contact with the atmosphere so that the reduced species could oxidize. Analysis of these fluids and the precipitates that formed provided the basis for the Phase 1 experiments, determining how trace metals would partition between the fluids and the precipitates as the iron oxidizes. Analysis of the mineral phases that formed was conducted over a period from several days to several years after FP fluid collection.

Two additional sets of experiments (Phase 2 and Phase 3) were conducted on FP fluids from the UPP-S3 and UPP-S4 wells (collected in September, 2016). These fluids were stored at room temperature and exposed to the atmosphere for about a year before the experiments were started. The carboy of raw UPP-S3 (no chemical additions) flowback fluid was first vigorously shaken to re-suspend precipitate and make a homogeneous mixture for sampling. 200mL of the fluid was added into each of nine 250mL bottles. Additions of either H$_3$PO$_4$ or H$_2$SO$_4$ were to induce the formation of sulfate or APS (aluminum phosphate sulfate) mineral phases $\text{AB}_3(\text{XO}_4)_2(\text{OH})_6$ such as Alunite supergroup minerals (Bayliss et al., 2010), while the addition of sodium carbonate solution was to increase pH and induce the formation of carbonate minerals. The control and hydrochloric acid addition experiments were intended to serve as controls. A 1mL trace metal spike (1 ppm) was placed into each bottle. The additives for Phase 2 experiments are listed in Table 1.

<table>
<thead>
<tr>
<th>Bottle #</th>
<th>Additive</th>
<th>Volume/concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control</td>
<td>No addition</td>
</tr>
<tr>
<td>2</td>
<td>Low H$_2$SO$_4$</td>
<td>0.8 mL/2.5M</td>
</tr>
<tr>
<td>3</td>
<td>High H$_2$SO$_4$</td>
<td>8.0 mL/2.5M</td>
</tr>
<tr>
<td>4</td>
<td>Low H$_3$PO$_4$</td>
<td>1.3 mL/1.5M</td>
</tr>
<tr>
<td>5</td>
<td>High H$_3$PO$_4$</td>
<td>13 mL/1.5M</td>
</tr>
<tr>
<td>6</td>
<td>Low HCl</td>
<td>2.0 mL/1.0M</td>
</tr>
<tr>
<td>7</td>
<td>High HCl</td>
<td>20 mL/1.0M</td>
</tr>
<tr>
<td>8</td>
<td>Low Na$_2$CO$_3$</td>
<td>2.0 mL/1.0M</td>
</tr>
<tr>
<td>9</td>
<td>High Na$_2$CO$_3$</td>
<td>20 mL/1.0M</td>
</tr>
</tbody>
</table>

Table 1. List of additives, concentrations, and volumes for Phase 2 experiments.
Based on the results of these experiments, a third set of experiments (Phase 3) was conducted with mixtures of UPP-S4 flowback fluid, an artificial acid mine drainage fluid (1 N H$_2$SO$_4$, 0.01M FeCl$_3$, 0.01M FeSO$_4$) and a mixed trace metal solution (100 ppm each of Cu, Ag, Se, V, Zn, Ga, Y, Dy, Yb, and 1000 ppm La). These experiments were set up similarly to those in Phase 2. Details of these additions are given in Table 2.

Table 2. Additives for Phase 3 experiments with artificial acid mine drainage fluid (AMD) and trace metal (TM) spike.

<table>
<thead>
<tr>
<th>treatment</th>
<th>Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 control</td>
<td>none</td>
</tr>
<tr>
<td>2 TM</td>
<td>10 ml TM spike</td>
</tr>
<tr>
<td>3 0.5 AMD</td>
<td>0.5 ml AMD</td>
</tr>
<tr>
<td>4 0.5 AMD TM</td>
<td>0.5 ml AMD and 10 ml TM</td>
</tr>
<tr>
<td>5 5.0 AMD</td>
<td>5.0 ml AMD</td>
</tr>
<tr>
<td>6 5.0 AMD TM</td>
<td>5.0 ml AMD and 10 ml TM</td>
</tr>
<tr>
<td>7 50 AMD</td>
<td>50 ml AMD</td>
</tr>
<tr>
<td>8 50 AMD TM</td>
<td>50 ml AMD and 10 ml TM</td>
</tr>
<tr>
<td>9 50 AMD</td>
<td>50 ml AMD</td>
</tr>
</tbody>
</table>

For the Phase 2 and 3 experiments, the first supernatant samples were collected within a few hours of the experimental set up, and then at one week and two weeks after the start of the experiments. Approximately 10 ml volume was removed from each bottle with a plastic syringe and then filtered with a 0.2 μm syringe filter into a clean 15 ml falcon tube. A small aliquot was removed for pH analysis. At the end of the two-week experiments, a sample of the precipitates that formed were removed using a long pipet and placed on a 0.2 micron nucleopore filter in a polycarbonate filter flask. The solution was removed by vacuum filtration and the precipitates were rinsed with ~ 2 ml of milliQ water to remove residual salts, and the precipitates were allowed to air dry. An additional set of fluid and precipitate samples was collected from experiment three after approximately 8 months to investigate long-term changes in mineral composition and morphology.

Fluids and precipitates for the Phase 1 experiment were sampled similarly, except instead of collecting samples from a single bottle over time to determine changes in composition, samples were removed from larger volumes flowback fluids that had been collected previously and allowed to oxidize in the laboratory, and then compared to the original unoxidized sample.

**Analytical Methods**

Because the total dissolved solids (TDS) of these brines is about 200g/L, solution samples were diluted before analysis using a Perkin-Elmer Optima 3000DV and 4300DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and a Perkin-Elmer Sciex ELAN 6000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Two dilutions were made for each sample. The first was a 201-fold dilution in 2% HNO$_3$ with a 10 ppb spike of indium for analysis of selected trace metals by ICP-OES and ICP-MS. This aliquot was diluted again (2211 fold) in 2% HNO$_3$ to measure major cations and silica by ICP-OES.
Precipitate samples were analyzed by scanning electron microscopy (SEM) using a FEI Quanta FEG 250 Field Emission Scanning Electron Microscope equipped with a Bruker EDX detector, and X-ray diffraction (XRD) using a PANalytical X’Pert Pro powder diffractometer. The SEM samples were placed on double sided carbon tape on aluminum specimen stubs and coated with Au-Pd with a Denton Desk V precious metal coater before analysis. For XRD analysis, the filters with precipitate on them were placed on cut glass slides with double-sided tape and then adhered to XRD sample mounts. Sample height was adjusted using modeling clay. Precipitate samples were typically scanned at 45 KeV, 45 ma from 5 to 70 degrees 2-theta.

Analysis of Ra in the supernatant from selected experiments was conducted by Neil Sturchio and colleagues in the Department of Geological Sciences, University of Delaware. Solution aliquots from the week-long experiments were analyzed, and then an aliquot collected after approximately 6 months was analyzed to determine the longer term fate of Ra that had partitioned into the solid phase.

Results

Phase 1 experiments

Analyses for Phase 1 experiments were conducted on fluids that were collected earlier and had already started to oxidize, in order to better determine the time scales required for geochemical changes to occur. Aliquots were analyzed to characterize the supernatant fluid and secondary precipitates, the percent of trace elements associated with these phases, and the partitioning of trace elements into the solid phase(s).

The primary mineral phase formed from the oxidation of reduced iron from complex brines collected from the Utica/Point Pleasant is akaganeite (β-FeO(OH,Cl)). SEM analysis shows fine grained elongated nanometer sized precipitates in micron sized “tubular” and/or “hollow” aggregates that are reminiscent of mineralized microbial cells (Fig 1). However, EDX analysis of this phase reveals a more complex chemistry, (FeO(OH,Cl) with Si. However, it is not clear whether Si substitutes into the mineral structure, is sorbed onto surfaces, or is present as very fine-grained silica precipitates intermixed within the akaganeite. XRD analysis of these precipitates are consistent with akaganeite (Si rich). Other peaks for quartz, barite, and halite (residual from evaporated brine) are frequently observed.
**Figure 1** - SEM images of fine grained akaganeite formed from the oxidation of FP fluids from the A) UPP-W4 and B) UPP-S3 wells. EDX spectra (not shown) reveal peaks for Fe, Cl and Si, suggesting these precipitates are akaganeite with SiO₂ either sorbed or coprecipitated. C) XRD spectra of precipitates from FP brines collected from Utica-Point Pleasant hydraulically-fractured wells, the peaks in the spectra correspond to akaganeite (ak), quartz (q) and halite (ha).

Major and trace element uptake by these phases was determined by comparing the composition of an aliquot of the fluid sample that was filtered and acidified (FA) within hours of when the fluid was collected onsite at the well, to the residual supernatant after the fluid was allowed to age in the batch reactor (Raw). There was little difference in the major element concentrations (Na, Mg, K, Ca, Sr, Ba, Li and even Mn) between the FA and Raw samples. However, approximately 50% of the Fe in the UPP-W4, and 80-90% in the UPP-S1-4 samples precipitated as akaganeite, with a corresponding decrease in pH from near neutral (~ 6.4 to 6.6 at the well) to ~ 2.8 in the UPP W4 fluid, and ~ 3.1 in the UPP S1-4 samples. There was little evidence of uptake of alkali (Li, Rb, or Cs), alkaline earth metals (Sr, Ba) or transition metals (Ni, Cu, and Zn) into the solid phase in these acidic brines. Although several studies have shown that these elements can be sorbed onto akaganeite or other FeOOH phases, this behavior is strongly pH-dependent (eg Ponthieu et al., 2006; Webster et al., 1998; Smith, 1999; Bau, 1999; Verplanck et al., 2004) increasing with increasing pH. Therefore in these unbuffered experiments, acidity generated by iron oxidation and precipitation limits trace metal sorption onto these phases. The geochemical behavior of the rare earth and actinide elements measured was more complex. The light rare earth elements, for example La, remained in solution, while the middle and heavy rare earth elements were preferentially partitioned into the solid FeOOH phase. This behavior has been observed previously in both natural waters and in experiments (Bau, 1999; Verplanck et al., 2004) though the sorption-coprecipitation varies depending on solution speciation of the REE. Approximately 70 to 100% of the Th and U measured in the fresh flowback fluid was partitioned into the precipitates, while other toxic heavy elements, such as Pb, do not appear to be partitioned into the solid phase under these conditions.
Phase 2 experiments

Phase 2 experiments were conducted with several different acid or base additives in order to induce precipitation of sulfate, phosphate, APS-Alunite supergroup, or carbonate minerals that would sequester trace elements from these complex brines. Analysis of the solution compositions from these experiments shows that the concentrations of some elements did not change substantially over time after the various treatments, whereas others showed either a decrease or increase in concentration as a result of mineral precipitation/dissolution reactions. Analysis of the precipitates collected at the end of the bench scale experiments (by both XRD and SEM) show changes in mineralogy that are consistent with the measured changes in solution composition determined using ICP-OES and ICP-MS analyses.

Ba and Sr were removed by the addition of sulfuric acid, though their concentrations, and the resultant mineralogy, depended on the amount of sulfate added (Figure 2). In both the low and high SO4 treatments, precipitation was instantaneous upon addition of the acid due to the formation of sulfate minerals. In the low SO4 treatment, Ba decreased from ~ 1500 mg/L to ~ 600 mg/L within minutes, and then decreased slowly over the two-week experiment, while Sr varied only slightly. XRD and SEM analysis of the minerals formed indicate primarily barite (Figure 3). In the high SO4 treatment, Ba concentrations decrease to undetectable before the first sample was collected, but in contrast, Sr decreased within the first hour after acid addition, and then increased over the two week experiment. XRD and SEM show that the precipitates formed in the high SO4 experiments were gypsum and celestite.
[[Sr,Ba]SO₄]. However, despite the almost complete removal of Ba from solution, no discrete barite phases were observed (Figure 3). The changes in solution chemistry, as well as the SEM images of the solid phases in both sulfate treatments suggest that these minerals were undergoing dissolution-reprecipitation reactions throughout the experiments.

**Figure 2** Sr and Ba in the phase two experiments with different acid and base amendments. Solutions were sampled after ~ 1-2 hours (T1), one week (T2) and two weeks (T3).

Addition of carbonate increased solution pH from an initial ~ 2.4 up to ~ 6.5, and resulted in the precipitation of calcium carbonate (Figure 3C), however, with the exception of Ca, there was little change in the concentrations of other elements. Even Sr and Ba, which can substitute into calcite, exhibited only ~ 10% decrease in concentration in the FP fluids after the high carbonate treatment.

The geochemical behavior of trace elements in these experiments was complex. The addition of sulfuric acid, or sodium carbonate and subsequent precipitation of barite, celestite, gypsum and calcite had no measureable effect on the concentrations of alkali metals (Li, Rb, or Cs) and surprisingly, had very little effect on most of the transition metals measured (Ni, Cu, and Zn), with only small decreases (< 10%) observed from the high carbonate treatment. Most of the REE elements showed little to no change in concentrations in solution in any of the acid addition treatments as compared to the control, but were effectively scavenged by the carbonate addition treatments (Figure 4). In contrast, La was removed in both the carbonate and sulfate addition experiments, suggesting that larger ions like La can substitute into the sulfate phases.
La and Ho concentrations in the phase two experiments. La was scavenged from solution in both the sulfate and carbonate amendment treatments, while heavier REE, such as Ho, were primarily scavenged in the carbonate addition treatments where its concentration was below detection.

Figure 3 SEM images of precipitates collected from the phase 2 experiments. A) (top left) large tabular gypsum (darker phase) and smaller spiked globules of celestite (Sr(Ba)SO₄) from the high sulfate treatment; B) (top right) barite (Ba(Sr)SO₄) from the low sulfate treatment and C) (left) calcite from the high carbonate treatment.

Figure 4 La and Ho concentrations in the phase two experiments. La was scavenged from solution in both the sulfate and carbonate amendment treatments, while heavier REE, such as Ho, were primarily scavenged in the carbonate addition treatments where its concentration was below detection.
**Phase 3 experiments**

Based on the results of the phase 2 experiments, we conducted third set of experiments using FP Fluids, a synthetic acid mine drainage fluid, and a trace metal solution to investigate the formation of sulfate and APS mineral phases from mixtures of these solutions, the stability of these phases over time (several months), and their potential to incorporate trace elements from solution. The sulfate minerals observed in SEM images, the chemistry from spot analysis from EDX, and the mineralogy determined by XRD were consistent with the changes in solution chemistry. The sulfate phases formed immediately upon addition of the artificial AMD to FP Fluids, but varied among the three different sulfate addition experiments, and also appeared to change in morphology and relative abundance over time. The sulfate phases observed in the 0.5 AMD treatment were small (~ 5 μm) nearly pure endmember barite with characteristic barite rose morphology, as well as euhedral orthorhombic crystals (Figure 5).

The formation of these phases is consistent with the changes in solution chemistry. For example, Sr in the 0.5 AMD treatment is not significantly different than the control experiment, while Ba is approximately 10% lower. The chemistry and morphology of precipitates in the 5 ml AMD are very different; in this case the precipitates are barite-celestite balls and euhedral bricks, but these phases are extensively etched and have sharp features indicative of dissolution-precipitation reactions. Analysis of precipitates formed early in these experiments showed some discrete SrSO₄ phases were present as elongate needles or as fibrous aggregates resembling sheaths, however these were not abundant and were not observed in samples collected after several months.

Solution chemical analysis from the first week of the Phase 3 experiment showed that both Sr and Ba varied, indicating dissolution-precipitation occurs. In the 50 ml AMD treatment, large tabular crystals of gypsum as well as smaller elongated crystals of celestite were observed in SEM images and detected with XRD. Although barium was completely removed from solution in this treatment, and geochemical modelling using PHREEQC indicated solutions were supersaturated with respect to barite, there were no discrete barite phases observed in the precipitates. Ba was detected as a trace element in both the gypsum and celestite by EDX spot analysis. Trace elements Cu and La were sorbed/co-precipitated into the solid phase, however their concentrations varied over time, particularly in the 50 mL AMD treatment, suggesting continued exchange between the solution and precipitates. Sodium concentrations did not exhibit any significant change throughout the experiments other than those predicted for simple dilution. Potassium, however, was systematically lower in the highest sulfate addition experiment (Figure 6), suggesting the formation of K-jarosite, although this what was not detected by XRD or SEM.
Figure 5 SEM images from A, B), 0.5 ml AMD; C, D), 5 ml AMD; and E, F), 50 ml AMD.
Radium activity in the supernatant was analyzed from aliquots collected in the 1 week experiments, as well as in an aliquot collected after approximately 6 months, to determine whether Ra is stable in the precipitates. Results show that Ra activity is correlated with Ba concentration. Approximately 20% of the Ra was removed in the 0.5 mL AMD treatment within hours of the addition of SO4, and Ra activity remained unchanged after ~ 6 months, suggesting co-precipitation as barite. In the two higher AMD treatments, Ra activity decreased to ‘detection activity’ and remained at these levels throughout the experiments, suggesting that Ra was effectively sequestered into the sulfate precipitates.
**Figure 6** Ra activity in phase 2 experiments- a) Ra 226 activity over time, the final point was collected after approximately 6 months, and b) Ra 226 activity versus Ba concentration. The solid blue lines represent approximate detection level activities.

**Summary and Conclusions**

Considering the Utica-Point Pleasant (UPP W4; UPP S3 and S4) hydraulic fracturing FP fluids measured in this study, akaganeite is the major Fe oxy-hydroxide phase identified in all control samples as well as samples prepared with chemical additives. Both XRD, which provides crystallographic (mineral atomic structural) data, and EDX (microanalytical elemental) data support this result. This phase contains significant Cl and Si. Akaganeite of this composition has been synthesized in the laboratory for its unique physical properties as a nano-scale material (Tadic et al., 2015). Because it is not as common as a ferric iron phase in most geological materials it has received less attention as compared to the more abundant natural Fe\(^{3+}\) (hydr)oxide minerals, such as hematite, goethite or ferrihydrite (Cornell, 1992). Akaganeite does occur in nature in brines (Font et al., 2017; Chilkoor et al., 2018). Cornell (1992) synthesized akaganeite in the presence of silica to form a structure that she suggests incorporates about 4 percent Si into the crystal structure, with some silica also sorbing onto the surface of hollow rods of the akaganeite crystals. The potential for akaganeite to sorb trace elements from hydraulic fracturing fluids is likely to be dramatically different as compared to the more common natural Fe oxyhydroxide phases.

The mineralogical composition of precipitates varies with the type and concentrations of chemical additions mixed with the flowback fluids. As expected, sulfates precipitate with the introduction of sulfuric acid, and carbonates precipitate with introduction of sodium bicarbonate. But in the case of sulfuric acid addition, the concentration of the acid determines the phases that precipitate. Barite precipitates upon addition of lower levels of sulfate, discrete barite and celestite phases were observed at intermediate SO\(_4\) amendments, and gypsum and celestite were observed at the highest sulfate treatments. This result has important implications for the sequestration of cations with large atomic radii into the sulfate, including some that are of environmental concern, such as radium (Rosenberg et al., 2014; Zhang et al., 2015).


Chilkoo G., Shrestha N, Soeder D, Gadhamshetty V, 2018, Corrosion and environmental impacts during the flowback water disposal associated with the Bakken shale, Corrosion Science, 133, 48-60.


Daly RA, Borton MA, Wilkins MJ, Hoyt DW, Kountz DJ, Wolfe RA, Welch SA, Marcus DN, Trexler RV, MacRae JD, Krzycki JA, Cole DR, Mouser PJ, and Wrighton KC. 2016 Microbial metabolism in new 2.5 km deep ecosystem created by hydraulic fracturing in shales. *Nature Microbiology* 16146 | DOI: 10.1038/NMICROBIOL.2016.146


Welch, Sheets and Cole in prep Geochemistry of Flowback fluids from the Utica-Point Pleasant.


2. Publication citations (all journal articles, proceedings and presentations at conferences)

In prep  Welch, Sheets, Adamaitis, Sturchio and Cole, Remediation of Hydraulic Fracturing Fluid by Trace Element Extraction, in prep for Applied Geochemistry

3. Students Supported - Number and name of students supported by the project (MS/PhD/undergraduate/post docs) as well as their majors,

Chandler Adamaitis received her BS in Geology

4. Profession Placement of Graduates including sector (if known and applicable) and Teaching Assistantship

None as of yet. Chandler Adamaitis has applied for graduate school for Fall Semester, 2018

5. Awards or Achievements (patents, copyrights),

None as of yet

6. Any additional funding for this project

Chandler Adamaitis received a SURE summer scholarship (2017) to work with us on this project.