**Co-treatment of Abandoned Mine Drainage and Marcellus Shale Flowback Water
for Use in Hydraulic Fracturing**

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Abstract

Flowback water generated during shale gas extraction in Pennsylvania is mostly reused for hydraulic fracturing operation. Abandoned mine drainage (AMD), one of the most widespread threats to water quality in Pennsylvania, can potentially serve as a make-up water source to enable flowback water reuse. This study demonstrated co-treatment of flowback water and AMD produced in northeastern Pennsylvania in a pilot-scale system consisting of rapid mix reactor, flocculation tank and sedimentation tank. Sulfate concentration in the finished water can be controlled at a desired level (i.e., below 100 mg/L) by adjusting the ratio of flowback water and AMD in the influent. Fe^{3+} contained in the AMD can serve as a coagulant to enhance the removal of suspended solids, during which Fe^{2+} is co-precipitated and the total iron is reduced to a desirable level.

Solid waste generated in this process (i.e., barite) will incorporate over 99% of radium present in the flowback water, which offers the possibility to control the fate of naturally occurring radioactive materials (NORM) brought to the surface by unconventional gas extraction. Sludge recirculation in the treatment process can be used to increase the size of barite particles formed by mixing flowback water and AMD to meet specifications for use as a weighting agent in drilling fluid. This alternative management approach for NORM can be used to offset the treatment cost and promote flowback water reuse, reduce environmental impacts of AMD and reduce pressure on fresh water sources.

1. Introduction

Marcellus shale in the Appalachian Basin is one of largest unconventional gas reservoirs in the U.S. and is estimated to contain 7.42 to 14.2 trillion m³ (262-500 trillion cubic feet) of natural gas reserves (Engelder and Lash, 2008; Milici and Swezey, 2006). The success in unconventional gas extraction from Marcellus Shale formation has significant economic impacts for Pennsylvania (Kinnaman, 2011) but there is an increasing public concern about environmental risks associated with the management of flowback/produced water that has the second highest salinity and highest radioactivity among all sedimentary basins in the U.S. (Gregory et al., 2011; Kargbo et al., 2010; Rowan et al., 2011; U.S. Department Of Energy, 2009; He et al., 2014a).

Abandoned mine drainage (AMD) represents one of the most significant and persistent water quality problems in Pennsylvania, which affects the water quality of over 4000 miles of streams. (Gray, 1998; He et al., 2013; Johnson, 2003). Considering the proximity of AMD sites to shale gas wells, AMD can potentially serve as an alternative water source for flowback water reuse (Kondash et al., 2013; He et al., 2013). In Pennsylvania, approximately 6.1×10^{11} gal of AMD is annually discharged (Kondash et al., 2013), while 7.1×10^8 gal of flowback/produced water was generated from shale gas extraction activities in 2011 (Maloney and Yoxtheimer, 2012).

The merits of using AMD for hydraulic fracturing include reduced pressure on fresh water sources, reduced water transportation costs and associated greenhouse gas emissions, and mitigation of adverse environmental impacts caused by AMD. The major technical concerns with the use of AMD are high sulfate and iron concentrations in this impaired water. Dissolved sulfate can react with barium in the formation resulting in

severe scaling that may decrease well productivity, while iron may interfere with friction reducing chemicals or with the cross-linking of the gel that is sometimes added to increase the viscosity of fracturing fluid and enhance its ability to carry proppant sand into deeper fractures (He et al., 2013). Bench-scale studies were performed to understand precipitation of barite (BaSO_4) under the conditions created by mixing flowback water and AMD (Zhang et al., 2014; He et al., 2014b) and to optimize potential subsequent solids separation processes (He et al., 2014a; He et al., 2014c). Creation of fairly fine-grained precipitant requires particle coagulation (He et al., 2014c) or microfiltration (He et al., 2014a) to ensure effective separation of solids that are formed when AMD and flowback water are mixed.

Co-precipitation of Ra with BaSO_4 results in the enrichment of NORM in the solid phase, which may be of concern for the management of this solid waste (Zhang et al., 2014; He et al., 2014b). Ra concentration in the solid waste generated through sulfate precipitation, which is also a common approach in centralized wastewater treatment plants (CWT) that are employed in flowback water reuse, far exceeds the limits for disposal of technologically enhanced naturally occurring radioactive material (TENORM) in municipal solid waste landfills (5-50 pCi/g depending on state regulations) (Zhang et al., 2014). Municipal waste landfill disposal is the main alternative for managing this waste, but is limited by the allowed source term loading for TENORM on an annual basis (i.e., amount of TENORM that can be disposed in a given landfill) (PA DEP, 2004). Therefore, alternative management option for Ra-enriched solids generated by co-treatment of flowback water and AMD is needed in Marcellus Shale play.

As barite is the main component of the solids generated in this process, it can potentially be utilized as a weighting agent in drilling mud. Barite used in drilling mud formulation is typically produced from commercial barite ores. American Petroleum Institute (API) specification for physical and chemical characteristics of barite used in this process includes minimum density (4.2 g/cm^3), maximum water-soluble alkaline earth metals (250 mg/kg), maximum mass fraction of particles that are smaller than $6 \mu\text{m}$ (30%), and maximum mass fraction of particles that are larger than $75 \mu\text{m}$ (3%) (API, 2010). Generally, freshly precipitated BaSO_4 is relatively small in size ($<6 \mu\text{m}$) with the mean particle size decreasing with an increase in saturation level (Kucher et al., 2006; Wong et al., 2001). Therefore, the size of BaSO_4 formed under typical conditions employed when mixing flowback water and AMD is the main barrier for its use as a weighting agent.

This study was designed based on previous laboratory-scale results to demonstrate the feasibility of using AMD as an alternative make-up water and a source of chemicals for the treatment of flowback water in a pilot-scale treatment system operated using actual flowback water and AMD that is available in its vicinity. In addition, the treatment process was optimized to enable recovery of BaSO_4 solids that can be used as weighting agent in drilling mud.

2. Materials and Methods

2.1 Characteristics of flowback water and AMD

Flowback water and AMD were collected from sites in northeastern Pennsylvania and stored in 20,000 gallon frack tanks for use in the pilot-scale study. Characteristics of

these impaired waters sampled from the frack tanks are summarized in Table 1. The flowback water used in this study contains much higher concentrations of divalent cations compared with the flowback water from southeastern PA reported previously (He et al., 2013; He et al., 2014a; He et al., 2014b; Kondash et al., 2013) and is in agreement with the flowback/produced water quality model developed by Barbot et al. (2013).

Table 1 Characteristics of flowback water and AMD

Constitutes	Flowback Water	AMD
Na ⁺ (mg/L)	31,382±1207	37.6±1.7
Ca ²⁺ (mg/L)	31,270±621	66.3±1.2
Mg ²⁺ (mg/L)	1,590±49	82±2.1
Ba ²⁺ (mg/L)	19,115±166	-
Sr ²⁺ (mg/L)	16,141±210	-
Cl ⁻ (mg/L)	152,213±5670	266±4
SO ₄ ²⁻ (mg/L)	-	275±3
Fe ³⁺ (mg/L)	-	29.7±1.1
Fe ²⁺ (mg/L)	28.2±1.1	5.9±0.2
Ra-226 (pCi/L)	15,570±1823	-
Ra-228 (pCi/L)	1,385±339	-
TSS	246±4	6±0.1
pH	6.2±0.01	2.6±0.01

Based on the analysis of 140 AMD samples, Cravotta demonstrated that pH of AMD varies from 2.7 to 7.3, with the majority being either acidic or neutral (Cravotta, 2008a). AMD generally contains dissolved iron that varies from below 0.1 mg/L to a few hundred mg/L (Cravotta, 2008b). Low-pH AMD can contain both Fe²⁺ and Fe³⁺, and the ratio depends on geological conditions (Wei and Viadero, 2007; Druschel et al., 2004). The non-treated AMD used in this study is acidic and rich in ferric iron, which is typical for AMD from this region (Ott, 1986). Although precipitation of amorphous ferric

hydroxide is thermodynamically feasible, it would take several months to reach equilibrium considering the pH and ferric iron concentration of the AMD sample used in this study (Cornell et al., 1989).

Sulfate concentration in the AMD collected for this study was very low compared to barium concentration in the flowback water (Table 1), and was adjusted by adding Na₂SO₄ to the AMD stream prior to feeding it to the pilot-scale system to reflect more challenging treatment conditions. The actual initial concentrations of key constituents (i.e., Ba²⁺ and SO₄²⁻) in the two feed streams to the pilot-scale unit that were tested in this study are shown in Table 2.

Table 2. Adjusted initial barium and sulfate concentrations in flowback water and AMD fed to the pilot-scale system

Concentration	Barium (Flowback Water)	Sulfate (AMD)	Flowback/AMD mixing ratio
Low	11,474±299	1,172±19	1:9
High	19,115±451	2,150±31	1:8
The adjustment of barium and sulfate was determined in the field with turbidimetric analytical method and validated by sample analysis in the laboratory.			

2.2 Bench-scale tests

Bench-scale beaker tests were conducted in the laboratory to evaluate the reaction rate as a function of saturation index ($SI = \log \frac{\text{Ion Activity Product}}{K_{sp}}$) for barium sulfate using various flowback water and AMD samples collected previously as well as synthetic BaCl₂ and Na₂SO₄ solutions (Table S1 in the Supporting Information). The reaction rate

was calculated based on the data collected in the first two minutes of the test when it can be assumed that homogenous nucleation (i.e., formation of new particles in the bulk phase) governs the reaction in the absence of any seed particles.

Prior to pilot-scale tests, a set of bench-scale jar tests using a six-paddle jar tester (Phipps & Bird, Richmond, VA) was conducted in the field to find optimal operating conditions for turbidity and iron removal. Rapid mixing in these tests was conducted for 1 min at 300 rpm followed by slow mixing for 25 min at 25 rpm and settling for 30 min, during which turbidity and dissolved iron concentration were measured.

2.3 Pilot-scale operation

Unit processes in the pilot-scale treatment system include rapid mixing, flocculation, sedimentation and bag filtration (Figure 1). Two 25-gallon tanks equipped with variable-speed electric mixers (80-4,000 rpm) were used as rapid mixing tank and AMD mixing tank. The mixing speed of rapid mixers was adjusted to 1,600 rpm to ensure effective mixing (Gt value of 87,000). A 350-gallon tank equipped with paddle mixer was used as a flocculation tank. The mixing speed used for flocculation was adjusted to 8 rpm to achieve Gt value of 83,800. A 500-gallon cone-bottom settling tank was equipped with tube settler to ensure efficient separation of suspended solids and sludge thickening. The total influent flow rate of flowback water and AMD was targeted at 5 GPM, while the flow rate of the recycled sludge was adjusted based on the solids content at the bottom of the clarifier and the desired solids concentration in the rapid mixing tank. The TSS of the return sludge was 7.5 wt.% and the diaphragm pump was

used to recycle sludge with such high solids concentration back to AMD mixing tank at a flow rate of 5 gpm.

Each experiment was conducted for a period of about 6-8 hours to ensure steady-state conditions in the pilot-scale system as evidenced by constant levels of key operating parameters (i.e., influent and effluent barium, sulfate and iron concentrations, effluent turbidity, solids concentration in the recycled sludge).

Figure 1. Schematic of the pilot-scale treatment system

2.4 Analytical Methods

Cation and anion analysis in the laboratory was performed using atomic absorption spectroscopy (AAS) (Model 1000, PerkinElmer, Waltham, MA) and ion

chromatography (Dionex ICS-1100, Thermo Scientific, Waltham, MA), respectively. For AAS analysis, samples were filtered through 0.45- μ m membrane, and diluted with 2% nitric acid and 0.15% KCl solution to eliminate ionization interference during AAS analysis for Ba and Sr (He et al., 2014b; Barbot et al., 2013). Samples for total dissolved iron analysis were filtered through 0.22- μ m membrane to eliminate interference of sub-micron particles with dissolved iron measurement (He et al., 2014a).

A high-resolution Apex Gamma spectrometry system (Ortec, Oak Ridge, TN) with a high-purity Germanium detector was used to quantify the activity of radionuclides. Prior to NORM analysis, samples were placed in 47 mm petri dishes, sealed with vinyl electrical tape, and kept for at least 2 days to ensure equilibrium between Ra-228 and Ac-228. Ra-226 activity was analyzed by measuring gamma ray emission at 186 KeV, while Ac-228 activity was analyzed based on multiple gamma ray emissions at 270, 338, 911, and 964 KeV. Ra-228 activity was calculated based on the activity of its progeny Ac-228.

The on-site analysis for barium and sulfate was conducted using Hach Method 10251 and Hach Method 8051, respectively. Validation of the Hach methods was performed by comparison with AAS for dissolved barium and ion chromatography for sulfate measurement under the conditions that are relevant for shale gas wastewater. It was found that the dissolved sulfate measurements by these two analytical methods were in good agreement (data not shown). However, the turbidimetric method for barium analysis was reliable only when the strontium concentration was lower than the barium concentration. The total dissolved iron and Fe²⁺ on site analyses were conducted by FerroVer Method (Hach Method 10249) and 1,10-phenanthroline method (Hach Method

8146), respectively. The Fe^{3+} concentration was calculated as the difference between the total dissolved iron and Fe^{2+} concentration.

Characterization of solids that precipitated in the mixing reactor in terms of morphology and chemical composition were performed using scanning electron microscopy (SEM, Philips XL30, FEI Co., Hillsboro, OR) and energy dispersive X-ray spectroscopy (EDX, EDAS Inc., Mahwah, NJ), respectively. The solid samples from the mixing reactor were diluted 500-1,000 times with DI water and deposited on a 0.45 μm nylon membrane on site. After the membrane samples were completely dried in the field, they were transferred to the laboratory and sputter coated with palladium for 60s in a vacuum at a current intensity of 40 mA to avoid the charging effect (Tang et al., 2006). The particle size distribution was statistically analyzed by measuring the size of at least 200 particles from at least five SEM images (Murdoch et al., 2011; Shoults-Wilson et al., 2011).

Water-soluble alkaline earth metals content (as calcium) was measured in solid samples collected from the sludge return line. The sludge samples were filtered through 0.7- μm glass fiber membrane, washed with 150 mL of DI water and dried in an oven. 1g of dry solids was collected from the membrane, mixed in 50mL of DI water, and placed on a rotary shaker to equilibrate for 1 hour. The suspension was then filtered through 0.45- μm membrane and the total alkaline earth metals in the liquid permeate was measured using EDTA titration method (Standard Method 2340, APHA et al., 2012).

3. Results and Discussion

3.1 Sulfate Removal

234 Presence of dissolved sulfate in the fracturing fluid is of concern because of the
235 potential to cause mineral scaling in the subsurface, particularly in Marcellus Shale that is
236 rich in Ba, Sr and Ca (He et al., 2013; He et al., 2014c). Therefore, sulfate concentration
237 in the hydraulic fracturing fluid is generally limited to 100 mg/L (He et al., 2013). It was
238 previously reported that mixing of AMD and flowback water requires more than 10 hours
239 to reach precipitation equilibrium as indicated by conductivity analysis (Kondash et al.,
240 2013). He et al. reported that barite precipitation is very rapid and will reach equilibrium
241 within 30 min when excess sulfate is added to flowback water, while celestite
242 precipitation will proceed for more than 24 hours (He et al., 2014b). As it is desirable to
243 minimize the size of the treatment plant, slow celestite and gypsum precipitation
244 reactions were not considered in this study for the control of sulfate in the finished water.

245 Figure 2 shows average sulfate concentration throughout the treatment system
246 from at least 3-5 measurements at steady-state operation. Sulfate analysis revealed that
247 barite precipitation proceeded rapidly in the mixing reactor and reached equilibrium after
248 the flocculation tank. Such behavior is expected because the saturation index calculated
249 using PHREEQC software with Pitzer activity corrections was above 4.0 for all
250 experimental conditions evaluated in this study, which corresponds to rapid barite
251 precipitation (He et al., 2014b). As shown in Figure 2, sulfate concentration in the
252 finished water was reduced to below 100 mg/L for all three experimental conditions,
253 which was the target concentration to enable unrestricted use of this water for hydraulic
254 fracturing.

Figure 2. Sulfate concentration in the pilot-scale treatment units for various experimental conditions (error bars indicate 95% confidence interval of the mean)

The decrease in saturation index will lead to slower homogeneous nucleation rate, while the increase in seed concentration will promote the seeded growth rate (Nancollas and Purdie, 1964). The sulfate consumption rate as a function of saturation index observed in bench-scale and pilot-scale tests is shown in Figure 3. As can be seen in this figure, the reaction rate increases sharply for $SI > 3.0$, which is in agreement with rapid barite precipitation reported previously (He et al., 2014b). Bench-scale tests were designed to evaluate homogenous nucleation reaction (Supporting Information) and the rate expression is fitted well with an exponential curve ($R^2=0.95$). The average sulfate

consumption rate in the rapid mix reactor of the pilot-scale test without sludge recycling was 2.0 and 4.2 mM/(min) for low (SI=4.4) and high (SI=4.7) concentration, respectively, and was in excellent agreement with the bench-scale tests (Fig. 3).

Experiments conducted at low concentration with sludge recycling reduced SI from 4.4 to 4.0 due to dilution, but the total suspended solids (TSS) in the mixing reactor increased from 0.2 to 3.9 wt.%. The average sulfate consumption rate in the mixing reactor increased from 2.0 to 2.2 mM/(min) despite a 50% reduction in hydraulic retention time in the reactor caused by sludge recycling. Sulfate consumption with sludge recycling was significantly above the values observed for homogenous nucleation. These results indicate that the seeded growth was effectively promoted by sludge recycling and that growth of existing barite particle comprised a significant portion of sulfate consumption (i.e., 48%) under these conditions.

Figure 3. Sulfate consumption rate as a function of saturation index (the two highest SI conditions in bench-scale tests were achieved by mixing Na_2SO_4 and BaCl_2) (error bars indicate 95% confidence interval of the mean)

3.2 AMD as a source of coagulant

While dissolved sulfate can be reduced to acceptable level, coagulation may be required prior to settling to facilitate removal of fine barite particles formed in this process (He et al., 2014c). Dissolved iron typically present in AMD can potentially serve as the internal coagulant to reduce the cost and total life cycle impact of the proposed AMD use as make up water for hydraulic fracturing. Salama et al. (2015) reported that AMD was useful for coagulation of microalgae biomass at pH between 7 and 9, while

Sun et al. (2013) studied As removal by coagulation with in-situ formed Fe^{3+} from AMD. Previous lab-scale studies found that coagulation with ferric chloride was an effective process for the removal of suspended solids formed by mixing flowback water and AMD and that the finished water turbidity can be reduced to below 5 NTU with ferric chloride dosage of 20-60 mg/L as Fe at pH 6.0-7.0 (Zheng, 2013).

The pilot-scale experiment with pH adjustment by adding NaOH was conducted at low concentration conditions. Initial concentrations of Fe^{3+} and Fe^{2+} in the mixture were 26.7 mg/L and 8.1 mg/L, respectively. Bench-scale jar tests revealed that the optimum pH for turbidity and iron removal was between 7.0 and 7.5, when the turbidity of the supernatant was reduced to 2 NTU and the total iron was reduced to 0.1 mg/L. The coagulant dosage used in this study is in agreement with the range of ferric chloride dosages reported previously (Zheng, 2013).

Turbidity and total iron in the effluent from the pilot system operated at pH 7.5 were 3 NTU and 0.1 mg/L, respectively, indicating that iron contained in the wastewater effectively served as coagulant to enhance solids removal. Although aeration was not applied in the pilot-scale system, the total iron was reduced to a desired level at pH 7.5. The Fe^{2+} concentration in the effluent of the rapid mix reactor, flocculation tank and settling tank was 0.66 mg/L, 0.18 mg/L and 0.08 mg/L, respectively, while the Fe^{3+} concentration was reduced to below the detection limit (0.1 mg/L for Hach Method 10249) in the rapid mix reactor.

The rate equation developed by Singer and Stumm (1970) was incorporated in the PHREEQC model to predict Fe^{2+} removal. The kinetic model predicted that Fe^{2+} would be reduced from 8.1 to 5.8 mg/L after 1 min of contact time at the dissolved oxygen

concentration of 4 mg/L. Jar tests revealed that the Fe^{3+} concentration decreased from 26.7 mg/L to 0.12 mg/L after 1 minute of rapid mixing, while the Fe^{2+} concentration was reduced from 8.1 mg/L to 0.78 mg/L. The difference between the measured and predicted Fe^{2+} concentrations is likely due to the presence of heavy metals (e.g, Cu^{2+}) that can catalyze the oxidation reaction (Stumm and Lee, 1961) and/or the incorporation of ferrous ion into ferric hydroxide by coprecipitation (Wei and Viadero, 2007; Tronc, et al. 1992).

The effective use of iron contained in AMD as coagulant for solids separation reveals the additional merits for using this wastewater as make-up water for flowback water reuse.

3.3 Management of Ra-enriched solid waste

As listed in Table 3, the quality of finished water from the proposed treatment process enables unrestricted use for hydraulic fracturing. However, the management of the solid waste generated from this process is still a concern due to its elevated radioactivity.

Table 3. Finished water quality for low concentration conditions

Ra-226 in Effluent	<60 pCi/L
Ra-228 in Effluent	<10 pCi/L
Ra removal	>99%
Total Iron (mg/L)	0.1
Sulfate (mg/L)	73 ± 3
Turbidity (NTU)	3
pH	7.3 ± 0.01

As sulfate concentration in the influent was in excess compared to barium, complete removal of barium resulted in complete Ra removal as evidenced by Ra concentration in the finished water below the detection limit (60 pCi/L for Ra-226 and 10 pCi/L for Ra-228), which is in agreement with previous results (Kondash et al., 2013; Zhang et al., 2014). The solids generated in the pilot-scale system contained 648 pCi/g Ra-226 and 53 pCi/g Ra-228, respectively, which far exceeded the limits for TENORM disposal in municipal solid waste landfills (5-50 pCi/g depending on state regulations). Reuse of Ra-enriched BaSO₄ particles formed in this treatment process as weighting agent in drilling mud formulation can potentially reduce the TENORM loading in municipal landfills in Pennsylvania. Previous study has demonstrated that the radioactivity from Ra-enriched barite particles is not a concern even for workers at centralized waste treatment facilities that store their TENORM solids as long as they are separated from these solids by about 3-5 m (Zhang, 2015). Therefore, safe handling/storage of the radioactive sludge produced from the co-treatment of flowback water and AMD can be easily achieved. In essence, this approach for management of barite produced in this process will result in the deposition of Ra-enriched BaSO₄ in the shale formation because most of the weighting agent in the drilling mud is lost by adsorption to the shale formation during horizontal drilling. However, the barite particles formed in this process would have to be much bigger to meet the API standards (API, 2010) so that they can be used for unconventional well drilling.

Growth of precipitated solids is a common goal in many industrial processes (Demopoulos, 2009; Nason and Lawler, 2008). The fundamental idea behind these applications is to promote seeded growth, while limiting the generation of new particles

through homogeneous nucleation. At high supersaturation, which is typical for barite precipitation from flowback water due to its high barium concentration (Barbot et al., 2013), homogenous nucleation governs the precipitation process. Therefore, sludge recirculation was utilized at low concentration conditions in this study to reduce supersaturation by dilution of the feed stream with recycled sludge and to increase the concentration of seed particles in the mixing reactor in an effort to suppress homogenous nucleation and promotes seeded growth.

The feasibility of enhancing the growth of barite particles through sludge recirculation was conducted in a pilot-scale system without pH adjustment (pH of the mixture was 2.8). Particle size analysis of samples collected from the rapid mix reactor revealed the average barite particle size of 5.42 ± 1.61 and 3.77 ± 1.23 μm for low and high concentration conditions, respectively. These results illustrate that the increase in saturation level yields smaller particles (Fig. 4a), because homogeneous nucleation dominates at high barite supersaturation (Kucher et al. 2006). The number percent of particles that are smaller than 6 μm was 63% and 89% for the low and high concentration levels, respectively, which is not compatible with the size requirement for drilling mud specified by API.

As illustrated in Figure 4b, introduction of sludge recirculation reduced cumulative frequency of the particles that are smaller than 6 μm from 63 to 27%, which meets the API requirement. This result is consistent with the reaction rate analysis discussed earlier (Fig. 3).

Figure 4. Particle size distribution of barite particles: (a) low sulfate and high sulfate conditions (b) low sulfate condition with and without sludge recirculation

EDX analysis revealed that the precipitant formed in the pilot-scale system is strontian barite (i.e., BaSrSO_4) with relatively uniform Ba content (about 84% of cations) for all three experimental conditions evaluated in this study. As can be seen in Figure 5, Sr content in strontian barite particles is not dependent on the morphology of solids formed in the system. Sanchez-Pastor et al. reported that the incorporation of Sr into barite particles would result in the elongation of the precipitant (Sánchez-Pastor et al., 2006). However, such phenomenon was only observed under low concentration conditions (i.e., low supersaturation) used in that study. At high concentration condition, the reaction is governed by homogeneous nucleation rather than crystal growth. EDX analysis also revealed that Ca incorporation into the precipitant was negligible, which can be explained by the difference in the ionic radius between barium and calcium (McIntire, 1963). The atom percent of barium in strontian barite obtained in this study is slightly higher than that reported elsewhere (Kondash et al., 2013), which is likely due to differences in the composition of feed solution, reaction time and measurement method.

Figure 5. Morphology and chemical composition of mineral precipitant formed at various experimental conditions: (a) low concentration; (b) high concentration and (c) low concentration with sludge recycle.

Particle density measured by submersion method (Klute, 1986) revealed average density of 4.3 g/cm³ based on triplicate measurements while the water-soluble alkaline earth metal content (as calcium) was 44 mg/kg. Therefore, BaSO₄ particles recovered from this process meet API specification and can be reused in drilling mud formulation, which can potentially reduce the cost of unconventional gas extraction and relieve the pressure on the management of TENORM associated with flowback water reuse. Ra levels in the solids produced in the centralized wastewater treatment (CWT) facilities that employ sulfate precipitation for divalent ion removal (mainly Ba and Sr) are also

significantly above the TENORM disposal limit (Zhang et al., 2014). Therefore, the approach for barite reuse developed in this study can also be used to improve waste management practices in these facilities. Laboratory and field-scale experiments conducted in this study also demonstrated that the effluent produced by co-treatment of abandoned mine drainage and flowback water can meet industry requirements for unrestricted use in hydraulic fracturing in Marcellus Shale. These results indicate that it is possible to reduce the use of fresh water for hydraulic fracturing while at the same time helping to alleviate adverse environmental impacts of abandoned coal mine discharges in Pennsylvania.

4. Conclusion

A pilot-scale study was conducted to evaluate the co-treatment of flowback water and AMD for use in hydraulic fracturing. The results of the pilot-scale tests revealed that sulfate was rapidly removed from liquid phase at high supersaturation with respect to barium sulfate. Sulfate concentration in the finished water could be reduced to below 100 mg/L by using the appropriate mixing ratio between flowback water and AMD. Ferric ion contained in AMD was useful as coagulant to assist the separation of suspended solids by settling. This practice can reduce the cost and total life cycle impact of the use of AMD as a make-up water source for flowback water reuse. When the AMD is rich in ferrous iron, a separate reactor with aeration will be required for Fe^{2+} oxidation and Fe^{3+} that is formed in situ can be used for the subsequent flocculation process.

The Ra-rich solid waste generated through this process poses a serious management problem, as it exceeds the TENORM limit for municipal solid waste

landfills. The feasibility of recovering barium sulfate for use as a weighting agent in drilling mud was evaluated in this study. Experimental results demonstrated that the barium sulfate particle size decreases with an increase in the initial supersaturation level and is typically smaller than the size required for barite use as a weighting agent. The increased surface area of primary particles and reduced supersaturation level resulting from sludge recirculation promoted the growth of barium sulfate particles. The physical and chemical properties of the barium sulfate particles obtained with sludge recirculation can fulfill the API requirements, which offers an alternative management option for the TENORM solid waste generated from the process of blending flowback water AMD.

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