OPTIMIZATION OF TREATMENT OPTIONS TO ENABLE THE USE OF ABANDONED MINE DRAINAGE (AMD) FOR HYDRAULIC FRACTURING IN MARCELLUS SHALE

by

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Abandoned Mine Drainage (AMD) is a promising make-up water source for hydraulic fracturing in Marcellus Shale as it is often available in the vicinity of planned natural gas wells and can be used to reduce fresh water utilization. When mixing AMD with Marcellus Shale produced water, the high sulfate concentration in AMD could precipitate a significant amount of barium and strontium in produced water as a pre-treatment for produced water prior to reuse for hydraulic fracturing. In order to promote the recycling of AMD and produced water, it is necessary to optimize treatment processes to remove solids created by mixing these waters.

Conventional coagulation/flocculation process was optimized with respect to mixing/settling time, coagulant dosage, pH, sludge handling and clarifier design using two different Marcellus Shale flowback waters and actual AMD that is available in their vicinity. This conventional process is compared against ballasted flocculation that has smaller footprint and may be more suitable as a mobile treatment system. The mixing ratio of flowback water and AMD was studied in order to meet potential effluent quality requirement for sulfate of 100 mg/L that may be imposed by gas companies and was compared to chemical equilibrium calculations by Phreeqc and MINEQL models.

The effluent quality from the conventional and ballasted flocculation processes are comparable with turbidity below 5 NTU despite the fact that the contact time required for the
ballasted flocculation is just 10 min compared to 1 hour required for conventional treatment process. Careful optimization of the AMD : Marcellus Shale Produced water mixing ratio is needed to ensure effluent quality with respect to sulfate concentration. The solids produced by ballasted flocculation had better settling characteristic and higher sludge density than the solids produced by conventional process.

**Keywords:** Marcellus Shale, Flowback water, Abandoned Mine Drainage (AMD), Coagulation/flocculation, Ballasted flocculation, Sludge handling
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1.0 INTRODUCTION

Shale gas is a promising and vast energy source that is developed and produced from continental shale formations. Among all the shale formations, the Marcellus Shale of the Appalachian Basin is one of the most expansive and largest shale reservoirs in play in the United States. The Marcellus Shale underlies a large portion of Pennsylvania, eastern West Virginia, parts of New York, Ohio, as well as Maryland. It contains as much as 489 Tcf (trillion cubic feet) of natural gas recoverable reserves (Engelder, 2009; Kargbo et al., 2010). In 2012, a total of 6,165 Marcellus wells were drilled, 3,550 (58%) of these were completed drilling while the other wells were still in process (Pennsylvania Department of Environmental Protection, 2013).

Development of the Marcellus Shale has been made possible by recent advances in two key technologies: horizontal drilling and hydraulic fracturing (Matthews and Malone, 2007). Hydraulic fracturing requires large amounts of frac fluid, which is made up of 90.5% water, 9% proppant (a propping agent, typically sand, used to hold open cracks in the formation) and 0.50% additives, to create cracks that allow natural gas to escape freely and rise to the surface. According to a recent study of Susquehanna River Basin, the average horizontal Marcellus well requires approximately 16.5 million liters of water about 104,000 barrels (Yoxtheimer et al., 2012).

Possible water sources include surface water, private water sources, municipal water, and groundwater, as well as reused produced water. A study conducted by the Appalachian Shale
Water Conservation Management Committee in 2008 identified surface water withdrawals as the primary source (60–70%) of the total water demand for drilling and completion activity in the Marcellus Shale Basin (Gaudlip et al., 2008). As the number of gas drilling operations continues to grow, efficient water use strategies are becoming critical aspects of shale operations, especially under drought conditions, low seasonal flow, or in locations with already stressed water supplies (Kargbo et al., 2010).

One solution to the management of hydraulic fracturing water is the reuse of the flowback or produced water. However, the high concentration of scale-forming divalent cations, including barium, calcium, iron, magnesium, and strontium (Ba\(^{2+}\), Ca\(^{2+}\), Fe\(^{2+}\), Mg\(^{2+}\) and Sr\(^{2+}\)), could readily form precipitates that may block the fractures in gas bearing formations required for economic gas production (Engelder, 2009; Kargbo et al., 2010). In addition, only 10% - 30% of the injected frac fluids return to the surface during the first 10-14 days of fracturing operation as flowback water in Marcellus Shale (Kidder et al., 2011). The low water recovery requires large amounts of fresh water to serve as make-up water for hydraulic fracturing activities in the Marcellus Shale development.

Another promising approach to manage frac fluid is using abandoned mine drainage (AMD) in the vicinity of planned natural gas wells as a source of frac water. That approach can help mitigate the problems (potential pollution of groundwater, surface water and soil, which in turn, may have harmful effects on humans, animals and plants) caused by the drainage itself, while lessening the pressure on other freshwater withdrawal. Coal-mining activities in the Appalachian Basin have left behind an environmental legacy of AMD, which collectively discharges more than 1.2 billion liters of low-pH contaminated water per day into fresh-water streams (Button et al., 1998). As compared with the volume of water required for hydraulic
fracturing in Marcellus Shale, it is clear there is a sufficient volume of water to make AMD utilization feasible from a water-supply perspective.

In addition to serving as source water for hydraulic fracturing, AMD also provides a source of sulfates, which could precipitate a significant amount of divalent cations, such as $\text{Ba}^{2+}$, $\text{Sr}^{2+}$, and $\text{Ca}^{2+}$, in the flowback water as preliminary treatment; AMD may also reduce the potential for scale formation in the gas wells (Akcil and Koldas, 2006). Precipitates formed by the reaction of AMD with flowback water should be removed prior to water reuse to minimize the potential for porosity reduction of the proppant packing.

As numbers of wells keep increasing, a greater volume of both fracturing flowback water and produced water could be readily available from the wells. In turn, as the total volume of water requiring treatment grows, the proportion of produced water will also increase significantly. Large amounts of produced water, along with efforts to improve efficiency and lower costs, will stimulate producers and engineers to continue developing cost effective treatment technologies (Jenkins, 2012).

Using abandoned mine drainage (AMD) water, which is often available in the vicinity of planned natural gas wells, can reduce the need for fresh water utilization and induce precipitation of divalent cations from flowback water as a pre-treatment. Designing a cost effective and long-term use treatment system is necessary to secure the cost competitiveness of using AMD water compared to freshwater. Treatment processes are focused on the reduction of the concentrations of sulfates and metals through chemical precipitation, as well as the removal of total suspended solids to acceptable levels by coagulation/flocculation followed by clarification. The specific objectives of this work include:
1) Optimize conventional coagulation/flocculation treatment processes to achieve potential effluent quality requirement for turbidity (<10 NTU) sulfate of (<100 mg/L) and compare the performance with that of ballasted flocculation using actual flowback water and actual AMD.

2) Compare performance of conventional and ballasted flocculation using actual flowback and AMD samples.

3) Compare experimental results with equilibrium predictions for finished water quality.

4) Develop strategies for handling the sludge produced in the proposed treatment process.
2.0 LITERATURE REVIEW

2.1 WATER SUPPLY AND WASTE DISPOSAL REGULATION

2.1.1 Flowback water

The Pennsylvania Department of Environmental Protection is making efforts to protect surface water because that valuable water resource could be removed from the hydrologic cycle through injection into the shale. The department requires operators to submit a Water Management Plan with drilling permit applications to identify water sources to be used, as well as safe yield calculations for surface water withdrawals for each well (Gaudlip et al., 2008). In this case, operators are likely to deal with a variety of water regulatory agencies as the increasing development of shale gas take place in the Marcellus Shale.

The disposal of flowback and produced water is another crucial issue. Regulations and laws related to flowback water disposal are governed by the Underground Injection Control Program (UIC) of the Federal Safe Drinking Water Act, the Federal Clean Water Act and the National Pollutant Discharge Elimination System (NPDES). Prior to generation of waste, the operator should prepare and implement a plan for control and disposal of drilling wastes. In Pennsylvania, flowback water is likely to be regulated by a number of options for disposal that may include using commercial waste treatment facilities, on-site recycling for re-use in
subsequent fracturing jobs, as well as for Class II injection wells. Among these opinions, underground injection is expected to be limited in the Marcellus Shale play, as there are few areas that have suitable injection zones.

2.1.2 Abandoned mine drainage

Abandoned mine drainage (AMD) is water that is polluted from contact with abandoned mines, and is a common form of water pollution in Pennsylvania and in other states where vast amounts of mining took place in the past. Mine drainage includes both active-treatment mines (i.e., mines whose drainage waters are already treated and released into rivers and streams) and abandoned mines (i.e., mines whose drainage waters are not treated, and where liability for pollution they cause is not clear) (Yoxtheimer et al., 2012).

Abandoned mine drainage is commonly known as acid mine drainage; however, not all of that drainage is acidic. The generation of acidity due to sulfide oxidation occurs by two processes: proton acidity and metal acidity. The former occurs during the oxidation of sulfides, and the latter is from the hydrolysis of metal species in solution (Younger, 1998). Iron pyrite, the most common mineral influencing the AMD quality, reacts with oxygen and water (Stumm and Morgan, 1996). The resulting fluids may be highly toxic and, when mixed with groundwater, surface water and soil, may have harmful effects on humans, animals as well as plants.

For mines that have clearly assigned liability for treating drainage and releasing to rivers and streams, operators must obtain National Pollutant Discharge Elimination System (NPDES) permits. Mining companies are also required to treat and reduce sulfate levels, in order to meet Clean Water Act standards. However, the liability for ensuring abandoned mines discharged water conforms to Clean Water Act standard is not clear.
2.2 UTILIZATION OF AMD FOR SHALE GAS EXTRACTION

2.2.1 Factors affect AMD utilization

Remediation of surface waters contaminated with AMD could bring considerable environmental, social, and economic benefits, because it can improve ecosystem health, public water availability, as well as promote recreational opportunities (Button et al., 1998). The co-treatment of flowback water and produced water with AMD can not only solve public concerns regarding depletion of the fresh water supply in the Marcellus shale development area, but also put polluted water source to good use and provide a reduction of dissolved solids content in treated water.

In 2011, Pennsylvania Department of Environmental Protection issued a white paper about the utilization of AMD in Well Development for Natural Gas Extraction. It prescribes draft guidelines for promoting AMD use in hydraulic fracturing that is focusing on storage issues and liability. Treatment, transportation, and storage costs are the most important factors affecting water-utilization decisions in shale-gas development (Yoxtheimer et al., 2012). Pennsylvania has proposed policy reforms to address environmental liability issues associated with AMD use, but its implementation will likely raise costs for its use in hydraulic fracturing as compared to the use of freshwater.

Abandoned (untreated) mine drainage poses a larger environmental challenge. Issues regarding handling liability and storage costs for abandoned-mine waters in particular represent significant regulatory barriers. Study indicated that reducing sulfate levels without the use of additional freshwater may involve costs of several dollars per barrel versus less than one dollar per barrel for freshwater purchased directly (Yoxtheimer et al., 2012). However, AMD use may become cost competitive with the development and use of low-cost AMD treatment technologies.
in centralized locations designed for long-term use, along with efficient water transfer and storage facilities (Yoxtheimer et al., 2012).

### 2.2.2 Sulfate scale and related problems

Sulfate scale deposits are hard, adherent, almost insoluble in mineral acids or other common solvents, and thus difficult to remove mechanically (Bader, 2006). When forming sulfate scale deposits in the downhole environment, severe flow restriction will occur, which in turn, will lead to additional capital cost and substantial operating cost. As the underground has significant amounts of scale-forming divalent cations, such as barium and strontium, the sulfate concentration should be decreased to a relatively low level before AMD is reused as frac water.

Sulfate reducing bacteria (SRBs) are anaerobic microorganisms that are often found under slime and other deposits. Under highly reducing conditions in the presence of adequate sulfates and organics, sulfate reducers will generate hydrogen sulfide (H$_2$S) as a metabolic product and cause microbial influenced corrosion (MIC) (Hamilton, 1985). SRBs have created souring of some conventional reservoirs from injection of waters, both produced and semi-fresh. The sour gas generated through this process would decrease the purity of gas product (Guidotti, 1994), and thus ought to be removed via gas scrubbing or other treatment processes prior to being sold. Hydrogen sulfide gas is also lethal at levels above 1000 ppm by volume for exposures over 2 min, and therefore, worker-health safeguards monitoring systems are required.

Besides, sulfate scale could also include Naturally Occurring Radioactive Materials (NORM) related problems because flowback water contains Radium is readily incorporated in sulfate scale. As such, external processing equipment could pose radioactive hazards due to NORM adherent to scales created during water processing (Bader, 2006).
Ballasted flocculation, known as the ACTIFLO\textsuperscript{®} technology, is a compact process that operates with micro-sand as a seed for floc formation. The microsand provides a surface area that enhances flocculation and acts as ballast to form robust and rapidly settling flocs. A different concept for ballasted flocs formation is provided by Young and Edwards (2003). Their microscopic observations of differences between iron-polymer flocs and iron-polymer-plus-ballasted-agent flocs suggested that the ballasted sand did not function as a “seed” for floc formation but was incorporated uniformly into the floc matrix. Ghanem et al. (2007) proposed a comprehensive evaluation of the fundamental physical and chemical factors governing ballasted flocculation reactions, including micro-sand dosage, time of coagulant and polymer dosage, and mixing intensity, etc.

Ballasted flocculation is ideally suited for industrial applications and is applied successfully in the wastewater treatment industry. It is especially ideal for plants with limited building areas. The unique settling characteristics performed by the micro-sand ballasted flocs allow for clarifier designs with high overflow rates, short detention times and minimal sludge volumes. These designs result in system footprints between 5 and 20 times smaller, compared to conventional clarification designs of similar capacity.

The schematic description of the ACTIFLO\textsuperscript{®} process is shown in Figure 1. Influent is pumped to a rapid-mix basin where coagulant is added to neutralize charges on the suspensions. The flow is then transferred to a flocculation basin where polymer and micro-sand are added to form the ballasted flocs. When suspensions are passed to a clarifier, ballasted flocs settle and are removed along with the ballasting agent. The micro-sand and sludge is recycled to the flocculation basin by a sand-solids separator, hydrocyclone.
2.4 SLUDGE HANDLING

2.4.1 Sludge settling

The characteristics of sludge produced in industrial water treatment can vary tremendously from plant to plant and even, from time to time, within the same plant, due to the different types of wastewater, and changes in the operation of wastewater treatment plants. As sludge handing is responsible for about 30%-40% of the capital cost, the importance of sludge handling and disposal cannot be overestimated (Vesilind, 1974).

The primary clarifier simply operates by settling heavier solids to the bottom and floating lighter solids to the top. The solids removed from the bottom of the clarifier are known as raw primary sludge which commonly contains a dry solids concentration of 4% to 8%. The
secondary clarifier typically has two zones that control the design of the clarifier. In the sludge blanket (zone 1), the settling velocity of the particles should govern the design for this zone. The mass of solids per unit area per unit time (lb/ft²/min) is defined as the gravity flux. In the concentrated sludge zone (zone 2), the rate of sludge drawoff controls the sludge thickening process. In this zone, the solids flux is defined as underflow flux.

Clarifiers and thickeners are separation devices, common in waste treatment as well as in other chemical operations. These devices separate two phases by differences in their density. Clarifiers and thickeners are essentially identical units: a clarifier produces clean water, while a thickener concentrates solids slurry.

2.4.2 Sludge dewatering

After the solid/liquid separation via gravity sedimentation, the concentration of solids in sludge ranges from 7% to 10% by weight (based on this study). The ultimate disposal of sludge is often facilitated by removing enough of the liquid portion so that the sludge behaves as a solid. Dewatering reduces the moisture content of the sludge so that it can more easily be disposal of by landfill, in terms of less storage space and less vehicle cost. However, the higher capital/operating costs, as well as increased equipment maintenance and replacement must be considered for selecting the cost-effective device. Sludge dewaterability, yield rates, as well as the overall cost analysis should be carefully studied before dewatering operation.

Generally, sludge dewatering can be accomplished by several processes, including drying beds, vacuum filtration, pressure filtration, centrifugation, cyclone, or capillary suction. Compared with thermal evaporative processes, mechanical dewatering via filtration and compression is often selected because of its low energy requirement (Vaxelaire et al., 1999).
Most mechanical dewatering processes comprise two stages: the filter cake formation stage and the compression stage. In the second stage, water is further squeezed from the cake by the application of a mechanical force. Tarleton and Wakeman (2006) gave a descriptive overview of the generic equipment types and main alternatives available to a design engineer. Three widely used dewatering processes are highlighted as potentially effective approaches that could handle sludge generated by the co-treatment of flowback water and AMD water.

### 2.4.2.1 Filtering centrifuges

Filtering centrifuges use centrifugal forces to efficiently perform batch and continuous cake filtration and deliquoring. Figure 2 depicts a cone centrifuge that could handle solids concentration ranging from 10% to 40% by weight. The worm screen centrifuge causes solids to move along the cone via an internal screw conveyor. The compromise between throughput and final cake moisture is governed by the conveyor speed. A short cake residence time, typically 4-15 seconds, could effectively produce sludge cake with high final dry solids content. (Tarleton and Wakeman, 2006)

![Figure 2. Schematic description of single stage worm screen centrifuges (Tarleton and Wakeman, 2006)
2.4.2.2 Belt press filters

Belt presses are characterized by two continuous, tensioned filter cloths. Schematic of the belt arrangement on a belt press filter is indicated in Figure 3. Flocculated sludge is introduced to the lower belt and is then progressively compressed under pressure as the cloths move over a sequence of successively smaller diameter rollers. The feed solids concentration typically ranges from 0.2% to 30% in a belt press process (Tarleton and Wakeman, 2006). Extra liquor is removed through the cloths by mechanical expression to produce a very dry cake.

![Figure 3. Schematic description of the belt arrangement on a belt press filter (Tarleton and Wakeman, 2006)](image)

2.4.2.3 Filter presses

The schematic representation of a typical bar horizontal filter press is shown in Figure 4. The process is commonly used in batch processing of solids forming incompressible and moderately compressible filter cakes. The feed sludge is introduced to the square, rectangular or circular chambers through a variety of plate porting arrangements and a suitable positive displacement or centrifugal pump. The chambers, formed between hollow frames and flat filter plates or between adjacent recesses filter plates, allow for filter cake formations as well as washing and gas-blown
deliquoring operations. Typical feed solids concentration ranges from 1% to 30% by weight. (Tarleton and Wakeman, 2006)

![Diagram of a typical bar horizontal filter press showing aspects of filter cycle operations (top) and cloth washing (bottom) (Tarleton and Wakeman, 2006)](image)

**Figure 4.** Schematic description of a typical bar horizontal filter press showing aspects of filter cycle operations (top) and cloth washing (bottom) (Tarleton and Wakeman, 2006)

### 2.4.3 Sludge disposal

Dewatering of sludge is often desirable and even necessary. However, it must be emphasized that dewatering is simply a preparation for ultimate disposal. Landfill disposal of sludge is one of the more common disposal practices (Smith et al., 1999). Disposal sites should be operated either by the waste generator who will maintain responsibility for its own waste or by a properly managed disposal facility.
3.0 MATERIALS AND METHODS

3.1 FEED WATER CHARACTERISTICS

Characteristic of Marcellus shale flowback water varied with shale formation locations as well as flowback period. Water samples were collected from two representative well sites located in southwest Pennsylvania. Site A is located in Washington County (South West of Allegheny) which had five wells that were connected in a common manifold, while Site B lies in Westmoreland County (East of Allegheny) which had only one well on the pad.

The volume of fracturing fluid injected for the hydraulic fracturing was 18 million gallons for the five wells at site A (which corresponds to an average of 3.6 million gallons per well) and 4.33 million gallons for the single well at site B. The flow-composite flowback water sample from each site was used in this study. The mixing ratio of flowback water sampled at different time was based on the flow-rate profile with time. The flowback and AMD water pair is summarized in Table 1. The main characteristics of the composite flowback water and AMD samples are shown in Table 2.

Flowback water usually contains high levels of calcium, magnesium, sodium, barium and strontium. As shown in Table 1, Site A has lower Barium concentration (236 mg/L) and higher Strontium concentration (1,799 mg/L) compared to Site B which has higher Barium concentration (1,204 mg/L) and lower Strontium concentration (590 mg/L). AMD 1 and 2 are
nearby Site A while AMD 3 and 4 are available in the vicinity of Site B. Each flowback water sample was mixed with two distinct AMD waters in terms of sulfate concentration. AMD 5 was taken from the vicinity of Site C while AMD 6 was closed to Site D. The AMD 1, 3 and 4 are untreated abandoned mine drainage, while AMD 2, 5 and 6 are treated mine drainage.

<table>
<thead>
<tr>
<th>Mixture No.</th>
<th>Flowback water</th>
<th>AMD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A (composite)</td>
<td>1 (untreated)</td>
</tr>
<tr>
<td>2</td>
<td>A (composite)</td>
<td>2 (treated)</td>
</tr>
<tr>
<td>3</td>
<td>B (composite)</td>
<td>3 (untreated)</td>
</tr>
<tr>
<td>4</td>
<td>B (composite)</td>
<td>4 (untreated)</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>5 (treated)</td>
</tr>
<tr>
<td>6</td>
<td>D</td>
<td>6 (treated)</td>
</tr>
</tbody>
</table>

The preliminary research is carried by using Mixture 1 to set up general test procedures of conventional coagulation/flocculation and ballasted flocculation, in terms of coagulation dosage range, and pH adjustment range, as well as slow mixing and settling time. Mixtures 2, 3 and 4 follow the same jar test procedures and are compared to Mixture 1 because they have different \( \text{Ba}^{2+}/\text{SO}_4^{2-} \) ratio. Mixtures 5 and 6 have significantly higher barium concentrations and were used to confirm that this treatment process could also effectively treat mixtures with higher cations and anions concentrations, as well as to see if they could handle larger amounts of sludge.
Table 2. Flowback and AMD water characteristics

<table>
<thead>
<tr>
<th>Constitutes</th>
<th>Flowback Water</th>
<th>Acid Mine Drainage (AMD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>27,946</td>
<td>18,766</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>15,021</td>
<td>3,496</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>1,720</td>
<td>614</td>
</tr>
<tr>
<td>Ba (mg/L)</td>
<td>236</td>
<td>1,204</td>
</tr>
<tr>
<td>Sr (mg/L)</td>
<td>1,799</td>
<td>625</td>
</tr>
<tr>
<td>Fe (Total) (mg/L)</td>
<td>ND</td>
<td>2.8</td>
</tr>
<tr>
<td>Cl (mg/L)</td>
<td>104,300</td>
<td>35,380</td>
</tr>
<tr>
<td>SO₄ (mg/L)</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>Alkalinity (mg CaCO₃/L)</td>
<td>44</td>
<td>ND</td>
</tr>
<tr>
<td>pH</td>
<td>6.43</td>
<td>7.38</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>42</td>
<td>54</td>
</tr>
</tbody>
</table>
3.2 CONVENTIONAL COAGULATION/FLOCCULATION

Conventional coagulation/flocculation process is evaluated using six different combinations of actual Marcellus Shale flowback waters and actual AMD (both treated and untreated) that is available in their vicinity. As shown in Figure 5, jar tests were carried out in PB-700 six paddle jar tester (Phipps & Bird, Richmond, VA). Each 1000 mL beaker was filled with 500 mL of flowback and AMD water mixture. The pH was accurately checked by a digital pH-meter that was calibrated daily with buffer solutions. Settled water samples were analyzed for turbidity and sulfate concentration.

Sulfate concentration was measured using a Hach DR/890 portable colorimeter (Hach, Loveland, CO) and a Hach Sulfavēr® 4 Sulfate Reagent following the method 8051 (Hach, Loveland, CO). Turbidity was measured using the same Hach colorimeter following the method 8237 (Hach, Loveland, CO). Further cation analyses were performed using a Perkin-Elmer 1100B atomic absorption spectrophotometer while anions analyses were measured by ion chromatography (DX-500, Dionex, Sunnyvale, CA). All experiments were performed at room temperature (20°C).
Flocculation time governs floc formation and is generally expressed, along with mixing intensity, as a product (G\text{s}). Selection of G and Gt are important parameters in determining the proper mixing for both rapid mix and flocculation reactor design. Velocity gradient G is a parameter that can be used to express the power input as follows:

\[
G = \left( \frac{P}{\mu V} \right)^{1/2}
\]

where:

- G = mean velocity gradient (s\(^{-1}\))
- P = the power dissipated in the water (N \(\cdot\) ms\(^{-1}\))
- V = volume of water to which the power is applied (m\(^3\))
- \(\mu\) = absolute viscosity of the water (N \(\cdot\) sm\(^{-2}\))
Acceptable Gt factors range between $10^4$ and $10^5$ (Warren and Hammer, 1985). For high turbidity solids removal in this study, G typically ranges from 30 s$^{-1}$ to 80 s$^{-1}$, while Gt is in the range of 36,000 to 96,000 (Davis and Cornell, 2008). As shown in Table 3, Gt values for coagulation and flocculation process were 45,600 and 64,800, respectively.

Table 3. The Gt value of coagulation/flocculation process

<table>
<thead>
<tr>
<th>Mixing rate (rpm)</th>
<th>Mixing time (min)</th>
<th>G value (sec$^{-1}$)</th>
<th>Gt</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1</td>
<td>760</td>
<td>45,600</td>
</tr>
<tr>
<td>25</td>
<td>30</td>
<td>36</td>
<td>64,800</td>
</tr>
</tbody>
</table>

Process optimization is done in terms of pH, coagulant dose, mixing/settling time. The specific procedures are as follows:

pH optimization is performed by mixing flowback water with its AMD pair at a desired mixing ratio calculated by Phreeqc and MINEQL$^+$ (will be discussed in Section 4.3). Ferric chloride was dosed at 20 mg/L as Fe and 0.1 M sodium hydroxide solution was used to adjust the pH. For Mixture 1, pH was adjusted to 5.00, 5.50, 6.00, 6.50, and 7.00; for Mixtures 2, 3 and 4, pH was adjusted to 6.25, 6.50, 6.75, and 7.00. Within five minutes from the start of mixing flowback water with AMD, rapid mixing was conducted for one minute at 300 rpm (G = 760 sec$^{-1}$) followed by slow mix for 30 minutes at 25 rpm (G = 36 sec$^{-1}$) and settling for 30 minutes. 50 mL of supernatant was collected from the beaker (depth of sample collection is 50 mm) and analyzed for finished water quality.

Once the optimum pH was achieved, studies were carried out to determine the effect of coagulant dosage optimization on turbidity removal efficiency. Flowback water was mixed with its AMD water pair at a desired mixing ratio and pH was adjusted to optimized value determined
in the previous step. For Mixture 1, coagulant dosage was adjusted at 20, 30, 40, 50, 60, 70 mg/L as Fe. For Mixtures 2, 3 and 4, coagulant dosage was adjusted to 15, 20, 25 and 30 mg/L as Fe. The rest of the procedure was identical to that used in the previous test.

Slow mixing and settling time optimization was performed at pH and coagulant dosage at the optimum values obtained in previous steps. Slow mixing was varied between 15 or 30 minutes at 25 rpm and settling was conducted for 30 or 45 minutes. 50 mL of supernatant was collected from the beaker (depth of sample collection is 50 mm) and analyzed for finished water quality. Slow mixing and settling time optimization was only investigated for Mixture 1.

3.3 BALLASTED FLOCCULATION

Ballasted flocculation was tested using the pH and coagulant dosage at the optimum values obtained from conventional coagulation/flocculation jar-tests. A total of 2.5 grams of microsand was added to a total mixture volume of 500 mL to achieve typical microsand dose in this process of five grams per liter.

The initial mixing period of two minutes is followed by another three minutes of rapid mixing at 300 rpm. At that time, flocculant aid is added to the solution and mixing continued for another 15 seconds. Mixing intensity was reduced to 200 rpm for a period of 45 seconds followed by four min of settling time. 50 mL of supernatant is collected from the beaker (depth of sample collection is 50 mm) and analyzed for finished water quality. Turbidity and sulfate concentration are analyzed immediately after jar-test by Hach colorimeter.
3.4 EQUILIBRIUM PREDICTIONS

MINEQL⁺ 4.6 and Phreeqc Interactive 2.17 were used for equilibrium predictions in this study. MINEQL⁺ is software for chemical equilibrium calculations and was developed by Westall, et al. (1976). Phreeqc I is software for geochemical speciation calculation that was developed by US Geological Survey. Both of MINEQL⁺ and Phreeqc I use similar computer codes on the basis of the mass action law, with the differences in databases and equations that are used to calculate activity coefficients. MINEQL⁺ uses the MINTEQA2 database and extended Debye Huckel equation to predict the activity coefficient, which means that this model gives relatively high accuracy results as long as the ionic strength below 0.5 molality. For ionic strength above 0.5 molality, Phreeqc model, which uses Pitzer equation and “Pitzer.dat” database, gives accuracy results for activity coefficients calculation (Li, 2011).

Equilibrium of sulfate precipitation was studied at three different reaction times (i.e.: 10, 20 and 60 min) to understand the potential of conventional and ballasted flocculation process to achieve effluent sulfate concentration of 100 mg/L that may be required by E&P companies. Experimental results were compared to chemical equilibrium calculations by standard thermodynamic models like Phreeqc and MINEQL⁺.

3.5 BENCH-SCALE SLUDGE SETTLING STUDY

Two methods of design are commonly used for clarifier design. The method developed by Talmadge and Fitch (1955), based on work by Kynch (1952), and requires calculations of a
clarifier area required for clarification and a thickening area based on the interface settling velocity of sludge with a single initial concentration. However, experiments have shown that clarifier design methods based on Kynch's theory are not applicable to wastewater sludge (Vesiland, 1974).

The widely accepted method of design is based on work by Coe and Clevenger (1916) and Cho et al. (1993). They used total solids flux, including settling of the sludge induced by gravity (bulk movement of sludge) and that induced by recycling water from the clarifier bottom. The settling properties of flocculated sludge were evaluated in a 1-L cylinder equipped with a diffuser stone. Aeration was used to suspended solids in order to obtain a more homogeneous aliquot for analysis. After mixing for two minutes, suspensions were allowed to settle and the sludge settling velocity was determined by observing sludge interface with time.

### 3.6 PILOT-SCALE CLARIFIER DESIGN PARAMETERS

Sludge settling characteristics are studied to provide basis for clarifier design with respect to sludge loading, sludge recycle ratio, clarification area, and thickening area. Design of pilot-scale clarifier is based on parameters listed in Table 4, the influent flow is 20 GPM and the underflow solids content is 7%. The mass ratio, 1:10, is the weight of the barium sulfate solids generated from the recycled sludge compared to the weight of the newly precipitated barium sulfate solids generated in the wastewater during the precipitation reaction.
Table 4. Pilot-scale clarifier design parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent flow</td>
<td>20 GPM</td>
</tr>
<tr>
<td>Underflow solids content</td>
<td>7%</td>
</tr>
<tr>
<td>Recycle sludge mass ratio</td>
<td>1:10</td>
</tr>
<tr>
<td>(new produced sludge : recycled sludge)</td>
<td></td>
</tr>
</tbody>
</table>

3.6.1 Sludge recycle ratio

Recycled sludge could provide barite crystal seed to accelerate barium sulfate precipitation. The recycle ratio necessary to maintain a MLSS in the tank of desired solids content is obtained by performing a mass balance on solids in the reactor. Specified recycle rate ($Q_r$) could be obtained by Equation (2) as well as the maximum solids flux ($X_u$) that can be applied to this clarifier.

$$Q_r X_u + Q (X_0) = (Q + Q_r) X_u$$

where:

- $Q = \text{influent wastewater flowrate (ft}^3 \text{ min}^{-1})$
- $Q_r = \text{recycle sludge flowrate (ft}^3 \text{ min}^{-1})$
- $X_0 = \text{total suspended solids concentration in influent flow (mg L}^{-1})$
- $X_u = \text{underflow solids concentration (mg L}^{-1})$
3.6.2 Thickening area

The area required for thickening corresponding to each limiting flux and recycle ratio using the expression:

\[
A_t = (Q + Q_r) \frac{t_u}{H_0}
\]  

where:

- \( A_t \) = thickening area (ft²)
- \( Q \) = influent wastewater flowrate (ft³ min⁻¹)
- \( Q_r \) = recycle sludge flowrate (ft³ min⁻¹)
- \( t_u \) = ultimate time (min)
- \( H_0 \) = initial interface height (ft)

3.6.3 Clarification area

The zone settling velocity (ZSV) is defined as the gradient of the linear part of settling curve. The minimum required clarifier area is computed by equation as follows:

\[
A_c = \frac{Q}{ZSV}
\]

where:

- \( Q \) = the effluent flow over the weir (ft³ min⁻¹)
- \( ZSV \) = zone settling velocity (ft min⁻¹)
3.6.4 Overflow rate

Overflow rate is one of the guidelines for the design of settling tanks and clarifiers in treatment plants. It is used by operators to determine if tanks and clarifiers are hydraulically over or underloaded. Surface overflow rate, similar to hydraulic loading rate (flow per unit area), is used to determine loading on sedimentation basins and circular clarifiers. However, hydraulic loading rate measures the total water entering the process, whereas surface overflow rate measures only the water over-flowing the process. The overflow rate is computed using the following equation:

\[
OR = \frac{Q}{S}
\]

(5)

where:

- OR = overflow rate (gpm ft\(^{-2}\))
- Q = flowrate (gallons min\(^{-1}\))
- A = surface area (ft\(^2\))
4.0 RESULTS AND DISCUSSION

4.1 CONVENTIONAL COAGULATION/FLOCCULATION JAR-TEST

Conventional coagulation/flocculation process was optimized with respect to mixing/settling time, coagulant dosage, and pH. The aim of this work is to produce reliable data for optimal turbidity removal by coagulation with Fe (III) on the basis of experimental work carried out with two different Marcellus Shale flowback waters and actual AMD that is available in their vicinity. The performance of the conventional flocculation process was compared with that of the ballasted flocculation.

4.1.1 The results for Mixture 1

The initial jar-test used Mixture 1 comprised of 20% Flowback (FB) water A and 80% AMD 1 based on the result of previous research. As indicated in Table 2, FB water A has 236 mg/L barium and AMD 1 contains 700 mg/L sulfate. According to the mixing ratio and composition of original feed water, the initial barium and sulfate concentration of Mixture 1 were 47 mg/L and 560 mg/L, respectively.
4.1.1.1 The effects of pH

It is well known that pH is one of the key parameters that are controlling the efficiency of coagulation/flocculation of wastewater. The impact of pH on turbidity and sulfate concentration in Mixture 1 is shown in Figures 6 and 7, respectively.

Figure 6. Impact of pH on effluent turbidity in conventional flocculation process for Mixture 1

Figure 7. Impact of pH on effluent sulfate concentration in conventional flocculation process for Mixture 1
Results indicate that the optimum pH for turbidity removal in Mixture 1 is 6.0. The variation of sulfate concentration with is not significant. High sulfate concentration in the effluent was mainly due to low barium concentration (47.2 mg/L) in flowback water A, which was not significant to precipitate much of the sulfate (560 mg/L) in AMD 1.

4.1.1.2 The effects of settling/slow mixing time and coagulant dosage

The dosage of coagulant depends on the content of suspended solids in the mixture. Generally, the treatment efficiency, in terms of turbidity, is assumed to increase with increasing dose of coagulant. When the treatment efficiency reaches a maximum, turbidity increases with the further addition of coagulant. Figure 8 demonstrates the results of coagulant dosage optimization experiments using 15 and 30 minutes of slow mixing time and followed by 30 minutes settling time.

When the slow mixing time was just 15 minutes, it seems that the optimal coagulant dose was 50 mg/L. However, when the slow mixing time increased to 30 minutes, there were no significant differences between the coagulant dosages in the range from 20 to 70 mg/L as Fe as the final turbidity of all samples was below 2.0 NTU (the effluent turbidity decreased two to five times compared with the results obtained with the slow mixing time of 15 minutes. Therefore, the coagulant dosage of 20 mg/L and slow mixing time of 30 minutes would be optimal process parameters for the conventional flocculation process.
Figure 8. Impact of coagulant dose and slow mixing time on effluent turbidity in conventional flocculation process for Mixture 1 with 30 min settling time

Figure 9. Impact of coagulant dose and settling time on effluent turbidity in conventional flocculation process for Mixture 1 with 30 min slow mixing time

Optimization of the settling time using 30 minutes of slow mix time is shown in Figure 9. The impact of settling time variation between 30 and 45 minutes on final water turbidity was not obvious. In sum, the optimum pH, coagulant dose, slow mixing time and settling time for Mixture 1 was 20 mg/L as Fe, 30 minutes and 30 minutes.
4.1.2 The results for Mixtures 2, 3 and 4

4.1.2.1 The effects of pH

Characteristics of feed water for these three mixtures are listed in Table 2 (in chapter 3.1). Mixture 2 comprises of 30% Flowback (FB) water A and 70% AMD 2. Mixture 3 consists of 40% FB water B and 60% AMD 3. Mixture 4 contains 25% FB water B and 75% AMD 4. The initial sulfate concentration of Mixtures 2, 3 and 4 were 174 mg/L, 433 mg/L and 236 mg/L, respectively. The initial barium content of Mixtures 2, 3 and 4 were 71 mg/L, 496 mg/L and 291 mg/L, respectively.

Mixture 2 had about two times higher sulfate concentration than barium concentration, while Mixtures 3 and 4 had similar sulfate and barium mass ratios. The only difference between Mixtures 3 and 4 is that both sulfate and barium concentrations in Mixture 3 were nearly two times higher than in Mixture 4. All flocculation optimization tests with these three mixtures were performed with one minute rapid mixing time, 30 minutes slow mixing time and 30 min settling time.

The optimization of pH for conventional flocculation of Mixtures 2, 3 and 4 using 30 minutes slow mixing time and 30 minutes settling time is shown in Figure 10. As can be seen in this figure, pH variations in the range from 6.25-7.0 had significant impact on effluent turbidity. Based on these results, it can be concluded that all three mixtures achieved the lowest effluent turbidity at pH 6.50. As can be seen in Figure 11, coagulation pH had very little impact on sulfate concentration in the effluent.
Figure 10. Impact of pH on effluent turbidity for conventional flocculation process with Mixtures 2, 3 and 4 (Ferric Chloride Dosage = 20 mg/L as Fe)

Figure 11. Impact of pH on effluent sulfate concentration in conventional flocculation process with Mixtures 2, 3 and 4 (Ferric Chloride Dosage = 20 mg/L as Fe)

4.1.2.2 The effects of coagulant dosage

The results of coagulant dose optimization at pH 6.5 for Mixtures 2, 3 and 4 are shown in Figure 12. These results indicate that the optimal coagulant dose for Mixture 2 is 25 mg/L as Fe while 20 mg/L as Fe was sufficient to remove most of the turbidity for Mixtures 3 and 4. Figure 13
shows the impact of coagulant dose on sulfate concentration in the effluent. For Mixtures 2 and 3, sulfate concentration in the effluent was nearly constant for all coagulant doses evaluated in this study. However, sulfate concentration in the effluent for Mixture 4 decreased slightly as the coagulant dose increased. It is highly unlikely that the ferric sulfate would precipitate under these conditions.

This error may be due to the unique characteristics of Mixture 4. The barium concentration in flowback water B was very high while the sulfate concentration in AMD 4 was comparatively low. In this case, a slight variation of the mixing ratio has a significant influence on the equilibrium barium and sulfate concentrations in the mixture. These results suggest that mixing ratio of flowback water and AMD should be carefully adjusted, especially in the case of significant “unmatched” barium or sulfate concentration.

Figure 12. Impact of coagulant dose on effluent turbidity in conventional flocculation process with Mixtures 2, 3 and 4 at pH 6.5
Figure 13. Impact of coagulant dose on effluent sulfate concentration in conventional coagulation/flocculation process for Mixtures 2, 3 and 4 at pH 6.5

Figure 14 shows the color and turbidity of flowback water A, AMD 2 and effluent from the conventional coagulation/flocculation/sedimentation process. Visible decrease in color and turbidity of treated water compared with both flowback and AMD is apparent in this figure.

Figure 14. Observation of feed water and effluent characteristics
4.1.3 The results for Mixtures 5 and 6

4.1.3.1 The effects of pH

Characteristics of feed water for these three mixtures are listed in Table 2 (in chapter 3.1). The initial sulfate concentration of Mixtures 5 and 6 are 405 mg/L, 493 mg/L, respectively. The initial barium content of Mixtures 5 and 6 are 588 mg/L, 706 mg/L, respectively. Compared with Mixtures 1, 2, 3 and 4, Mixtures 5 and 6 have greater concentrations of sulfate and barium contents, and could produce more barite and increase total suspended solids.

Figure 15 indicates the impact of pH on effluent turbidity. As can be seen in this figure, pH variations in the range from 6.25-7.0 had remarkable impact on effluent turbidity. Based on these results, it can be concluded that all three mixtures achieved the lowest effluent turbidity at pH 6.50. As can be seen in Figure 16, coagulation pH had very little impact on sulfate concentration in the effluent. These results are relatively consistent with those using Mixtures 2, 3 and 4.

![Figure 15. Impact of pH on effluent turbidity in conventional flocculation process with Mixtures 5 and 6 (Ferric Chloride Dosage = 20 mg/L as Fe)](image-url)
4.1.3.2 The effects of coagulant dosage

The results of coagulant dose optimization at pH 6.5 for Mixtures 5 and 6 are shown in Figures 17 and 18. These results indicate that the optimal coagulant dose for Mixtures 5 and 6 is 25 mg/L as Fe. As discussed, these two mixtures contain high levels of barium and sulfate, and thus need more coagulant to neutralize electric charge of colloidal particles, and induce colloidal particles to settle. Similar with previous results, coagulant dosage variation had limited effect on effluent sulfate concentration.
Figure 17. Impact of coagulant dose on effluent turbidity in conventional flocculation process with Mixtures 5 and 6 at pH 6.5

Figure 18. Impact of coagulant dosage on effluent sulfate concentration in conventional flocculation process with Mixtures 5 and 6 at pH 6.5

4.1.4 The comparison of Mixtures

The optimized conventional coagulation/flocculation process for the removal of barite formed after mixing of flowback water and AMD included rapid mixing at 300 rpm for one minutes, slow mixing at 25 rpm for 30 minutes and settling for 30 minutes. The optimal pH for this process is between 6 and 6.5 and the optimal Ferric Chloride dosage of 20 mg/L or 25 mg/L as Fe could achieve expected effluent turbidity (i.e., below 5 NTU) for most mixtures.
In addition, coagulant dosage and pH variation has limited effect on final sulfate concentration that is governed primarily by the concentration of Ba$^{2+}$ in flowback water. The mixing ratio of flowback water and AMD should be carefully adjusted to achieve a desired sulfate concentration in the finished water.

4.2 BALLASTED FLOCCULATION

Ballasted flocculation has smaller footprint comparing to conventional process and might be more suitable as a mobile treatment system for flowback and AMD water. The impact of adding anionic and cationic flocculant aids was evaluated for the flowback water and AMD mixtures and their dosages were optimized to achieve lowest effluent turbidity. The impact of ten minutes pre-mixing on sulfate removal by ballasted flocculation process was investigated for all four flowback water and AMD mixtures.

4.2.1 The results for Mixture 1

4.2.1.1 Flocculant aid optimization

The optimization of flocculant aid is shown in Figure 19. Four types of anionic polymers and four types of cationic polymers were tested at the concentrations of 2 and 1 ppm. Anionic flocculant aids performed better than most of the cationic polymers. Higher dosages of anionic polymer accomplished better results than lower dosages. Among four different anionic flocculant aids tested in this study, Hydrex 6161 yielded best results with effluent turbidity below 1 NTU at 1 ppm dose.
**4.2.1.2 Flocculant aid dosage minimization**

The minimization of Hydrex 6161 as flocculant aid is aimed for decreasing the cost, and is depicted in Figure 20. Effluent turbidity was below 1 NTU for 0.5 ppm dose while it increased to 4 NTU when the dose was further reduced to 0.2 ppm. Consequently, the minimum dose of anionic polymer Hydrex 6161 should be 0.2 ppm.
4.2.2 The results for Mixtures 2, 3 and 4

4.2.2.1 Flocculant aid optimization

The results of flocculant aid optimization for Mixtures 2, 3 and 4 are shown in Figure 21. Four types of anionic polymers and four types of cationic polymers were tested at the concentration of 1 ppm. The results shown on Figure 21 suggest that anionic flocculant aids also performed better than cationic polymers for these mixtures. Hydrex 6161 yielded best results as the effluent turbidity for all three mixtures was below 2 NTU. These results are very similar to those obtained for Mixture 1.
Figure 21. Impact of flocculant aid type on turbidity of the effluent from ballasted flocculation with Mixtures 2, 3 and 4 at flocculant aid dosage of 1 mg/L.

### 4.2.2.2 Flocculant aid dosage minimization

Figure 22 indicates that adding 0.5 ppm of Hydrex 6161 to Mixture 2 could achieve effluent turbidity of 6 NTU while 0.2 ppm was sufficient to achieve equal or better effluent turbidity for Mixtures 3 and 4.
4.2.3 The results for Mixtures 5 and 6

Basing on the results obtained for Mixtures 1, 2, 3 and 4, anionic flocculant aid Hydrex 6161 was investigated for use with Mixtures 5 and 6. Figure 23 shows that adding 0.5 ppm of Hydrex 6161 to Mixtures 5 and 6 had the ability to decrease turbidity to below 5 NTU.
4.2.4 The impact of pre-mixing

As the reaction time of ballasted flocculation is very short, the impact of pre-mixing on sulfate removal in ballasted flocculation was evaluated by adding a 10 minutes pre-mixing step (i.e., prior to the addition of microsand) to the experimental procedure. As can be seen in Figure 24, significant amount of barite precipitation could be observed after just two minutes of reaction time.

*Figure 24. Changes in Mixture 3 color and turbidity with time variation from 0.5 to 2 min*

Final sulfate concentration after 10 minutes and 20 minutes of the reaction in these tests was compared to the results obtained in a conventional coagulation process that lasted 60 minutes (30 minutes of slow mixing and 30 minutes of settling) in Figure 25. This figure clearly shows that the increase in the reaction time from 10 to 60 minutes did not have significant impact on the overall sulfate removal. Therefore, a pre-mixing is not necessary for ballasted flocculation when treating a mixture of flowback water and AMD.
4.2.5 Summary of findings

The effluent quality from the conventional and ballasted flocculation processes were of comparable quality (i.e., below 5 NTU) despite the fact that the contact time required for the ballasted flocculation is just ten minutes compared to one hour required for conventional treatment process.

Anionic flocculant aid was found to work better than cationic flocculant aid for ballasted sand flocculation. In fact, some cationic flocculant aids lead to a turbidity increase while most anionic flocculant aids helped to decrease turbidity of the finished water. Among the anionic polymers, Hydrex 6161 performed the best for all flowback and AMD mixtures tested in this study. The minimum flocculant aid dosage ranged from 0.2 mg/L for Mixtures 1, 3 and 4 to 0.5 mg/L for Mixtures 2, 5 and 6.
It was found that there will be no need to add a pre-mixing stage for ballasted flocculation process since barite precipitation was essentially more than 90% complete in the first ten minutes of contact between AMD and flowback water.

4.3 EQUILIBRIUM PREDICTIONS

4.3.1 Sulfate precipitation

The sulfate concentration in the effluent of conventional and ballasted flocculation is compared to chemical equilibrium predictions in Figure 26. The initial sulfate concentration was calculated based on the water quality characteristics and mixing ratios of flowback water and AMD. The sulfate concentration after 10 and 20 minutes was determined from the experiments designed to optimize ballasted flocculation and ballasted flocculation with pre-mixing period of 10 minutes. The sulfate concentration after 60 minutes was determined from the experiments designed to evaluate the performance of conventional coagulation process. Chemical equilibrium calculations were performed using Phreeqc model with Pitzer equation for activity corrections and MINEQL+ with extended Debye–Hückel equation for activity corrections (Li, 2011).

As indicated in Figure 26, majority of sulfate precipitated in the first ten minutes of contact with barium. Sulfate removal in Mixtures 1 and 2 were relatively low compared to that observed in Mixtures 3, 4, 5 and 6. Experimental results are consistent with the predictions using Phreeqc and MINIQL+ models with calculations obtained using the Phreeqc model being a bit closer to experimental results.
Comparison of experimentally measured barium and strontium removal with equilibrium predictions are shown in Figures 27 and 28, respectively. Strontium removal was low as barium sulfate precipitation dominated chemical precipitation. Similar results were obtained by Li (2011) which suggested that sulfate is a very effective precipitating reagent for barium but fails to remove strontium and calcium.

The only differences between experimental results and predictions may be due to the unique characteristics of Mixture 4. The barium concentration in flowback water B was very high while the sulfate concentration in AMD 4 was comparatively low. In this case, a slight
variation of the mixing ratio has a significant influence on the equilibrium barium and sulfate concentrations in the mixture.

**Figure 27.** Comparison of barium removal after 60 minutes with equilibrium predictions
4.3.2 Impact of $\{\text{Ba}^{2+}/\text{SO}_4^{2-}\}$ ratio on sulfate removal

Saturation index (SI) is the logarithm of the quotient of the ion activity product (IAP) and solubility product constant ($K_{sp}$).

$$SI = \frac{\log IAP}{K_{sp}}$$

(7)

In Equation (7), IAP is the product of free ion species activities; $K_{sp}$ is thermodynamic equilibrium constant (solubility product constant) and was determined already for different minerals in Phreeqc and MINEQL$^+$ databases. The IAP for BaSO$_4$ is shown in Equation (8).

$$IAP = \{\text{Ba}^{2+}\} \cdot \{\text{SO}_4^{2-}\}$$

(8)
Table 5. Impact of $\{\text{Ba}^{2+}\}/\{\text{SO}_4^{2-}\}$ activity ratio on sulfate removal

<table>
<thead>
<tr>
<th>Flowback Water</th>
<th>AMD Water</th>
<th>Initial SO$_4$ (mg/L)</th>
<th>Initial Ba (mg/L)</th>
<th>Ion Activity Ratio ${\text{Ba}^{2+}}/{\text{SO}_4^{2-}}$</th>
<th>Mass ratio ${\text{Ba}^{2+}}/{\text{SO}_4^{2-}}$</th>
<th>Ionic Strength</th>
<th>Saturation Index $I_{\text{BaSO}_4}$</th>
<th>Effluent SO$_4$ (mg/L)$^a$</th>
<th>Sulfate Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% FB A</td>
<td>80% AMD 1</td>
<td>560</td>
<td>47.2</td>
<td>0.06</td>
<td>0.08</td>
<td>0.465</td>
<td>2.57</td>
<td>530.0</td>
<td>5.4</td>
</tr>
<tr>
<td>65% FB A</td>
<td>35% AMD 1</td>
<td>253.3</td>
<td>153.4</td>
<td>0.42</td>
<td>0.61</td>
<td>2.186</td>
<td>2.23</td>
<td>172.0</td>
<td>32.1</td>
</tr>
<tr>
<td>70% FB A</td>
<td>30% AMD 1</td>
<td>219.3</td>
<td>165.2</td>
<td>0.53</td>
<td>0.75</td>
<td>2.374</td>
<td>2.17</td>
<td>128.0</td>
<td>41.6</td>
</tr>
<tr>
<td>30% FB A</td>
<td>70% AMD 2</td>
<td>174.2</td>
<td>70.8</td>
<td>0.28</td>
<td>0.41</td>
<td>0.976</td>
<td>2.04</td>
<td>140.0</td>
<td>19.6</td>
</tr>
<tr>
<td>35% FB A</td>
<td>65% AMD 2</td>
<td>162.8</td>
<td>82.6</td>
<td>0.36</td>
<td>0.51</td>
<td>1.141</td>
<td>2.02</td>
<td>126.0</td>
<td>22.6</td>
</tr>
<tr>
<td>40% FB A</td>
<td>60% AMD 2</td>
<td>151.4</td>
<td>94.4</td>
<td>0.44</td>
<td>0.62</td>
<td>1.309</td>
<td>2.00</td>
<td>102.0</td>
<td>32.6</td>
</tr>
<tr>
<td>35% FB B</td>
<td>65% AMD 3</td>
<td>467.2</td>
<td>434.0</td>
<td>0.66</td>
<td>0.93</td>
<td>0.372</td>
<td>3.65</td>
<td>165.0</td>
<td>64.7</td>
</tr>
<tr>
<td>40% FB B</td>
<td>60% AMD 3</td>
<td>432.7</td>
<td>496.0</td>
<td>0.81</td>
<td>1.15</td>
<td>0.423</td>
<td>3.62</td>
<td>85.0</td>
<td>80.4</td>
</tr>
<tr>
<td>45% FB B</td>
<td>55% AMD 3</td>
<td>398.2</td>
<td>558.0</td>
<td>0.99</td>
<td>1.40</td>
<td>0.475</td>
<td>3.60</td>
<td>20.0</td>
<td>95.0</td>
</tr>
<tr>
<td>20% FB B</td>
<td>80% AMD 4</td>
<td>250.8</td>
<td>232.8</td>
<td>0.65</td>
<td>0.93</td>
<td>0.261</td>
<td>3.25</td>
<td>120.0</td>
<td>52.2</td>
</tr>
<tr>
<td>25% FB B</td>
<td>75% AMD 4</td>
<td>236.3</td>
<td>291.0</td>
<td>0.86</td>
<td>1.23</td>
<td>0.269</td>
<td>3.13</td>
<td>65.0</td>
<td>72.5</td>
</tr>
</tbody>
</table>

$^a$: 60 min reaction.
As listed in Table 5, all mixtures had similar saturation index of BaSO₄, which ranged from 2.00 to 3.65. In this case, sulfate removal efficiency as a function of \( \frac{[\text{Ba}^{2+}]}{[\text{SO}_4^{2-}] } \) ratio was investigated based on the assumption that saturation conditions were similar. Sulfate removal efficiency as a function of \( \frac{[\text{Ba}^{2+}]}{[\text{SO}_4^{2-}] } \) ion activity ratio in conventional coagulation/flocculation process with one hour reaction time is shown in Table 5 and plotted in Figure 29. The correlation between sulfate removal efficiency and \( \frac{[\text{Ba}^{2+}]}{[\text{SO}_4^{2-}] } \) mass ratio is shown in Figure 30. When \( \frac{[\text{Ba}^{2+}]}{[\text{SO}_4^{2-}] } \) ion activity ratio increased from 0.06 to 0.99, the sulfate removal efficiency increased from 5.4% to 95%. Similar results were observed in the case of the \( \frac{[\text{Ba}^{2+}]}{[\text{SO}_4^{2-}] } \) mass ratio where the increase in the mass ratio from 0.08 to 1.40 resulted in a linear increase in sulfate removal efficiency.

![Graph](image.png)

**Figure 29.** The correlation of \( \frac{[\text{Ba}^{2+}]}{[\text{SO}_4^{2-}] } \) ion activity ratio with sulfate removal efficiency after 1 hour of contact time
**Figure 30.** Correlation of \( \text{Ba}^{2+}/\text{SO}_4^{2-} \) mass ratio with sulfate removal efficiency after 1 hour of contact time
4.4 CHARACTERISTICS OF TREATED EFFULENT

Predicted and measured sulfate concentrations for different mixing ratios of flowback water and AMD are shown in Table 6. Sulfate concentrations decreased with a decrease in the blending ratio of AMD water. Careful adjustment of the flowback water and AMD blending ratio is required to guarantee effluent sulfate concentration below 100 mg/L.

As the major goal of using AMD water for natural gas extraction is serving as makeup water, blending a large quantity of AMD water is of practical significance. The optimum Flowback water : AMD water mixing ratio is calculated based on equilibrium values and is shown in Figure 31. The blending ratio of AMD water ranges from 30% to 88% depending on the $\{\text{Ba}^{2+}\}/\{\text{SO}_4^{2-}\}$ ion activity ratio of Flowback water and AMD water. Except for AMD 1, mixing with AMD water could potentially produce 1.5 to 7.3 times larger volumes of frac water compared to reusing flowback water only.
Table 6. Comparison of predicted and measured SO$_4$ concentration for different mixing ratios of flowback water and AMD

<table>
<thead>
<tr>
<th>FB water</th>
<th>AMD</th>
<th>volume ratio</th>
<th>Sulfate concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FB water</td>
<td>AMD</td>
<td>AMD/FB</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>20%</td>
<td>80%</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>65%</td>
<td>35%</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>70%</td>
<td>30%</td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>30%</td>
<td>70%</td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>35%</td>
<td>65%</td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>40%</td>
<td>60%</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
<td>35%</td>
<td>65%</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
<td>40%</td>
<td>60%</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
<td>45%</td>
<td>55%</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>20%</td>
<td>80%</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>25%</td>
<td>75%</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>12%</td>
<td>88%</td>
</tr>
<tr>
<td>D</td>
<td>6</td>
<td>25%</td>
<td>75%</td>
</tr>
</tbody>
</table>
The primary goal of coagulation-flocculation process is turbidity removal. As shown in Table 7, all effluent water had turbidity below 5 NTU. The other concern is that control of effluent sulfate concentration in order to decrease the occurrence of sulfate scaling. The final water quality of the conventionally treated flowback water : AMD blend was also evaluated in terms of its ability to meet the sulfate concentration below 100 mg/L. As discussed in chapter 4.3, carefully adjusting the mixing ratio could achieve desirable results.

The concentration of total iron in all mixtures was below 1 mg/L. Other ions of interest, including barium, strontium, magnesium, sodium and calcium, decreased significantly compared to initial value in the raw flowback water. Effluent pH values ranged from 6.0 to 6.5.
### Table 7. Effluent water quality from conventional coagulation and flocculation

<table>
<thead>
<tr>
<th>No</th>
<th>FB water</th>
<th>AMD</th>
<th>SO₄</th>
<th>Ba</th>
<th>Sr</th>
<th>Fe</th>
<th>Mg</th>
<th>Na</th>
<th>Ca</th>
<th>pH</th>
<th>Turbidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20% (A)</td>
<td>80% (1)</td>
<td>530</td>
<td>0.2</td>
<td>362</td>
<td>&lt; 1</td>
<td>268</td>
<td>7470</td>
<td>2479</td>
<td>6.13</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>30% (A)</td>
<td>70% (2)</td>
<td>140</td>
<td>18</td>
<td>566</td>
<td>&lt; 1</td>
<td>604</td>
<td>10107</td>
<td>5205</td>
<td>6.46</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>40% (B)</td>
<td>60% (3)</td>
<td>85</td>
<td>2.5</td>
<td>238</td>
<td>&lt; 1</td>
<td>190</td>
<td>7633</td>
<td>1280</td>
<td>6.40</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>25% (B)</td>
<td>75% (4)</td>
<td>63</td>
<td>43</td>
<td>148</td>
<td>&lt; 1</td>
<td>137</td>
<td>4769</td>
<td>624</td>
<td>6.38</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>12% (C)</td>
<td>88% (5)</td>
<td>2</td>
<td>7.3</td>
<td>980</td>
<td>&lt; 1</td>
<td>494</td>
<td>5087</td>
<td>3394</td>
<td>6.45</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>25% (D)</td>
<td>75% (6)</td>
<td>1</td>
<td>14</td>
<td>2167</td>
<td>&lt; 1</td>
<td>1305</td>
<td>8094</td>
<td>8496</td>
<td>6.46</td>
<td>3</td>
</tr>
</tbody>
</table>

4.5 SLUDGE HANDLING AND CLARIFIER DESIGN

4.5.1 Sludge quantities

Sludge quantities that would be generated in a pilot-scale test operated at the flow rate of 20 gpm with an 8-hr shift are estimated on the basis of barium sulfate precipitation. Total influent solids and sludge volume prior to dewatering process was calculated assuming 7% solids content and solids density equal to barite density (4.48 g/cm³) and is shown in Table 8. The six mixtures generated considerable barite solids, ranging from 140 mg/L to 1196 mg/L, and a daily sludge volume of 16.2 to 138.8 m³.
Table 8. Sludge quantities estimation based on barite precipitation

<table>
<thead>
<tr>
<th>No.</th>
<th>FB water</th>
<th>AMD</th>
<th>Barite Solids</th>
<th>Total Influent Solids (kg/day)</th>
<th>Solids Volume (m³/day)ᵃ</th>
<th>Sludge Volume (m³/day)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20% FB A</td>
<td>80% AMD 1</td>
<td>281</td>
<td>10.2</td>
<td>2.3</td>
<td>32.6</td>
</tr>
<tr>
<td>2</td>
<td>30% FB A</td>
<td>70% AMD 2</td>
<td>140</td>
<td>5.1</td>
<td>1.1</td>
<td>16.2</td>
</tr>
<tr>
<td>3</td>
<td>40% FB B</td>
<td>60% AMD 3</td>
<td>844</td>
<td>30.7</td>
<td>6.8</td>
<td>98.0</td>
</tr>
<tr>
<td>4</td>
<td>25% FB B</td>
<td>75% AMD 4</td>
<td>495</td>
<td>18.0</td>
<td>4.0</td>
<td>57.5</td>
</tr>
<tr>
<td>5</td>
<td>12% FB C</td>
<td>88% AMD 5</td>
<td>1196</td>
<td>43.5</td>
<td>9.7</td>
<td>138.8</td>
</tr>
<tr>
<td>6</td>
<td>25% FB D</td>
<td>75% AMD 6</td>
<td>983</td>
<td>35.7</td>
<td>8.0</td>
<td>114.1</td>
</tr>
</tbody>
</table>

ᵃ: Solids density equal to barite density (4.48 g/cm³).
ᵇ: Assuming 7% solids. Water density at 20°C is 0.9982 g/cm³.

As flowback water A has low barium content, the solids generated by Mixtures 1 and 2 are relatively small. Flowback water B, C and D had higher barium concentration compared against flowback water A. Thus, Mixtures 3, 4, 5 and 6 produced more solids than Mixtures 1 and 2. AMD 4 had low sulfate concentration, and thus generated comparatively small amount of sludge.

4.5.2 Clarifier design for a pilot-scale unit

The schematic of treatment process flow is indicated in Figure 32. For the pilot-scale treatment process, clarifier and thickener designs are based on the parameters indicated in this figure. The influent flow rate is 20 GPM with a concentration of 1,000 mg/L total suspended solids. Chemicals are dosed in the rapid mix tank, while polymers are dosed in the slow mix tank. The
underflow solids content is 7%. Partially concentrated barite sludge is pumped to the reaction basin to accelerate barite crystallization. The mass ratio of recycled sludge over newly generated sludge is 10 : 1.

![Figure 32. Schematic description of treatment process flow](image)

**4.5.3 Sludge recycle ratio**

The sludge recycle ratio is calculated based on mass balance, and is described as follows:

Mass Balance 1: \[
\frac{\text{mass of recycled dry TSS}}{\text{mass of influent TSS}} = 10 \]

\[
10 \times (Q_{in} \times C_{in} \times t) = Q_r \times C_u \times t
\]

\[
10 \times (20 \text{ GPM} \times 1,000 \text{ mg/L}) = Q_r \times 70,000 \text{ mg/L}
\]

\[
Q_r = 2.86 \text{ GPM}
\]

Mass Balance 2: Reactor mass input = Reactor mass output
\[ Q_{in} \cdot C_{in} + Q_r \cdot C_u = (20 + Q_r) \cdot C_0 \]

\[ 20 \text{ GPM} \cdot 1,000 \text{ mg/L} + 2.86 \text{ GPM} \cdot 70,000 \text{ mg/L} = (20 + 2.86) \cdot C_0 \]

\[ C_0 = 9,625 \text{ mg/L} \]

4.5.4 Sludge settling characteristics

Sludge settling characteristics are studied for Mixture 3 with solids concentration around 10,000 mg/L. Under this circumstance, interactions between particles are important factors to hinder settling. Settling is classified as Type II settling as the solid suspension tends to settle as a zone or blanket, and maintain the same position relative to each other. There is usually a distinct clarified zone showing a liquid-solid interface.

The settling and compaction curves are developed by plotting the height of the sludge interface versus the time of settling. Figure 33 shows the settling curve of conventional flocculated sludge, while Figure 34 presents the settling curve of ballasted flocculated sludge.

![Figure 33. Settling curve of conventional flocculated sludge](image-url)
In designing a thickener, the area required for the clarification and thickening functions are calculated separately. The larger of the two areas determines the size needed to achieve the specified performance. Clarifier design parameters are calculated separately for conventional and ballasted flocculated sludge.

For conventional flocculated sludge: $t_u = \text{from plot} = 12 \text{ min}$

For ballasted flocculated sludge: $t_u = \text{from plot} = 5 \text{ min}$

### 4.5.5 Design parameters

#### 4.5.5.1 Area required for thickening ($A_t$)

$$H_o = 1.15 \text{ ft}$$

$$H_u = \frac{C_0 * H_o}{C_u} = \frac{1,000 \text{ mg/L} * 1.15 \text{ ft}}{9,625 \text{ mg/L}} = 0.12 \text{ ft}$$

For conventional flocculated sludge:
For ballasted flocculated sludge:

\[
A_t = (Q + Q_c) \frac{t_u}{H_0} = (20 + 2.86) \frac{\text{gallons}}{\text{min}} \times \frac{6.79 \text{ lbs}}{\text{gallon}} \times \frac{12 \text{ min}}{1.15 \text{ ft}} \times \frac{8h}{24h} = 540 \text{ ft}^2
\]

4.5.5.2 Area required for clarification (Ac)

For conventional flocculated sludge:

\[
ZSV \text{ (zone settling velocity)} = 0.115 \text{ ft/min}
\]

\[
Ac = \frac{Q}{ZSV} = \frac{Q}{0.115 \text{ ft/min}} = \frac{20 \frac{\text{gallons}}{\text{min}} \times 6.79 \text{ lbs}}{0.115 \text{ ft/min}} \times \frac{8h}{24h} = 393.7 \text{ ft}^2
\]

For ballasted flocculated sludge:

\[
ZSV \text{ (zone settling velocity)} = 0.25 \text{ ft/min}
\]

\[
Ac = \frac{Q}{ZSV} = \frac{Q}{0.25 \text{ ft/min}} = \frac{20 \frac{\text{gallons}}{\text{min}} \times 6.79 \text{ lbs}}{0.25 \text{ ft/min}} \times \frac{8h}{24h} = 181.1 \text{ ft}^2
\]

4.5.5.3 Clarifier diameter

Based on the calculation above, clarifier design is limited by thickening stage. The clarifier area for conventional flocculated sludge is 540 ft\(^2\), and for ballasted flocculated sludge is 225 ft\(^2\).

Diameter of the clarifier is given by following calculation:

For conventional flocculated sludge: \(D = [(540 \text{ ft}^2) * 4/3.142]^{0.5} = 26.22 \text{ ft}\)

For ballasted flocculated sludge: \(D = [(225 \text{ ft}^2) * 4/3.142]^{0.5} = 13.30 \text{ ft}\)
4.5.5.4 Overflow rate (OR)

For conventional flocculated sludge:

\[
OR = \frac{20 \text{ gpm}}{540 \text{ ft}^2} = 0.037 \text{ gpm/ft}^2
\]

For ballasted flocculated sludge:

\[
OR = \frac{20 \text{ gpm}}{225 \text{ ft}^2} = 0.088 \text{ gpm/ft}^2
\]

4.6 CHEMICAL ADDITION

The mixing of coagulants and polymers, or both with wastewater increases the removal efficiency of suspended solids. When feed water contains large amounts of total suspended solids, the dosage of coagulant and flocculant aid will increase. As it is summarized in Table 9, dosages of 20-25 mg/L coagulant and 0.2-0.5 ppm flocculant aid achieved satisfactory turbidity removal. Mixtures 2, 5, 6 required higher dosages because of high total suspended solids. Compared with Mixtures 5 and 6, Mixture 2 has fairly low barite precipitation. High total suspended solids may be generated by calcium carbonate precipitation, as the alkalinity of AMD 2 is relatively high.
Sodium hydroxide addition are mainly depends on the alkalinity of flowback water and AMD water, as well as coagulant dosage. pH would decrease when adding ferric chloride to the mixed solutions. As discussed above, AMD 2 has considerable alkalinity and thus the sodium hydroxide dosage for Mixture 2 is lower than for other mixtures, which ranged from 0.0032 g/L to 0.0170 g/L.

### 4.7 TREATMENT PROCESS SUMMARY

A schematic description of the overall treatment process is shown in Figure 35. The co-treatment of Marcellus Shale produced water and AMD is started by water characterization. AMD water is then transferred to gas well site aiming for minimizing transportation costs. The blend ratio of flowback water and AMD is dependent upon [Ba]/[SO₄] mass ratio. Conventional coagulation/flocculation process is operated by dosing optimum coagulant dosage, as well as by controlling pH and mixing time/intensity. For ballasted flocculation process, ballasted sand and
flocculant aid are added as well. The water and solids are separated by clarifier: water is stored in frac tank for reuse as frac water; partial sludge is recycled back to reactor, and thus provides barite crystal seed to accelerate barium sulfate precipitation, while the rest is dewatered for disposal.

Figure 35. Schematic description of the overall treatment process
5.0 SUMMARY AND CONCLUSIONS

Abandoned mine drainage (AMD) water, which is often available in the vicinity of planned natural gas wells, can reduce the need for fresh water utilization and induce precipitation of target divalent cations from flowback water as a pre-treatment step. Successful completion of this novel water management strategy would be beneficial for producers of natural gas in the Marcellus Shale and potentially any shale or coal bed methane development where produced water must be managed and/or freshwater withdrawals may be limited.

Conventional coagulation/flocculation/sedimentation process for all mixtures evaluated in this study included 1 min rapid mixing at 300 rpm (G = 760 sec\(^{-1}\)) followed by 30-min slow mixing at 25 rpm (G = 36 sec\(^{-1}\)) and 30-min of settling time. Gt values for coagulation and flocculation process were 45,600 and 64,800, respectively. The optimum coagulation pH for this process was between 6.0 and 6.5. Ferric chloride dose of 20 mg/L as Fe could achieve fairly low effluent turbidity for most mixtures (i.e., below 5 NTU). Mixtures with higher total suspended solids, above 1,000 mg/L, may require larger coagulant dosage. In addition, coagulant dose and pH variations had limited impact on sulfate concentration in the effluent.

For ballasted flocculation process, anionic flocculant aid worked better than cationic flocculant aid for the mixtures of flowback water and AMD investigated in this study. Among anionic polymers, Hydrex 6161 performed the best for all for mixtures tested in this study. Minimum flocculant aid dose of 0.5 ppm was needed for Mixtures 2, 5 and 6, while 0.2 ppm was
sufficient for Mixtures 1, 3 and 4. Although the total reaction time in ballasted flocculation was just 10 min, addition of a pre-mixing step is not necessary to achieve maximum barite precipitation and associated sulfate removal.

Careful optimization of the AMD : Marcellus Shale Produced water mixing ratio is needed to ensure effluent quality with respect to sulfate concentration. Equilibrium calculations that included appropriate ion activity corrections for high ionic strength (i.e., Phreeqc with Pitzer Equation) are similar to experimental results obtained in experiments with 1 hr reaction time. Sulfate removal efficiency increased from 5.4% to 95% when \( \frac{\text{Ba}^{2+}}{\text{SO}_4^{2-}} \) ion activity ratio increased from 0.06 to 0.99 or when \( \frac{\text{Ba}^{2+}}{\text{SO}_4^{2-}} \) mass ratio increased from 0.08 to 1.40.

Sludge handling strategies were evaluated in terms of sludge generation rate and settleability. Study found that ballasted flocculated sludge has higher density and better settling characteristics compared to that of conventional flocculated sludge. Clarifier designed for a pilot-scale unit based on influent flow rate of 20 GPM with an eight-hour daily operation required minimum clarifier area for conventional process of 540 ft\(^2\), while the minimum clarifier area for ballasted flocculation was 225 ft\(^2\).

Application of this water treatment process will greatly reduce the volume of concentrated brine, which must be disposed, minimize withdrawals of freshwater and the associated pumping costs, and add value to AMD waters that are abundant resources often located in proximity to the Marcellus shale.
Based on the results of this research, maintaining appropriate mixing ratio of flowback water and AMD is critical to guarantee effluent sulfate concentration below 100 mg/L. Pilot-scale studies are needed to validate laboratory results and optimize strategies for managing variability of water quality in the field.

For co-treatment of flowback water with AMD containing high sulfate content, more data are required to better understanding the equilibrium and kinetics of barite precipitation, as well as that of celestite and calcite precipitation. Meanwhile, when blended mixtures produce large quantity of precipitates, high chemical dosage (i.e., coagulant, sodium hydroxide, flocculant aid) may be required. The cost efficiency of conventional coagulation/flocculation process compared against ballasted flocculation treatment process need to be further investigated based on the pilot-scale studies.

The cost and effectiveness of the proposed treatment process are highly depending on fracturing fluid quality criteria with respect to TSS, TDS, as well as the concentrations of other cations, including iron, barium, and calcium, that may be of concern for the design of fracturing fluids. The impacts of their concentrations on well permeability and gas production should be explored so that the appropriate water quality treatment criteria can be incorporated in the design of the proposed treatment process.
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