

# **DEVELOPMENT AND VALIDATION OF AN ACID MINE DRAINAGE TREATMENT PROCESS FOR SOURCE WATER**

## **Final Technical Report**

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## Abstract

Throughout Northern Appalachia and surrounding regions, hundreds of abandoned mine sites exist which frequently are the source of Acid Mine Drainage (AMD). AMD typically contains metal ions in solution with sulfate ions which have been leached from the mine. These large volumes of water, if treated to a minimum standard, may be of use in Hydraulic Fracturing (HF) or other industrial processes. This project's focus is to evaluate an AMD water treatment technology for the purpose of providing treated AMD as an alternative source of water for HF operations. The HydroFlex™ technology allows the conversion of a previous environmental liability into an asset while reducing stress on potable water sources. The technology achieves greater than 95% water recovery, while removing sulfate to concentrations below 100 mg/L and common metals (e.g., iron and aluminum) below 1 mg/L. The project is intended to demonstrate the capability of the process to provide AMD as alternative source water for HF operations.

The second budget period of the project has been completed during which Battelle conducted two individual test campaigns in the field. The first test campaign demonstrated the ability of the HydroFlex system to remove sulfate to levels below 100 mg/L, meeting the requirements indicated by industry stakeholders for use of the treated AMD as source water. The second test campaign consisted of a series of focused confirmatory tests aimed at gathering additional data to refine the economic projections for the process. Throughout the project, regular communications were held with a group of project stakeholders to ensure alignment of the project objectives with industry requirements. Finally, the process byproduct generated by the HydroFlex process was evaluated for the treatment of produced water against commercial treatment chemicals. It was found that the process byproduct achieved similar results for produced water treatment as the chemicals currently in use. Further, the process byproduct demonstrated better settling characteristics in bench scale testing.

The field testing conducted in the second project budget period demonstrated the ability of the HydroFlex technology to meet industry requirements for AMD water chemical composition so that it can be used as source water in HF activities. System and operational improvements were identified in an additional series of confirmatory tests to achieve competitive cost targets. Finally, the application of the HydroFlex process byproduct in produced water treatment was demonstrated, further supporting the commercial implementation of the technology. Overall, the project results demonstrate a path to the economic treatment of AMD to support its increased use as source water in HF, particularly in regions with limited local freshwater availability.

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## 1.0 Executive Summary

Hydraulic Fracturing (HF) is becoming an increasingly common method of unconventional resource extraction allowing access to previously uneconomical natural gas reserves. This has contributed to increasing utilization and potential strain on local freshwater sources due to the large volume of water required during the fracturing process. This project's focus is to evaluate an Acid Mine Drainage (AMD) water treatment technology for the purpose of providing treated AMD as an alternative source of water for HF operations. The HydroFlex™ technology allows the conversion of a previous environmental liability into an asset while reducing stress on potable water sources. The technology achieves greater than 95% water recovery, while removing sulfate to concentrations below 100 mg/L and common metals (e.g., iron and aluminum) below 1 mg/L. This project demonstrated the capability of the process to provide AMD as alternative source water for HF operations.

During the second budget period both a structured test campaign, Test Campaign 1 (TC1), as well as shorter, discrete confirmatory tests, Confirmatory Test Campaign (CTC), were performed using the field demonstration HydroFlex system. Data collected as part of the field trials was used to project costs for operation of the system. During TC1, several extractant to aqueous (E:A) ratios were evaluated to determine which would remove sulfate most effectively. It was determined that a 1:2 E:A ratio provided the best sulfate removal. Therefore, this ratio was used during long duration, steady state operation to evaluate the long term ability of the HydroFlex system to remove sulfate. A summary of the sulfate removal capabilities at this E:A ratio is shown in Figure 1. Using a single extraction stage, sulfate levels in the AMD were reduced to less than 150 mg/L from an average influent concentration of approximately 550 mg/L. When a second extraction stage was brought online at 120 hours, the sulfate levels in the AMD were reduced to below 100 mg/L.

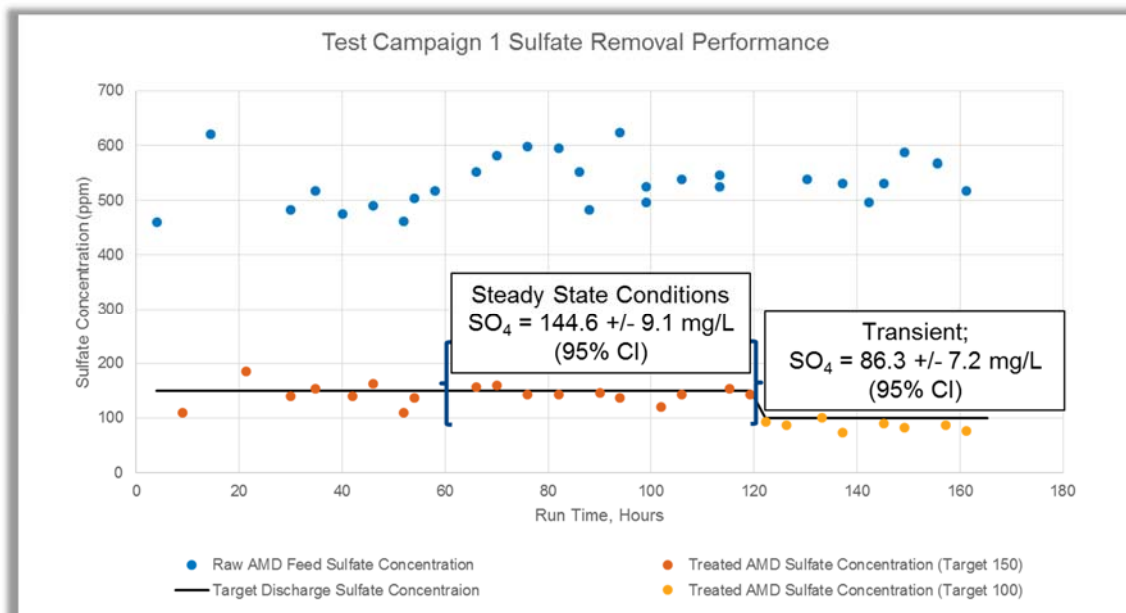


Figure 1. TC1 sulfate removal performance of the HydroFlex system.

The CTC was conducted after the conclusion of TC1 to further evaluate the primary system economic drivers. Process chemical feed rates, filtration requirements, and chemical makeup procedures were identified to be primary system cost drivers and were tested to determine if operational cost savings could be realized. It was found that system operational costs were able

to be reduced approximately 50% during the CTC when compared to operating costs during TC1. Further operational cost projections from the CTC results indicate that an additional 30% reduction may be realized through additional process modifications.

As part of the BP2 activities, regular project updates were provided to the project stakeholder committee. The results of the test campaigns were shared with the project stakeholders, who confirmed that reducing sulfate levels to less than 100 mg/L achieves the requirements for use of treated AMD as a source water.

Byproducts which were generated as part of field testing were characterized and evaluated against industrial chemicals used in the treatment of produced water. It was found that the sodium sulfate solution which the HydroFlex process produces is effective at treating produced water for the removal of barium and strontium, which are constituents of concern when recycling or disposing of produced water. While both the HydroFlex process byproduct and the industrial softening solution provided adequate reduction of barium and strontium levels in produced water samples, the HydroFlex process byproduct reduced turbidity in the treated effluent samples substantially when compared against the commercially available solution.

Results of the comparative testing conducted were shared with companies currently providing treatment for produced water to determine the interest in using the HydroFlex byproduct as a softening agent for removal of barium. It is believed that the increased settling rate will translate into smaller settling tanks required for the treatment of produced water.

The field testing conducted in the second project budget period demonstrated the ability of the HydroFlex technology to treat AMD to meet industry requirements for source water in HF activities. System and operational improvements were identified during the confirmatory test campaign to achieve competitive cost targets. Finally, the application of the HydroFlex process byproduct in produced water treatment was evaluated, further supporting the commercial implementation of the technology by validating an outlet for the process byproduct stream. Overall, the project results demonstrate a path to the economic treatment of AMD to support its use as source water in HF, particularly in regions with limited local freshwater availability and proximity of HF operations to AMD sources.

## 2.0 Project Background

The National Petroleum Council estimates the volume of recoverable gas from tight sands, gas shales, and coal bed methane within the United States is in excess of 25 trillion cubic meters (900 trillion cubic feet) (National Petroleum Council, 2011). The United States, on average, consumes 0.6 trillion cubic meters (22 trillion cubic feet) of natural gas per year, substantiating the largely untapped resource as a critical contributor to the nation's energy portfolio (National Petroleum Council, 2011). A method employed and improved upon for more than 60 years to access the gas from the underground formations is hydraulic fracturing (HF). HF is a well-stimulation process that aims to maximize the extraction of underground resources, including oil and natural gas, by injecting large volumes (on the order of millions of liters) of pressurized water with a mixture of chemicals and proppant into underground rock formations to create pathways for the natural gas and oil to migrate from the rock pores to the surface.

An estimated 117 billion liters (31 billion gallons) of freshwater was used from 2011 to 2013 for HF among eight major shale plays, as shown in Figure 2 (Lux Research, 2012). In 2013, the hydraulic fracturing industry was projected to double its freshwater usage over the next 3 years,

Source: Lux Research, "Risk and Reward in the Frac Water Market", Mar 2012

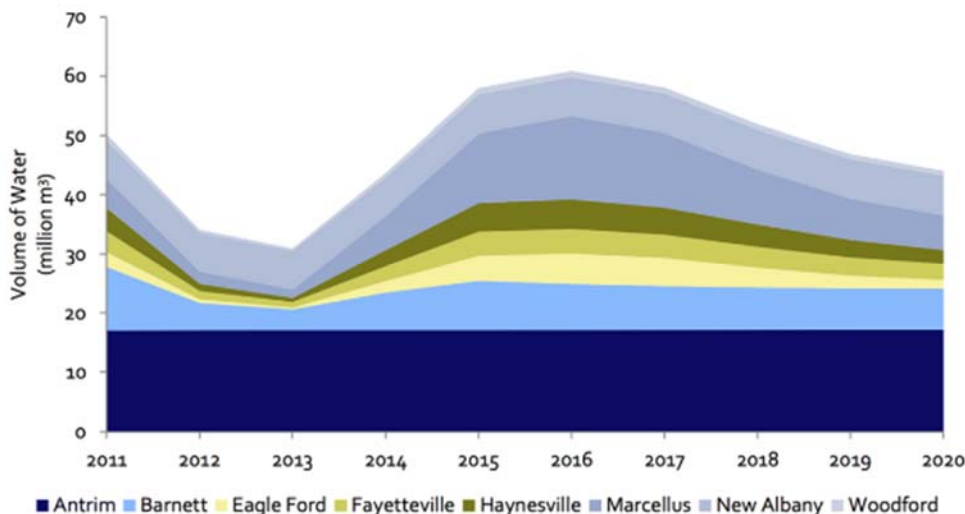


Figure 2. The yearly volume of water injected during hydraulic fracturing at the eight major shale plays was previously projected to exceed the volume used in 2013 each year through 2020.

and, if the current freshwater sources continue to be used, the strain on public water supplies may negatively impact the price and availability of natural gas and oil for residential and industrial consumers. The Department of Energy (DOE) has a goal to advance the environmentally sound development of unconventional, domestic natural gas and oil resources that is dependent on identifying novel technologies that reduce water usage and resource degradation through less freshwater-intensive approaches.

Acid mine drainage (AMD) is an abundant source of marginal water that is frequently disregarded as a water source for hydraulic fracturing. As the US looks to the future of energy with unconventional resource development, the legacy of pollution from past resource extraction is noted with AMD. AMD is formed by a natural process that generates sulfates and metals in solution in almost any case where large volumes of earth or rock are disturbed. It is especially prevalent in areas of coal and mineral mining, and the highly contaminated drainage can continue for centuries after mining production is discontinued. In Pennsylvania alone AMD affects more than 8,800 kilometers (5,500 miles) of waterways (Cavazza & Cavazza, 2011). AMD's main components, iron and sulfate, are not suitable for fracturing water due to downhole considerations; however, under the right conditions, iron is a powerful water treatment chemical, and sulfate an effective precipitant for scale-causing metals.

Current AMD remediation technologies are not able to provide water that meets the quality standards desired by the oil and gas industry. Limestone neutralization (i.e., liming) is the most common method currently employed for treating AMD water; however, it does not meet the stringent HF water standards for sulfate concentration. Liming is dependent on the water solubility of calcium sulfate and is frequently unable to remove sulfates below the level of 1,000 (mg/L). Nanofiltration with liming in succession helps to improve the water quality, but adds a level of complexity and is not a "one solution fits all" approach that can meet the sulfate discharge level requirement of less than 250 mg/L. Another drawback of liming is that it generates large volumes of high-density waste that may require costly disposal.

The HydroFlex process is a platform technology that is capable of meeting the sulfate discharge requirements of <250 mg/L (and potentially lower concentrations) and common metals to levels below surface discharge requirements. It recovers greater than 95 percent of the incoming water,



produces byproducts of potential use to the industry rather than a waste sludge, and operates with modified commercial off-the-shelf (COTS) equipment.

The HydroFlex process for the remediation of AMD has been tested in the lab and demonstrated successfully in the field at St. Michael, PA. The previous laboratory and field testing confirmed the consistent removal of aluminum, iron, and sulfate from AMD source water for a range of starting concentrations. These demonstration efforts were targeted solely for AMD remediation for discharge. The work conducted under this project is focused on adaptation of the process to provide water and byproducts useful for the unconventional resource development industry. This DOE program supports the optimization and large scale demonstration of the HydroFlex technology for treatment of AMD water for use in hydraulic fracturing.

## 3.0 Project Objectives and Approach

The objectives of this project are: (1) to develop an innovative treatment process to support the use of AMD water for HF, (2) to evaluate the use of the process byproducts in produced water treatment processes, and (3) to determine the environmental, regulatory and commercial implications of using treated AMD as source water in HF.

These objectives were met through a multi-task technical approach conducted in two budget periods. As part of the activities of the first budget period, laboratory testing was conducted to determine process operating parameters, and field shakedown testing was conducted by Battelle's subcontractor, Winner Water Services (Winner). During the second budget period the field demonstration HydroFlex system was operated in support of both a structured test campaign as well as shorter, discrete confirmatory tests aimed at supporting specific process development objectives. Data collected as part of the field trials was used to project costs associated with operation of the system, providing estimated costs for the treatment of AMD for source water use using the HydroFlex technology.

The byproduct generated during field testing were characterized and evaluated against industrial chemicals used in the treatment of produced water. Use of the byproduct solution in other oil and gas applications reduces the cost for operation of the system by avoiding waste disposal costs and potentially providing an additional revenue stream. Results of the comparative testing conducted were shared with companies currently operating produced water treatment facilities to determine their interest in using the HydroFlex byproduct as a softening agent for removal of barium.

As part of BP2 activities, regular project updates were provided to the project stakeholder committee. Throughout the project, the committee provided valuable information regarding required water quality characteristics for source water as well as acceptable economics for water treatment. Additionally, stakeholders were able to share challenges that the industry is currently struggling with regarding use of AMD as source water in HF operations.

## 4.0 Technical Tasks

### 4.1 Task 1.0: Project Management and Planning

Project management activities were conducted throughout the second budget period (BP2). Battelle managed the project as stated in the Project Management Plan (PMP) which was updated whenever a significant change was made to the project. All work conducted under BP2's

Tasks 3 and 4 was planned and managed through the project management task, including the field work and reporting completed by Winner Water Services (Winner). Throughout BP2, project scope and budget was managed against the PMP.

Due to concerns with the system's ability to successfully execute a second test campaign, a GO/NO GO decision point was added between the first and second planned test campaigns to ensure that the data collected during the first test campaign supported the need for a second test campaign. The SOPO and PMP were updated to reflect these changes. At the conclusion of the first test campaign, a NO GO decision was made regarding execution of the second test campaign. Instead of a second test campaign, the remaining project funding was used to complete the originally proposed tasks associated with byproduct testing and stakeholder outreach. In addition, a series of discrete confirmatory field tests were conducted to further refine the system operating cost projections. The report submitted as part of the GO/NO GO decision point included the Field Testing Report for the first test campaign and replaced this deliverable as per the SOPO.

## **4.2 Task 3.1: AMD Treatment Process Testing and Evaluation-Test Plan Development**

A test plan was created for the first field test campaign using data from the lab and shakedown testing performed in Budget Period 1. The test plan is included as Appendix B. Test campaign one (TC1) consisted of two parts; the first part encompassed initial testing of extractant to AMD (E:A) ratios to select the ratio most likely to achieve sulfate removal goals. The second portion included a steady-state run performed at the E:A ratio selected during the range-finding portion of TC1.

Sulfate removal results from the continuous lab testing in Phase 1 were used to estimate the sampling requirements for the E:A range finding tests. It was determined that the data are not likely to be normally distributed, so the data was treated as nonparametric. Using two different standard deviations, one a pooled value and the other a worst case estimate, power calculations were performed assuming a nonparametric test for a difference in medians of two populations. In Figure 3, the estimated number of samples per E:A to detect a difference in medians between two E:A groups is shown. Based on this graph, it was decided that 5 samples would be collected and run at each E:A to detect a difference of 50 mg/L achieved in the sulfate concentration between test conditions.

Additionally, during the process shakedown testing of Phase 1, sulfate samples were collected from the extraction stage. The number of samples needed to provide a confident assessment of steady state sulfate removal during the second portion of TC1 was predicted using the variability in the sulfate values from Phase 1. In Table 1 the estimated 95% confidence interval precision is provided by sample size. It should be noted that in both these cases, the actual confidence interval width and test power changed according to the variability actually realized in the samples collected.

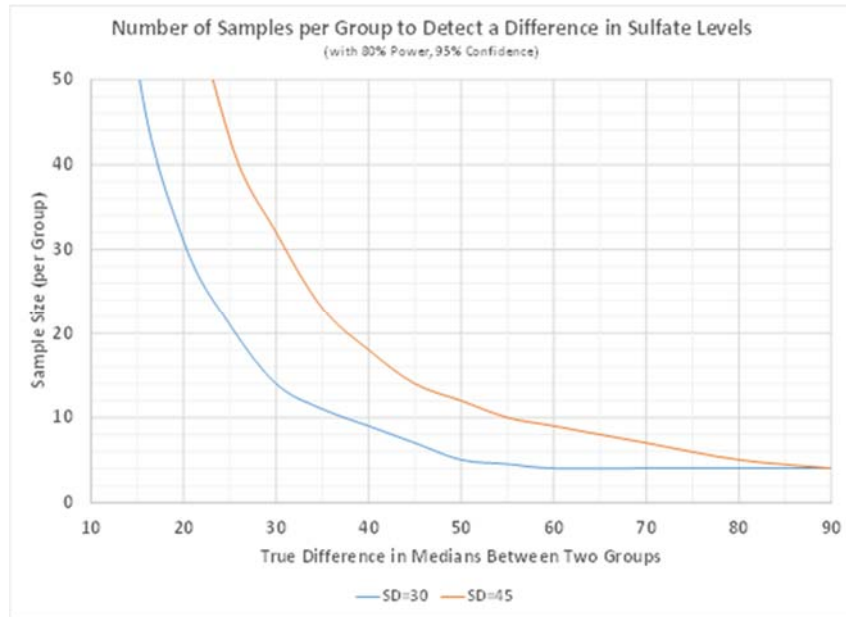


Figure 3. This graph shows the estimated number of samples required to detect a difference in medians between two E:A test cases during the first portion of test campaign one.

Table 1. The estimated 95% confidence interval precision by sample size is shown.

Sample Size	Confidence Interval Precision
3	Mean +/- 147
4	Mean +/- 43
5	Mean +/- 28
10	Mean +/- 15
25	Mean +/- 8
50	Mean +/- 6
100	Mean +/- 4

The number of samples required to draw statistical conclusions from the test data was used to inform the number of tests and required test length of the E:A ratio screening test runs, as well as the overall duration and sampling frequency of the steady state portion of TC1.

## 4.3 Task 3.2: AMD Treatment Process Testing and Evaluation-Process Testing

### 4.3.1 EXTRACTANT EVALUATION

Prior to the start of the first test campaign in BP2, additional laboratory and field testing was performed to evaluate the extractant material on the field system and identify any adjustments needed to the process operation based on the extractant's anticipated performance. The primary concern behind these tests were losses of the organic extractant observed in the Phase 1 testing due to entrainment of the extractant in the treated AMD water. Because organic loss has a significant impact on the process economics, several tests were run to reduce organic losses from the system. These tests identified changes to the process chemistry, unit operations operating parameters, and maintenance procedures. More detailed results of the testing performed are included in Appendix A.

First, the type and quantity of extractant material that was not recovered during the operation of the process in BP1 was estimated. Next, the impact of various process changes on the amount of unrecovered material was evaluated, and finally operational changes were made to capture the extractant for recovery and return to the system. The following sections outline the testing performed to quantify and reduce the loss of entrained extractant.

#### *QUANTIFICATION OF LOSSES*

In the laboratory testing conducted as part of BP1, total organic carbon (TOC) tests were used to estimate the amount of extractant carry over observed during testing. Operational parameters, such as mixing speed, were configured to minimize TOC readings in the process discharge, thus maximizing phase disengagement and recovery of extractant material. Similarly during the field shakedown testing, TOC tests allowed quick characterization of the level of entrained extractant. However, TOC tests do not measure the concentrations of individual constituents in the extractant mixture, rather they determine the bulk organic concentration.

To identify which process changes would best reduce extractant carry over during B2 testing, information regarding the carry-over of individual extractant components was needed. Therefore, additional analysis of organics both in the aqueous phase as well as bulk analysis of the extractant remaining on the system was conducted. In both cases, Battelle ran samples taken from the field system using 2-dimensional gas chromatography with time-of-flight mass spectral detection. Samples of treated AMD were pulled immediately after the final extraction stage (upstream of GAC beds), as well as at the overall process discharge point (downstream of GAC beds). Response factors for the extractant components were determined by analyzing neat samples of each, and blank and spiked samples were also run. For analysis of components in the aqueous phase, the sample was first extracted with dichloromethane to concentrate the target compounds.

The extractant mixture is composed of three components in a predetermined ratio; the components include the active ingredient, the diluent and a modifier to improve phase disengagement. At the beginning of TC1, the bulk extractant was analyzed and compared to virgin extractant to determine how the composition had changed during the previous year of operation, using the method described above.

This analysis indicated that concentration of the active ingredient had decreased by approximately 20% with relation to the diluent and modifier components. This indicates that organic losses tend to favor the active ingredient rather than being an entrained mixture of composition similar to the bulk extractant. Figure 4 shows a 3-dimensional plot representing the spectra obtained in the two dimensional GC work. The active ingredient is a mixture of amines, which tend to elute from the GC column later due to their ionic nature. It should be noted that the

alcohol modifier used in the extractant could not be separately distinguished from the hydrocarbons in the spectra. Additionally, recovery of hydrocarbons was low, at around 4%, versus an 89% recovery for the amine components.

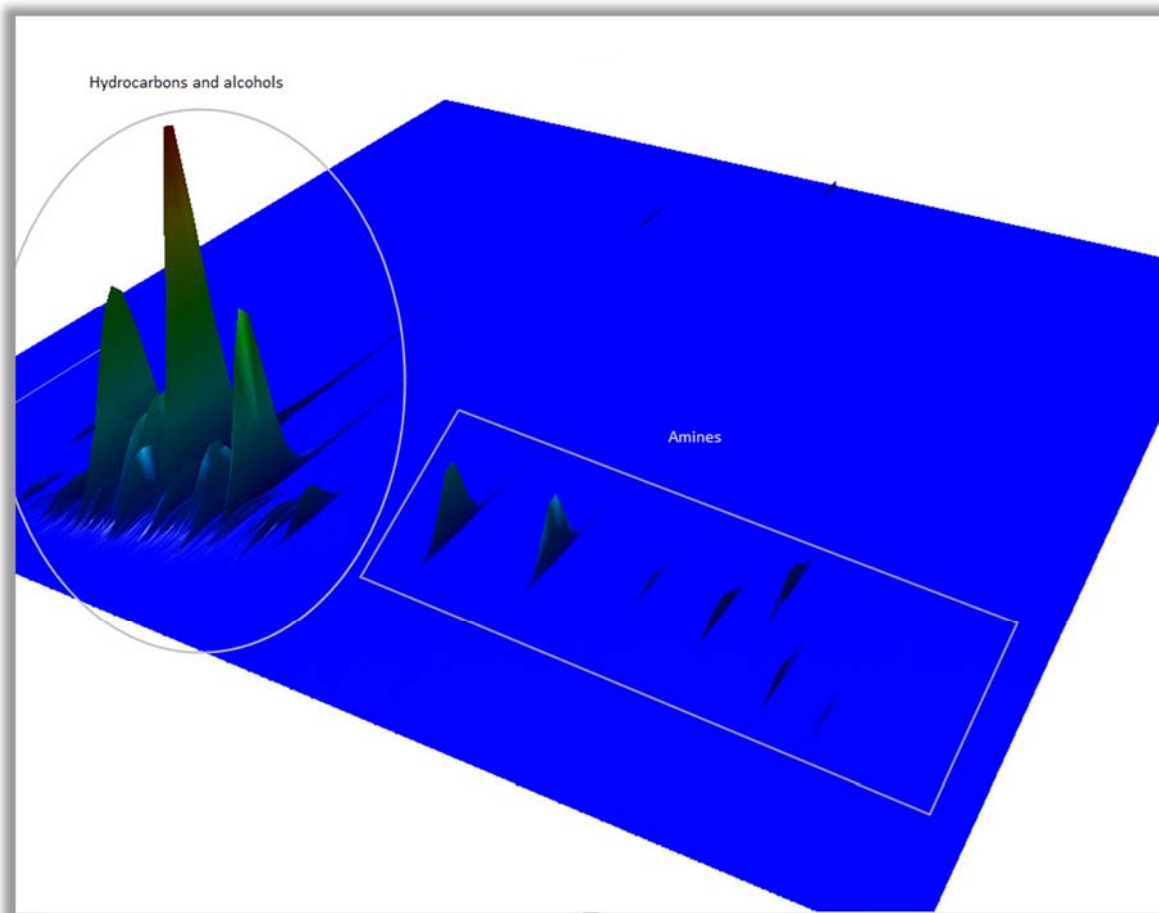


Figure 4. 3 dimensional plot of 2 dimensional GC spectra of the extractant used for the testing.

Analysis of the organic components extracted from the process water using dichloromethane also indicated an enrichment of active ingredient in the aqueous phase. The observed concentrations were adjusted by the recovery observed in the positive control, and showed that the concentration of active ingredient in the aqueous phase relative to the modifier and diluent is higher than in the bulk extractant (see Appendix A). Another finding from the GC work was that the concentration of extractant components was slightly higher after the activated charcoal filter than before, indicating that the extractant had built up in the charcoal beds, blinding the media and resulting in bypass of the media. A change in the maintenance procedures for the charcoal beds to incorporate more frequent backwashing was incorporated to prevent bypass of the filters by the extractant components. More detailed results of the GC work are provided in Appendix A.

### **PROCESS CHANGES**

Several process changes were investigated to prevent extractant loss in the HydroFlex system, including changing the extractant formulation, filtration/centrifugation of the treated AMD effluent, adjustment of the pH of the extraction step, addition of iron coagulant, extraction of residual extractant using individual extractant components, use of bicarbonate instead of carbonate to regenerate the extractant, and ion exchange for polishing of the AMD effluent.

Extractant formulation was investigated during Phase 1 testing; however, some of the higher ratios of modifier to extractant were not previously tested. These values were examined to see if a more beneficial effect could be realized. In this testing, the linear relationship between extractant:modifier ratio and residual TOC in the AMD was consistent with that observed previously, as shown in Figure 5. Since adjustment of the extractant:modifier ratio was determined to provide only a limited benefit to the process economics, no change was made to the extractant formulation prior to the continuous run in TC1.

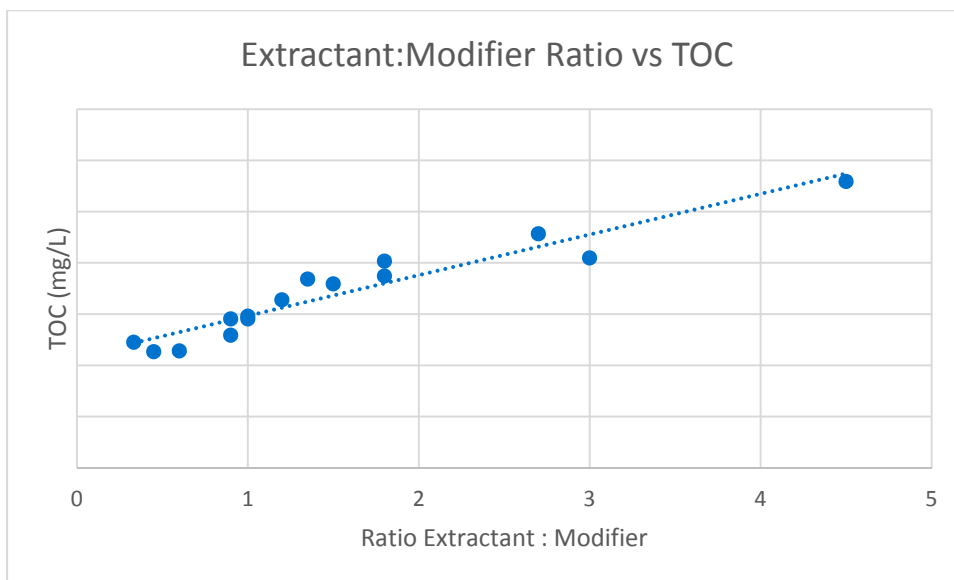


Figure 5. A linear correlation was observed between the ratio of active ingredient to modifier in the extractant to the residual TOC in the AMD water.

The pH was also adjusted in the extraction stages to lower levels in expectation that a lower pH would affect the surface chemistry of both the organic colloids and the calcium carbonate solids. There was no significant effect of pH on the residual TOC in the AMD water, and so pH adjustment was not investigated further or implemented in TC1. Results of the pH adjustment testing can be found in Appendix A.

As a possible process change filtration and centrifugation of the effluent water was tested. A polysulfone micro filter was used to filter the effluent to judge whether extractant was entrained preferentially in the calcium carbonate solids formed due to the high calcium content in the AMD source. Centrifugation was also employed to fully clarify the effluent. Analysis of the effluent for TOC pre and post centrifugation indicated that a portion of the organic material was associated with the calcium carbonate solids, and a portion was not removed through filtration or centrifugation, remaining in the treated effluent. These results helped to guide future evaluation of methods to reduce extractant entrainment, but were not implemented due to the relatively low concentration of extractant present in the recovered calcium carbonate solids.

An additional process change evaluated was the dosage of iron to assist in clarifying the effluent. The HydroFlex process was originally designed to remove iron from water streams by formation of an oxyhydroxide floc that is floated by the organic extractant. At correct iron doses and process conditions, the floc collects the entrained portion of extractant and floats it to the top of the sample. The floc would then require processing through the currently unused metal stripping section of the HydroFlex system, designed to separate the iron from the extractant, recovering the entrained extractant and producing a separate ferric sulfate solution.

This mechanism was tested for recovery of both the soluble and insoluble entrained extractant by addition of ferric sulfate pentahydrate solution. Figure 6 shows iron applied to processed AMD water in varying conditions, with the best performance seen in samples -11 and -13, where the floc is floated and the water is clarified.



Figure 6. Several tested conditions of iron addition for recovery of entrained extractant.

Although the iron was effective at recovering the entrained portion of extractant, the associated cost of dosing the iron and recovering it in the metal stripping stages outweighed the benefit of reclaiming the extractant. Accordingly, the approach of iron addition was omitted from further consideration.

Another method evaluated to recover extractant material associated with the treated AMD was to perform a second extraction step using another organic based extractant to pull the dilute amount of organic material out of the bulk treated AMD. Re-extraction of the entrained organic was tested using specific fractions of the extractant mixture. The expectation was for contact with the diluent to break any emulsions and pull the organic from the aqueous stream with a clean phase break. This diluent could then be reused in the process. However, testing indicated that this approach would not be feasible for this application, as it recovered only a small fraction of the extractant, and would be difficult to implement during the field test campaign.

Normally, the extractant used in the HydroFlex process is loaded in a carbonate form to exchange for and remove sulfates, but can also be loaded with other salts or bicarbonate. Bicarbonate was tested to determine whether it would improve phase disengagement in the extraction section versus carbonate-loaded extractant. A small improvement was observed in the entrainment with bicarbonate-loaded extractant. However, use of bicarbonate requires twice the stoichiometric dose to regenerate the extractant compared to carbonate, and additional testing would have been required to validate efficient stripping performance. The measured improvement in entrainment did not justify these expenses, so no changes were made to the form of salt loaded on the extractant.

Finally, ion exchange resins were tested for their efficiency in recovering soluble active ingredient from the extractant. The ion exchange testing considered four separate resins, ultimately settling upon a weak acid cationic resin due to its relatively high loading for extractant and economical

regeneration. Initial screening tests of the resins were performed by mixing a gram of resin with 40 mL of HydroFlex effluent and comparing the TOC removal. Loading capacities for the resins were then found by making flow through columns to pass an excess of effluent over the bed. Effluent samples were collected at fixed intervals to calculate the TOC loading on the resins. Resin for the regeneration tests was also loaded in the flow through columns, then regenerated with sulfuric acid according to the engineering specification sheets for each resin. The TOC removal capability for each resin was then assessed after regeneration and compared to a virgin resin sample to judge the efficiency of the regeneration.

No resins appeared to be economical for this recovery when sulfuric acid is used as the regenerant due to high volumes of waste, but if hydrochloric acid is used, value could be realized from an ion exchange (IX) bed. The demonstration site was not permitted for hydrochloric acid, so this was not implemented in the testing, but can be considered to improve the process economics going forward.

Overall, most of the process changes evaluated did not produce a large enough reduction of the organic carry over to be economically applied to the field test unit while maintaining the project scope and schedule guidelines.

### ***OPERATIONAL CHANGES***

In addition to process changes, operational changes were investigated to determine their effect on reducing the quantity of organic carryover including changing the mixing parameters and the scheduled maintenance of the activated charcoal beds installed as a polishing step downstream of the HydroFlex process. Sufficient mixing to remove the sulfate from the AMD was achieved with the mixer off in the extraction stage, but this left very little room for adjustment. Options to improve the range of adjustability in the mixer were investigated. Additionally, as the process was operated, it was noted that the TOC levels in the effluent became higher after the granular activated charcoal (GAC) beds than before, so the maintenance schedule for the GAC was amended. Finally, additional residence time was added to the system to facilitate additional phase break time.

In BP1 testing, it was found that operation of the extraction stage without the mixer operating allowed for sufficient contact between the extractant and AMD to remove sulfates. The mixing in this case came from the turbulence of the two flows entering the false bottom in the mixer and passing by the vanes in the impeller. However, despite effective sulfate removal, this layout did not allow flexibility in adjusting the mixing as flows or sulfate levels changed. Accordingly, a simple modification to the mixing compartment was tested. This modification is shown schematically in Figure 7, where the feed was redirected through a two inch pipe which could be slid up and down inside a pre-existing three inch perforated pipe. A gasket at the bottom of the two inch pipe sealed the interior and directed the height at which extractant entered the mixing chamber, which in turn affected the level of mixing. When the pipe was at its lowest, the fluids experienced higher mixing, while the fluids experienced the least mixing at the highest pipe location.



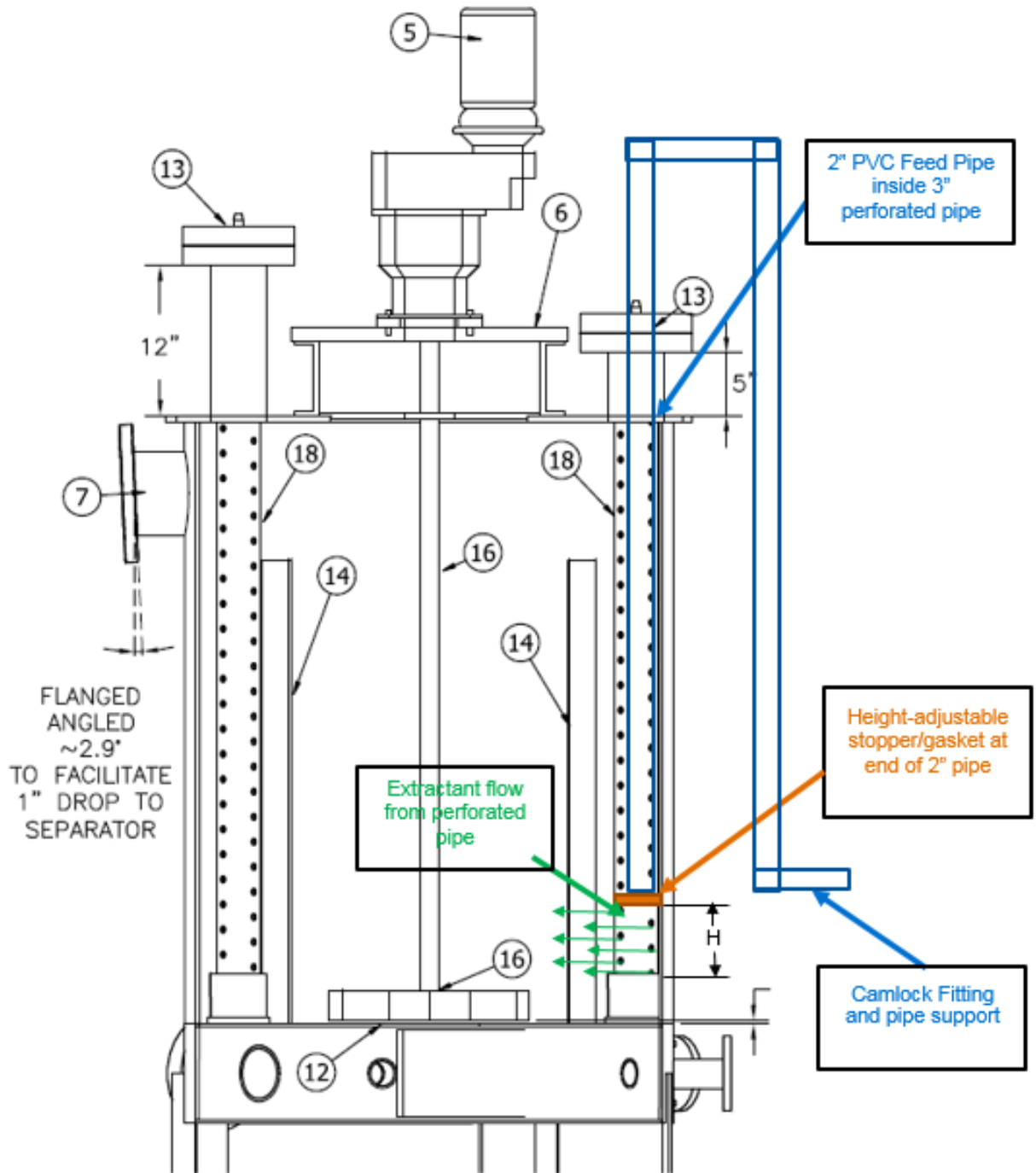


Figure 7. Conceptual diagram of the modification made to the mixing compartment during mixing tests.

With the modified mixing compartment, equivalent sulfate removal was achieved but with lower entrainment, as measured by turbidity in the sample as it overflowed from the mixer. However, the TOC measurements from the aqueous overflow after the settling section were not meaningfully affected by changes in the mixing compartment. Due to these results, the mixer was reverted to its original design with the mixer turned off.

The original design of the HydroFlex system included a GAC unit to ensure that volatile organic carbon (VOC) compounds were not released by the process. During regular VOC sampling around the GAC, it was discovered that the total organic carbon in the effluent increased across the carbon bed. Inspection revealed that a layer of organic had accumulated in the carbon vessels and was adding to the TOC in the effluent. To remedy this, backwashing of the GAC beds was added as a weekly maintenance item. Following this modification to the GAC maintenance procedures, no additional TOC was detected in samples of GAC effluent during the remainder of the field testing. Appendix A contains additional information of the operational changes made to the process.

### **4.3.2 TEST CAMPAIGN ONE: EVALUATION OF SULFATE REMOVAL CAPABILITIES**

The first test campaign was started on August 3, 2015. The test campaign was comprised of two phases. During the first phase, the E:A ratio of the system was varied to determine its impact on sulfate removal. In the second phase, the system was run for three weeks under steady state conditions at the E:A ratio which resulted in the best sulfate removal. The average flow rate of AMD through the treatment system was 45 gallons per minute, driven primarily by the availability of the AMD blend on site.

#### ***E:A RATIO EVALUATION DISCUSSION***

The system was operated at a single E:A ratio each day for the first week of operation. Sulfate samples were pulled after several hours of run time at each E:A ratio. Figure 8 shows the sulfate extraction performance observed at each E:A ratio. As expected, at higher E:A ratios, when the ratio of extractant to aqueous phases was increased, more sulfate was extracted. Analysis of variance indicated that there was significant difference between the test groups, and pairwise comparisons showed that all results were significantly different at 95% confidence.

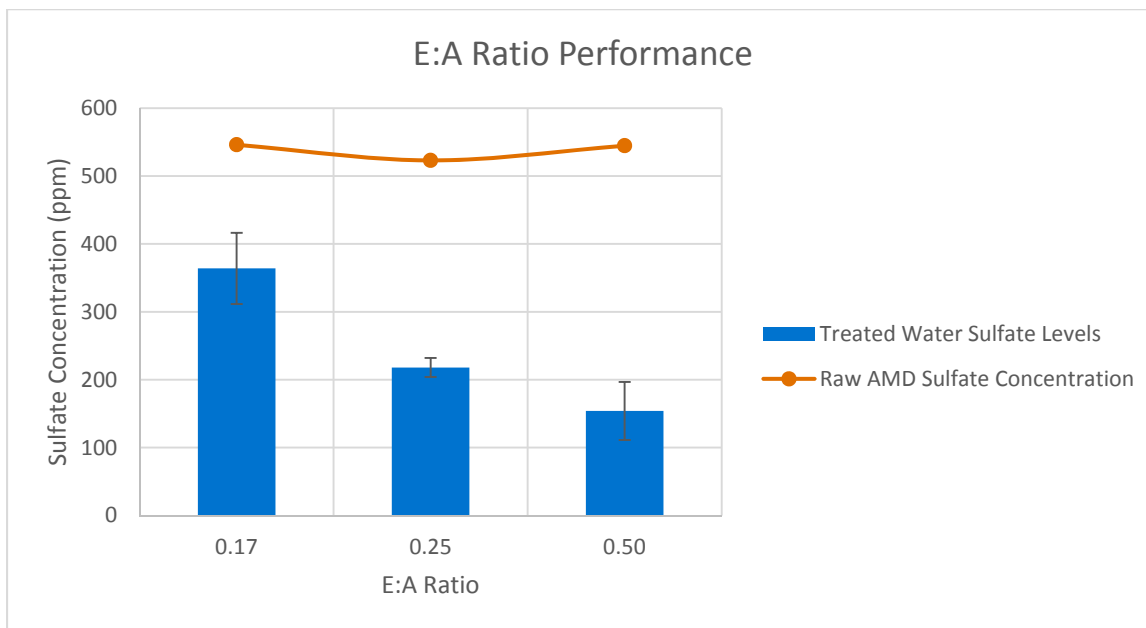


Figure 8. Comparison of E:A ratios evaluated during the first week of the test campaign. Error bars represent a 95% confidence interval.

In general, the lowest E:A ratio capable of providing the sulfate removal required is optimal, as a smaller overall volume of extractant is required to treat a given water source, resulting in lower capital and operating expenses. From the run data collected, it was determined that a 1:2 E:A ratio would be required to reduce sulfate to the required levels. This E:A ratio differs from the 1:10 E:A ratio previously used during field test runs conducted during the first budget period.

The original design for the process included a small makeup feed stream to address minor extractant losses. Due to the complexity of incorporating this makeup feed in daily operations, extractant makeup was not routinely performed during the field testing conducted prior to the first test campaign. It is believed that gradual degradation to the extractant health over a year of operations contributed to the need to run at a 1:2 E:A to achieve sulfate removal similar to that of the 1:10 E:A used when the extractant was fresh. Prior to the start of the second phase of TC1, additional extractant was added to the system to enhance the sulfate removal capabilities of the system; however, the extractant already loaded on the system was not able to be restored to its original strength observed during the two-30 hour demonstration runs conducted in BP1.

### **STEADY STATE RUN DISCUSSION**

The system was operated for approximately 150 hours to collect performance data during steady state operation at the 1:2 E:A ratio. During the three weeks of run time, the process feed to the HydroFlex process was maintained, on average, between 500 and 600 mg/L sulfate. For the majority of the test campaign (approximately 120 operational hours), a single extraction stage achieved a sulfate level of below 150 mg/L. This equates to a sulfate removal of an average of 403 mg/L or a 74% reduction in sulfate content. Figure 9 and Figure 10 show the sulfate concentration of influent AMD stream and the process discharge stream.

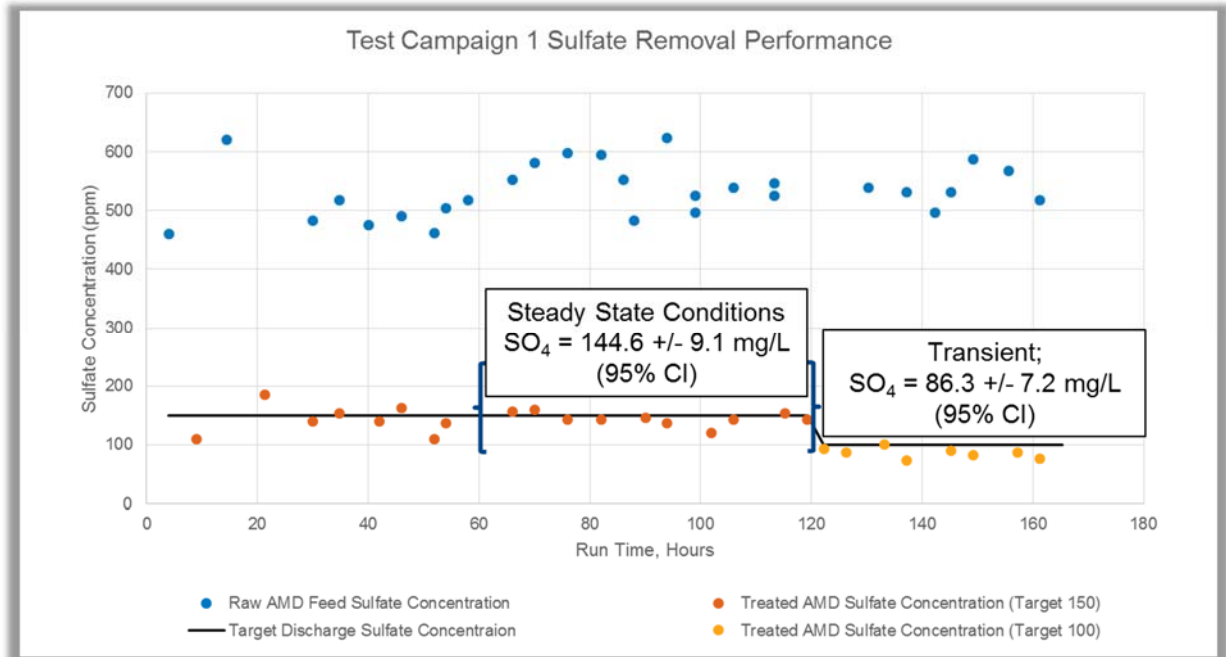


Figure 9. AMD feed sulfate concentration and treated water sulfate concentration for both 150 mg/L and 100 mg/L targets.

After approximately 120 hours of operation, a second extraction stage (E2) was brought online to provide additional sulfate removal capability, achieving sulfate levels below 100 mg/L per the guidance of our stakeholder committee. The impact of the second extraction stage is illustrated by the step change in the sulfate removal targets shown in Figure 9 and Figure 10. Under these conditions, sulfate was consistently reduced to levels below 100 mg/L, removing an average of 448 mg/L of sulfate or a reduction of sulfate by 85%.

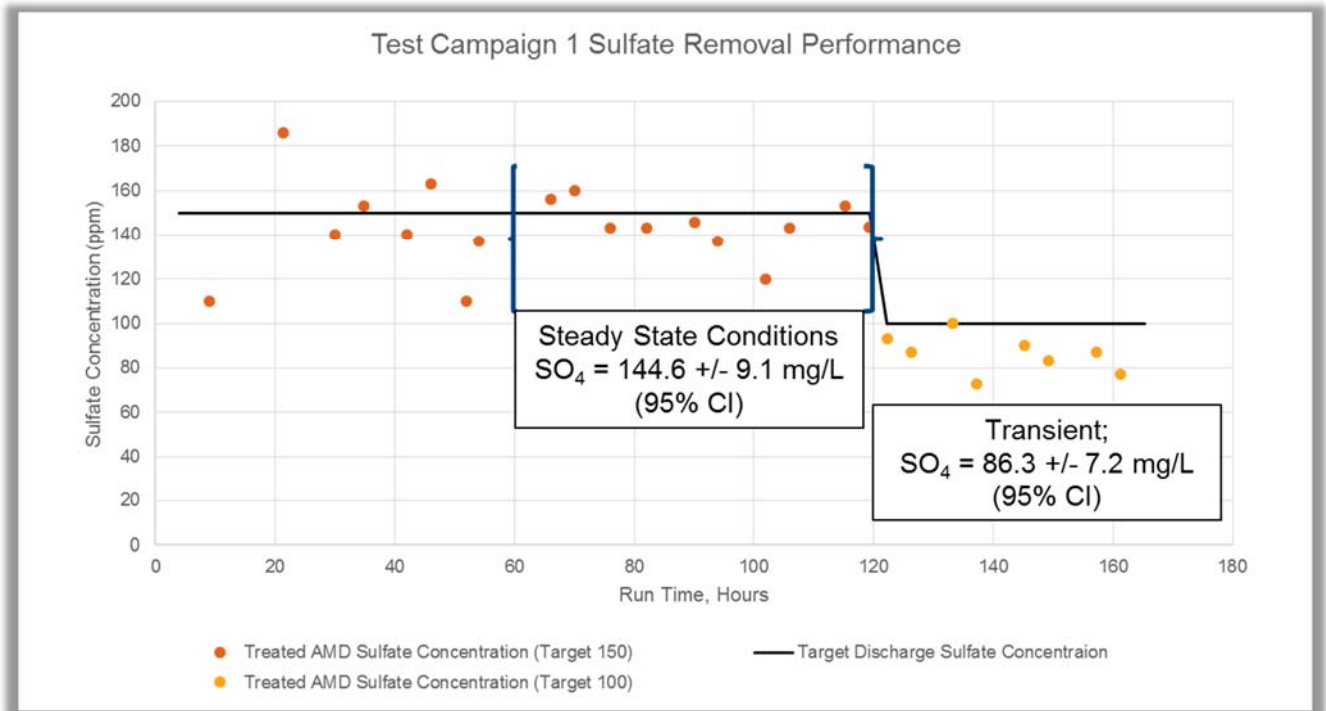


Figure 10. Zoomed view of Figure 2, showing only discharge water sulfate concentration.

**PROCESS BYPRODUCT GENERATION**

The HydroFlex process generates a process byproduct which is a mixture of sodium carbonate and sodium sulfate. A 6% sodium carbonate solution is fed to the S4 stage of the sulfate stripping stages to regenerate the extractant for reuse in the extraction stages. The stripping stages generate a byproduct which is concentrated and collected from the S1 stage. To preserve the process mass balance, the volume of byproduct dosed to the system is equivalent to the volume of carbonate dosed. Every 12 hours of operation, the sulfate concentration of the produced byproduct was sampled and recorded. The sulfate concentration of the generated byproduct, as well as the carbonate feed rate to the sulfate stripping stages is shown in Figure 11 below.

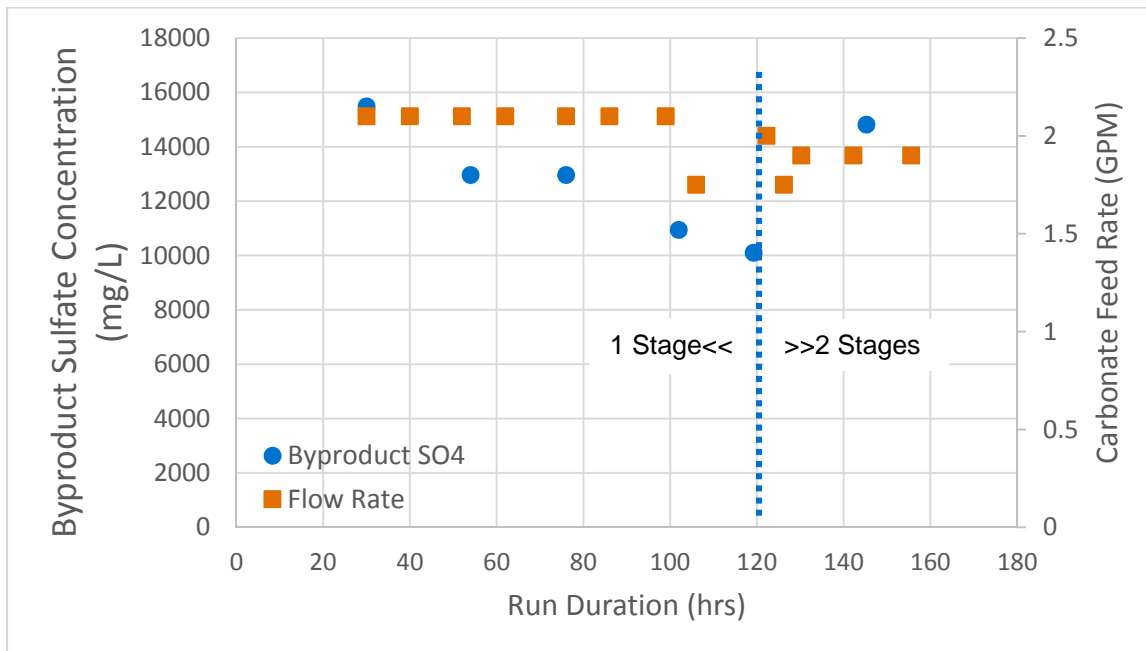


Figure 11. Byproduct sodium sulfate concentration and process sodium carbonate feed rate shown for steady state portion of TC1.

The volume of byproduct produced is equivalent to the volume of sodium carbonate fed to the process, and is directly proportional to the concentration of the contaminants being removed from the AMD source. Pumps and level controllers ensure that the flow rates of carbonate solution fed to the process and byproduct solution which leaves the process are equal. Throughout the test campaign, the concentration of the byproduct decreased, indicating that carbonate was dosed in excess during this phase of testing, diluting the sulfate concentration in the byproduct stream. This was intentional to maintain extractant performance at the highest possible level during TC1 to provide maximum sulfate extraction, so during TC1 sodium carbonate dosing rate was maintained at approximately 2.1 GPM throughout the test. TC2 was originally intended to identify optimal carbonate dosing rates for best possible process economics, but to evaluate the benefit of a lower carbonate feed in TC1, the sodium carbonate dosing rate was decreased to 1.9 GPM near the end of the second phase of TC1 after the second extraction stage was brought online. With the incorporation of the second extraction stage, the test results determined that the extraction performance was maintained at this lower carbonate feed rate.

### **EXTRACTANT CARRY OVER**

Throughout the test campaign, TOC was measured at the E1 aqueous discharge to estimate the amount of net extractant losses (or carryover into the aqueous phase) during operation of the system. Minor extractant losses are expected, and would be compensated for in a production system by dosing a small volume of makeup extractant to the process on a continual basis. It should be noted that TOC measures all organic-based carbon sources in the water, so it can only be used as a comparative indicator of extractant losses rather than an accurate measurement.

During the E:A screening runs, TOC was measured at each E:A ratio to determine the potential impact of E:A ratio on extractant carry over. The results are shown in Figure 12.

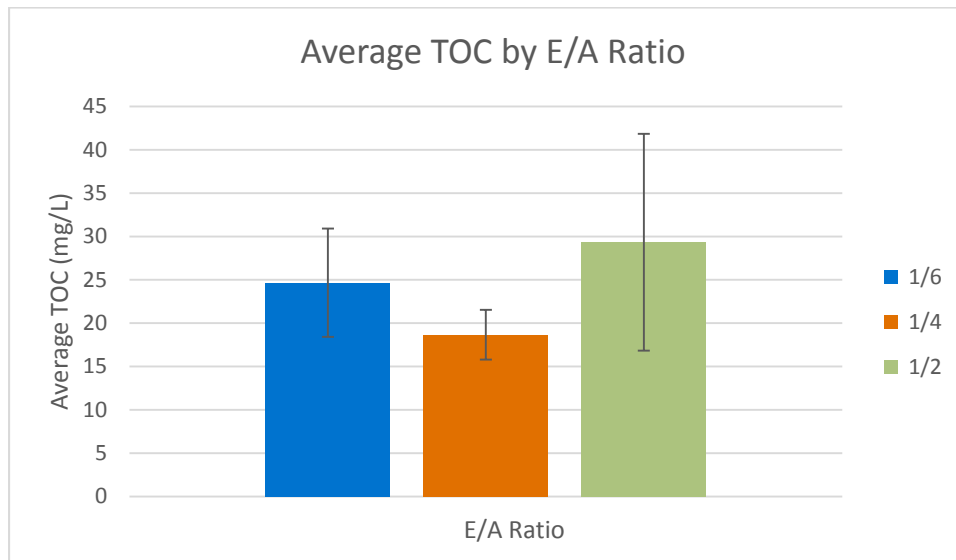


Figure 12. E:A ratio vs average TOC reading, error bars represent the 95% confidence interval.

It can be seen that the highest level of TOC observed occurs at the maximum E:A ratio tested (1:2). The highest amount of sulfate removal was also observed at this E:A ratio. During BP1 laboratory testing, it was also found that the higher E:A ratios exhibited greater TOC values, while simultaneously providing better sulfate removal. These data are aligned with projections, as it is believed that there is improved contact between the aqueous and extractant phases at higher E:A ratios. This allows for more efficient exchange of sulfate ions from the aqueous phase into the extractant phase, but also increases the potential for extractant to become entrained in the aqueous phase and be discharged from the system. Although the TOC is lowest at a 1:4 E:A, this reading is suspected to be within the error range of the measurement instruments. Based on this data and observations from previous laboratory testing, it is believed that TOC content generally increases as E:A ratio increases.

At the end of the first test campaign, the decision was made to increase the sulfate removal to provide treated AMD with less than 100 mg/L of sulfate. To achieve this, the process was adjusted to incorporate a second extraction stage. While the sulfate removal targets of less than 100 mg/L were met, a large spike in the TOC of the product water was observed. Figure 13 shows how the addition a second extraction stage approximately doubled the residual TOC in the treated AMD.

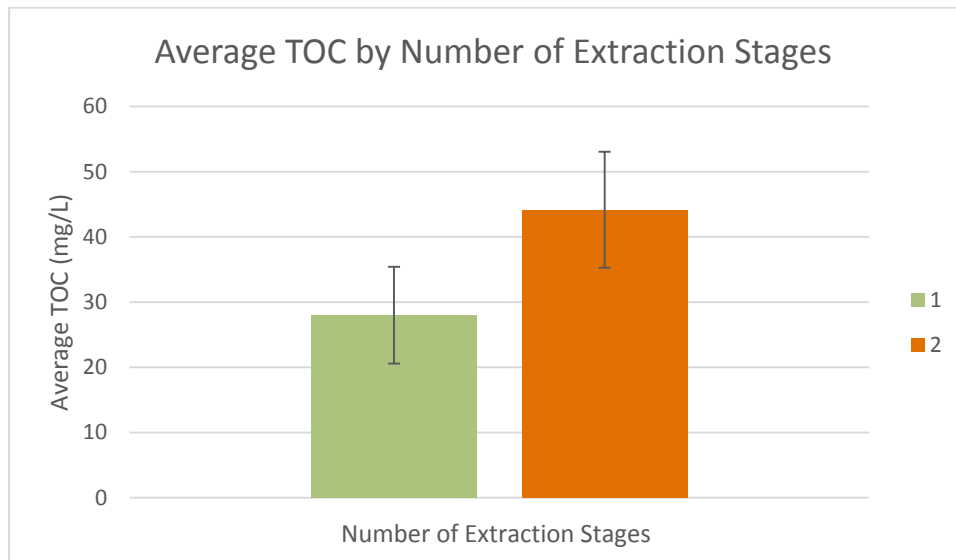


Figure 13. TOC vs Number of Extraction Stages.

It is therefore expected that the extractant losses of the system are elevated when operating a second extraction stage. This likely occurs because a second extraction stage requires operation of a mixer at high RPM to achieve inter-stage liquid transfer. Once again, it can be seen that a balance must be struck between the degree of sulfate removal required and the financial costs associated with the extractant lost from the system. This information is important design information for future commercial implementation of the HydroFlex process, as an appropriate balance between sulfate removal and extractant carryover must be found for the specific operation.

In general, throughout TC1 the TOC of the treated AMD decreased as the run duration increased, as shown in Figure 14. This suggests that if the run were to have continued past the planned duration, the TOC in the treated discharge may have further decreased before reaching some steady state minimum TOC level. This indicates that estimates for extractant makeup based on the TOC results measured during TC1 will result in conservative economic projections.



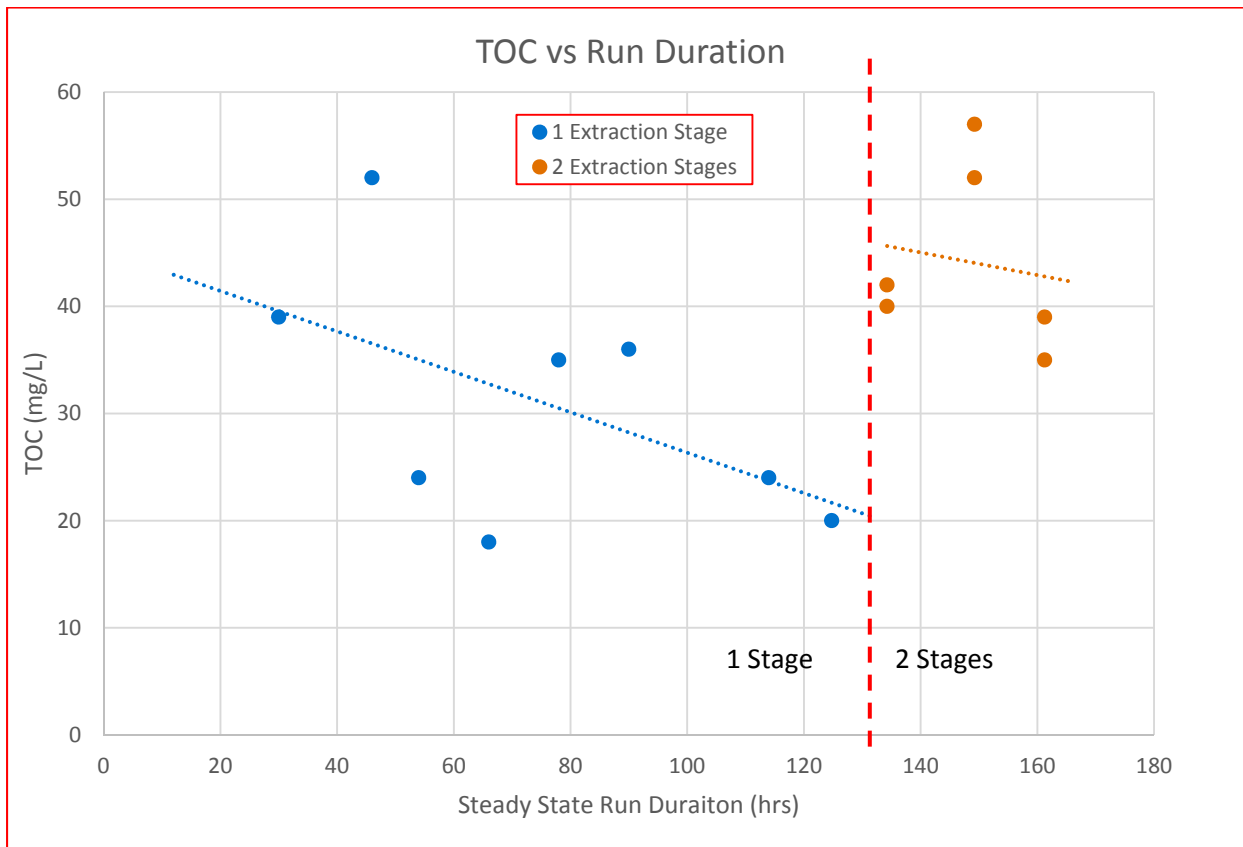


Figure 14. TOC vs Run Duration for operation of a single and dual extraction stages.

### TEST CAMPAIGN 1 CONCLUSIONS

Test Campaign 1 demonstrated long term, steady state system behavior. Data from the first test campaign indicates that sulfate levels are effectively reduced through operation of the HydroFlex platform. An initial screening of the E:A ratio effect on sulfate removal performance indicated that to achieve the required sulfate levels under the Sarver, PA site conditions requires operation at an E:A approaching 1:2. A lower E:A ratio is sufficient at higher extractant strength, as evidenced by the results from the demonstration runs conducted in BP1 with fresh extractant.

Operation of a second extraction stage resulted in the reduction of the sulfate levels to below 100 mg/L during the test campaign, but increased extractant entrainment in the AMD discharge. Over TC1, sulfate removal and TOC measurements consistently improved throughout the entire test campaign, indicating that the results may be further improved as the system is operated over a longer period of time.

At the conclusion of TC1, a preliminary estimate of the process economics was conducted and the key cost drivers for the process were identified. These preliminary estimates, illustrated in Figure 15, indicate that carbonate consumption, extractant maintenance and filtration are key cost drivers. If an outlet for the byproduct cannot be established, then waste disposal will also be a key cost, but it is expected that the byproduct can be dispositioned at cost as a treatment chemical for produced water (see Sections 4.5 through 4.7). Additional discussion of the process economics can be found in Section 4.4.1.

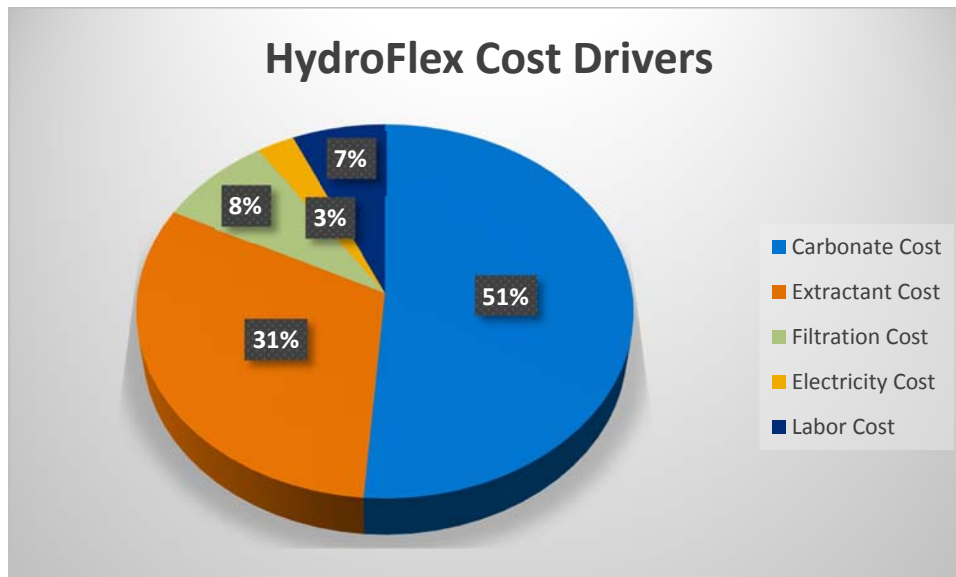


Figure 15. Key cost drivers for the HydroFlex process based on TC1 results.

### 4.3.3 CONFIRMATORY TESTING: LIMITED OPERATIONAL COST REDUCTION TESTS

Based on these results, the original objectives of test campaign two were redirected toward reducing the process cost drivers; specifically carbonate usage and filtration costs. The field unit was used for additional runs to evaluate the impact of reduced carbonate feed rate on the process performance. Additionally, centrifugal pumps in the system susceptible to fouling were replaced with diaphragm pumps and the filters removed to determine whether filtration costs could be eliminated. A full test plan and report for the Confirmatory Test Campaign (CTC) is included in Appendix C.

This additional testing was performed over the course of four weeks, during which the feed rate of carbonate was reduced from roughly 1.9-1.7 gpm at the end of the TC1 testing to 0.73 gpm. As in TC1, AMD water from both the mine and leach pile were blended to provide a feed between 500 and 600 mg/L  $\text{SO}_4$ , and two countercurrent extraction stages were operated to target a sulfate residual of 100 mg/L  $\text{SO}_4$  or less. Titrations were done on each batch of sodium carbonate feed solution to determine the concentration, and removal was tracked by mass of sodium carbonate fed per mass of  $\text{SO}_4$  ion removed. This accounted for variability of the feed carbonate concentration during the test run.

During the four week test, the sulfate feed concentration was 523 +/- 20 mg/L  $\text{SO}_4$ . The sulfate residual was 103 +/- 18 mg/L  $\text{SO}_4$ . This was accomplished with a specific utilization of 2.84 +/- 0.29 lb  $\text{Na}_2\text{CO}_3$  feed per lb of  $\text{SO}_4$  removed, almost half that of the 5.25 lb  $\text{Na}_2\text{CO}_3$  feed per lb of  $\text{SO}_4$  removed during the TC1 testing.

Besides carbonate consumption, the omission of fabric filters to prevent pump fouling in the output was evaluated. During BP1 testing and TC1, sub 100 micron bag filters were used prior to the product water pumps to prevent calcium carbonate scale from plugging the centrifugal pumps. Prior to TC1 the centrifugal pumps were replaced with diaphragm pumps, but the filters left in line as a safety precaution to prevent plugging of the oil water separator. Replacement of bag filters is a significant cost driver as shown in Figure 15. Use of 200 micron filter bags prior to the confirmatory tests resulted in no observed impact in oil water separator performance, so it was

hypothesized that removal of the bags completely would still allow good performance at improved cost.

The bag filters were removed from the system during the second week of the confirmatory testing and the oil water separator monitored for plugging by solids. The diaphragm pumps did not suffer from scaling without the filters in place. The oil water separator did experience some fouling with precipitated solids at the leading edge of the packing, but it is anticipated that pressure washing of the packing on a regular schedule will allow for continued operation.

The confirmatory testing also included investigation of an alternate means to measure the level of extractant present in the treated AMD entering the granular activated carbon beds. Total organic carbon tests were previously used as an indicator of all organic compounds, but in this round of field testing a traditional Gas Chromatography-Mass Spectroscopy (GC-MS) method was evaluated for extractant component identification. This GC-MS work did not identify any components of the extractant compounds in the effluent water, which suggests that actual losses could be quite low. However, this work is not conclusive as the GC method used needs further validation to properly identify the extractant components, including running of reference materials. A discussion of how the findings from the confirmatory testing affected the process economics is given in Section 4.4.1.

## **4.4 Task 3.3: AMD Treatment Process Testing and Evaluation- Evaluation of Process Performance**

### **4.4.1 PROCESS ECONOMIC DISCUSSION**

Among the primary considerations behind adoption of the HydroFlex process by industry are the costs associated with the operation of the system. Data collected during the testing conducted as part of TC1 and the CTC were used to determine operating cost estimates for the process. As discussed in Section 4.3.3, operational cost projections were first made based on the results of TC1, which were the basis of the test objectives for the CTC. CTC results were then used to project the anticipated operating costs for a commercial system.

Table 2 presents the operational cost estimates determined as an outcome of TC1, the CTC, and production system cost projections. The basis of estimates for each operational parameter were continuously refined for each version of operational cost projections.

Table 3 defines the basis of estimate for each of the cost scenarios examined. Based on the cost analysis presented in Table 2, it is anticipated that the treated AMD costs will range from ~\$4-10/kgal for future implementation of the HydroFlex technology.

**Table 2. Operational cost projections based on TC1 and CTC results, as well as productions system operational cost estimates.**

<b>Operational Costs</b>			
<b>Parameter</b>	<b>TC1 Results</b>	<b>CTC Results</b>	<b>Projected for Commercial Operation</b>
<b>Carbonate Cost</b>	\$5.34	\$2.89	\$2.48
<b>Extractant Cost</b>	\$3.26	\$1.94	\$0.41*
<b>Filtration Cost</b>	\$0.85	\$0.00	\$0.00
<b>Byproduct Disposal</b>	\$10.20	\$4.70	\$0.00
<b>Electricity Cost</b>	\$0.28	\$0.24	\$0.17
<b>Labor Cost</b>	\$0.69	\$0.69	\$0.69
<b>Total Cost per kgal</b>	<b>\$20.61</b>	<b>\$10.46</b>	<b>\$3.76</b>
<b>Total Cost per bbl</b>	<b>\$0.87</b>	<b>\$0.44</b>	<b>\$0.16</b>

\*requires confirmation by long term process operation results.

**Table 3. Basis of estimates for each of the costing exercises conducted.**

Basis of Estimate			
Parameter	TC1 Results	CTC Results	Projected Production
<b>Carbonate Cost</b>	TC1 Results, using excess carbonate feed	CTC Results, reduced feed rate; avg for final week of test period	Theoretical utilization of carbonate based on stoichiometric dosing and using bulk carbonate pricing
<b>Extractant Cost</b>	Estimated extractant loss based on TOC measurements during TC1; assumes replacement of active ingredient	CTC TOC Results; Assumes replacement of bulk extractant mixture	Based on 10 ppm target loss; anticipated long term system performance
<b>Filtration Cost</b>	TC1 Results, based on filter replacement cost and change out frequency	CTC Results, assumes no filters required	CTC Results, assumes no filters required
<b>Byproduct Disposal</b>	TC1 Results, \$0.30/gal of waste disposed	CTC Results; avg for final week of test period. \$0.265/gal of waste disposed	Disposition at no cost
<b>Electricity Cost</b>	TC1 Results, higher electricity rates due to higher tiered rate	CTC Results; based on observed load, lower tiered rate	Typical industrial sector costs
<b>Labor Cost</b>	Engineering estimate for commercial system; assumes operator on site 2 hrs/day	Engineering estimate for commercial system; assumes operator on site 2 hrs/day	Engineering estimate for commercial system; assumes operator on site 2 hrs/day

One of the primary cost drivers for the process is the amount of carbonate fed to the sulfate stripping stages to regenerate the extractant. During TC1, carbonate was fed to the stripping stages at an average flow rate of 2.1-1.9 GPM which results in a contribution of \$5.34 to the operational costs associated with TC1. During the CTC, the carbonate flow was reduced to 0.73 GPM, which is less than half of the carbonate flow rate fed during TC1, while still maintaining extraction performance. By achieving more efficient utilization of carbonate fed to the system, operational cost reductions were not only realized in the carbonate cost, but also in the waste disposal of the byproduct stream as the byproduct volume produced during operation of the system was reduced. Under steady state operation, the byproduct generation rate is nominally equal to the carbonate feed rate to the stripping stages. For a production system, the cost for procurement of carbonate is further reduced as carbonate purchased in bulk vs. bagged is less expensive. In addition, it is assumed that the process byproduct will be able to be dispositioned at cost (see byproduct testing discussion in Section 4.5). Additional process improvements are

projected to provide carbonate utilization rates which approach theoretical stoichiometric predictions.

Continued process modifications to reduce organic losses from the system are expected to reduce the costs associated with extractant maintenance, with final production system costs consisting of a minor makeup stream for the extractant material.

During the CTC, it was demonstrated that the filtration skid used in the process to protect process equipment was not required to achieve required equipment reliability thresholds. Therefore, filtration costs were removed from the CTC and projected production system cost estimates. Additionally, more refined estimates of electrical consumption were made for the cost of electricity to operate the process, as large industrial processes typically receive lower cost rates.

From previous conversations with stakeholders who utilize source water for HF purposes, water is typically purchased for \$0.12-0.50 per barrel (i.e., \$2.86-\$11.90 per thousand gallons). This indicates that the HydroFlex system has the capability to meet industry cost targets for provision of treated AMD water under the assumptions used in the economic projections. However, adaptations made to the system during the field trials will require permanent incorporation in the commercial system, and a low cost disposal route will need to be identified for disposal of the process byproduct. Finally, the current pilot process requires an operator to be present at all times during system operation. This is due, in part, to the current set up of the HydroFlex system as an experimental pilot facility. Additional automation and process control equipment would reduce operator requirements to only a few hours per shift, translating to reduced labor costs.

#### 4.4.2 STAKEHOLDER OUTREACH DISCUSSION

Regular communications with the project stakeholder committee was maintained throughout BP2 to facilitate feedback on the HydroFlex process performance and economics. There were no changes to the stakeholder group membership during BP2. Table 4 shows the stakeholders who provided feedback throughout the project.

**Table 4. Stakeholder committee for source water quality requirements.**

Stakeholder	Type
StatOil	Industry
XTO Energy	Industry
PADEP Oil & Gas Program	Regulatory
PADEP Conservation and Restoration	Regulatory
PADEP Office of Surface Mines	Regulatory
Water Research Institute	Academic

The stakeholder committee was briefed approximately quarterly on the project activities. During the stakeholder briefing held at the end of April 2015, the stakeholders were briefed on the planned field test campaigns and were asked to provide feedback to ensure that the testing was aligned with industry requirements. Stakeholders confirmed that the planned testing was an appropriate demonstration of the technology's ability to meet their requirements for AMD water treatment.

After the BP2 field testing was completed, the stakeholders were briefed on the test results. Water quality characteristics achieved by the HydroFlex process were shared and compared against the requirements for source water defined in BP1. Table 5 shows the water quality

characteristics achieved by the HydroFlex process during TC1 compared against the stakeholder committee established source water benchmark characteristics.

**Table 5. HydroFlex process water quality compared to projected water requirements for source water.**

Parameter	Sarver Site AMD	Slickwater Target	Gel Target	HydroFlex Sarver Site
Chlorides (mg/L)	N/A	< 70,000	<25,000	N/A*
Iron (mg/L)	<1	< 10	< 10	<1
Carbonate/Bicarbonate (mg/L)	< 10	< 400	< 500	350-450
Calcium (mg/L)	<5	< 8,000	< 100	<5
Magnesium (mg/L)	20	< 1,200	< 100	20
Sulfates (mg/L)	550-650	< 400	< 300	<100
pH	8-9	5 to 7	6 to 8	9-10
Total Dissolved Solids (mg/L)	600-800	< 120,000	N/A	500-700

Additionally, stakeholders were briefed on the projected process economics based on the results of TC1. Industry stakeholders agreed that the projected price point based on TC1 data for water treatment of less than \$0.50/bbl, which does not include markup for profits or delivery charges, seems like a reasonable cost for treatment. One of the industry stakeholders discussed potential transportation issues associated with using treated AMD for source water. They discussed that they are working toward taking water transportation trucks off the roads wherever possible, as transportation costs associated with trucking and bonding frequently used roads is not economically sustainable. They are transitioning to piping their source water when geography allows, and stated that if the AMD treatment sites were located within a feasible pipeline radius from the well sites, it would make for a more attractive water source. Both industry stakeholders highlighted the importance of process economics as the driving factor behind industry acceptance, and that the overall cost of source water needs to include not only treatment costs, but also transportation and/or storage costs.

#### 4.5 Task 4.1: Process Byproduct Testing and Evaluation-Test Plan Development

The HydroFlex process produces a byproduct which is primarily an aqueous solution of sodium sulfate and sodium carbonate. Exploration of use of this process byproduct in produced water treatment was conducted as part of this project for several reasons. First, reuse of the process byproducts in other industries helps to reduce the costs associated with handling and disposal of the byproduct as a process waste. Second, by providing a cost effective means to recycle produced water, freshwater burdens of HF operations are further reduced. Finally, if the process



byproduct is able to be dispositioned at reduced cost or at a profit, the operational economics of the HydroFlex process are further improved.

Preliminary discussions with water treatment facilities revealed that the byproduct from the HydroFlex stripping stages has potential value as a softening/precipitation solution. Of particular concern when recycling produced water is the presence of barium and strontium, which in the presence of sulfate will precipitate out of solution causing scaling of process equipment and formation damage downhole. Additionally, polyvalent metals commonly present in the produced water such as calcium and magnesium can interfere with the crosslinking behavior of gel frac fluid formulations. Battelle tested the effectiveness of the HydroFlex process byproduct for removal of metals and reduction of hardness and turbidity from produced water. The byproduct was compared to solid sodium sulfate which is representative of the treatment chemicals currently used by oil and gas service companies.

A series of experiments were developed to evaluate the performance of the HydroFlex process byproducts against a standard, industrial grade sodium sulfate. Approximately 5 gallons of the sodium sulfate byproduct was collected from the S1 vessel of the HydroFlex plant during TC1 on August 5, 2015 and stored in a sealed, 5 gallon container until analysis/testing. The collection of this sample was timed to ensure that a representative sample of process byproduct was used for the comparative testing. A 5 gallon sample of produced water was collected from a produced water disposal facility site in the Marcellus region and stored in a sealed 5 gallon Nalgene container for analysis and testing. The produced water sample was collected from a well-mixed reservoir of produced water and is considered a representative sample of typical Marcellus Shale produced water.

#### **4.6 Task 4.2: Process Byproduct Testing and Evaluation-Laboratory Testing**

The produced water sample was first analyzed for pH, SO<sub>4</sub>, alkalinity, turbidity, and concentrations of calcium, magnesium, barium, strontium, and iron. The concentrations of Ba and Sr in the produced water sample were totaled to determine the total moles of target cations that will react and precipitate with SO<sub>4</sub>. The sample of HydroFlex process byproduct was analyzed for pH, alkalinity, and SO<sub>4</sub>. For each test conducted, byproduct solution (34.1 g/L) was added to 0.35 L of produced water in a 500 mL beaker to equal a stoichiometric ratio of 1 (moles sulfate to moles Ba and Sr). This was repeated for stoichiometric ratios of 0.5 and 2. The entire procedure was repeated using sodium sulfate powder obtained from Sigma Aldrich at the same three stoichiometric ratios. All reaction products were allowed to settle for 5 minutes after which turbidity was analyzed on the clarified sample. Clarified samples were collected and sent to a third party laboratory for total recoverable metals determination by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES).

#### **4.7 Task 4.3: Process Byproduct Testing and Evaluation-Evaluation of Performance**

The byproduct testing indicated that the HydroFlex byproduct provides similar performance as technical grade sodium sulfate powder with regard to barium and strontium removal from produced water. However, the byproduct also demonstrated better iron removal, better calcium removal, and better settling characteristics. These results are promising as an outlet for the process byproducts is pursued.

Table 6 summarizes all analyses performed. The pre- and post-mixing test concentration in the produced water sample was evaluated for total recoverable metals (Fe, Al, Ba, Sr, Mg, and Ca),

pH, sulfate and alkalinity (ICP-AES per EPA method 200.7 was performed by an outside lab). All precipitation reaction effluent samples were analyzed in triplicate for statistical analysis.

**Table 6. Analysis plan for reaction effluent**

Sample	Parameters	Analyses
<b>Precipitation Reaction Product</b>	pH, SO <sub>4</sub> , alkalinity, turbidity, Ca, Mg, Ba, Sr, Fe	<ul style="list-style-type: none"> <li>• 2 tests (byproduct and prepared NaSO<sub>4</sub>);</li> <li>• x 3 concentrations (0.5, 1.0, 2.0 x stoichiometric value);</li> <li>• x 3 reactions (triplicate for statistical analysis) = <b>18 total samples</b></li> </ul>

Metals were analyzed by EPA method 200.7, and the results are summarized in Table 7. In general, both the process byproduct and standard sodium sulfate addition reduced all metals by the same order of magnitude. Reduction of all metals increased with increasing concentration of byproduct and sodium sulfate. Both the quantity of sulfate added to the reaction effluent and alkalinity increased with increasing concentration of HydroFlex byproduct.

**Table 7. Summary of Precipitation Reactions with HydroFlex Byproduct and Sodium Sulfate Powder**

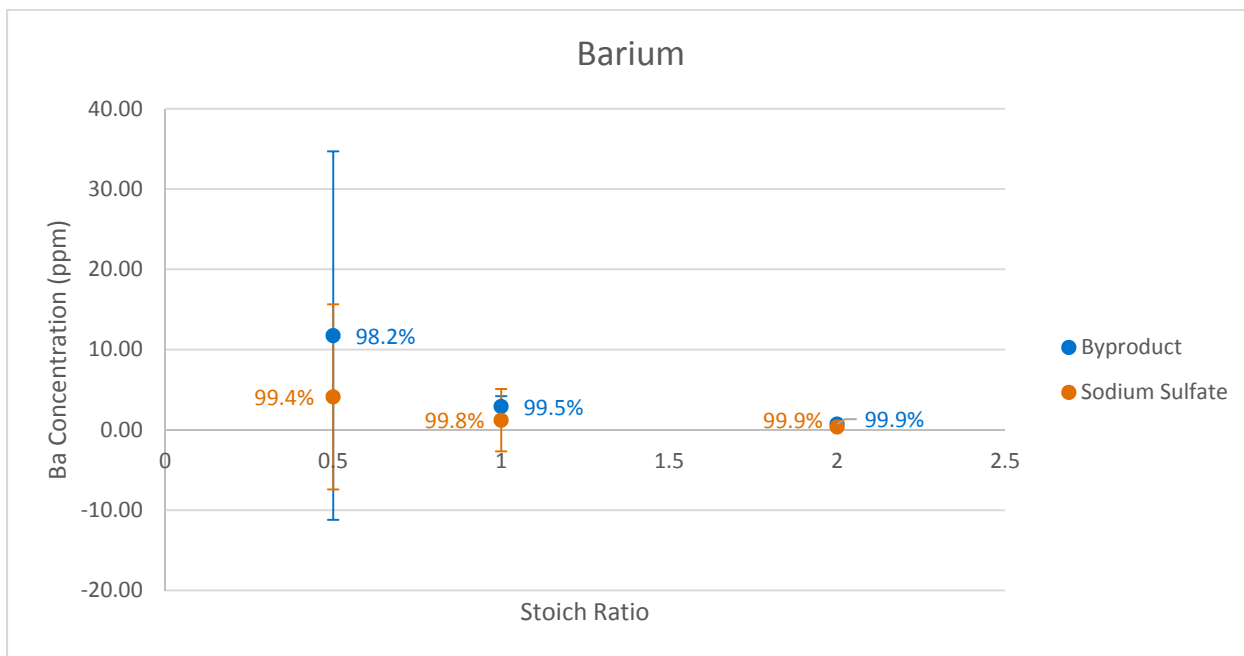
Analyte	Raw Produced Water (mg/L)	Treatment with HydroFlex Byproduct (mg/L)			Treatment with Sodium Sulfate Powder (mg/L)		
		0.5	1	2	0.5	1	2
<b>Ba</b>	641	11.74 (+/-10.5)	2.92 (+/-0.58)	0.72 (+/-0.23)	4.11 (+/-5.3)	1.21 (+/-1.8)	0.37 (+/-0.18)
<b>Ca</b>	12,200	12,733 (+/-1507)	11,433 (+/-1051)	9,963 (+/-72)	13,167 (+/-570)	13,267 (+/-1099)	12,567 (+/-663)
<b>Fe</b>	133	2.11 (+/-0.99)	0.73 (+/-0.82)	0.171 (+/-0.34)	26.5 (+/-3.1)	24.5 (+/-1.1)	23.1 (+/-1.78)
<b>Mg</b>	1290	1,437 (+/-136)	1,340 (+/-128)	1,300 (+/-45)	1,450 (+/-88)	1,470 (+/-120)	1,413 (+/-124)
<b>Sr</b>	2120	1,823 (+/-52)	1,480 (+/-85)	1,197 (+/-103)	1,833 (+/-73)	1,483 (+/-137)	1,057 (+/-36)
<b>Alkalinity</b>	0	287 (+/-33)	347 (+/-13)	393 (+/-24)	123 (+/-68)	133 (+/-52)	77.5 (+/-20)
<b>Sulfate</b>	2.1	589 (+/-87)	1,553 (+/-6.5)	3,490 (+/-118)	544 (+/-15)	1,073 (+/-86)	1,863 (+/-288)
<b>Turbidity</b>	>2000	100 (+/-49)	50 (+/-0.98)	36 (+/-27)	>1,100	>1,100	>1,100

Note: 95% confidence intervals are shown in parentheses.

**Table 8. Percent Removal of Precipitation Reaction Metals**

Analyte	Raw Produced Water (mg/L)	Hydroflex Byproduct (mg/L)			Solid Sodium Sulfate (mg/L)			Byproduct Removal Capacity
		0.5	1	2	0.5	1	2	
Ba	641	98.2%	99.5%	99.9%	99.4%	99.8%	99.9%	Similar
Ca	12,200	N/A	6.3%	18.3%	N/A	N/A	N/A	Increased
Fe	133	98.4%	99.5%	99.9%	80.1%	81.6%	82.6%	Increased
Mg	1290	N/A	N/A	N/A	N/A	N/A	N/A	Similar
Sr	2120	14.0%	30.2%	43.6%	13.5%	30.0%	50.2%	Similar

The HydroFlex byproduct and sodium sulfate powder demonstrated similar ability to remove key metals Ba and Sr from the produced water sample, as seen in Figure 16 and Figure 17. Sufficient sample analysis was conducted such that confidence intervals for the analysis could be determined. Note that percent removal values are shown next to each data point in addition to error bars which represent the 95% confidence interval. These test results indicate that the HydroFlex process byproduct is able to achieve similar removal rates as existing chemicals used in softening operations. Calcium and iron removal may also be important to O&G end users of the processed water since calcium, iron, and other polyvalent metals can interfere with the performance of crosslinkers in gel frac fluids. The byproduct appeared to have better removal of iron at all doses as shown in Figure 19, and calcium at the higher doses as in Figure 18. This is expected since the byproduct is likely to have a higher pH which aids in iron precipitation, while the carbonate present in the byproduct results in precipitation of insoluble calcium carbonate.



*Figure 16. Barium Removal Results for Byproduct and Sodium Sulfate Powder*

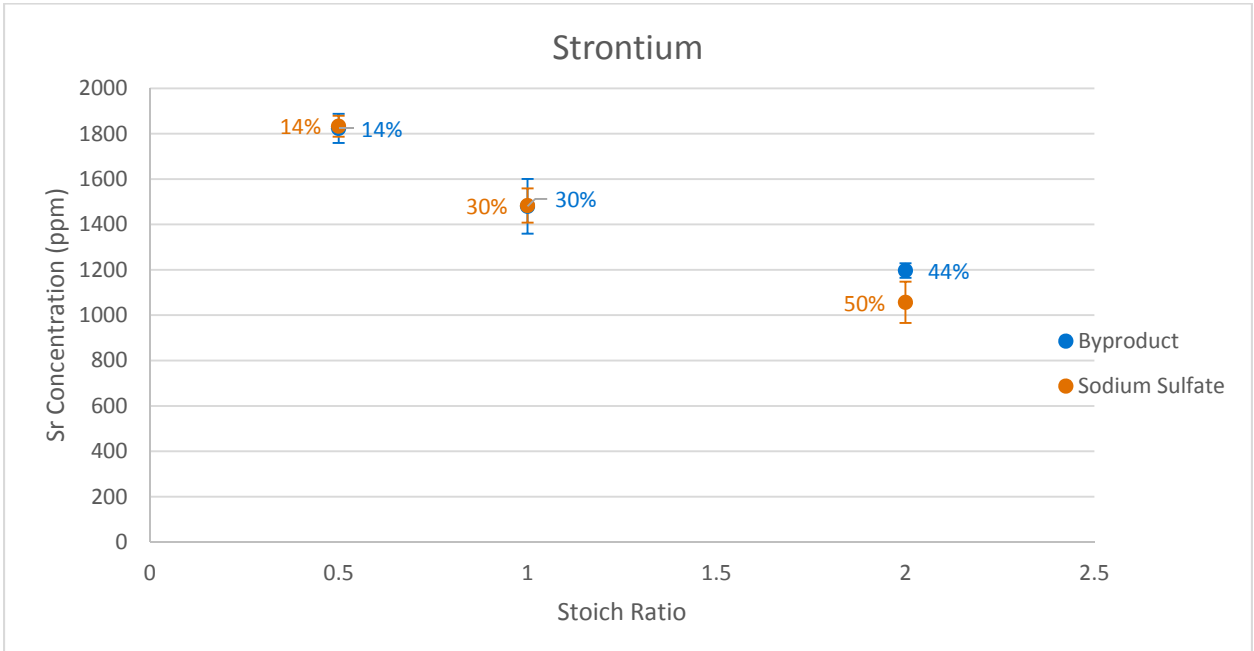


Figure 17. Strontium Removal Results for Byproduct and Sodium Sulfate Powder

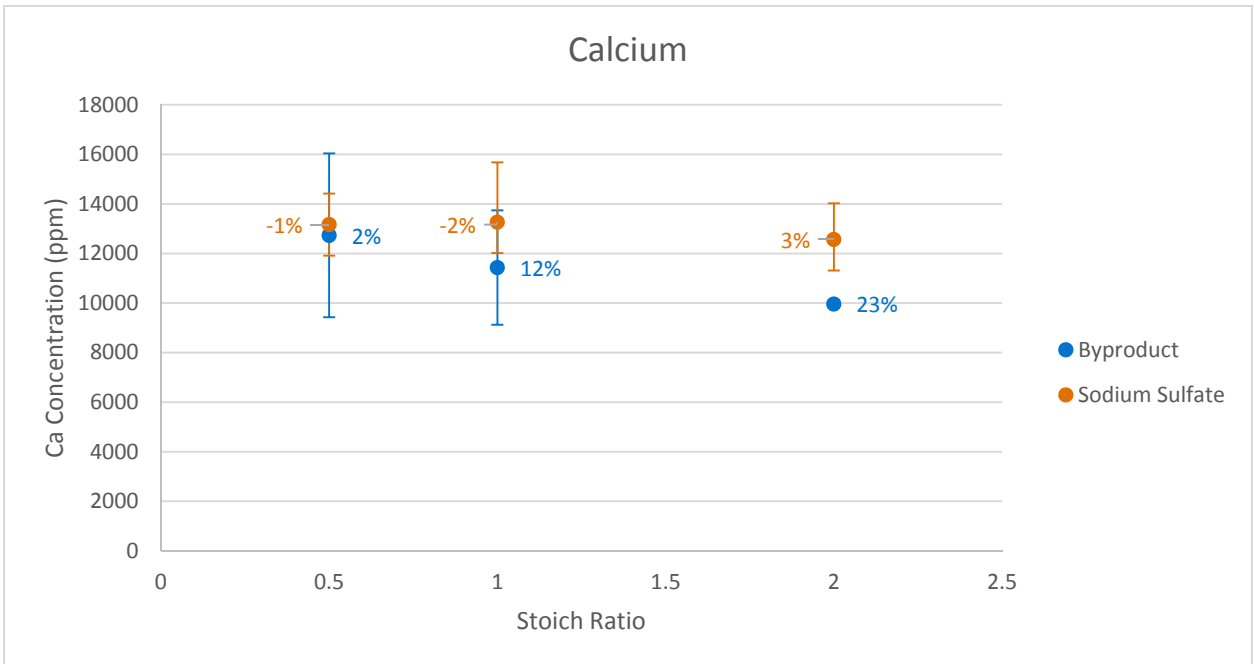


Figure 18. Calcium removal results for byproduct and sodium sulfate powder. Error bars represent the 95% confidence interval, while percentage labels show the average percentage removal.

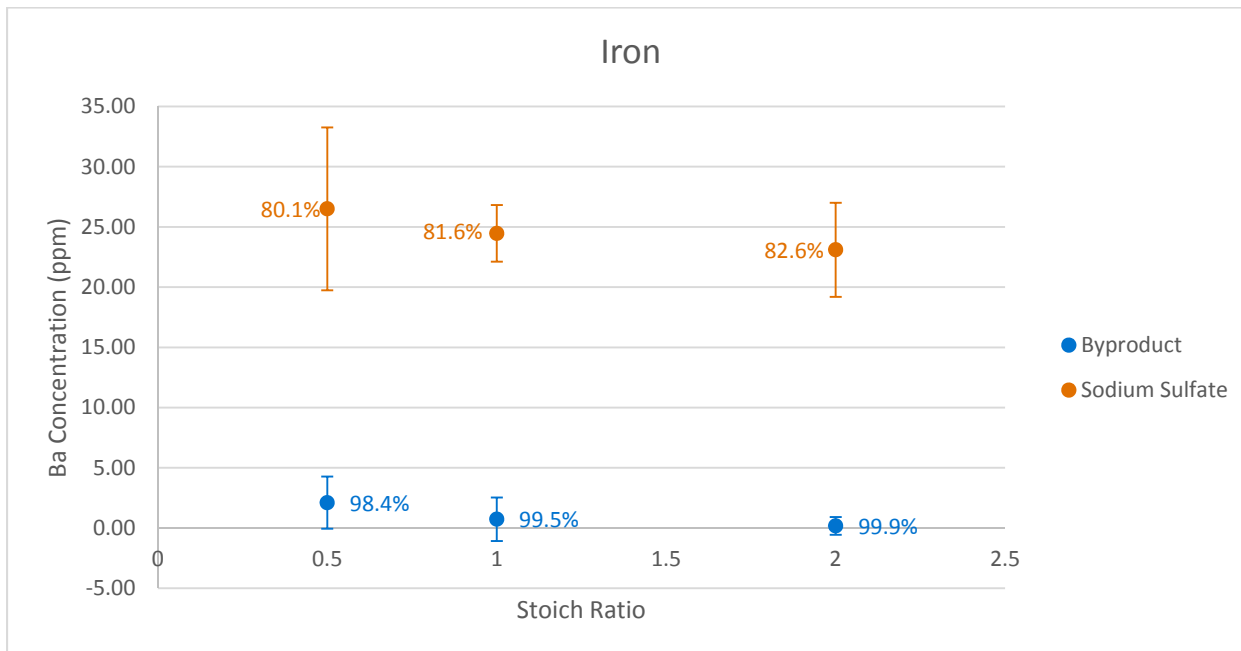


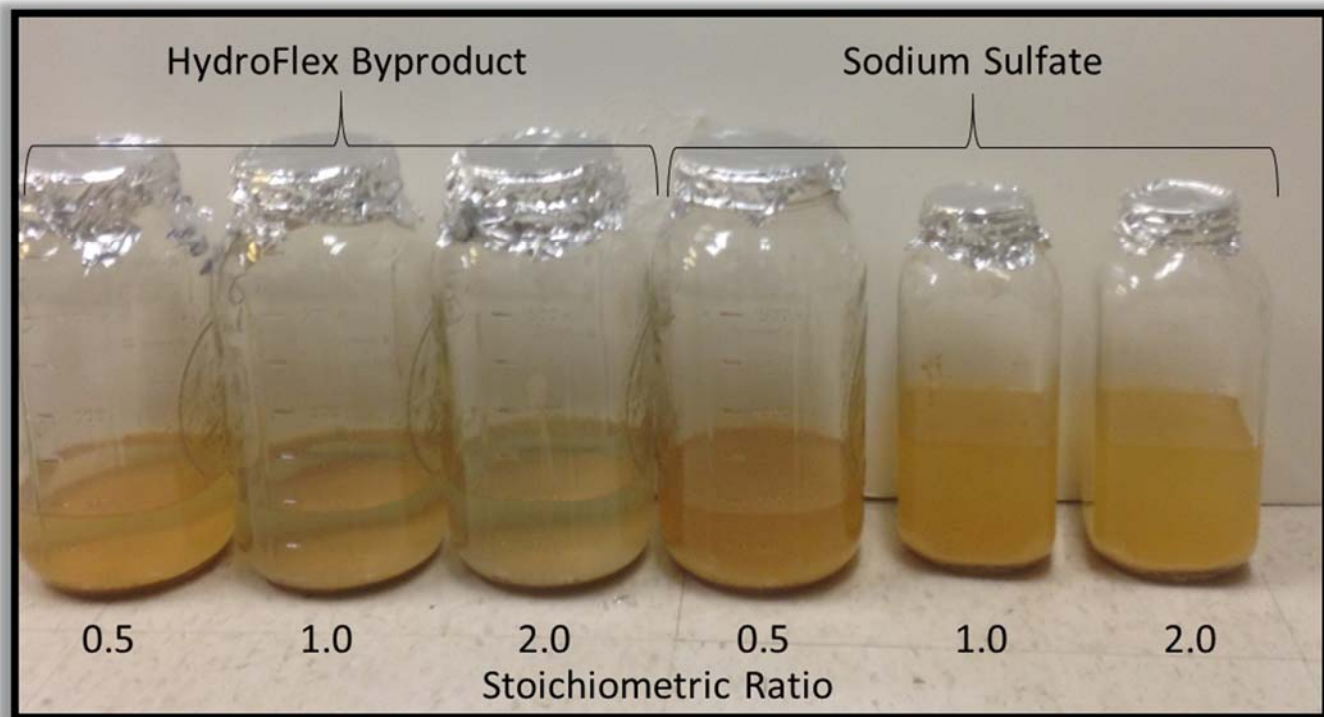
Figure 19. Iron removal results for the process byproduct and solid sodium sulfate

During the tests, it was observed that the samples treated with the HydroFlex byproduct settled much faster than the samples treated with the standard sodium sulfate powder. To quantify this observation, turbidity measurements on all samples were taken after 5 minutes of settling time. The results of this testing are shown in Table 9.

**Table 9. Turbidity measurements (NTU) by stoichiometric dose rate for byproduct and sodium sulfate after 5 minutes of settling time.**

	HydroFlex Byproduct			Na <sub>2</sub> SO <sub>4</sub>		
	0.5	1	2	0.5	1	2
<b>Ave Turbidity (NTU)</b>	<b>100</b>	<b>49.5</b>	<b>36</b>	<b>&gt;1100</b>	<b>&gt;1100</b>	<b>&gt;1100</b>

As shown, the turbidity of the samples treated with the HydroFlex effluent is lower by at least an order of magnitude when compared to the standard sodium sulfate powder. This is believed to be advantageous for a treatment process which may use similar chemicals to achieve a softening reaction, as more rapid clarification of the sample typically results in decreased residence time, helping to reduce the footprint required for settling tanks and ponds and increasing the throughput of the process. Figure 20 shows representative samples of the treated effluent, illustrating the difference in clarity between samples treated with byproduct and with standard sodium sulfate. While specific analysis regarding why clarification is improved when using the HydroFlex process byproduct was not conducted, it is believed it is due to the presence of dilute constituents from the AMD source, including trace metals, which assist in flocculation and settling of particles.



*Figure 20. Samples of produced water treated at different stoichiometric ratios with byproduct and sodium sulfate solids. Note that byproduct treated samples appear clearer than those treated with sodium sulfate.*

While initial tests of the process byproduct for produced water treatment were promising, additional testing is required to fully validate the process. Future testing should include processing of multiple samples of produced water from several different formations to ensure that the process chemistry is effective across all anticipated water chemistries. Additionally, scale up of the process should be considered, and future tests should be conducted on a continuous system. Finally, the dilute concentration of the process byproduct may pose challenges for treatment facilities, as its use may result in a larger volume of water resulting from the treatment process. This should also be considered in future testing.

## 5.0 Communication of Project Results

To address the program objective to support transition of the technology and project results into implementation by the oil and gas industry, the project results to date were presented in this budget period at two conferences by Battelle's subcontractor, Winner. These conferences were selected because of the opportunity to disseminate project information to industrial, regulatory, and academic parties of interest, as well as to receive feedback on the challenges encountered when unconventional water sources are used as a source water.

**Table 10. Conference attendance information.**

Event	Location	Date	Presenter	Presentation Title
Society of Petroleum Engineers, Annual Technical Conference and Exhibition	Houston, TX	9/28/15-9/30-15	Todd Beers, Winner Water Services	Paper No. SPE-174947-MS Treating Acid Mine Drainage for Use as Source Water: A Pilot Study
Ohio Mineland Partnership	Marietta, OH	10/13/15	Carolyn Kotsol, Winner Water Services	Development and Validation of an Acid Mine Drainage Treatment Process for Hydraulic Fracturing Source Water

## 6.0 Conclusions

The objectives and milestones set forth for BP2 have been accomplished, although continued optimization of the HydroFlex technology is required to meet the industry cost targets. Test campaigns were conducted using the 100 GPM HydroFlex unit to collect data pertaining to the sulfate removal abilities of the system as well as the associated operating costs. During TC1, it was determined that the system was consistently able to remove sulfate from the AMD to levels below 150 or 100 mg/L, depending on the number of extraction stages in operation. Removal of sulfate to this level is aligned with industry stakeholder feedback on threshold sulfate levels for source water.

System operational costs were estimated based on TC1 data. These data were used to identify discrete tests conducted as part of the CTC which demonstrated adjusted operating conditions capable of achieving similar sulfate removal performance at a reduced operating cost. Based on the results of the CTC, treatment costs of ~\$0.44/bbl were estimated, however these costs do not include transportation or any mark-up for profit. With further modifications and long term operation of the HydroFlex system, it is projected that water can be treated for \$0.16/bbl, leaving room for the addition of transportation and mark-up costs, while still meeting typical source water costs of \$0.12-\$0.50/bbl. However, to achieve this would require identification of an outlet for the process byproduct.

Laboratory testing conducted on the process byproduct stream against industrial water softening chemicals indicate that use of the byproduct sodium sulfate solution for the removal of barium from produced water may be advantageous. Testing indicates that both industrial sodium sulfate solutions and the HydroFlex process byproduct solution are capable of removing more than 99% of barium present and over 50% of strontium present. It was found that produced water samples



treated with the HydroFlex process byproduct clarify more rapidly than samples treated with industrial sulfate solutions. Decreased turbidity in the treated produced water effluent indicates that smaller settling areas may be required to achieve similar removal efficiencies, potentially allowing for increased production from existing produced water treatment facilities.

This project allowed for the demonstration and validation of a novel technology to treat AMD and provides a means to convert an environmental liability to a benefit for the HF industry. The technology has evolved significantly over the course of the program, and process improvements were identified which allow the system to operate more efficiently. Future steps taken by Winner will include implementation of the process improvements identified as part of this study, as well as continued efforts to improve process efficiency. Additionally, Winner is working to translate the findings from this project into other industrial applications, further increasing the versatility of the HydroFlex technology.

## 7.0 Bibliography

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## 8.0 List of Acronyms and Abbreviations

Acronym	Definition
AMD	Acid Mine Drainage
BP1	Budget Period 1
BP2	Budget Period 2
CTC	Confirmatory Test Campaign
DOE	Department of Energy
E:A (or E/A)	Extractant to Aqueous phase ratio
EDP	Experimental Design Plan
HF	Hydraulic Fracturing
NCTE	No Cost Time Extension
PADEP	Pennsylvania Department of Environmental Protection
RPM	Revolutions per Minute
TC1	Test Campaign 1
TC2	Test Campaign 2
TOC	Total Organic Content
VOC	Volatile Organic Compound

## 9.0 Appendices

Appendix A: (Confidential – not included in this document)

Appendix B: Test Campaign 1 Test Plan

Appendix C: (Confidential – not included in this document)

Appendix D: Selected Stakeholder Meeting Minutes

Appendix E: Selected Stakeholder Project Update Communications

Appendix F: Cost Information Back-Up

Appendix G: Technology Introduction

## Appendix A: (Confidential – not included in this document)

## Appendix B: Test Campaign 1 Test Plan

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## Appendix D: Selected Stakeholder Meeting Minutes

## Appendix E: Selected Stakeholder Project Update Communications



## Appendix F: Cost Information Back-Up

## Appendix G: Technology Introduction