Organic and Inorganic Controls on Barite Precipitation in Unconventional Shale Systems

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Abstract: Barite scale precipitation is an important problem in hydraulic fracturing systems. During fracture fluid injection, organic additives are added to control scale precipitation. It is assumed that these additives are effective at inhibiting barite scale, but given the long shut-in times, changes to solution chemistry down borehole, and the tendency for fluids to imbibe into the shale matrix, the actual efficacy of these chemicals is difficult to evaluate. In particular, unconventional reservoirs are subject to large variations in pH (often strongly acidic at the beginning of injection), ionic strength, and variability in organic amendments. This work focuses on the effects of these geochemical parameters on the precipitation of barite from fluids containing Ba-SO_4. Of the three major parameters, pH was shown to have the greatest impact on barite precipitation. At low pH (≤ 2), which occurs with the initial injection of a 15% HCl acid slug, barite precipitation is completely inhibited. As pH approaches near circum-neutral conditions, precipitation rates increase, with maximum rates at pH ≥ 5. Ionic strength is the second most important factor for barite precipitation rates. At high I.S. (≥ 1M), precipitation was inhibited, while precipitation rates increased with lower I.S. reaching a plateau at I.S.'s ≤ 0.01M. Surprisingly, nearly all organics tested either had no effect on barite precipitation rates compared to control reactors or, in some cases, actually accelerated precipitation. Though organics with high chelating properties (citric acid and guar gum) did retard barite precipitation rates, no organic completely inhibited barite scale formation. Analysis of the barite crystals precipitated during the experiments showed surprisingly high consistency in particle size for all reactors, suggesting barite inhibition is due more to the control of nucleation rates rather than crystal surface poisoning. These results indicate that organic additives injected to control barite scale have little to no impact on reducing scale precipitation and in some cases exacerbate the problem.

Introduction:

In conventional and unconventional oil/gas systems, the precipitation of mineral scale, defined here as any inorganic precipitation on fracture/piping surfaces and/or in the shale matrix, is of significant concern. One of the most important scale types that is common in both systems is barite ($BaSO_4$). Given the low solubility of barite ($K_{sp} = 10^{-9.97}$)[1], even at low concentrations of Ba^{2+} and SO_4^{2-} in solution (≥ 1.4 ppm Ba^{2+} and ≥ 1 ppm SO_4^{2-}), barite can precipitate rapidly. Depending on where the scale precipitation occurs (piping, fracture surfaces, pores, pore necks, etc.), a substantial impact on permeability, and subsequently overall recovery/production can occur.

In unconventional systems, chemicals are injected into the subsurface and then shut-in with times ranging from 3 days to 6 weeks before production begins. During this period of time, significant variations in the chemical composition of the injected fluid will occur due to fluid imbibition into and reaction with the host shale, including the neutralization of acidic fluids (accompanied by an increase in total dissolved solids (TDS)), alteration of chemical additives under elevated temperatures, mixing with formation water, etc. It is of significant practical interest to identify how the solubility of barite, and the rates at which it precipitates, are modified by these downhole geochemical variables. For example, barite in pure water at pH 5 is predicted to be ~3-fold less soluble than at pH 2 (a typical stimulation fluid pH). Therefore, a worst-case scenario that should be avoided would be dissolution of Ba from shale followed by either pH neutralization or the injection of chemical additives that trigger massive precipitation of barite within micro-fractures and shale matrix, reducing production from these zones. In principle, the chemical additives that are chosen to inhibit this type of formation damage tend to be guided by research performed on conventional oil/gas systems. However, the geochemical environment within unconventional shale reservoirs is very different than conventional systems, and we have little knowledge that can be used to optimize chemical stimulation practices to avoid such problems. Organics in the system may also affect Ba scale formation. Previous work on Fe(III)-precipitation in unconventional shale systems has shown that organics can moderate Fe-cycling[2]. Thus, and additional objective of this study is to determine *(1)* if organics injected to mitigate mineral scale are effective and *(2)* determine whether organics in the system accelerate mineral scale formation.

The majority of research investigating scale precipitation has focused on conventional oil/gas systems [3-10]. Though these studies provide valuable insights, there are some major geochemical differences between conventional and unconventional systems. The two most striking differences are the time intervals over which scale precipitation may occur and the volumes of injected chemicals. Overall, the total timeframe considered for scale precipitation in conventional oil/gas systems is 2-3 hours [3, 4, 6, 7, 11, 12], which corresponds to transit time through production piping of produced water that is capable of producing barite scale. In these systems, produced water is the first fluid to travel through the piping followed by the main crude. In comparison, in unconventional systems, chemicals are injected into the subsurface and then shut-in for upwards of 6 weeks before production begins. At a minimum, this means that contact time during which precipitation of barite scale can occur is > 330-fold longer than what is considered in dealing with conventional systems. However, imbibition of fluids into the shale matrix will subject them to evolving pH and salinity conditions, potentially over even longer timeframes. Additionally, there is a significant difference between extraction methods with regards to chemical additives. In order to reduce barite scale precipitation in conventional systems, scale inhibitors (e.g. dietylenetriamine penta(methylene phosphonic) acid, sulfonated polycarboxylic acid, polyvinylsulfonate polymer, carboxy methyl inulin, phosphorus incorporated maleic acid, phospine polycarboxylic acid, and nitrilo trimethylene phosphonic acid)[3, 4, 6] are injected into produced water as it is traveling from the reservoir into the piping. Because of the shut-in period in unconventional production substantial variations in chemistry such as pH variations, increasing of total dissolved solids (TDS), imbibition of fluids into the rock, alteration to the additives due to temperature, mixing with formation water, etc., will occur. For example, the acid initially injected into the subsurface is at pH = 0, while produced water is often pH = 7-8. Ionic strength can also vary significantly from 4.25 mM (freshwater injection) to > 2 M in produced water. The possibility of these highly complex chemical reactions necessitates additional study of barite scale precipitation in the presence of different organic additives and inorganic parameters that do not occur in conventional oil/gas shale systems.

In order to determine the important parameters affecting the precipitation of barite scale in hydraulic fracturing systems, a series of experiments were conducted using varying pH, ionic strength (I.S.), and various organics (injection additives, formation water, and produced water) conditions. It is assumed that very low pH or high I.S. will retard Ba precipitation, but the impact of organics (either to accelerate or retard precipitation) is unknown. The organics selected for this work are common organics used in fluid injections, along with common organics inherent to formation and produced waters (ethylene glycol, kerosene, cyclohexanes, etc.). These experiments were carried out without the presence of shale in order to determine the factors required for precipitation from solution without the influence of sorption to oil/gas shales. Because of the high Ba concentrations often detected in produced waters (> 1,000 mg/L[13, 14]), thermodynamic modeling using Visual Minteq[15] has shown that the sorption capacity of Ba should be met, resulting in additional scale precipitation occurring directly from solution. The results of these experiments provide information on the impact of organics common to unconventional systems and inorganic parameters on barite scale precipitation while also indicating which parameters have the greatest effect on barite scale precipitation from solution. This information will provide insight into potential changes to fracture fluid additive formulations to help mitigate barite production that can negatively impact recovery/production.

Methods:

Reactor Experiments:

In order to minimize the variables being tested at any one time, a single parameter (pH, I.S., or organic) was adjusted at a time. Initial barium and SO_4^{2-} concentrations were fixed throughout the experiment at a 1:1 molar ratio to minimize the effect of Ba:SO_4 on the precipitation rate. Preliminary experiments showed that a starting saturation index (S.I.) of 1.3 (total Ba^{2+} and SO_4^{2-} = 1 mM) was ideal in order to provide slow enough Ba precipitation to allow monitoring of Ba concentrations over a total of 1-week incubation time. All experiments were conducted at 80^{o}C under constant agitation via an end-over-end tumbler with a rotation rate of 70 rpm. The range of variables used in these experiments, outlined in **Table 1,** are common in unconventional systems where pH and I.S. can vary up to 7-orders of magnitude, along with the presence of additional organics not included in the injected fracture fluid.

Barite precipitation reactions were conducted in acid-cleaned 50 mL borosilicate I-Chem vials with Teflon© lined lids. Reactors were initially filled with double de-ionized (DDI) water and the chemical to be tested (**Table 1**) at concentrations consistent with real world conditions without the addition of Ba or SO_4. One additional set of experiments was conducted using a fracture fluid recipe used at the NETL Greene Co. Well E site, both with and without added HCl, to determine the effects of the various organics on Ba precipitation when mixed together at ratios used in the field[16]. These vials were placed on the end-over-end mixer at 70 rpm (up to 20 reactors at a time) in a convection oven at 80^{o}C for 12 hours prior to experimentation to allow full mixing and temperature equilibration. Additionally, vials of 20 mM $BaCl_2$ and 20 mM Na_2SO_4 were placed in the oven, unagitated, in order to equilibrate the stock solutions and remove effect of temperature fluctuations on the precipitation reactions. In all experiments, the Na_2SO_4 stock was added to all vials, capped, and agitated prior to the addition of the $BaCl_2$ stock. Though T_0 samples were sampled immediately after the addition of Ba stock to all the reaction vials, due to the time required for sampling, T_0 time points varied from 1-30 minutes from the addition of Ba. Sampling of these experiments was conducted every 24 hours for one week with additional sampling immediately after addition of the Ba and at 12 hours. A total of 1 mL was collected at each sampling point. Samples were immediately filtered through a 20 nm Anatop™ filter. In order to arrest additional barite precipitation following filtration, 0.75 mL of filtered sample was added to 50 mL of 10% trace metal grade HNO_3 for preservation. Total Ba concentrations were measured using a Thermo Scientific ICP-OES model iCAP 6300.

Barium Precipitate Analysis:

Due to the low total yield of Ba precipitates from the 50 mL vials, experiments were upscaled using 250 mL I-Chem borosilicate bottles in order to produce large enough quantities of precipitates for mineral identification, x-ray diffraction (XRD), and particle size, dynamic light scattering (DLS). Experiments using the 250 mL bottles had the same concentrations to the 50 mL vial experiments and were conducted at 80^{o}C using a modified end-over-end tumbler at 60 rpm. Following a 1-week reaction time, contents of the bottles were centrifuged at 10,000 rpm for 1.5 hours to separate the barite crystals from the supernatant. Prior to drying the samples, a subset of Ba precipitates, ~1 mg, was taken for DLS measurements. The remaining Ba precipitates were dried in a desiccator for XRD analysis.

The Ba precipitate subsampled for DLS measurements, ~1 mg, was diluted into 5 mL of DDI water and sonicated for 20 minutes to reduce aggregation. Particle size analysis was done using a Malvern Zetasizer Nano. A total of 25 scans were taken for each sample.

X-ray diffractograms of the Ba precipitates were collected using a Rigaku Micro-flex x-ray diffractometer. Diffractograms were collected using a Cu K_α x-ray source with a scanning range of 5-80^o in 2-theta. Mineral phase identification was completed using the JADE software package[17] by matching the 5 most intense diffraction peaks with reference diffractograms contained in the National Institute of Standards and Technology (NIST) reference library. The Ba precipitate diffractograms were also compared to a natural barite sample procured from the Stanford University research mineral collection.

Thermodynamic calculations of experimental conditions were conducted using Visual Minteq[15]. All calculations were carried out at 80^{o}C and 1 atm pressure with barite precipitation being allowed. Initial ion concentrations used in modeling were derived from ICP-OES, added concentrations, and pH measurements.

Results:

Effect of pH:

Due to the wide range of pH conditions in hydraulic fracturing systems, the effect of pH can be considered one of the most important inorganic variables with regards to barium precipitation. A range of pH conditions (2-7) relevant to stimulated reservoirs were tested to determine its impact on barium precipitation. Since hydrochloric acid is used in hydraulic fracturing operations, it was used to acidify these experiments. As seen in **Figure 1**, variations in pH had a strong impact on the precipitation of barium-bearing phases. At pH ≤ 2, detectable precipitation did not occur, but above pH 2, precipitation rates increased until pH 5 was reached. At pH 5 and above, Ba concentration curves were within error at each pH condition for a given time point (**Figure 1**). The similarity among precipitation rates for pH's 5-7 is also consistent with thermodynamic modelling of initial saturation indices (S.I.) for pH 5 to 7, which vary from 1.252 (pH 5) to 1.255 (pH 7). The calculated initial S.I. using Visual Minteq[15] for pH 2 is 0.271, indicating that precipitation is favorable at this condition. Thermodynamic modeling of the final experimental values show that the systems are slightly undersaturated at various pH's (**Table 2**), indicating more Ba precipitation was observed than was predicted using standard speciation calculations. At pH = 2, the extend of undersaturation is minimal (S.I. = -0.02) and becomes more excessive as pH approaches 7. Though there is apparent disagreement between the final steady-state experimental values and the thermodynamic data, the overall discrepancy in S.I. is less than one order of magnitude.

Effect of Ionic Strength:

A wide range of ionic strengths (I.S.) were tested. These concentrations varied from low (i.e. < 0.01 M), due only to the $BaCl_2$ and Na_2SO_4 added, to levels equivalent to produced waters (I.S. > 2.3 M)[18-20]. For all experiments except for the lowest I.S., the system I.S. was controlled using NaCl which is the most abundant electrolyte in produced water. For all I.S. reactors, pH was adjusted to pH = 7 using NaOH in order to negate any pH effects.

Ionic strength has a strong effect on the extent and rate of barium precipitation (**Figure 2**). At I.S. ≥ 1M, barium precipitation is inhibited, while at lower levels precipitation rate increases until a maximum rate (under these Ba and SO_4 concentrations) is reached at an I.S. of < 10 mM. Another set of experiments (data not shown) were conducted to determine if the type of electrolyte, Na^+ or Cl^-, in these systems is important for barite precipitation. To test this, experiments were conducted using NH_4Cl and $NaNO_3$ at identical I.S.'s. These experiments showed no difference in barium precipitation depending on the electrolytes used, indicating that the total I.S. and not the type of electrolyte, except for Ba and SO_4, is the important factor with regards to the effect of I.S. on barium precipitation. In the cases of both pH and I.S., the concentration changes required to go from no precipitation to maximum precipitation rates occur over a 3-order of magnitude range.

Effect of organics:

A wide range of organics were tested in order to determine their effect on barium precipitation: additives in fracture fluid (ethylene glycol, kerosene, etc.), present in formation waters (acetate, citrate, etc.), and present in produced waters (bitumen, cyclohexane, etc.). A summary list of organics tested is found in **Table 1**. Due to the large number of organics tested, the experiments that exhibited similar Ba precipitation behavior are plotted in **Figure 3**. Control experiments (no organics, same pH/I.S.) were run in conjunction with every organic experimental run. The Ba concentration versus time curves for the control experiments are highly consistent between experimental runs with a variation < 15% in Ba concentration for each sampling time point. **Figure 3** shows that the organics either do not impact the Ba precipitation rate or enhance precipitation. Of particular note, ethylene glycol, commonly added as a winterizing agent and scale inhibitor, enhances the precipitation rate of Ba. In order to confirm the result for ethylene glycol, the experiments were repeated twice more resulting in identical results. These results indicate that organics common to these systems do not appreciably inhibit the precipitation of Ba.

A subset of organics from **Table 1**, namely citrate and guar gum, show a different trend compared to the organic compounds presented in **Figure 3**. These organics are known to have substantial metal chelation properties. As seen in **Figure 4**, Ba precipitation is significantly slowed compared to the Control experiment and the other organics (**Figure 3**). Fracture fluid used in this study contained similar concentrations of guar gum compared to the guar gum only experiments. For fracture fluid at pH = 7, Ba concentrations mirrored those of guar gum, whereas fracture fluid at pH = 2 had no detectable Ba precipitation (data not shown). Though Ba precipitation rate is retarded compared to all other organics, precipitation is still not inhibited.

Effect of Ammonium Persulfate and 2-ethyl-1-hexanol

An additional additive that is commonly used in hydraulic fracturing formulations, especially in TX[21], is the breaker ammonium persulfate. This compound is also a good proxy for other persulfate containing breakers (Mg-, K-, and Na-)[21], which can be a source of significant quantities of sulfate in the subsurface. Due to the large amount of sulfate contained in this chemical, there is a high possibility of enhanced Ba precipitation compared to all other experiments. Indeed, as shown in **Figure 5**, when compared to the Control, Guar Gum, and Bitumen, Ba precipitation is rapid. At sampling point T0 which represents 6 minutes (**Figure 5**), 2/3 of the added dissolved Ba was lost via precipitation. In less than 24 hours no Ba in solution (< 20 nm diameter) was detected indicating rapid precipitation. 2-ethyl-1-hexanol, a commonly used corrosion inhibitor was also shown to cause precipitation of all of the Ba in solution within 24 hours (**Figure 5**).

Barium Precipitate Particle Characterization

Thermodynamic modeling of the various reactor formulations indicate that all Ba should precipitate as the mineral barite. X-ray diffraction was completed on the samples to verify the experimental products and to determine if there are any structural defects in the precipitated barite caused by the organic additives. The XRD diffractograms for all of the organic reactors were identical. When compared to the pure barite reference material (**Figure 6**), there is very little variation between barite solids precipitated in the presence of organics and the reference.

To determine average particle size for the Ba precipitates, dynamic light scattering (DLS) was completed on a subset of the precipitates. The results of the DLS analysis showed a high consistency in particle size for barite precipitates regardless of the organic present during precipitation. Overall particle size for these samples was 2.2 ± 0.3 μm. There is high consistency in XRD and DLS data between solids precipitated in the presence of organics indicating little to no impact on the type and size of Ba precipitate formed for various organic reactants.

Discussion:

Impact of Common Additives

The majority of organic molecules tested in our experiments have no effect, or in some cases enhance the formation of Ba-scale. Enhancement has been found previously in experiments testing barite precipitation in solutions containing methanol[8]. The most striking result of this work is that none of the organics tested were able to prevent the precipitation of barite at a saturation index (S.I. = 1.3), i.e., well below that which would be present in typical hydraulic fracturing systems (S.I. > 4, produced waters). If chemical additives, especially ones added to inhibit scale (ethylene glycol) are unable to control Ba precipitation at this low S.I., they are highly unlikely to be effective at the higher S.I.'s commonly observed. Of all the organics tested, only those with strong chelating properties, i.e., citrate and guar gum, slowed down precipitation. Nevertheless, these chemicals did not completely halt precipitation (**Figure 4**). In contrast to citrate and guar gum, several organics actually accelerated precipitation rates compared to controls (**Figure 3**). One of the most important of the organic components that enhanced precipitation is bitumen. Bitumen is native to the rock, abundant and is readily released into solution in presence of several common organic additives[22-25] and thus it is most likely an important molecule promoting barite scale precipitation in most systems. The ability of released bitumen to promote mineral precipitation has been previously shown in reference to bitumen-promoted oxidation of Fe released from pyrite in oil/gas shales[2, 26], in which the presence of bitumen resulted in Fe(III)-scaling under conditions where scale precipitation should have been minimal. Besides bitumen, another important group of additives to take into consideration are sulfate-bearing breakers such as ammonium persulfate. As shown in **Figure 5**, ammonium persulfate strongly scavenges any Ba in solution and rapidly forms a barite precipitate. This chemical alone illustrates the potential negative impact that ill-considered additives can have scale formulation. Because of the deleterious effect most additives have on Ba-scale mitigation, caution should be taken when a new fracture fluid formulation is being developed, especially if any of the additives contain significant quantities of sulfate.

Role of Inorganic Geochemical Parameters

In hydraulic fracturing systems, inorganic parameters (pH and I.S.) have a larger influence on the precipitation of barite than organics. When comparing pH and I.S. conditions that are present during injection and shut-in, one typically finds that pH of the system has a greater range than I.S (7-orders of magnitude for pH versus 3-orders of magnitude for I.S.). The initial 15% HCl acid slug that is universally used during the initial stage of injection will transiently drop the pH of the system locally to below pH = 0. Depending on the total amount of carbonate and its interaction with the acid slug, the extent and rate of acid neutralization can vary widely[2, 26, 27]. In systems where there is very low pH buffering capacity (Barnett Shale, portions of the Marcellus Shale, etc.), the overall solution pH in the fracture network can stay low for weeks, such as between pH 3 and 4, as shown in previous work[2, 26, 27]. As seen in **Figure 2**, such low pH conditions would result in a significant reduction in precipitation rate and potentially the overall quantity of precipitated barite. Conversely, in rocks with high pH buffering capacity, such as portions of the Eagle Ford shale, acid neutralization would be rapid (days) resulting in significant and rapid barite scale precipitation.

In stimulated shales systems, acidity is highest during the injection process and gradually decreases as the injected acid is neutralized by the dissolution of carbonate minerals contained in the shale. In contrast, as fracture fluid interacts with the shale, carbonates, pyrite, clays, feldspars, halite, and organic matter will dissolve, further increasing the I.S. of the solution. Unlike acidity, I.S. variability is inversely related to reaction time with the shale. Thus, depending on the rate of pH and I.S. increase in the system, a time window of maximum barite precipitation is likely to occur. The longer it takes for I.S. to increase to levels > 1M, the more barite can precipitate on fracture surfaces, in pores and pore necks, and piping.

Ba Precipitates

Under the vast majority of aqueous compositions, the most insoluble form of Ba is barite. Our thermodynamic modeling and corresponding experiments have shown that in every single scenario tested in which Ba precipitated, the form of precipitate was expected and observed to be barite (**Figure 6**). In all the reactors, regardless of the rate of precipitation, barite crystals precipitating directly from solution had a relatively narrow particle size range, 2.2 ± 0.3 μm. This particle size is large enough to completely block nano-pores, pore necks, and significant proportions of microfractures that are both natural to the rock and newly formed peripheral fracture regions. If such features are completely occluded, substantial reductions in porosity/permeability (primary and secondary) can occur. Another important consideration with respect to the average particle size of the precipitates is that these results suggest that the primary effect of the various chemical parameters (organics, pH, I.S.) is inhibition of nucleation of barite crystals and not poisoning of the crystal surface following nucleation. If crystal surface poisoning were a factor, then the range of particle sizes would be much greater. This observation suggests that if barite scale mitigation is to be optimized, it is important to control the initial nucleation of the barite crystals since it appears that no chemical additive has the ability to actually poison the crystal surface and limit the size of the particles.

Implications

In unconventional systems, depending on where barite precipitation occurs (e.g. piping, fracture surfaces, micro-fracture, pores, or pore necks), a significant reduction in porosity can occur resulting in loss of total production/recovery. Because microcracks and kerogen are often thought of as being the most important conduits for hydrocarbon movement out of the oil/gas shales[16, 28-34], any precipitation in these regions, along with precipitation in the shale matrix[2, 26], should have the potential to negatively impact the productivity of a well. With the high surface area and easy transmissivity of solution into microfractures versus the shale pores, the probability of substantial cementing of these natural fractures, and by extension peripheral fractures induced by injection, is high. Additionally, since it is shown that organics natural to the stimulated rock volume actually enhance precipitation (bitumen, acetate, aromatics), barite precipitation on the margins or within kerogen blebs is also a possibility. Substantial precipitation in either of these areas can be detrimental to production.

Our collective results suggest that organic molecules natural to the system or injected into the subsurface have either no impact on barite scale precipitation or may actually enhance precipitation. Thus far, only organics with high chelation ability, citrate and guar gum, have been shown to slow down scale formation. However, even these organics do not completely inhibit scale over longer time scales, such as those that occur during shut-ins. If organic additives to control Ba-scale are to be further explored, an alternative strategy required in order to optimize formulations.

We have also shown that the inorganic parameters in hydraulic fracturing systems have a stronger effect on Ba-scale formation than the organic components. Though it is possible to tailor a system via pH to reduce scale formation, due to the low pH conditions that would be required to inhibit barite precipitation, a litany of additional issues will occur. For example, by keeping solution pH ≤ 2, significant quantities of acid are required to overcome the pH buffering capacities of the rock. In regions with extremely high pH buffering capacity, such as portions of Eagle Ford with > 50 wt.% calcite, it may not be possible to keep the pH low enough to keep Ba-scale precipitation from occurring. Additionally, keeping a constant low pH is damaging to piping and casing of the wells which has the potential to cause significant infrastructure problems to a stimulated well. Besides maintaining a low pH, high I.S. could be used to combat Ba-scale precipitation. In a typical stimulation scenario using fresh water, I.S. is initially at levels below those which would inhibit barite formation. Through the course of shut-in and production, I.S. is expected to increase to high levels (generally between 1-3 M)[20, 35-37]. In general, high I.S. will naturally inhibit barite scale formation. Yet the rate of precipitation appears to be significantly faster than the increase in I.S. This implies that before I.S. levels have increased to levels that would stop precipitation, the precipitation is already finalized. As noted earlier, our thermodynamic modeling and laboratory experiments have both shown that high I.S. will solubilize some of the barite, but regretfully, only about 10% of the precipitate barite will be dissolved back into solution, which has the potential to precipitate elsewhere in the system when I.S. lowers, temperature lowers, or pH increases. Another important factor to consider in trying to control the barite scale with high I.S. is that if levels of salinity are too high other mineral precipitates such as gypsum and halite may start precipitating.

Barite scale precipitation is a known problem in both conventional and unconventional oil/gas systems. Due to the short contact time in conventional systems between piping and highly saline produced water, producers appear to have developed effective mitigation strategies in all but the most saline environments (off-shore). Unconventional systems though are significantly more complex due to the injection of chemicals into the formation, highly variable and changing pH, high I.S., chemical alteration of the formation rock, and significantly longer reaction times. With regards to barite scale, our present work shows that most chemical mitigation strategies may be insufficient to deal with scale build-up. To make matters worse some additives (*i.e.* sulfate-based breakers) can exacerbate the problem through rapid precipitation where nearly all the available Ba is precipitated. New strategies are therefore required to combat Ba-scale in unconventional systems in order enhance productivity and recoveries.

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References:

1. Krauskopf, K. B.; Bird, D. K., *Introduction To Geochemistry*. 3rd ed.; WCB/McGraw-Hill: **1995**.
2. Jew, A. D.; Dustin, M. K.; Harrison, A. L.; Joe-Wong, C. M.; Thomas, D. L.; Maher, K.; Brown, G. E., Jr.; Bargar, J. R., Impact of Organics and Carbonates on the Oxidation and Precipitation of Iron during Hydraulic Fracturing of Shale. *Energy & Fuels* **2017,** 31, 3643-3658.
3. Liu, Y.; Kan, A.; Zhang, Z.; Yan, C.; Yan, F.; Zhang, F.; Bhandari, N.; Dai, Z.; Ruan, G.; Wang, L.; Greenberg, J.; Tomson, M., An assay method to determine mineral scale inhibitor efficiency in produced water. *Journal of Petroleum Science and Engineering* **2016,** 143, 103-112.
4. Yan, F.; Dai, Z.; Ruan, G.; Alsaiari, H.; Bhandari, N.; Zhang, F.; Liu, Y.; Zhang, Z.; Kan, A.; Tomson, M., Barite scale formation and inhibition in laminar and turbulent flow: A rotating cylinder approach. *Journal of Petroleum Science and Engineering* **2017,** 149, 183-192.
5. Bhandari, N.; Kan, A. T.; Dai, Z.; Zhang, F.; Yan, F.; Ruan, G. G.; Alsaiari, H. A.; Zhang, Z.; Liu, Y.; Deng, G.; Tomson, M. B., Effect of Hydrodynamic Pressure on Mineral Precipitation Kinetics and Scaling Risk at HPHT. In *SPE International Oilfield Scale Conference*, Society of Petroleum Engineers: Aberdeen, Scotland, UK, **2016**; p 12.
6. Zhang, F.; Dai, Z.; Yan, C.; Bhandari, N.; Yan, F.; Liu, Y.; Zhang, Z.; Ruan, G.; Kan, A. T.; Tomson, M. B., Barite-Scaling Risk and Inhibition at High Temperature. *SPE Journal* **2017**, 69-79.
7. Shen, D.; Fu, G.; Al-Saiari, H.; Kan, A. T.; Tomson, M. B., Barite Dissolution/Precipitation Kinetics in Porous Media and in the Presence and Absence of a Common Scal Inhibitor. *SPE Journal* **2009**, (462-471).
8. Jones, F.; Piana, S.; Gale, J. D., Understanding the Kinetics of Barium Sulfate Precipitation from Water and Water-Methanol Solutions. *Crystal Growth & Design* **2008,** 8, (3), 817-822.
9. Dai, C.; Stack, A. G.; Koishi, A.; Fernandes-Martinez, A.; Lee, S. S.; Hu, Y., Heterogeneous Nucleation and Growth of Barium Sulfate at Organic-Water Interfaces: Interplay between Surface Hydrophobicity and Ba^{2+} Adsorption. *Langmuir* **2016,** 32, 5277-5284.
10. Antonious, M. S., Effect of Additives on the Crystallization of Barium Sulphate. *Phosporus, Sulfur, and Silicon and the Related Elements* **1996,** 112, (1-4), 235-245.
11. Yan, F.; Zhang, F.; Bhandari, N.; Wang, L.; Dai, Z.; Zhang, Z.; Liu, Y.; Ruan, G.; Kan, A.; Tomson, M., Adsorption and Precipitation of Scale Inhibitors on Shale Formations. *Journal of Petroleum Science and Engineering* **2015,** 136, 32-40.
12. Zhang, F.; Dai, Z.; Yan, F.; Ruan, G.; Bhandari, N.; Zhang, Z.; Liu, Y.; Kan, A. T.; Tomson, M. B., Acid/base and metal complex solution chemistry of sulfonated polyacrylate copolymer versus temperature and ionic strength. *Applied Geochemistry* **2017,** 76, 1-8.
13. Akob, D. M.; Cozzarelli, I. M.; Dunlap, D. S.; Rowan, E. L.; Lorah, M. M., Organic and Inorganic Composition and Microbiology of Produced Waters from Pennsylvania Shale Gas Wells. *Applied Geochemistry* **2015,** 60, 116-125.
14. Phan, T. T.; Capo, R. C.; Stewart, B. W.; Graney, J. R.; Johnson, J. D.; Sharma, S.; Toro, J., Trace metal distribution and mobility in drill cuttings and produced waters from Marcellus Shale gas extraction: Uranium, arsenic, barium. *Applied Geochemistry* **2015,** 60, 89-103.
15. Gustafsson, J. P. *Visual MINTEQ*, 2.61; **2009**.
16. Hammack, R. W.; Harbert, W.; Sharma, S.; Stewart, B. W.; Capo, R. C.; Wall, A. J.; Wells, A.; Diehl, R.; Blaushild, D.; Sams, J.; Veloski, G. *An Evaluation of Fracture Growth and Gas/Fluid Migration as Horizontal Marcellus Shale Gas Wells are Hydraulically Fractured in Greene County, Pennsylvania*; National Energy Technology Laboratory: Pittsburgh, **2014**; p 76.
17. Materials Data, Inc. *Jade XRD Pattern Processing Ver. 6.5*, **2002**.

18. Haluszczak, L. O.; Rose, A. W.; Kump, L. R., Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry* **2013,** 28, 55-61.
19. Lester, Y.; Ferrer, I.; Thurman, E. M.; Sitterley, K.; Korak, J. A.; Aiken, G.; Linden, K. G., Characterization of Hydraulic Fracturing flowback Water in Colorado: Implications for Water Treatment. *Science of the Total Environment* **2015,** 512-513, 637-644.
20. Zolfaghari, A.; Dehghanpour, H.; Noel, M.; Bearinger, D., Laboratory and Field Analysis of Flowback Water from Gas Shales. *Journal of Unconventional Oil and Gas Resources* **2016,** 14, 113-127.
21. Ground Water Protection Council; Interstate Oil & Gas Compact Commission. FracFocus Chemical Disclosure Registry.
22. Loeber, L.; Muller, G.; Morel, J.; Sutton, O., Bitumen in Colloid Science: A Chemical, Structural and Rheological Approach. *Fuel* **1998,** 77, (13), 1443-1450.
23. Redelius, P.; Soenen, H., Relation Between Bitumen Chemistry and Performance. *Fuel* **2015,** 140, 34-43.
24. Redelius, P. G., Solubility Parameters and Bitumen. *Fuel* **2000,** 79, 27-35.
25. Traxler, R. N., The Physical Chemistry of Asphaltic Bitumen. *Chemical Reviews* **1936,** 19, (2), 119-143.
26. Jew, A. D.; Harrison, A. L.; Dustin, M. K.; Joe-Wong, C. M.; Thomas, D. L.; Maher, K.; Brown, G. E.; Cercone, D.; Bargar, J., Mineralogical and Porosity Alteration Following Fracture Fluid-Shale Reaction. In *URTeC*, Austin, TX, **2017**.
27. Harrison, A. L.; Jew, A. D.; Dustin, M. K.; Thomas, D. L.; Joe-Wong, C. M.; Bargar, J. R.; Maher, K.; Brown, G. E., Jr., Element release and reaction-induced porosity alteration during shale-hydraulic fracturing fluid interaction. *Applied Geochemistry* **2017,** 82, 47-62.
28. Agrawal, S.; Sharma, M. M., Practical Insights into Liquid Loading Within Hydraulic Fractures and Potential Unconventional Gas Reservoir Optimization Strategies. *Journal of Unconventional Oil and Gas Resources* **2015,** 11, 60-74.
29. Bose, C. C.; Fairchild, B.; Jones, T.; Gul, A.; Ghahfarokhi, R. B., Application of Nanoproppants for Fracture Conductivity Improvement by Reducing Fluid Loss and Packing of Micro-fractures. *Journal of Natural Gas Science and Engineering* **2015,** 27, 424-431.
30. Davies, R. J.; Mathias, S. A.; Moss, J.; Hustoft, S.; Newport, L., Hydraulic Fractures: How Far Can They Go? *Marine and Petroleum Geology* **2012,** 37, 1-6.
31. Gale, J. F. W.; Laubach, S. E.; Olson, J. E.; Eichhubl, P.; Fall, A., Natural Fractures in Shale: A Review and New Observations. *AAPG Bulletin* **2014,** 98, (11), 2165-2216.
32. Gale, J. F. W.; Reed, R. M.; Holder, J., Natural Fractures in the Barnett Shale and Their Importance for Hydraulic Fracture Treatments. *AAPG Bulletin* **2007,** 91, (4), 603-622.
33. Karra, S.; Makedonska, N.; Viswanathan, H. S.; Painter, S. L.; Hyman, J. D., Effect of Advective Flow in Fractures and Matrix Diffusion on Natural Gas Production. *Water Resources Research* **2015,** 51, 8646-8657.
34. Wilkins, S.; Mount, V.; Mahon, K.; Perry, A.; Koenig, J., Characterization and Development of Subsurface Fractures Observed in the Marcellus Formation, Appalachian Plateau, North-Central Pennsylvania. *AAPG Bulletin* **2014,** 98, (11), 2301-2345.
35. Abualfaraj, N.; Gurian, P. L.; Olson, M. S., Characterization of Marcellus Shale Flowback Water. *Environmental Engineering Science* **2014,** 31, (9), 514-524.
36. Bai, B.; Carlson, K.; Prior, A.; Douglas, C., Sources of Variability in Flowback and Produced Water Volumes from Shale Oil and Gas Wells. *Journal of Unconventional Oil and Gas Resources* **2015,** 12, 1-5.
37. Balashov, V. N.; Engelder, T.; Gu, X.; Fantle, M. S.; Brantley, S. L., A Model Describing Flowback Chemistry Changes with Time After Marcellus Shale Hydraulic Fracturing. *AAPG Bulletin* **2015,** 99, (1), 143-154.

Table 1: List of organic and inorganic parameters tested in this study. Concentrations of organics used similar to those used during injection in the field or detected in formation/produced waters[18-21, 35, 36].

Chemical	Use
Acetate	Natural
Citric Acid	Natural, Iron Control
Bitumen	Natural
Kerosene	Friction Reducer
Ethylene Glycol	Winterizing agent, anti-scaling
Polyethylene glycol	Biocide
2-ethyl-1-hexanol	Corrosion inhibitor
Guar Gum	Gellant
Methanol	Corrosion Inhibitor
Glutaraldehyde	Biocide
Ammonium Persulfate	Breaker
Malonate	Produced water
n-alkane	Produced water
Cyclohexane (benzene)	Produced water

Inorganic Parameters
pH 2
pH 3
pH 4
pH 5
pH 6
pH 7
I.S. 0.6 mM
I.S. 0.01 M
I.S. 0.11 M
I.S. 0.99 M
I.S. 2.26 M

Table 2: Measured final Ba concentrations in reactors with corresponding Saturation Index. Theoretical total added Ba is equivalent to 13733 ppb.

pH	Measured Ba Conc. (ppb)	Saturation Index
2	9608 ± 905	-0.02
3	2868 ± 223	-0.16
4	1870 ± 142	-0.24
5	564 ± 25	-0.75
6	586 ± 30	-0.73
7	566 ± 20	-0.75

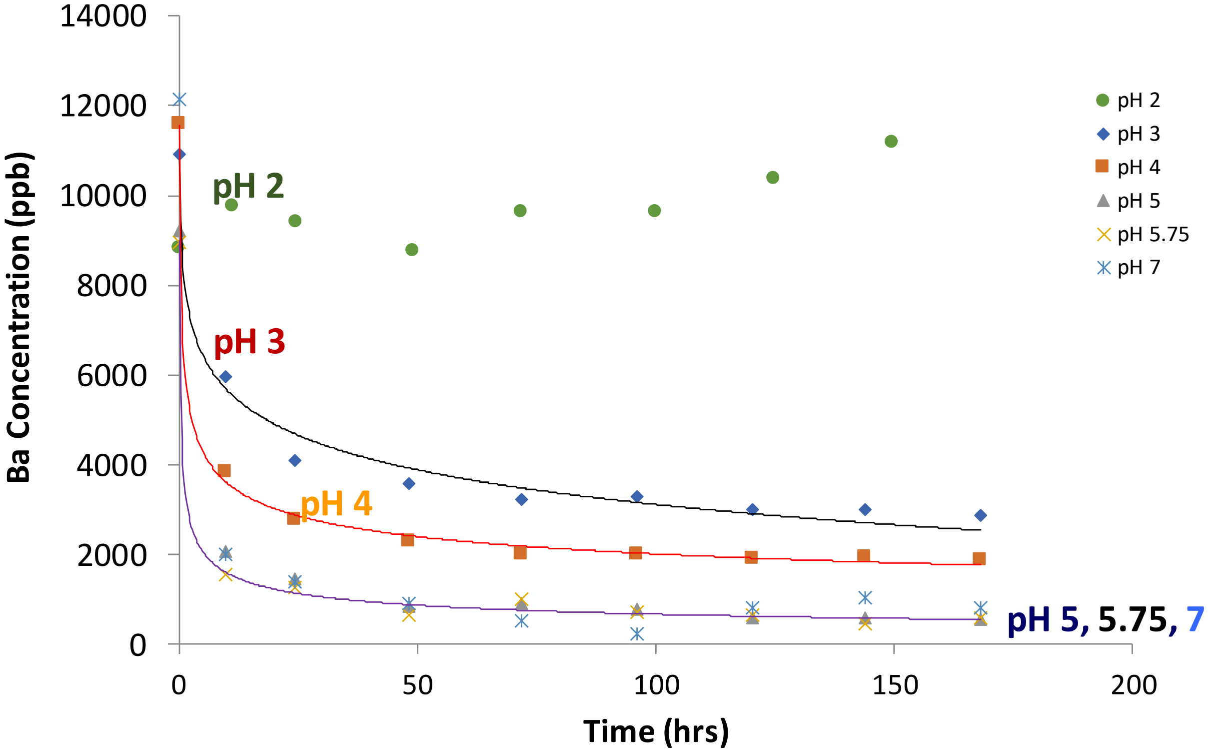

Figure 1: Effect of pH on Ba precipitation at 80°C. Ionic strength is primarily due to pH of the system. Measurement error for triplicate measurements was ≤ 8%. Plotted curves are logarithmic fits of the experimental data.

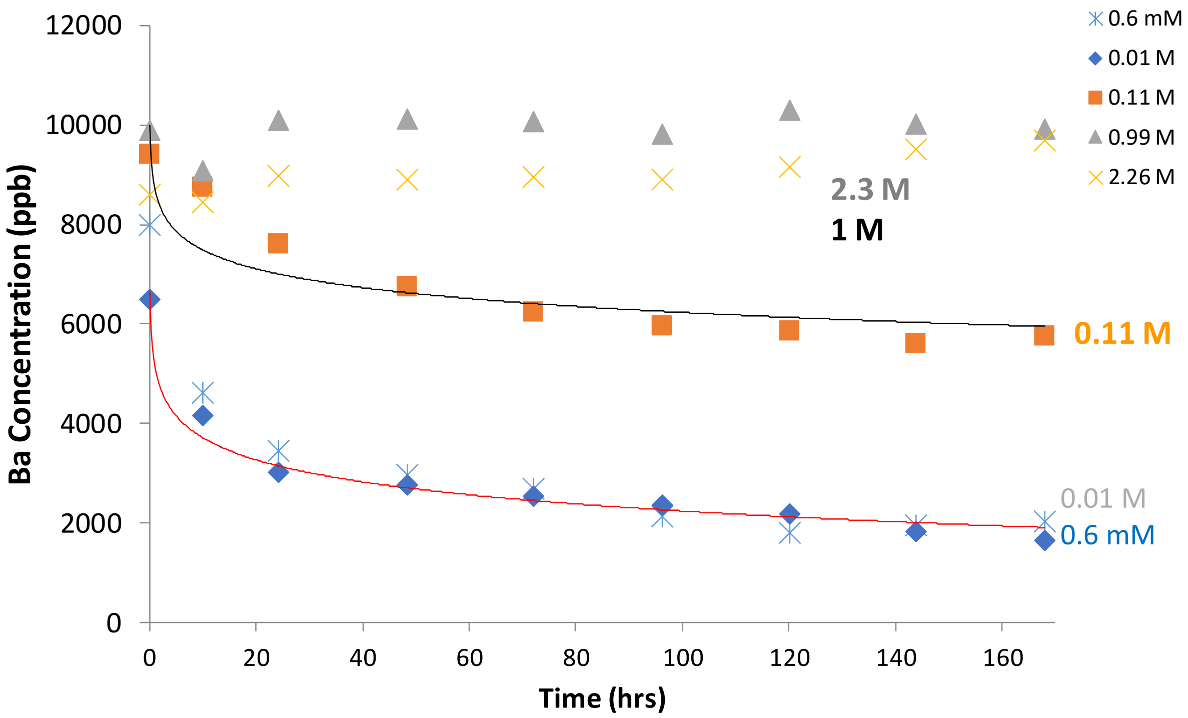

Figure 2: Effect of various ionic strengths on the precipitation of Ba. All experiments were conducted at pH = 7 and 80°C. Measurement error for triplicate measurements was ≤ 9%. Plotted curves are logarithmic fits of the experimental data.

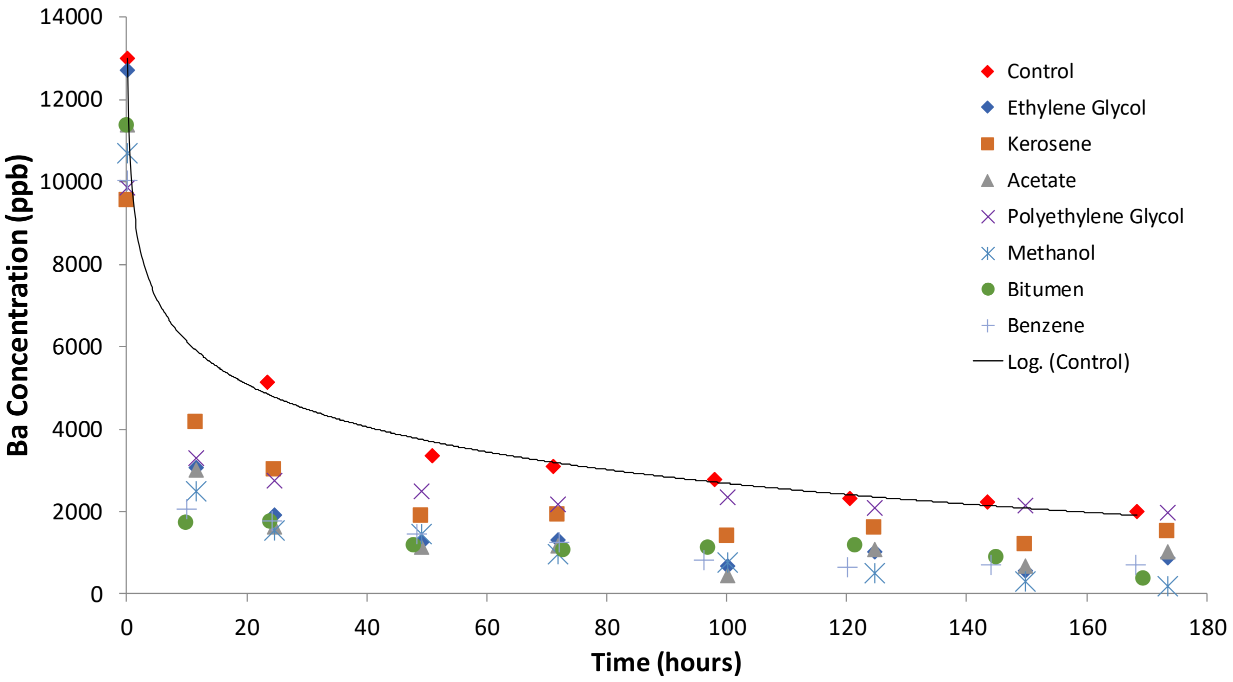

Figure 3: Barium precipitation in the presence of select organics at pH = 7 and 80°C. **Control** experiment consisted solely of added $BaCl_2$ and Na_2SO_4, no organics were added. Measurement error for triplicates was ≤ 10%. Plotted curves are logarithmic fits of the experimental data.

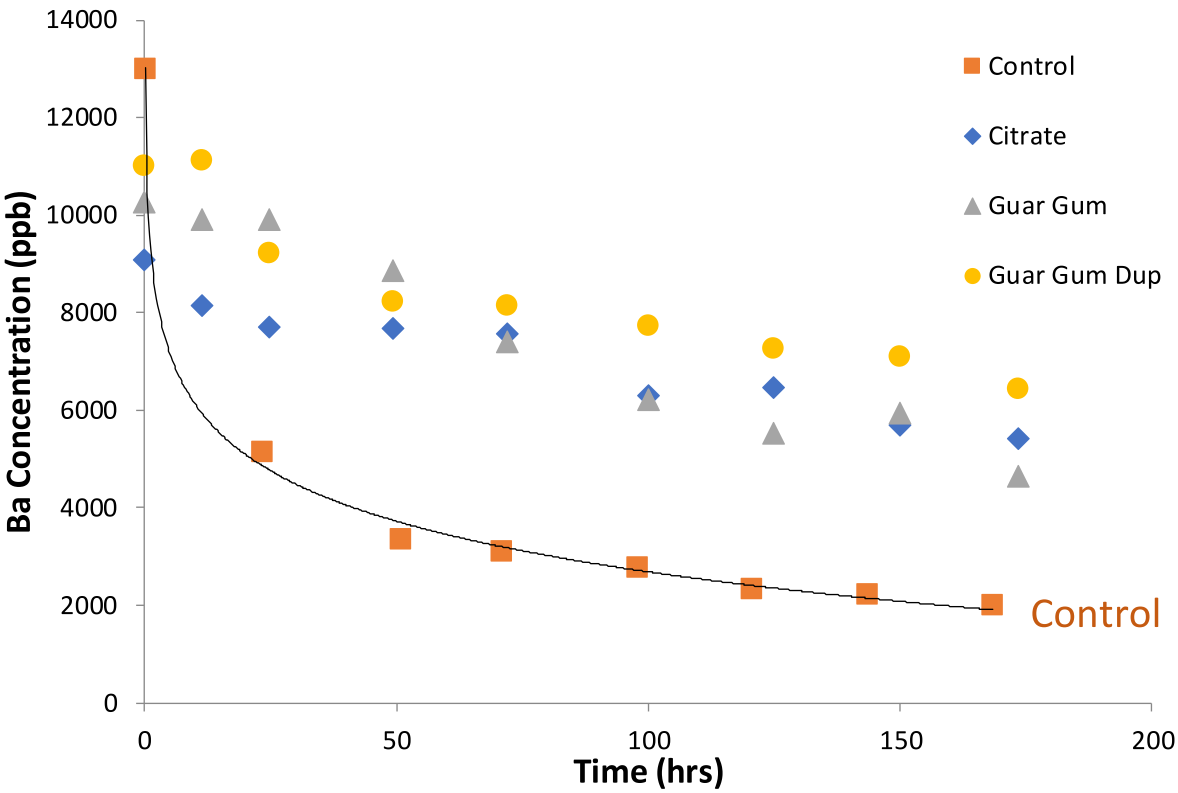

Figure 4: Barium precipitation in the presence of organics with high chelating potential at pH = 7 and 80°C. **Control** experiment consisted solely of added $BaCl_2$ and Na_2SO_4, no organics were added. Measurement error for triplicates was ≤ 10%. Plotted curves are logarithmic fits of the experimental data.

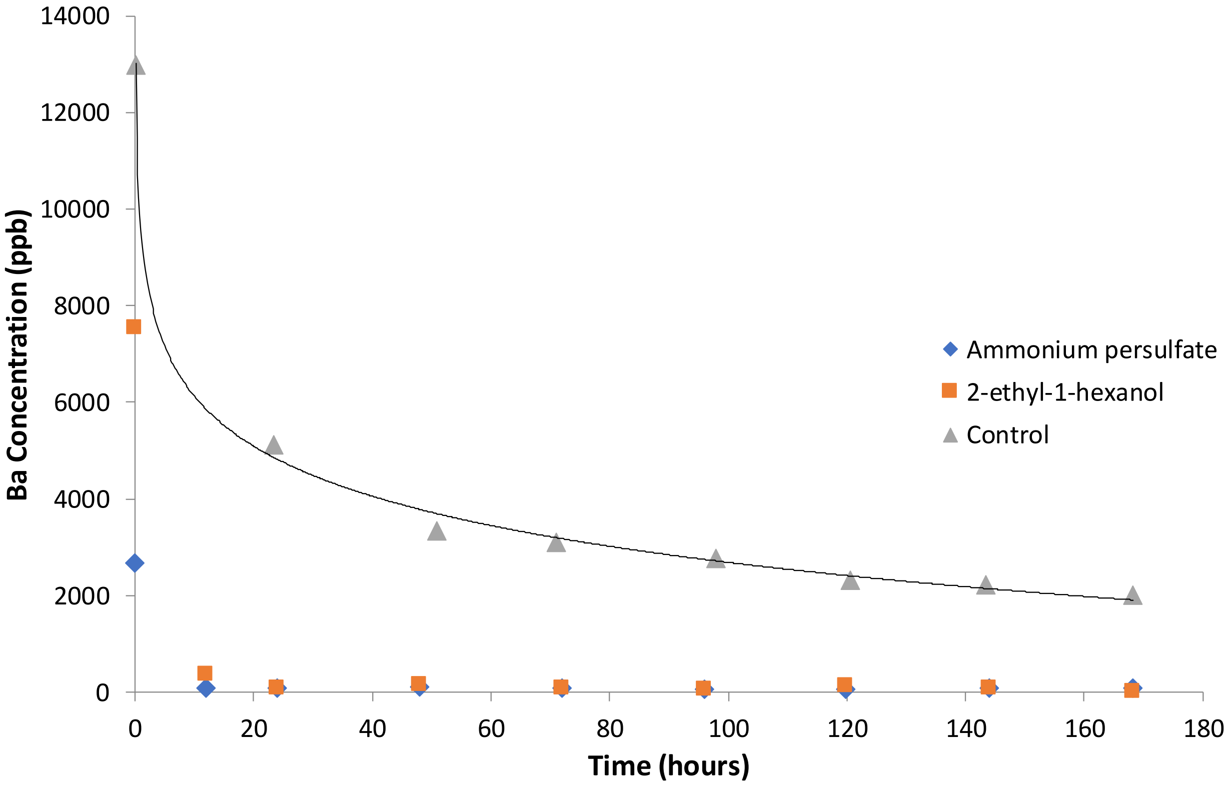

Figure 5: Barium precipitation in the presence of ammonium persulfate and 2-ethyl-1-hexanol at pH = 7 and 80^{o}C. **Control** experiment consisted solely of added $BaCl_2$ and Na_2SO_4, no organics were added. Measurement error for triplicates was ≤ 5%. Plotted curves are logarithmic fits of the experimental data.

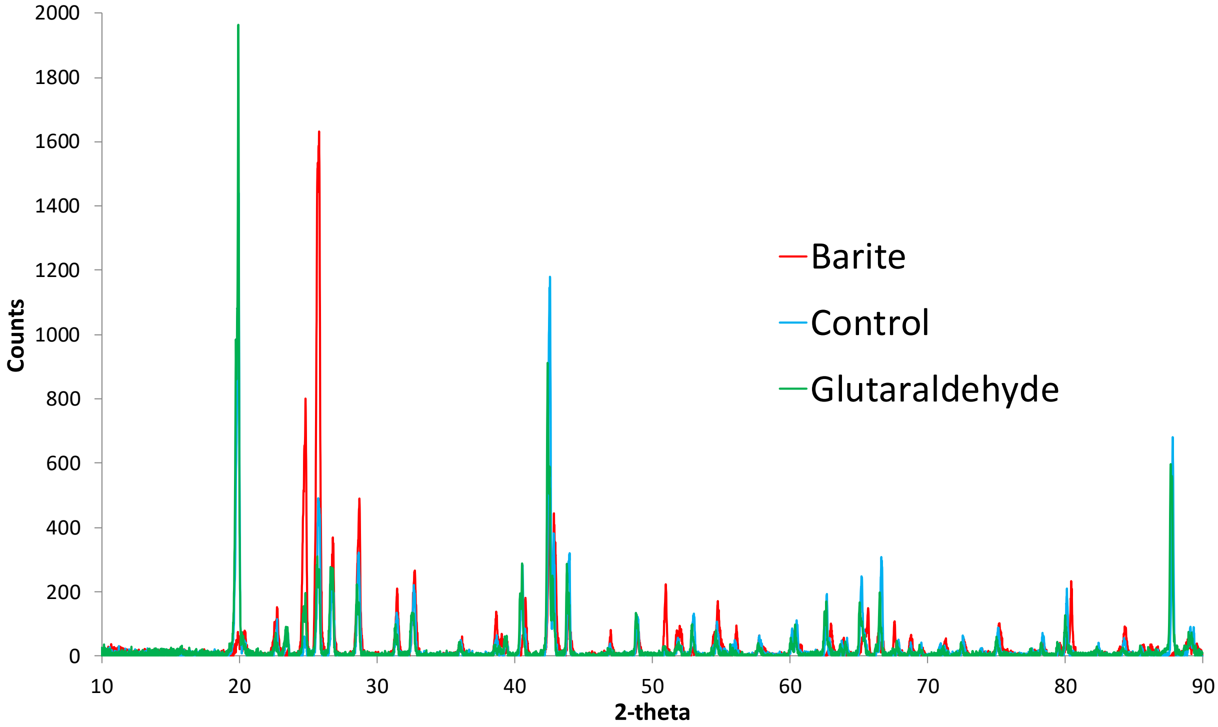

Figure 6: XRD diffractograms of three samples: Ground natural barite, Ba precipitates from Control experiment, and Ba precipitates from experiment containing glutaraldehyde. High consistency in peak positions between all three samples indicate that barite is the only solid phase precipitating.