The Pot of Gold at the End of the Rainbow:
The Chemistry of Shale Gas Fracturing and FLowback Systems

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Water treatment for shale gas fracturing (aka fracking) affords an enormous opportunity for the sale of the scale inhibitors that AWT member companies apply on a daily basis. The chemistry involved, however, can be extremely different than is typical for related water treatment fields such as cooling water, and even traditional oil and gas field brine treatment in vertical production wells.

Fracturing operations use a combination of hydraulic pressure, and mechanical force, to break up formation shale and release natural gas. The chemistry involved gamuts the extremes of water treatment. Down hole, many formations are a natural zeolite, and exchange “safe” ions with low solubility Barium and Strontium ions as the fracturing “fluid” is pumped down hole. The brine chemistry can be counter-intuitive for a traditional water treatment chemist involved with typical low to moderate ionic strength water. The extreme TDS involved in many flowback systems can actually depress scale potential. As the water is diluted, activity rises increasing scale potential at a rate faster than the decrease in scale potential effected by ion dilution. So dilution can actually create a scale problem in a flowback operation. Extreme iron levels are present in many cases, deactivating and rendering useless many common scale inhibitors. The reducing environment of any formation water present also contrasts the chemistry of the aerated surface water used by oil field chemists for dilution. Traditional waste treatment comes into play in the modeling the chemistry of ponds used for the recycle water used for fracking.

This paper discusses the water treatment opportunities presented by flowback systems, describes the chemistry of scale prediction and control under extreme conditions, and outlines some of the treatment philosophies used to minimize the impact of scale and suspended solids on gas production.

FRACKING 101

Natural gas and other petroleum products can be entrapped in shale layers. Traditional well drilling and production methods cannot release the natural gas.

Hydraulic fracturing, or fracking, allows natural gas and some petroleum products to be extracted from underground shale formations. As the initial well is drilled, mud is used to cool, stabilize, and bring fragments to the surface. Steel surface casing is set into the well with cement sealing to protect the aquifer ground water and prevent gas from escaping as it is brought to the surface (Figures 1, 2, 3).

In traditional oil and gas production, wells are drilled vertically into a reservoir that can be thousands of feet below the surface. In shale gas production, vertical wells are drilled and cased to the level of gas containing shale formation. The shaft drilling then proceeds horizontally through the shale formation (Figure 4).

Angled drilling is used to create a horizontal path. The sealed horizontal well tube is perforated to allow access to the shale and create an area for natural gas to flow (Figure 4). Sand, water, and chemicals are forced through to fracture the shale (Figure 5). The water is removed and brought back to the surface leaving sand behind to hold the perforations open. The flowback water goes into ponds to allow suspended solid precipitates to settle and super saturated mineral scales to move toward equilibrium. Downhole, iron and other metals may be in a reduced state (ferrous). Oxidation to ferric hastens removal by settling in the ponds.

This sophisticated drilling process takes a few months to create a well which can produce for decades if porosity is maintained.

Figures 1 – 5 outline the shale gas drilling procedure. Figure 6 depicts the process from the perspective of a water treater. Many resources are available online describing the process.[1]

Water Treatment Challenges

Flowback systems are subject to classical water treatment problems such as scale, corrosion, and microbial slime. They throw a few curve balls to the traditional water treatment specialist in the form of extreme TDS, extreme iron levels, and being subject to alternating reducing and oxidizing environments. Corrosion of well casings is not solely an economic problem. Pitting attack in well casings as they pass through aquifers, can lead to drinking water contamination.

MINERAL SCALE

Typical scale problems include traditional oil field scales such as calcium carbonate, barium sulfate and calcium sulfate. The use of waste water streams such as paper mill grey water, other reuse waters, can lead to unusual scales for oil and gas wells such as calcium phosphates and calcium oxalate. Iron is a major problem. Selection of water sources for the fracturing fluid, mixtures, and storage in settling ponds has a major impact upon the chemistry of the hydraulic fracturing and flowback reuse process.

Mxing Flowback with Dilution Water (Is dilution the solution?)

Many in the industry believe that “dilution is the solution “ to preventing scale in shale gas fracturing operation. If the flowback system is operated with brines of a total dissolved solids lower than seawater, this would be expected to be the case. Dilution with lower concentrations of scale forming species would be expected to reduce scale potetntial, possibly reducing or eliminating the need for scale inhibihotrs. When flowback waters pick up significant concentrations of scale forming species from the formation this is not necessarily the case. The same may be the case with extreme T.D.S. brines. In the first case, the use of a high T.D.S. brine may reduce the exchange of scale forming species such as barium, into the flowback. In the case of the extreme T.D.S. flowback, dilution can actually create a scale problem, as outlined in the next section.

Dilution water quality can be expected to decrease as regulations governing the use of fresh water become more stringent. Reuse water, industrial waste water, and mining discharge waters can be expected to be used for frac fluids and dilution in the future where higher quality waters are now in use..

Impact of Formation on Fracturing Fluid

Fracturing water dissolves minerals and in some cases exchanges ions such as Barium from the zeolite like formations. Barium levels and TDS can rise with time during the fracturing process (Figures 7, 8, 9). A summary of chemistry versus time is also included in government regulatory reports such as the study sponsored by the New York Independent Oil and Gas Association, which documents the same trends.(9) Similar trends have been observed in flowback water chemistry form the major shale gas formations through personal communication with our clients.

Typically, the flowback water concentrations, and in many cases scale potential, will rise with time through fracking. Flowback waters can reach extreme T.D.S. where ion activity is negligible. In some cases, barium and sulfate levels can reach a level where scale would be expected except under low to moderate ionic strength. The high ionic strength, however, reduces ion activity to an almost negligible level, resulting in an under-saturated solution. Dilution of these waters has been observed to create a scale problem as activity rises at a faster rate than the dilution decreases ion concentration. The net result is an initial increase in scale potential with dilution. Even diluting with deionized water could create a scale problem in these unusual waters.(2) The use of phosphate containing waters (such as sewage plant effluent, municipal waters) for dilution can also create an atypical phosphate scale downhole. Other waste waters, such as paper mill and sugar processing effluents, can create an oxalate scale problem. (3)

Iron levels can reach concentrations well in excess of 100 mg/L. Concentrations in excess of 1,000 mg/L have been reported. In reducing environments, the iron may stay in the ferrous state. Oxidation, and aeration in the ponds, oxidizes iron to the ferric state creating a suspended solids problem. Ferric forms will, ideally, precipitate in the settling/storage ponds.

Dilution waters can come from many sources including fresh waters such as lakes or rivers, reuse waters from industrial processes such as paper mills, and other sources which otherwise might be disposed of by deep well injection. Some fracturing operations work under the assumptions that “dilution is the solution.” Others prefer high TDS brines as dilution water to minimize exchange with the formation. Regardless, modeling is typically used to predict the properties of the blended flowback water and minimize the scale potential when injected downhole. [4]

Iron can have a major impact upon scale inhibitors. Many inhibitors are inactivated by iron, and can adsorb onto precipitating iron. Traditional phosphonates may be removed or inactivated by the iron. Polymers and copolymers can also be inactivated by the high iron levels.

SCALE PREDICTION AND CONTROL

Scale prediction at extreme TDS requires more rigorous calculations than those incorporated into simple indices[5] and rules of thumb.[6] Inhibitors used include the higher phosphonates such as DTMP,[7] copolymers, and other traditional inhibitors. Iron tolerance can be key in flowback treatment indicating the use of copolymers and above.

Fracturing fluids can reach total dissolved solids levels in excess of 300,000 mg/L. At these levels simple indices such as the Langelier Saturation Index (L.S.I.), similar simple indices for other scales such as barium sulfate and calcium sulfate, and rules of thumb, have no meaning, and can be misleading. Several major companies have used the L.S.I. as a reference for adding acid for pH adjustment to control calcium carbonate. At the high ionic strengths, indices based upon:

a) ion association models, to calculate the most likely free ion concentrations, and

b) activity coefficients such as Helgeson’s B-dot, Pitzer, or Uniquac estimations;

should be used to provide reasonable accuracy at the high ionic strengths involved. [2]

BIOCONTROL

Microorganisms in flowback systems present a threat to the casings. Microbial slime and deposits can create concentration cell effects and pitting attack. Slime and deposits can also harbor anaerobic corrosive bacteria. Loss of well casing integrity can result in contamination of aquifers through which the pipe passes, and environmental difficulties. Glutaraldehyde and chlorine dioxide are typical biocontrol agents.

SUMMARY

Shale gas fracturing has been heralded as a major energy source for now and in the future. Water treatment is critical to the water reuse process known as flowback. The process involves problems similar to those handled routinely by AWT member companies in cooling water, waste water, and pretreatment applications. Differences include:

The potential for extreme total dissolved solids;
Operation in both oxidizing and reducing environments;
Extreme iron levels;
Scales such as barium sulfate and calcium sulfate;
The use of blended waters.

Application of techniques for scale prediction and control at high T.D.S., and an understanding of barium sulfate, calcium sulfate and iron control, should be considered prior to a water treatment company undertaking the evaluation and treatment of problems in a shale gas flowback system.

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2) Ferguson, R.J.,*Mineral Scale Prediction and Control at Extreme TDS*, Paper No. IWC-11-77, *International Water Conference.*
3) *Ferguson, R.J., Predicting Calcium Oxalate Scale, National Association of Corrosion Engineers,Ppaer No. 02-239, 2002.*
4) Ferguson, R.J., *Predicting Properties of Blended Waters, Association of Water Technologies, 2010.*
5) *Ferguson, R.J., The Kinetics of Cooling Water Scale Formation and Control*, Association of Water Technologies, 2011.
6) Ferguson, R.J., *Water Treatment Rules of Thumb: Myths or Useful Tools,* Association of WaterTechnologies, 2004
7) diethylenetriamine penta(methylene phosphonic acid)
8) Baluch, M.E., Myers, R.R, Lipinski, B.A. and N.A. Houston, “Marcellus Shale Post-Frac Flowback Waters – Where is All the Salt Coming From and What are the Implications,” SPE Paper No. 125740, Easter Regional Meeting, 2009.
9) ALL Consulting , “NY DEC SGEIS Information Requests and Industry Responses,” Independent Oil & Gas Association of New York, 2010.

Figure 1: Aquifer and Gas Containing Shale Layer

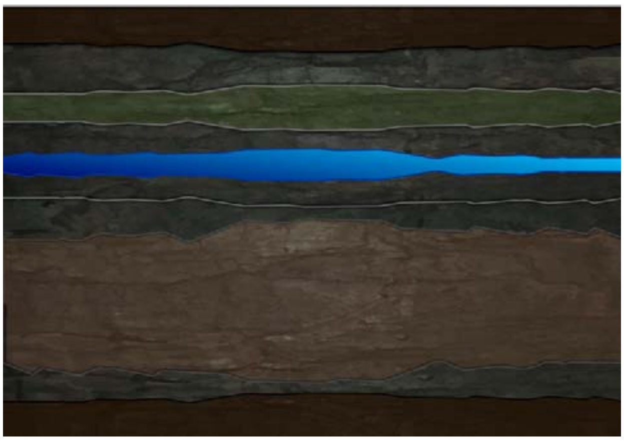


Figure 2: Drilling from the Surface

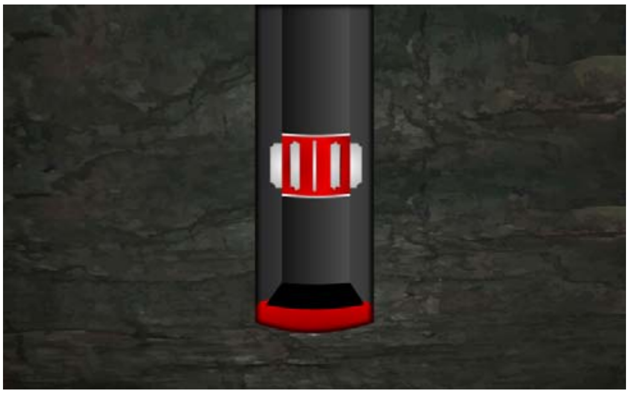


Figure 3: Casings Protect the Environment

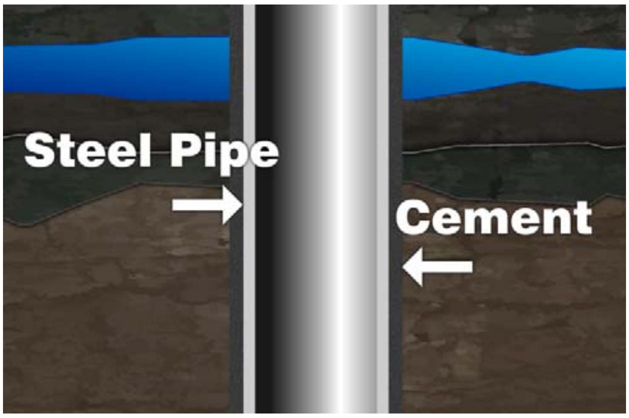


Figure 4: Wells Drilled Vertically To Shale Layer, Then Angled Drilling and Horizontal Shaft Creation

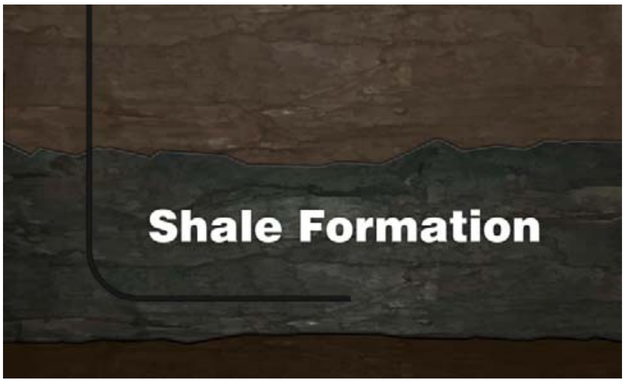
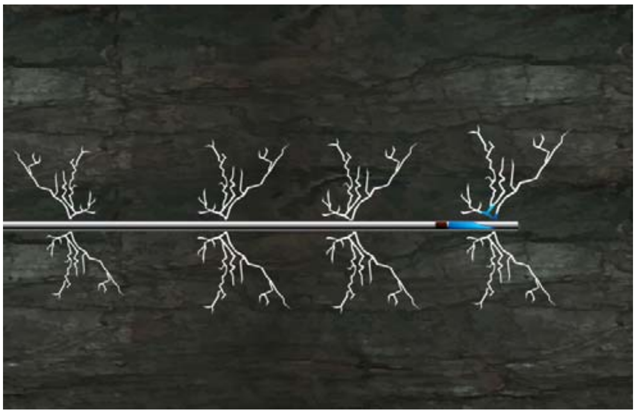


Figure 5: Fracturing Fluid Pumped Downhole Under Pressure Fractures Shale, Releasing Gas



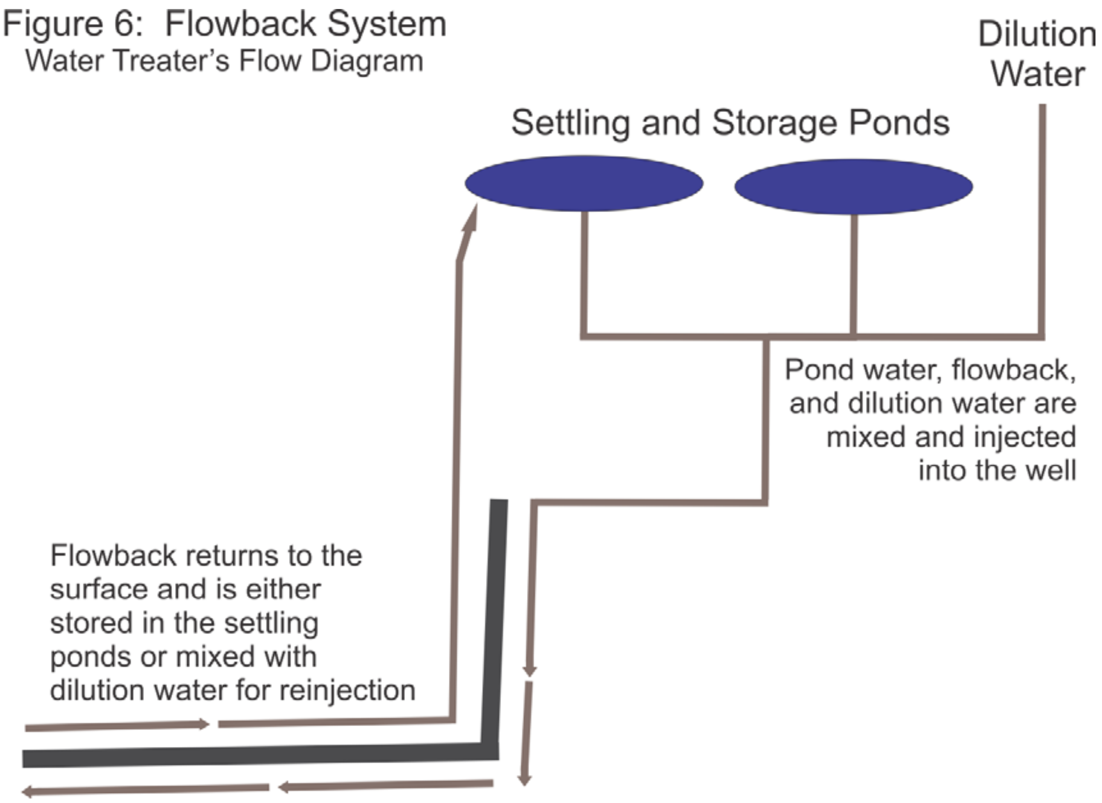


Figure 6: Flowback System
Water Treater's Flow Diagram
Dilution Water
Settling and Storage Ponds
Pond water, flowback, and dilution water are mixed and injected into the well
Flowback returns to the surface and is either stored in the settling ponds or mixed with dilution water for reinjection

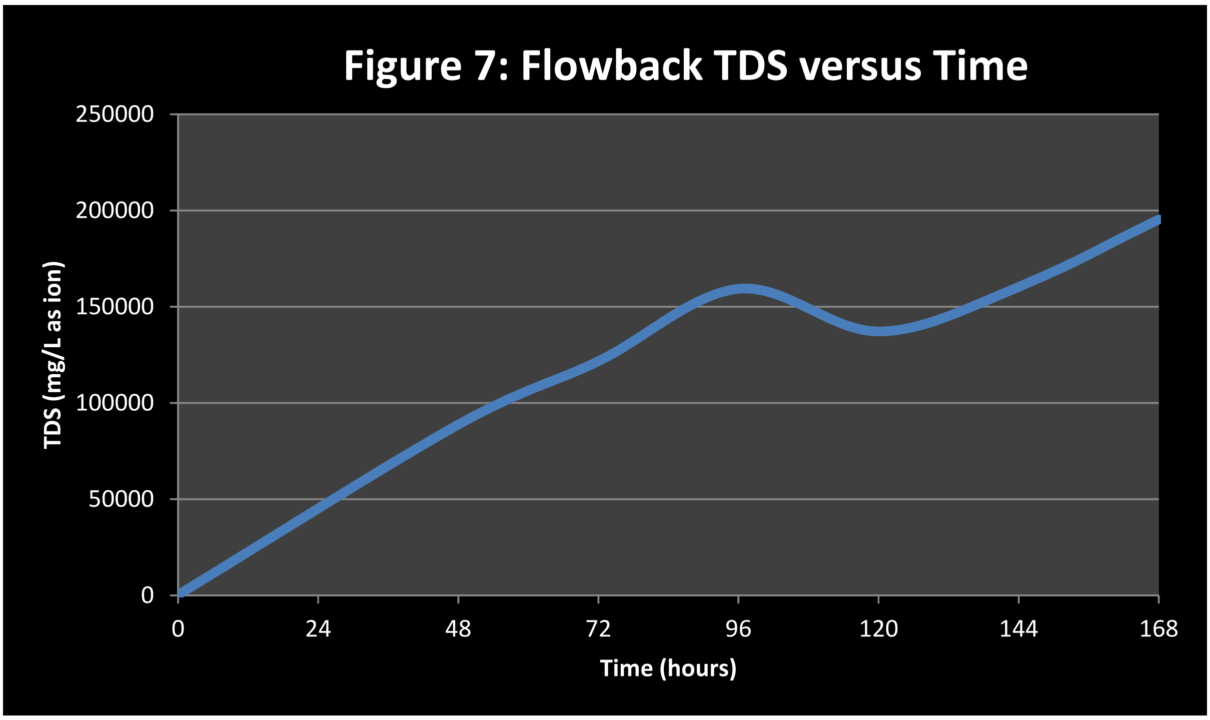


Figure 7: Flowback TDS versus Time
TDS (mg/L as ion)
250000
200000
150000
100000
50000
0
0
24
48
72
96
120
144
168
Time (hours)

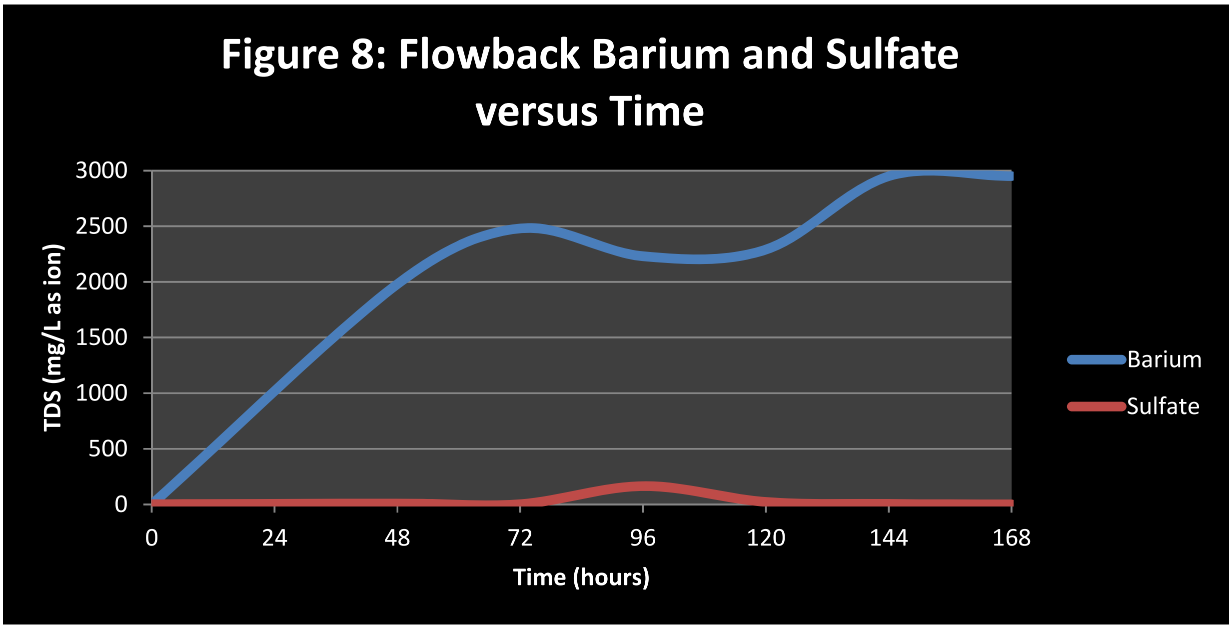


Figure 8: Flowback Barium and Sulfate versus Time
TDS (mg/L as ion)
3000
2500
2000
1500
1000
500
0
0
24
48
72
96
120
144
168
Time (hours)
Barium
Sulfate

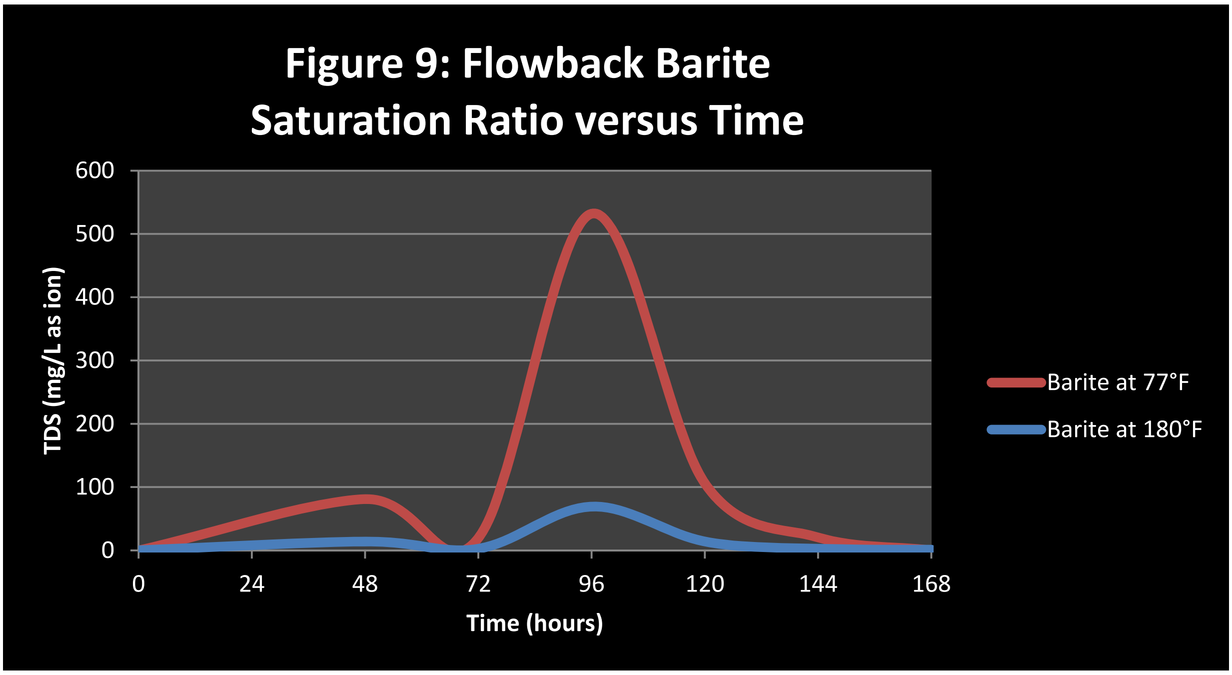


Figure 9: Flowback Barite Saturation Ratio versus Time
TDS (mg/L as ion)
600
500
400
300
200
100
0
0
24
48
72
96
120
144
168
Time (hours)
Barite at 77°F
Barite at 180°F