Workshop 4, Theme 2, Session 3
A Water Chemistry Perspective on Flowback Reuse with Several Case Studies

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TALISMAN ENERGY

Frac Flowback Reuse/Disposal – Early Shale Work

In the beginning, near fresh quality water was the standard for frac fluid preparation and flowback was disposed in deep wells. Deep well disposal is widely practiced. Approximately 3 billion cubic meters are injected in the USA annually from conventional energy production.

- Source water not a constraint and frac makeup was typically fresh water
- Some believed at the time that near fresh quality water was necessary for the frac ingredients to perform as intended
- Deepwell disposal was available for flowback. Frac flowback injection is small fraction of the total.

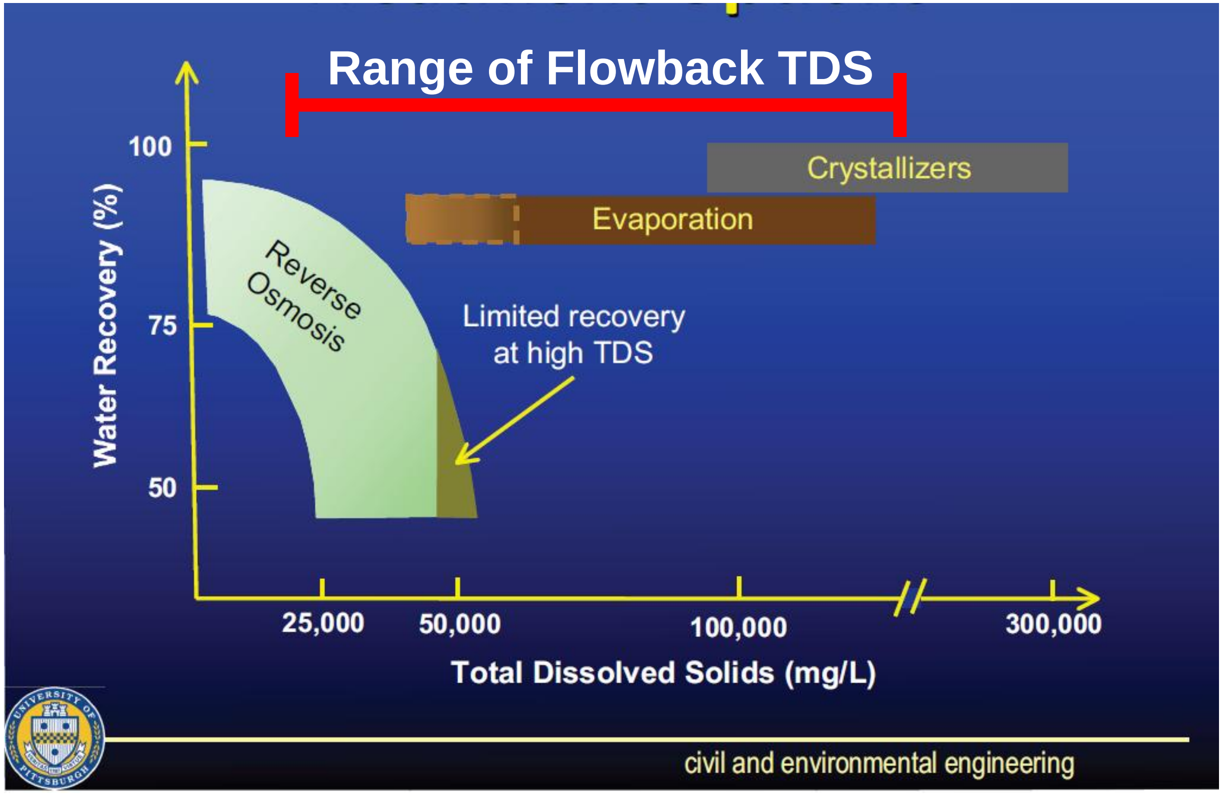
Injection Well and Tank Battery at Commercial Disposal Facility in Texas

from DOE Award DOE Award No.: FWP 49462 – Argonne Labs

Frac Flowback Reuse/Disposal – Dealing with Constraints

Disposal constraints in new plays provided the motivation to reuse flowback by treating it to near fresh quality by removing dissolved solids (TDS)

- High Total Dissolved Solids (TDS) flowback water and the presence of organics present treatment challenges
- Very difficult application for Reverse Osmosis due to organics and clay
- Only proven option is evaporation technology



Frac Flowback Reuse/Disposal – Dealing with Constraints

Application of water treatment technologies to create near fresh quality water from flowback

- Creating near fresh quality is feasible
- High capital and operating costs
- Evaporation does not allow 100% reuse of flow back

Pre-treatment

Evaporation Plant

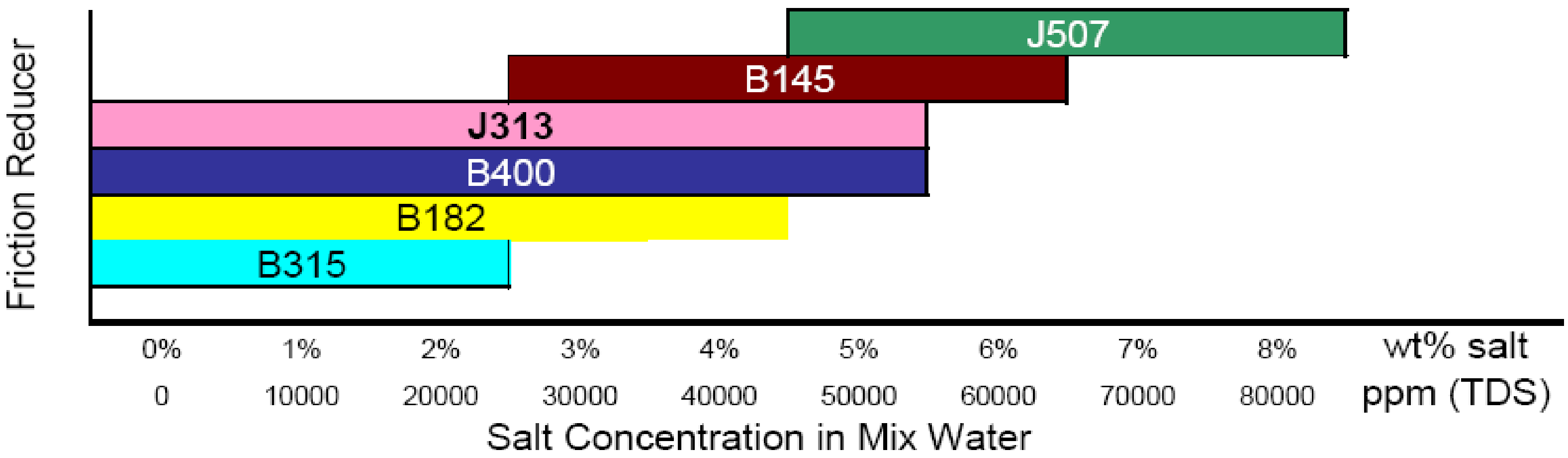
Fountain Quail, Texas

Frac Flowback Reuse/Disposal – Optimizing Constraints

Experience and testing shows that near fresh quality water is not always a requirement for fracking

- Options exist for saline tolerant chemical additives
- 100% Reuse has been demonstrated and practiced

Good Enough for Fracking in some Cases



Friction Reducer Source: Schlumberger Water Services

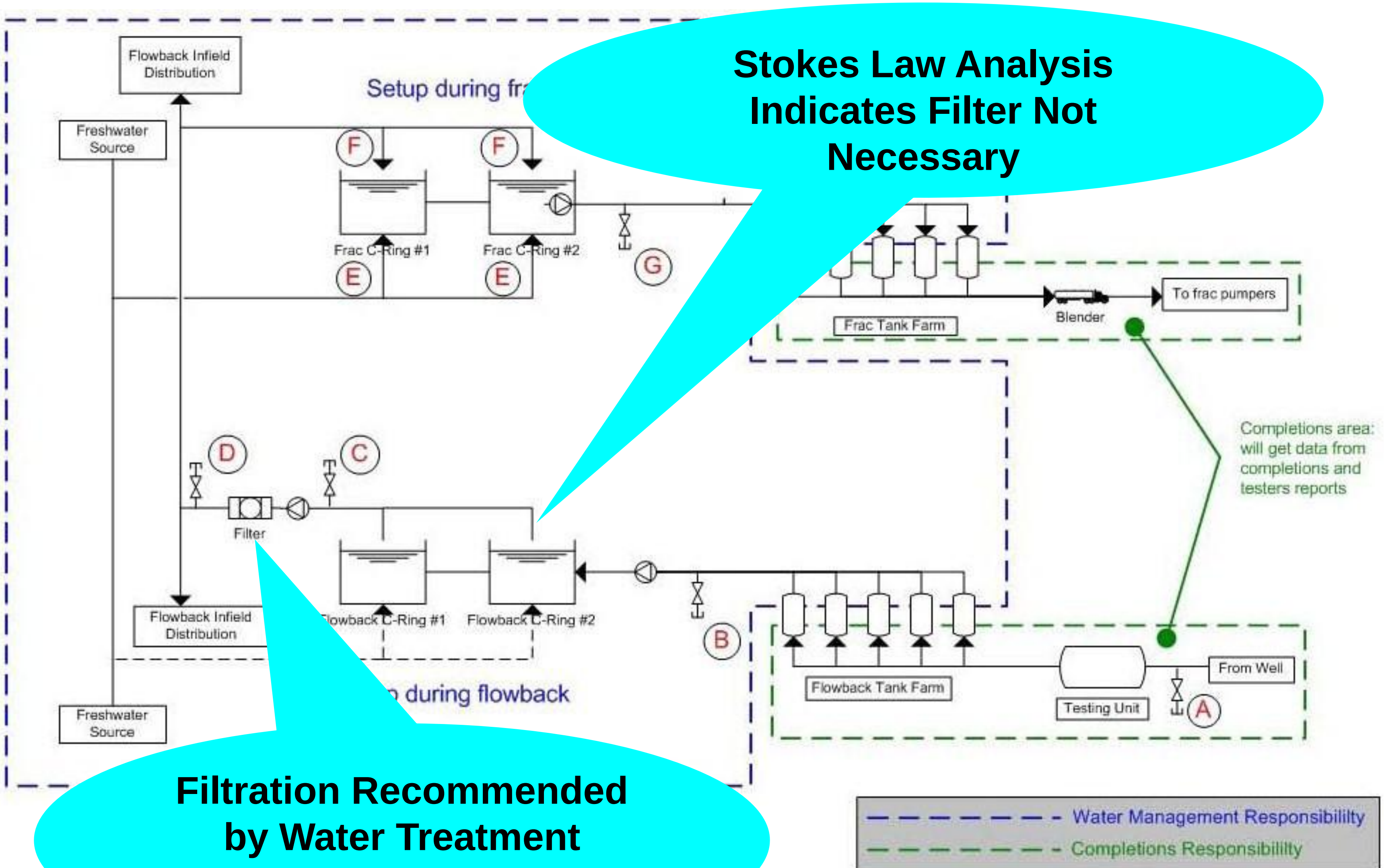
Two Perceived Obstacles to Flowback Reuse are Suspended Solids and Scaling Constituents

- Case Study 1; Removing Suspended Solids from Flowback, Is Filtration Necessary ?

- Case Study 2; Managing Metals and Hardness

- Logistics of Transporting and Storing Flowback
  - Any discussion on reuse must emphasize the differences between the North American (Western Canada, Eastern Canada, Eastern USA, and Southern USA) shale gas formations and the differences between different locations in the same formation. Reuse decisions and logistics will be site specific.

Data Collection to Support Reuse Water Management – Case Study 1; Removing Suspended Solids from Flowback Is Filtration Necessary ?



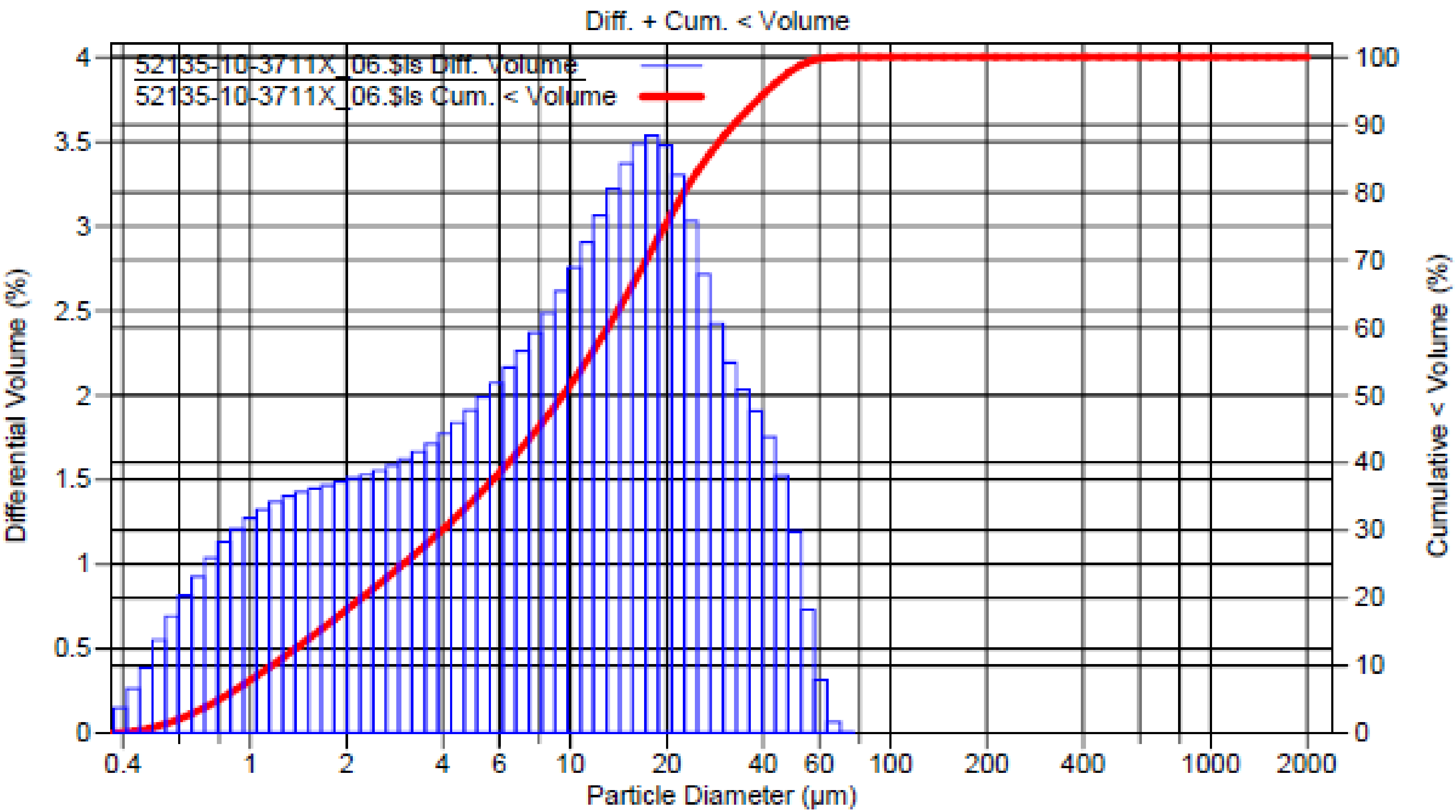
Stokes Law Analysis Indicates Filter Not Necessary

Filtration Recommended by Water Treatment Companies

Case Study 1; Flowback Filtration Necessary or Not?
Particle Size Distribution after Settling in Flowback Storage

Suspended Solids Profile after Surge Tanks

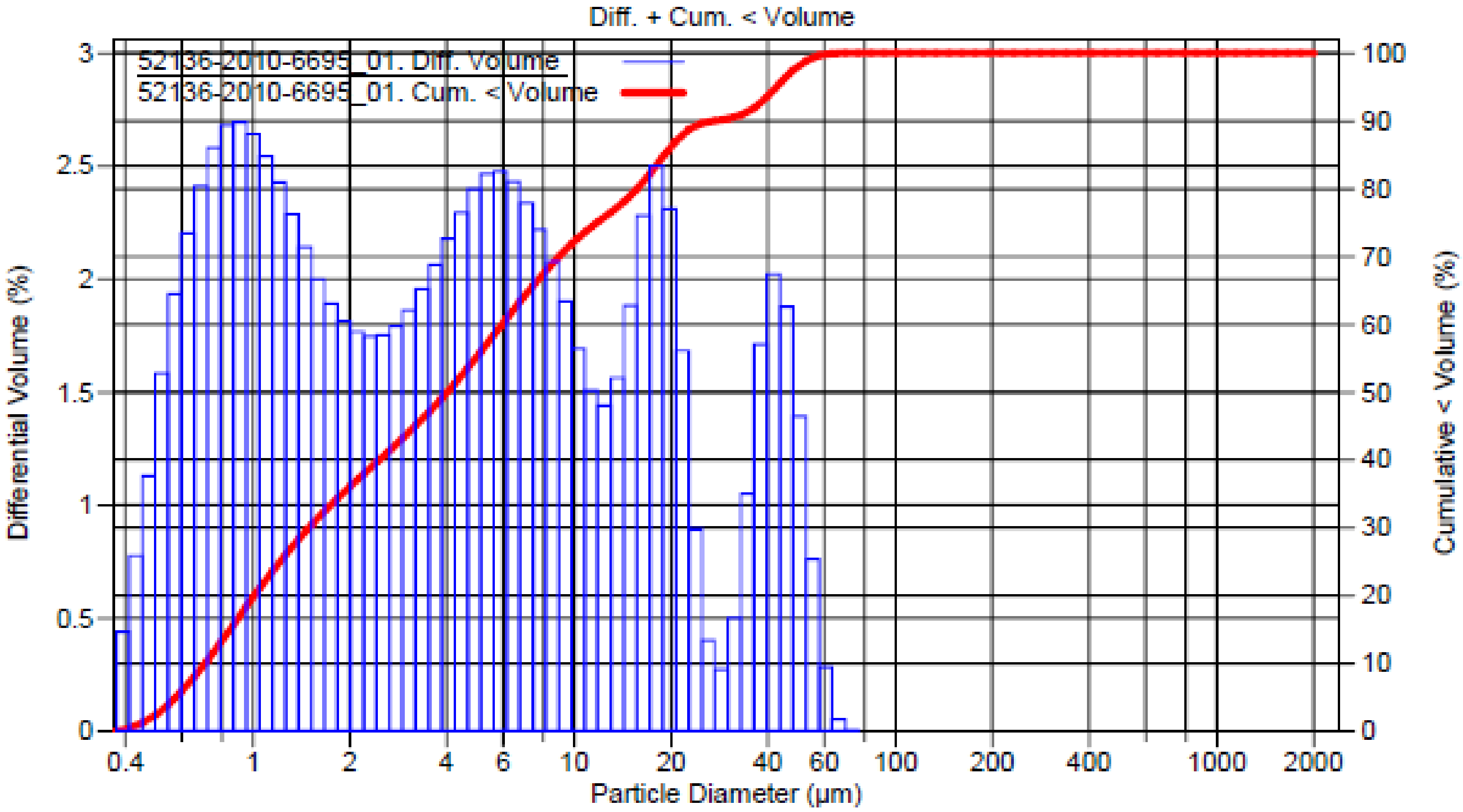
Total Suspended Solids ~ 1,500 mg/l



Case Study 1; Flowback Filtration Necessary or Not?
Particle Size Distribution after Settling in Flowback Storage

Suspended Solids Profile after Holding Tanks

Total Suspended Solids ~ 100 mg/l

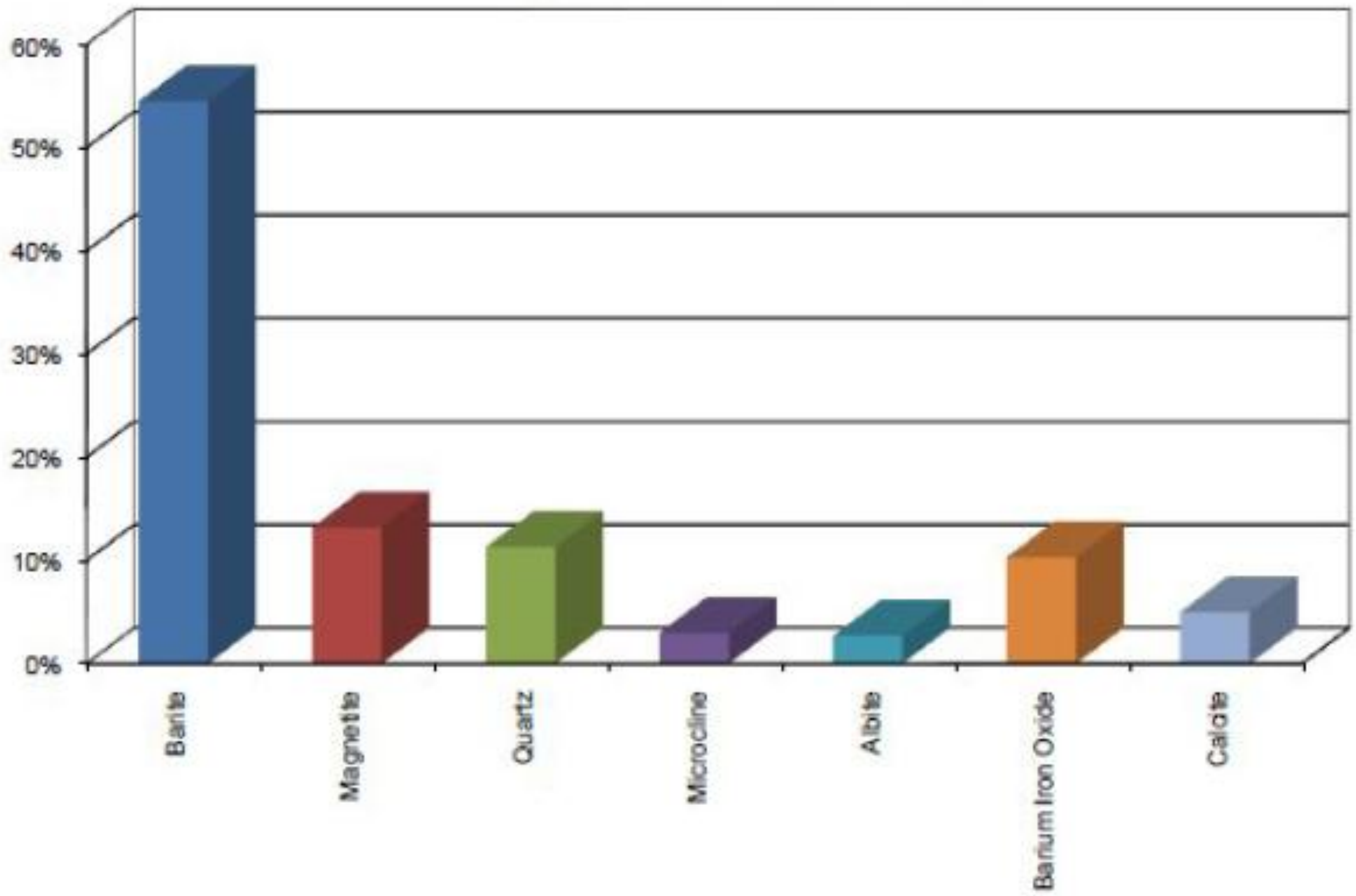


Case Study 1; Flowback Filtration Necessary or Not?
Particle Size Distribution after Settling in Flowback Storage

Particle Size Range, microns	Concentration at Holding Tanks, mg/l		Percent Removal
	Before	After	
0-10	728	75	-90%
10-25	442	22	-95%
25-100	346	17	-95%
>100	8	0	-100%
TOTAL	1523	113	-93%

Case Study 1; Flowback Filtration Necessary or Not?
Particle Composition after Settling in Flowback Storage

XRD Analysis shows Suspended Solids after settling consist primarily of Barite

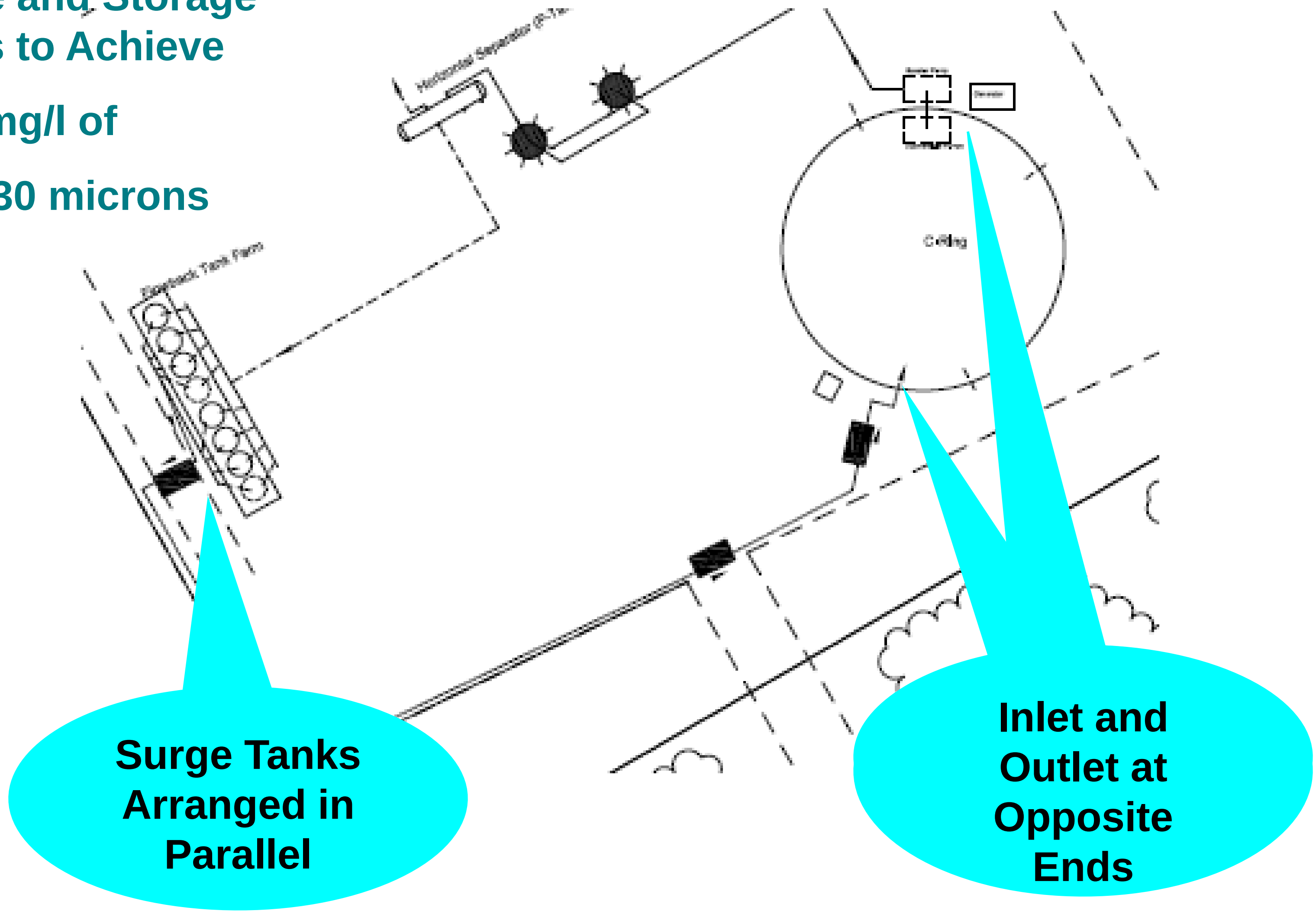


Case Study 1; Scheme for Removing Suspended Solids

Arrangement of Surge and Storage Tanks to Achieve

< 50 mg/l of

SS > 30 microns



Case Study 1 Summary; Removing Suspended Solids from Flowback

- Attempts to filter flowback resulted in filter blockage with fines, creating an obstacle to reuse of flowback.

- Settling in surge and storage tanks reduces suspended solids to < 50 mg/l of particles with a size range of 30 microns to 100 microns.

- The amount of suspended in the flowback has not had any noticeable impact on well performance. No long term studies have been made.

- Talisman has not observed biomass suspended solids which do not settle.

- Settled solids are removed from tanks by vacuum trucks and disposed in licensed landfills.

Case Study 2; Managing Metals and Hardness for Scale Control

Shale Flowback Water Analysis			Equivalents	
			Anions	Cations
Constituent	Units	Concentration		
Alkalinity as CaCO3	mg/L $CACO_3$	253.9	5.1	
Bromide	mg/L	901.9	11.3	
Chloride	mg/L	105,338.7	2,971.5	
Hardness as CaCO3	mg/L $CACO_3$	48,092.2		
Ammonia Nitrogen	mg/L	89.9		5.0
pH	STD Units	6.4		
TDS @ 180 C	mg/L	193,106.0		
Total Suspended Solids	mg/L	1,822.4		
Sulfate	mg/L	50.0	1.0	
Aluminum, Total	mg/L	13.0		1.4
Barium, Total	mg/L	9,082.7		132.3
Calcium, Total	mg/L	12,632.7		631.6
Iron, Total	mg/L	185.0		
Iron, Dissolved	mg/L	186.3		10.0
Lithium, Total	mg/L	633.9		91.3
Magnesium, Total	mg/L	1,185.0		97.5
Sodium, Total	mg/L	39,080.9		1,699.9
Strontium, Total	mg/L	3,715.6		84.8
			2,988.9	2,753.9

Ionic balance shows closure within 8.5%, which is acceptable

Case Study 2; Managing Metals and Hardness for Scale Control
Ions of Concern for Scaling

Shale Flowback Water Analysis		
Constituent	Units	Concentration
Alkalinity as CaCO3	mg/L $CACO_3$	253.9
Bromide	mg/L	901.9
Chloride	mg/L	105,338.7
Hardness as CaCO3	mg/L $CACO_3$	48,092.2
Ammonia Nitrogen	mg/L	89.9
pH	STD Units	6.4
TDS @ 180 C	mg/L	193,106.0
Total Suspended Solids	mg/L	1,822.4
Sulfate	mg/L	50.0
Aluminum, Total	mg/L	13.0
Barium, Total	mg/L	9,082.7
Calcium, Total	mg/L	12,632.7
Iron, Total	mg/L	185.0
Iron, Dissolved	mg/L	186.3
Lithium, Total	mg/L	633.9
Magnesium, Total	mg/L	1,185.0
Sodium, Total	mg/L	39,080.9
Strontium, Total	mg/L	3,715.6

Low concentrations of scale forming anions

Very high concentrations of scale forming cations

Enough iron to have a concern

Case Study 2; Managing Metals and Hardness for Scale Control
Potential Scaling Compounds

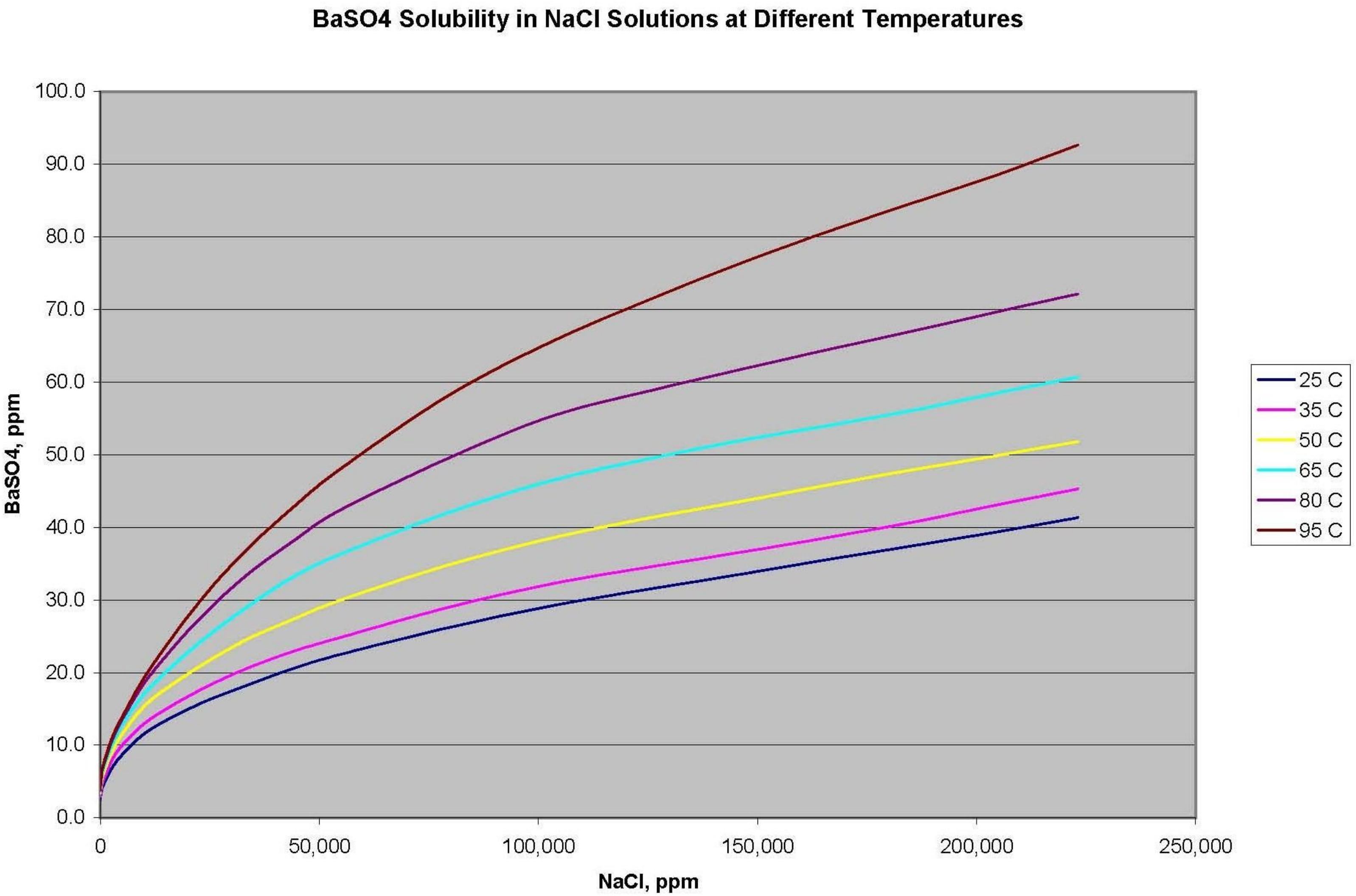
Compound	Concentration, mg/l	
	Compound	Chloride
CaHCO3	411	
BaSO4	122	
BaCl2 from Ba	13,663	4,652
CaCl2 from Ca	34,743	22,211
MgCl2 from Mg	4,641	3,456
SrCl2 from Sr	5,219	2,334
LiCl from Li	3,872	3,238
AlCl3 from Al	64	51
NH4Cl from NH4	267	177
FeCl2 from Fe	423	185
NaBr from Br	1,161	
NaCl from Cl	113,803	69,033
Sum of Cl Salts	176,695	105,339
Sum of All Salts	178,389	
Measured TDS	193,106	

There is some potential for CaCO3 or SrCO3 precipitation with large amounts of excess Ca and Sr

BaSO4 is at its saturation concentration with large amounts of excess Ba to precipitate with SO4 from fresh blend makeup or formation water

There is some potential for ferrous carbonate or other iron scale precipitation

Case Study 2; Managing Metals and Hardness for Scale Control Ionic Strength Increases BaSO4 Solubility, but not to a Significant Degree Compared to Ba Availability



Source: – Solubility of Barium Sulfate in Sodium Chloride Solutions from 25 C to 90 C, Charles Templeton, Journal of Chemical and Engineering Data, October 1960

Case Study 2; Managing Metals and Hardness for Scale Control Typical Recommendations for Scale Control and Alternative

- Scaling Potential
  - $BaSO_4$ is at saturation point with large amounts of excess Ba
  - Large amounts of excess Ca and Sr are present to drive $CaCO_3$ or $SrCO_3$ precipitation
  - Soluble iron is present to form $FeCO_3$ precipitate
  - SO_4 and alkalinity from fresh makeup increase potential for precipitation

- The traditional recommended approach is to remove Ba, Sr, Ca and Mg from flowback using Na_2SO_4 and Na_2CO_3 and CaO which requires large amounts of chemicals and also trucking:
  - 1.5 tons of Na_2SO_4 for every 500 bbl of flowback
  - 3.5 tons of $NaCO_3$ for every 500 bbl of flowback
  - Trucking chemicals and flowback to and from treatment facility
  - Solids generated by treatment must be landfilled

Case Study 2; Managing Metals and Hardness for Scale Control Typical Recommendations for Scale Control and Alternative

- Alternative is to take advantage of formation water chemistry in above ground blending of flow flowback and source water to reduce scaling potential
  - The constituents in flowback will react with the constituents in source water to reduce the scaling potential of the blend

Case Study 2; Managing Metals and Hardness for Scale Control Using Natural Barite Seed Crystals for Scale Control

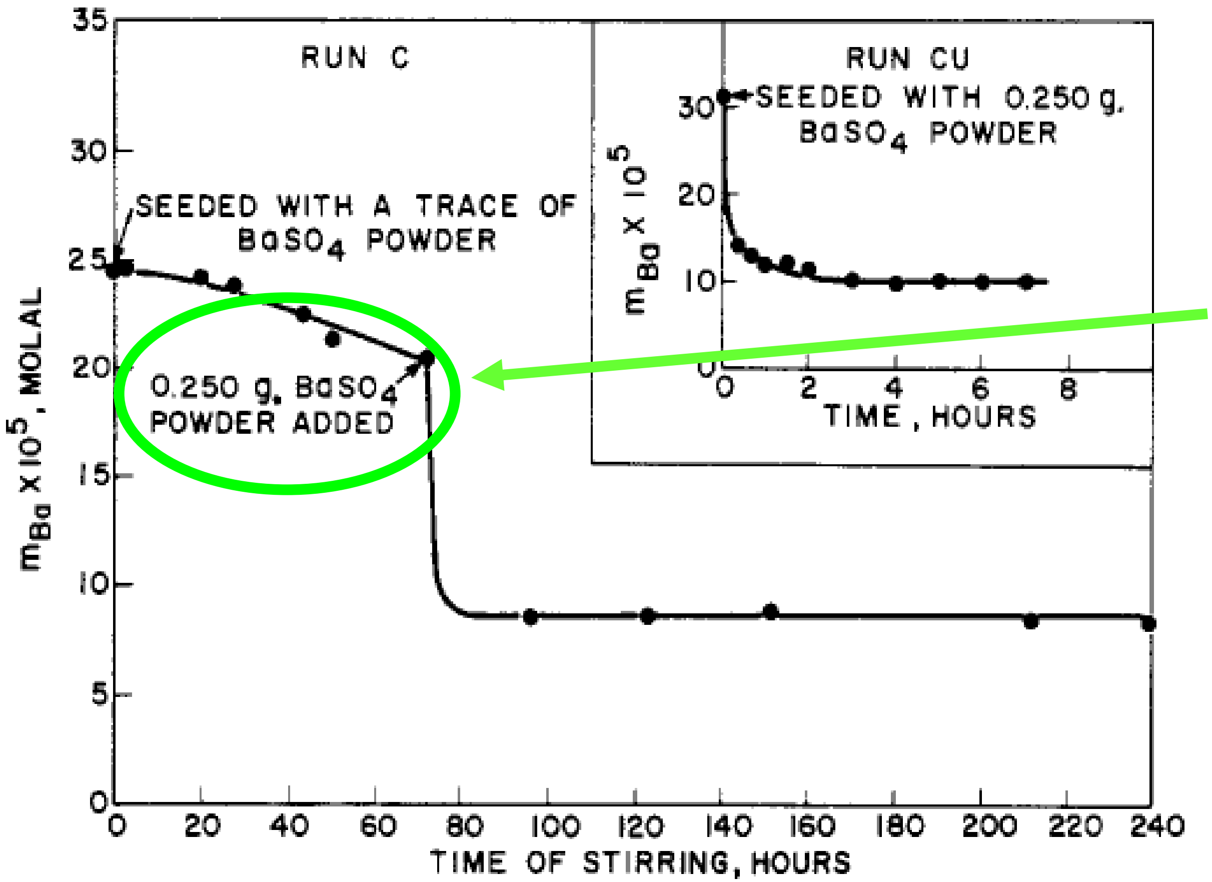


Figure 1. Kinetics of precipitation of $BaSO_4$ in 5% sodium chloride solution at 35° C.

Solution volume = 400 ml. $m_{Ba}/m_{SO_4} \approx 1$

625 mg/l of barite de-supersaturates

Flowback after settling has 250 mg/l of primarily barite SS

Co-precipitation of scaling salts is known from other applications – this has not been studied for flowback

Source: – Solubility of Barium Sulfate in Sodium Chloride Solutions from 25 C to 90 C, Charles Templeton, Journal of Chemical and Engineering Data, October 1960

Case Study 2; Managing Metals and Hardness for Scale Control
Typical Chemistry after Blending Flowback and Fresh Water

Shale Flowback and Fresh Water Blend		
Constituent	Units	Concentration
Alkalinity as CaCO3	mg/L $CACO_3$	250.0
Bromide	mg/L	180.4
Chloride	mg/L	21,067.7
Hardness as CaCO3	mg/L $CACO_3$	9,618.4
Ammonia Nitrogen	mg/L	18.0
pH	STD Units	6.4
TDS @ 180 C	mg/L	38,621.2
Total Suspended Solids	mg/L	364.5
Sulfate	mg/L	90.0
Aluminum, Total	mg/L	2.6
Barium, Total	mg/L	1,816.5
Calcium, Total	mg/L	2,566.5
Iron, Total	mg/L	37.0
Iron, Dissolved	mg/L	37.3
Lithium, Total	mg/L	126.8
Magnesium, Total	mg/L	237.0
Sodium, Total	mg/L	7,816.2
Strontium, Total	mg/L	743.1

- Talisman has reused flowback with only settling
- No chemical addition for precipitating metals and hardness
- Blend TDS of approximately 50,000 mg/l
- No apparent negative impact on the formation or gas production

Case Study 2 Summary; Managing Metals and Hardness for Scale Control Blending of Flowback and Fresh Water for Scale Control

- Talisman has reused flowback with only settling, and no chemical addition for metals and hardness reduction, for blend TDS of approximately 50,000 mg/l

- Why might blending of flowback and fresh water reduce scaling potential?
  - Iron is likely oxidized and precipitated as $Fe(OH)_3$ in surface tanks
  - Reduction in ionic strength reduces $BaSO_4$ solubility by 50%. SO_4 from surface water reacts with excess Ba and likely precipitates on seeds
  - Some $CaCO_3$ and $SrCO_3$ precipitation will occur. However, at this time scale control is indicated because of inverse solubility with respect to temperature and lack of definite information on co-precipitation

- What about formation compatibility?
  - The presence of barite "seeds" should reduce down hole and formation scaling due to preferential precipitation on the seeds
  - Caution is recommended for formations with soluble sulfate. However, barite "seeds" might be useful in such situations
  - In principle, fewer salts should be solubilized from the formation with higher TDS frac fluid
  - The impact of increased frac fluid density has not been investigated

Importance of Logistics for Managing Flowback Reuse

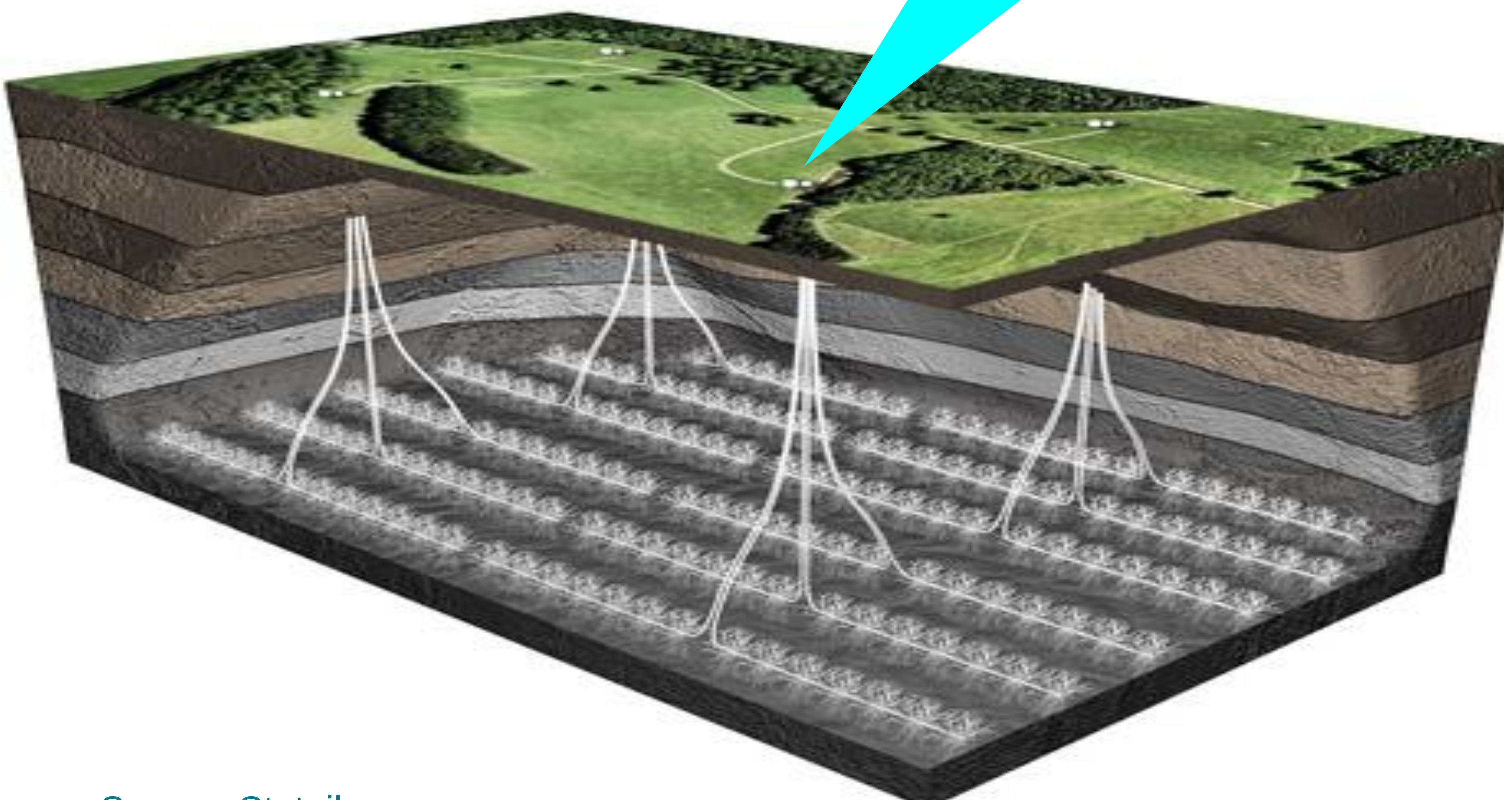
The logistics of transporting and handling flowback to minimize environmental and public health risks must take the following into consideration:

- Number of wells per pad – Flowback reuse on Multi-Well pads reduces movement of flowback off the pad
- Timing - storage required to deal with when flowback is available and when it is required
- Variations in the amount of flowback. The range is 10% to 50% of the injected frac fluid
- Location of fresh makeup
- Contiguousness of leases

Flowback Logistics – Multi-Well Pads Reduce Truck Traffic when Flowback is Reused

Reuse of flowback significantly reduces the amount of flowback removed from the pad versus no reuse of flowback

Multi-Well Pads
(6 to 24 per pad)



Source: Statoil

Flowback Logistics for < 20% Flowback

Flowback Storage

Portable tanks are suitable for smaller volumes of flowback

Flowback Storage for > 40% Flowback

Source Water

Portable tanks are less suitable for smaller volumes of flowback and field erected tanks are more practical

Flowback Storage

Logistics for Managing Flowback Reuse
Pipelines versus Trucks

- Trucks
  - Justified when flowback volumes are small
  - Truck traffic reduced substantially by multi-well pads
- Pipelines
  - Justified when flowback volumes are large
  - Reduces truck traffic
  - More land disturbance than trucks
- There is no specific rule for one versus the other

Shale Gas Flowback Water Reuse Summary

- Water chemistry considerations indicated that flowback does not require extensive treatment in all cases before it is reused
- Talisman Energy has successfully reused flowback with only settling of suspended solids for TDS of approximately 50,000 mg/l
- From a scale control perspective it might be advantageous not to remove metals and hardness before blending
  - Takes advantage of the de-supersaturation capability of naturally occurring barite seed crystals. Co-precipitation of other scaling salts might be a benefit.
  - The seed crystals might reduced down hole and formation scaling
- Reuse reduces truck traffic when disposal wells are not available
- Due to variations between locations, the flowback reuse and logistics issues are site specific

A Water Chemistry Perspective on Flowback Reuse with Several Case Studies

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Talisman Energy USA Inc.

Summary

Operators have tested the feasibility of using frac flowback water that has received only a minimum level of treatment. Successful fracture operations have been reported using frac solutions with total dissolved solids (TDS) in excess of 50,000 mg/l.

Any discussion on reuse must emphasize the differences between the North American (Western Canada, Eastern Canada, Eastern USA, and Southern USA) shale gas formations and differences between locations in the same formation make reuse decisions and logistics site specific. Operations must be conducted in compliance with applicable local laws and regulations.

This abstract discusses the reuse of frac flowback from a water chemistry perspective. Two examples of flowback reuse, where a minimal water treatment has been used, describe the rationale for why the practice is considered acceptable. Associated logistics considerations are also presented.

Introduction

Hydraulic fracturing is essential to the production of natural gas from tight shale. Fracture fluids are predominantly a water and sand mixture with a small percentage of other chemicals with specific functions. Fracturing requires high pressure. Friction reducers are used to decrease the frictional force in the pumped water allowing the pumping pressure to reach the formation. A mild acid prepares the stimulated area to accept the fracture treatment, biocide kills any bacteria collected in the water prior to pumping, scale inhibitors prevent mineral buildup from the water produced from the well, and corrosion inhibitors are added to protect equipment. Breakers to reduce the viscosity of friction reducers, clay stabilizers, and surfactants might also be used.

Approximately 10% to 50% of the water used for hydraulic fracturing may be returned quickly to the surface as frac flowback. Reuse of frac flowback has multiple benefits:

- Reduces demand for fresh water
- Reduces water disposed
- Reduces truck hauling to offsite disposal

Frac Flowback Reuse by Creating Near Fresh Water Quality

Until recently it was believed that near fresh quality water, or water with most metals and hardness removed, was required for use in fracturing fluid. Historically, most shale gas fracture flowback was disposed of by deep well injection. Deep injection wells are not always available and offsite disposal costs can be quite large relative to other water related costs.

Various technologies have been proposed to achieve near fresh quality standards by removing suspended solids, heavy metals, hardness, organics, and dissolved solids. In some cases, a relaxed requirement of specifying only the removal of heavy metals and hardness was considered acceptable.

These technologies are usually expensive, add operational complexity, increase environmental and safety risks, and generate by-products which require disposal in compliance with applicable laws and regulations.

There are clear advantages to reuse of frac flowback which requires only a minimum amount of treatment for removing suspended or dissolved solids. Several operators, including Talisman Energy, are routinely using frac flowback which has had a minimum amount of treatment.

Talisman Energy USA Goals for Flowback Reuse

Data collected from recent drilling in the Marcellus shale formations by Talisman Energy indicates initial flowback ranging between 10% and 25% of the injected volume. The initial flowback has lower dissolved solids than later flowback. The maximum concentration of Total Dissolved Solids (TDS) in the blended flowback is less than 200,000 mg/l. To consistently reuse virtually all of the flowback by blending with fresh water, frac fluids need to function effectively with a maximum TDS of 50,000 mg/l.

Water Chemistry Perspective on the Water Quality Requirements for Frac Flowback Reuse

The typical constituents in shale gas frac flowback water have been identified through various sampling programs. While the relative proportions of these constituents vary depending on the formation, there are some consistencies in the types of constituents present. Typically, the range of Total Dissolved Solids (TDS) is between 25,000 mg/l to 250,000 mg/l. The constituents which might impact the performance of the chemical additives to a frac fluid or impact the formation include:

- Suspended Solids – fine clay (could also include biosolids)
- Organics – both added and naturally occurring
- Scaling ions – barium, strontium, calcium, and magnesium along with alkalinity and sulfates
- Chlorides and oxygen – accelerate corrosion
- Residual friction reducers – interfere with constituents in the frac fluid
- Microbes – souring of the formation and microbiologically enhanced corrosion

The recommended functional performance considerations for reuse are:

- Friction reducer effectiveness
- Scale formation
- Microbiology control
- Corrosion
- Breaker
- Clay stabilization
- Long term impact on formation

Friction reducers with salinity tolerance of 90,000 mg/l or more have been advertised by several companies. Friction loop tests were performed for Talisman Energy and the acceptability of using a blend of flowback and fresh water with a TDS of 50,000 mg/l was demonstrated. Talisman's service providers were confident that the other functions could also be addressed. The two functional performance considerations which generated the most discussion were suspended solids and scale control.

Two case studies -- one for suspended solids and one for scale control -- are discussed below.

Water Chemistry Perspective; Case Study 1 - Suspended Solids

The recommendation for water used to prepare frac fluids is that it should be substantially free of suspended solids. There are various specifications to define what total amount of suspended solids and what particle size range meet the expectation of substantially free.

Talisman Energy conducted filtration of flowback tests for removing suspended solids but commonly experienced filter plugging. Thus the requirement to filter the flowback created an obstacle to reuse.

All of Talisman Energy's fracture operations include flowback storage. Application of Stoke's law to the various storage configurations suggested that under ideal conditions all particles greater than 30 micron in diameter would be removed from the frac flowback.

Samples were collected from several frac operations to determine the effectiveness of unaided gravity settling in flowback tanks whose primary purpose is surge control and storage.

- Slide 7 shows the sampling arrangement and the location of the filter recommended by water treatment companies.
- An investigation was made to compare a Stoke's law prediction to actual removal. The prediction indicated that under ideal conditions solids > 30 microns would be removed. It was understood that particle size and inlet/outlet configuration of the tanks were not ideal.
- Slides 8 and 9 show the particle size distribution of suspended solids before and after flowback holding tanks. The inlet and outlet of the surge and holding tanks were arranged to facilitate site set-up, not suspended solids removal, and the configuration was not ideal for settling. As a result, suspended solids removal was less than predicted. Side 10 summarizes the solids distribution before and after the holding tanks.

- Slide 11 show that most of the sand and clays are removed by settling, leaving primarily barite.
- Slide 12 shows the configuration of tanks to achieve performance which is closer to what is predicted by Stoke's law.
- The reuse of flowback with 50 mg/l or less of suspended solids, with a particle size range of greater than 30 microns and less than 100 microns, has not had a noticeable effect on well performance. No long term studies have been made.
- Talisman Energy has not observed interference from biomass.

Settled solids are periodically removed from the tanks by vacuum trucks and disposed in licensed landfills in compliance with applicable laws and regulations.

Water Chemistry Perspective Case; Study 2 – Scale Control

The scaling potential of barium, calcium, and iron with sulfate and carbonate ions has been discussed at length in the literature and there are both ongoing and new studies. There are many public and proprietary computer programs available to calculate scaling potential.

For the purpose of this case study a flowback chemistry for Northeast Central Pennsylvania chemistry is presented in Slide 14.

Slide 15 highlights that the chemistry is a high ionic strength, chloride based system with very high concentrations of the scale forming cations and very low concentrations of sulfate and carbonate.

When the ions are matched with each other the extent to which the salts are chloride based becomes more clear (refer to Slide 16).

Slide 17 shows the extent to which ionic strength has an impact on the total and relative solubility of salts.

It was recommended to Talisman Energy that metals and hardness be removed from the flowback before reuse. The open literature has examples of similar recommendations. Due to the high concentration of barium, strontium, calcium, and magnesium large amounts of sodium sulfate, soda ash, and lime are required.

In many cases the source of sulfate and carbonate alkalinity is the fresh make-up water. Since the high concentration of scaling cations are in the formation, it is best to remove the sulfate and carbonate alkalinity from the frac fluid before injection.

An alternative is to settle out the gross suspended solids, as described in Case 1 and then take advantage of the remaining barium sulfate "seeds" to quickly de-supersaturate sulfate. The chemistry of this approach is well established (refer to Slide 20). There are also literature references to co-precipitation of other scaling salts on seed crystals.

Talisman has reused flowback with only settling and no chemical addition for metals and hardness reduction for blend TDS of approximately 50,000 mg/l with no apparent negative impact on the formation or gas production.

Several hypotheses have been put forth for why blending of flowback and fresh water might be effective at reduced scaling potential of the blend:

- Iron is likely oxidized and precipitated as $Fe(OH)_3$ in surface tanks
- Reduction in ionic strength reduces $BaSO_4$ solubility by 50%. SO_4 from surface water reacts with excess Ba and likely precipitates on seeds
- Some $CaCO_3$ and $SrCO_3$ precipitation will occur. However, at this time scale control is indicated because of inverse solubility with respect to temperature and lack of definite information on co-precipitation

There are questions about the impact of flowback reuse on the formation:

- The presence of barite “seeds” should reduce down hole and formation scaling due to preferential precipitation on the seeds
- Caution is recommended for formations with soluble sulfate. However, barite “seeds” might be useful in such situations
- In principle, fewer salts should be solubilized from the formation with higher TDS frac fluid
- The impact of increased frac fluid density has not been investigated

Logistics Considerations for Frac Flowback Reuse

There are differences between the North American (Western Canada, Eastern Canada, Eastern USA, and Southern USA) shale gas formations and differences between locations in the same formation. Reuse decisions and logistics will be site specific. Operations must be conducted in compliance with applicable local laws and regulations.

The logistics of transporting and handling flowback to minimize environmental and public health risks must take the following into consideration:

- Number of wells per pad - flowback reuse on multi-well (refer to Slide 24) pads reduces movement of flowback off the pad
- Timing - storage required to deal with when flowback is available and when it is required
- Variations in the amount of flowback – flowback ranges from 10% to 50% of the injected frac fluid, which impacts the choice and style of storage (refer to Slides 25 and 26)
- Location of fresh makeup
- Contiguousness of leases

In general, reusing flowback on site with Multi-Well pads will reduce the amount of fresh water required at the pads and significantly reduce the movement of flowback from the pad.