A Common Clean Brine Specification for Reusing Recycled Produced Water – Draft Guidelines

A publication by the Produced Water Society – released for consultation 26th June 2020

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Executive Summary

Oilfield operators in the unconventional plays often have individualized water quality specifications for water to be used in their completions. This results in a myriad of specifications, which limits the scale of operation for treatment and reuse of these waters. If the industry can coalesce around a “common spec” for clean brine water quality, then water midstream entities could treat these waters on a larger scale. This would result in greater capital expenditure (CAPEX) and operating expenditure (OPEX) efficiency, resulting in a lower cost point for clean brine. A common spec would also allow water midstream companies to share clean brine across their pipeline systems, thus reducing the requirement for expensive surface storage. More recycling will reduce the demand on fresh- and brackish groundwater for completions, while reducing deep well injection volumes that may contribute to seismicity. The Produced Water Society (PWS) has canvassed stakeholders in shale plays to provide the basis for a common spec to be used as a guideline for minimum clean brine treatment. This guideline spec does not address potential compatibility issues that will be the responsibility of the buyer (operator) to evalute when using clean brine.

Table 1 – Common Clean Brine Minimum Specification for Reusing Recycled Produced Water

1.	Salinity	Reported
2.	pH	6.0 – 8.0
3.	Oxidation reduction potential (ORP)	>350 mV
4.	Turbidity	<25 NTU
5.	Oil	<30 ppm – no sheen
6.	Hydrogen sulfide (H_2S)	Non-detectable
7.	Particle size	Filter <25 micron

Background

Hydrocarbons production from unconventional formations using horizontal drilling and hydraulic fracturing technology generates huge quantities of byproduct water. These waters are from flowback of the fracturing fluids, as well as from formation connate water. In this paper "PW" will be used to refer to both flowback and connate produced waters, since they are often combined. Early in the development of shale plays, most of these waters were disposed of in UIC Class II saltwater disposal (SWD) wells. Eventually, fracturing fluids chemical packages were developed to be compatible with high-salinity waters. This development allowed for the recycling of PW as make-up water for fracturing fluids. Presently, produced water volumes are 200-400% in excess of the annual completion source water demand, which offers significant opportunity for reuse.

Early in the shale boom, PW recycling was widely adopted in the Marcellus play due to the high logistics cost of transporting PW to disposal wells in Ohio and West Virginia. The practice of PW recycling has been gradually adopted in the largest shale plays: the Midland and Delaware portions of the Permian Basin. As treatment technologies have improved and scales of operation have grown, it is now often more cost effective to recycle PW than to dispose of it in SWD wells. For this paper, "clean brine" (CB) will be used to refer to treated PW suitable for sale to operators for formulating fracturing fluids.

The development of the water midstream industry has created a new scale of operation that makes greater use of recycled PW more cost effective[1]. A barrier to wider use of PW has been the wide range of operator specifications for CB quality needed for completions. This requires water midstream companies to employ water treatment packages capable of meeting their most demanding customers' specifications. Since most operator customers may not require the most stringent specifications, water midstream companies are not using CAPEX and OPEX as efficiently as possible.

If the industry were to accept a common spec for CB quality, it would allow water midstream companies to treat PW at greater scale to reduce unit costs. A further – and perhaps more important – advantage is that it would be easier for water midstream companies to share CB across their pipeline systems. Sharing CB between adjoining water networks would substantially reduce the amount of CB storage capacity needed. This is a major CAPEX issue for water midstream companies. Furthermore, water going into CB surface storage ponds may require a greater level of treatment than water piped directly to completion sites due to natural degradation of water quality that occurs in ponds over time.

PWS is an independent third-party association of oilfield water professionals. As an interested party without a financial stake, PWS is in a good position to suggest a guideline for a common spec for CB used in fracs. A wide range of stakeholders including water midstream companies, operators, services providers, pumping companies, technology vendors, and oilfield water specialists have been consulted on this common spec for CB.

The common spec is not intended to meet every operator's internal spec for completion water. The goal is to provide good-quality CB that is suitable source water coming off a pipeline. Operators sourcing CB for frac fluid formulation will be able to plan for a minimum water quality at a low price point. Operators may then choose additional polishing treatment or freshwater blending at wellhead sites to meet their tighter internal specs. Ultimately, the goal is to reduce the overall costs of water management and reliance on freshwater. This paper proposes an initial common spec with the intent of establishing a starting point. It is fully anticipated that this spec will be updated as experience is gained by the industry working with this set of parameters.

Parameters

There are a wide range of parameters associated with the quality of CB generated from PW. Some of these components can be measured quickly in the field, while others require extensive time to measure in off-site labs. When water samples are taken in the field and go to an off-site lab for analysis, they may no longer be representative and the results from those sample analyses will certainly not be timely. To be most useful to the industry, the common spec needs to cover simple parameters that can quickly be measured in the field. Most useful will be properties that can be measured with on-line instruments in real-time reporting directly to water midstream companies' SCADA control systems. This data may also be available to buyers (operators) taking this water off the pipeline.

At the 2020 PWS Annual Seminar in Houston, Aaron Horn of XRI-FQ presented a paper[2] on trading CB at water terminals to facilitate greater water recycling. He stated, "Our first recommendation regarding the recycled produced water commodity market is for a quality standard." A portion of the presentation was on recommended parameters for assessing CB quality. Horn suggested a simple acronym, "SpOT", for determining CB quality:

Salinity
pH
ORP
Turbidity

All these parameters can easily be measured on-line in real time. This paper has used the SpOT parameters as a starting point for a CB common spec guideline. There are several parameters beyond the SpOT set that some stakeholders are also interested in such as bacteria, iron, oil, H_2S, total sulfides, corrosivity, and solids particle size. These other parameters will be discussed below.

Predictably, there was a range of values for water quality parameters among the stakeholders interviewed for this project[3]. A general consensus of acceptable values is provided in Table 1.

Table 1. Common Clean Brine Minimum Specification for Reusing Recycled Produced Water

Parameters	
Salinity	Reported
pH	6.0 – 8.0
ORP	>350 mV
Turbidity	<25 NTU
Oil	<30 ppm – no sheen
H_2S	Non-detectable
Particle size	Filter <25 micron

Discussion

This common spec is the Recommended Guideline for the Minimum Acceptable Criteria for CB Treatment. These parameters would be reported by entities putting water into CB pipelines for sale from their treatment facilities.

Primary parameters

a) Salinity

The salinity of CB may vary throughout the unconventional play and can fluctuate in individual wells over the course of their productive lives. This parameter will be measured and reported. Measurement will be performed via on-line conductivity probe and correlated to approximate salinity value.

b) pH

The pH parameter is easy to control and measure with on-line probes.

c) ORP

ORP is a valuable parameter that can be measured with on-line probes. Water with ORP >350 mV should be relatively free of bacteria. This level of ORP should oxidize any dissolved iron to the ferric state, which will precipitate. A combination of ORP and <50 NTU turbidity means that iron and oil levels should be acceptable. While the initial SpOT recommendation included ORP >250 mV, several operators and other stakeholders have expressed a strong preference for the spec going into the sales line to have ORP at 350-400 mV, since some excess oxidant will be consumed by reactive species in the CB stream. This level may be re-evaluated during the revision cycle for this spec.

d) Turbidity

Measurement of turbidity can be performed with an on-line light transmittance probe measuring NTU (nephelometric turbidity units). Turbidity is a measure used to determine the level of total suspended solids (TSS). Present suspended solids will show up as turbidity. Any present soluble iron will be oxidized to the solid ferric form (based on the ORP and the pH parameters), which will show up as turbidity.

Turbidity does not give any indication of particle size. Large particles would need to be captured in 25-micron solids filters at the point where the CB is transferred to the sales line. It is advisable for water buyers to also filter water at points of use to whatever particle size they are satisfied with. This would capture any solids picked up in the pipeline during transit.

e) Oil

It is in the water treater's interest to capture as much of the oil as possible that comes into their treatment facility, as recovered oil is a revenue stream. Furthermore, oil would likely interfere with downstream water treatment unit operations, driving up costs. In most cases, any oil coming through would likely show up as turbidity. Furthermore, at ORP >350 mV, some oil is oxidized. However, some high-API gravity unconventional oils may not register as turbidity.

Oil can be measured on-line with fluorescence technology. This is a more expensive instrument and must be calibrated when there is any change in source water. Studies have also indicated that there is great uncertainty associated with oil-in-water data obtained using existing laboratory-based methods, whether gravimetric, infrared absorption-based, or gas chromatography and flame ionization detection-based. This uncertainty may be as high as ±50% (at a 95% confidence level). The use of on-line oil-in-water monitors, particularly those installed in-line, could potentially reduce uncertainties associated with current sampling and analysis practices[4].

The 30-ppm oil limit intends to avoid oil sheens on CB storage ponds receiving this water. Free-phase oil sheens would require expensive bird protection measures around ponds.

f) H_2S

Operators will not accept CB waters with detectable H_2S. This parameter poses significant risk to personnel, as well as a corrosion risk for facilities. At ORP >350 mV, H_2S should be oxidized to elemental sulfur. High levels of H_2S will result in significant elemental sulfur that will require separation, without which will result in unacceptable turbidity levels.

It has been suggested that a total sulfides spec would be helpful. Water containing high sulfides could be mixed with lower-pH water and result in the generation of toxic H_2S gas. Since this parameter cannot be readily measured with on-line instrumentation, it is not included in this initial spec. CB buyers must be aware of this potential if they are blending waters with significant pH differences.

g) Particle size

Particle size can be measured with on-line laser spectroscopy, which are expensive instruments. A low-cost and practical approach is to simply filter CB with <25-micron nominal filters before going into pipelines, then buyers may choose to refilter at receiving locations if they have tighter particle size specs. Filtration with nominal 25-micron media will assure removal of 99.9% of particles exceeding 50 microns. Nutshell filters can meet this spec and are backwashable. Cartridge filters are also an option. While nutshell filters have higher capital costs versus cartridge filters, they will have far lower OPEX relative to cartridge filters for high-flowrate treatment plants. This filtration step must be the last unit process contacting the water before it is introduced into the sales pipeline. No additional chemistry or other fluids should be added downstream from this final treatment step.

Other best practice parameters

a) Bacteria

Several methods are available for measuring bacteria levels. The long-established approach of measuring bioassays takes 5-21 days and is not practical. Several new instruments are available that provide much quicker indications. However, by maintaining ORP >350 mV, there should be minimal living bacteria in the water. This ORP level may eliminate the requirement for further bacteria monitoring. This spec does not eliminate the potential need for water buyers (operators) to add oxidant or biocide at points of use.

b) Corrosivity

There has been some discussion about measuring corrosivity. On-line instruments are available that can provide an indication of a water's corrosivity. Most produced water pipeline systems are now constructed with high-density polyethylene (HDPE), which is generally impervious to typical chemistries used in oilfield waters. Some of the older legacy pipeline systems were constructed with steel pipe and are vulnerable to corrosion. It is up to owners of steel pipelines to determine the corrosivity parameters needed to protect their pipelines integrity.

Operators may have concerns about scaling and water compatibility with the formations in which they are used, which might impact how much freshwater is needed for blending or how much chemistry is employed to prevent scaling. Scaling potential is specific to the waters being blended, whether on the surface when mixing waters or when the frac water mixes downhole with connate water. Since these issues vary widely and are linked specifically to the working formation, no attempt is made to address these issues in this initial set of guidelines.

Instrumentation

Accurate analyses and chemical treatment can be achieved using proven advanced treatment systems[5]. Many vendors supply instruments for on-line measurement of the target parameters. Some of the types of useful instruments have been described above.

The key to delivering quality data is to properly maintain instruments and ensure regular calibration. Laboratory instruments have historically been calibrated against laboratory-produced solutions that are measured with standard test methods. This approach is not practical in the field. Most on-line instruments are now calibrated against calibration solutions from instrument manufacturers or chemistry vendors. These solutions are readily available and convenient to use. An exception is the oil-in-water measurement with fluorescence technology, which requires calibration against a solution formulated with the target oil to be measured.

Laboratory Methods

This section covers some of the most useful laboratory standard methods for measuring the target parameters. These methods are typically run in off-site labs and are generally impractical for in-field measurements. They are useful to cross-check against on-line data. Most of these methods are in line with current National Environmental Laboratory Accreditation Conference (NELAC)[6] standards.

Online measurements of the SpOT parameters will require calibration and periodic validation of sensors for quality and compliance purposes. Some on-line sensors are well adapted to providing accurate results as the nature of the water changes (e.g. conductivity) while the calibration of others is likely to measurably change as the conductivity of the produced water varies (e.g. ion-selective probes* and other sensors** that utilize combination probes with reference electrodes). How often on-line probes will need to be calibrated will depend upon how produced waters are treated, co-mingled, and stored, among other factors.

Depending on the formation where the CB buyer (operator) is using this recycled water, it may be necessary to measure other constituents (e.g. iron, sulfide, alkalinity, sulfate and barium) or other properties (e.g. corrosivity, saturation indices, tendencies to scale). Calibration methods will need to be appropriate for the expected brines and be capable of the minimum detection limits of the specifications. Accuracies of the calibration and testing methods should be dictated by the specifications. The proficiency test limits are proposed for methods discussed below. The following list of these testing methods are examples of those that can be considered. Alternate methods may also be acceptable, if they match the minimum detection limit (MDL) called for by the specification and are capable of generating the recommended accuracy at twice the MDL.

*Ion-selective probes typically include reference electrodes that make them quite susceptible to the ionic strength of the sample (and thus will require recalibration as the salinity of the sample changes).

**pH probes typically utilize a reference electrode (usually calomel [Ag:AgCl]) whose liquid junction forms a salt bridge with the sample. Produced water samples whose salinity varies will require frequent recalibration and verification.

Laboratory Methods[7]

Salinity measurement based on electrical conductivity and resistivity of water

1. Standard Method 2520A, 2520B or 2520C;
2. ASTM D1125-14; or
3. Alternate methods for salinity that can reliably provide salt content within ±10% of certified standards

pH

1. Standard Method 4500H+;
2. ASTM D1293-18; or
3. Alternate methods for pH determination that produce ±0.2 pH unit accuracies between 5.0 and 9.0

ORP

1. Standard Method 2580;
2. ASTM 1498-14; or
3. Alternate methods for ORP detection that can produce ±15% accuracy between ORP of 100-400 mV

Turbidity

1. Standard Method 2130;
2. ASTM 7315-17; or
3. Alternative nephelometric methods that can produce ±20% accuracy at 20 NTU

Oil and Grease

1. Standard Method 5520;
2. ASTM D8193-18; or
3. Alternative methods capable of generating ±20% accuracy

Sulfide

1. Standard Method 4500;
2. ASTM 4658-15; or
3. Alternative methods capable of generating ±20% accuracy

Other measurements that operators may want which will require calibration and validation:

Iron

1. Standard Method 3500;
2. ASTM D1068-15; or
3. Alternative methods capable of generating ±20% accuracy

Total Dissolved Solids (TDS) or Total Suspended Solids (TSS)

1. Standard Method 2540;
2. ASTM D5907-18; or
3. Alternative methods capable of generating ±20% accuracy

Sulfate

1. Standard Method 4500-SO42;
2. ASTM D4130-15; or
3. Alternative methods capable of generating ±15% accuracy

Calcium

1. Standard Method 3500;
2. Total Hardness Standard Method 2340; or
3. Alternate methods capable of generating ±20% accuracy between 20 and 100 mg/L calcium as CaCO3

Alkalinity

1. Standard Method 2320; or
2. Alternative methods capable of generating ±10% accuracy.

If applicable, NACE Standard TMO194-94 Field Monitoring of Bacterial Growth in Oilfield Systems

Benefits

Adoption of a guideline for a CB common minimum spec will provide important benefits, the most obvious of which is the encouragement of more water recycling by lowering the cost of recycled water. Greater use of recycled CB reduces the demand for fresh and brackish water that communities, agriculture, and industry compete for in arid regions. It provides more water availability to the operator that may struggle to acquire source water in some shale plays.

More recycling reduces the amount of water disposed of in SWD wells. In some areas, disposal pressures are increasing, which in turn limits volumes that can be injected. This creates problems for new wells that must be drilled through pressurized, shallower disposal zones, leading to disposal in more expensive deep-zone wells. Induced seismicity has been linked to high disposal volumes and pressures in some formations. It is in the industry's interest to proactively address this issue to avoid potential over regulation.. It could create a scenario in which waters must be highly treated to surface discharge requirements for National Pollutant Discharge Elimination System (NPDES) permits – an expensive option.

Increasing the scale of operations reduces CAPEX and OPEX for managing byproduct water, which has historically been a waste stream. Lowering the cost point for CB changes the game, allowing the water to become a tradable commodity rather than an expensive waste.[2]

Conclusion

The industry would benefit from adopting a common specification for minimum CB quality. The primary benefit would be to water midstream companies that can treat water at greater scale of operation, thus reducing CAPEX and OPEX unit costs. A common spec will also facilitate CB sharing across pipeline systems, reducing the amount of expensive storage capacity required. Ultimately, the water management cost savings will go to operators in the form of reduced CB supply and PW disposal costs. A common spec will allow the industry to coalesce around a set of controllable parameters that are measurable in real time. Further advantages of this initiative are to encourage CB recycling to reduce freshwater demand and water disposal. PWS endorses this

CB spec as a starting point, recognizing that it may be modified later as technologies for measurement improve and for other unconventional plays that may need to modify these limits.

References

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7 ASTM International West Conshohocken, PA, www.astm.org

Appendix A

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Special acknowledgement to Christopher Lloyd , Ph.D., Retego Labs who contributed significantly to the testing methods section