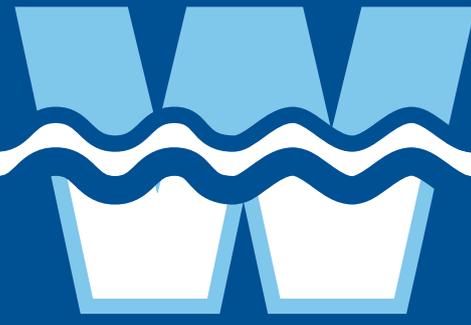


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Summer 2022

**An Overview of Some Water Treatment Processes, Phosphonates, and Polymers for the Oil & Gas Industry, in an Era of Water Recovery and Recycling**



# An Overview of Some Water Treatment Processes, Phosphonates, and Polymers for the Oil & Gas Industry, in an Era of Water Recovery and Recycling

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## Abstract

As a result of global population growth and an increased demand for energy and good quality water, the demand and supply positions for vital resources (especially water) varies considerably from country to country; but globally, freshwater withdrawals have increased six-fold over the last 100 years, and we all face an uncertain future due to critical worldwide water shortages and quality problems. In view of this crisis, this paper focuses on the oil and gas industry and their relatively large usage of water (e.g. for hydraulic fracturing fluids). It provides an overview on the types of standard water treatment separation processes available to implement the 3-Rs (i.e. Reuse, Recycle, Reclaim), and aims to further reduce water consumption. Additionally, this paper provides some guidance notes on the benefits, limitations, and application of phosphonates, polymers, and other waterside chemical inhibitors and performance additives, for selection by water treatment practitioners when confronted with more complex brine water chemistry.

## Background to population growth and an increased demand for energy and good quality water

Demographics tell us the number of people in the world increased more than 4-fold during the 20th century, and so we may ask what will humanity's future looklike.<sup>1</sup> Unfortunately, beyond trends on future population growth, it remains extremely difficult to predict with much certainty the future of the world's inhabitants. However, it is clear that the threads of mankind are closely intertwined with our impact on the natural environment, pandemics and other catastrophic events, fertility rates, and access to space, food, health services, education, and other resources.<sup>1</sup> It seems very unlikely that mankind's demand for energy and good quality water will ever diminish.

In spite of the politics of climate change and activist calls for a reduction in the world's dependence on fossil fuels - in favor of nuclear energy, solar and wind power, and other sustainable energy sources - global demand for crude oil (including biofuels) has in recent years been continuously climbing by approximately 10% per year. In 2006 daily global crude oil demand was 85.3 MMB/D. At the time of this writing in 2022, daily global crude oil demand is estimated to be 96.5 MMB/D, and the estimate for 2026 is 104.1 MMB/D. The only fall in demand in recent history was in 2020, when usage dropped to 91 MMB/D due to the economic and mobility impacts of widespread shutdowns across the world, due to the Corona virus pandemic.<sup>2</sup> Specific to the US, the Energy Information Administration (EIA) estimates that about 2.70 billion barrels of crude oil were produced directly from shale (tight) oil resources in 2020. This is equivalent to about 7.37 MMB/D - and equal to about 65% of total U.S. crude oil production - which shows how important unconventional resource development of shale oil (and gas) production is to the total annual output of US hydrocarbon production.<sup>3</sup>

The demand and supply positions for vital water resources vary considerably from country to country, but globally, freshwater withdrawals for agriculture, industry, and domestic/municipal use has increased six-fold over the last 100 years or so, with a sharp rise from the 1950s onward. Since 2000, however, the annual increase in global water withdrawals appears to be plateauing, or at least decelerating, at around 4 trillion cubic meters per year (nb: 1 cubic meter = 264.172 US gallons). However, it is clear that most conventional renewable water resources are declining in both output and quality in many countries as a result of population increases. Today, water shortages are affecting more than 3 billion people, and the amount of freshwater available per person has

plunged by a fifth over the last two decades.<sup>4</sup>

In the US, water use in 2015 was estimated to be about 322 billion gallons per day (Bgal/d), which was 9 percent less than in 2010. The 2015 estimates put total withdrawals at the lowest level since before 1970, following the same overall trend of decreasing total withdrawals observed from 2005 to 2010.<sup>5</sup> This lower (i.e. improved) water withdrawal position is likely due to significant changes in agricultural and horticultural irrigation practices, including use of surface- and sub-surface drip irrigation techniques. Additionally, in order to reduce demands on freshwater use, we see water/wastewater recovery, recycling, reinjection, purple pipes, and other water reuse techniques being increasingly practiced by municipalities and industries of all types. We are also seeing an increase in the commercial application of a wide range of modern water and wastewater treatment technologies that barely existed 30 or 40 years ago - particularly those processes that incorporate polymeric membranes, such as **wastewater membrane bioreactors (MBR)**, **seawater reverse osmosis (SWRO)**, and **electro-chemical deionization (EDI)**.

## The integral relationship between hydraulic fracturing and water

Hydraulic fracturing treatments aim to stimulate (increase the productivity) of low permeability oil and gas wells by creating a propped fracture (a crack in the reservoir rock) extending deep into the reservoir from the wellbore. The fracture is created by pumping a hydraulic fluid at high pressures that cause the reservoir rock to fail, creating the fracture at the wellbore and then extending it into the reservoir. Sand or other propping agents are pumped into the fracture during the frac treatment, which holds the fracture slightly open after the frac job is completed. The resulting propped fracture is highly-



conductive, which allows reservoir fluids to flow into the wellbore at much higher rates than those of non-stimulated wells.

The first frac job was pumped in 1947, and the early frac jobs were just a few hundred gallons in volume – a miniscule size by today's standards. Just about every fluid imaginable has been used as the base fluid for a frac job, with napalm (gelled gasoline) being used on the first job, and also including crude oil, gelled oils, inorganic and organic acids, acid/water/oil emulsions, foams...but the vast majority of frac jobs have used water as the base fluid, both fresh and brine, and both gelled and ungelled. Not surprisingly, water brings a number of benefits over the other alternatives:

- Water is benign, and much safer to work with.
- Water is generally far more plentiful and available.
- Water usually has a much lower cost.
- Water is a great solvent that can carry multiple desired chemistries into the reservoir.
- There are a larger variety of available chemical additives that allow for easier adjustment of the water-based frac fluid physical properties.

A fundamental design concern for frac treatments is compatibility between the frac fluid and the reservoir rock mineralogy and reservoir fluids. For example, in the presence of fresh (non-brine) water, **smectite** and mixed-layer clays will swell, while **illite** and **kaolinite clays** will break apart and migrate. The result in each of these cases can be a significant reduction in reservoir permeability due to plugging of pore throats in the rock caused by these physical changes in clay structure. Creating an artificial brine by adding an appropriate amount of a compatible salt (such as *potassium chloride* or a "KCl substitute" such as *choline chloride*) to the fresh water will reduce or eliminate these effects. Other potential concerns include dissolution and re-precipitation of iron compounds, precipitation of asphaltic sludge from the oil, deposition of paraffin (wax) from the oil, creation of emulsions with the oil, and creation of water blocks in the reservoir. Suffice it to say that ensuring compatibility between the water-based frac fluid and the reservoir

is critical. Intuitively, the ideal frac fluid would be made with a base fluid that is from (or mimics the composition of) the native reservoir water.

For many years each frac job was designed with the specific well, formation rock properties, and other reservoir parameters in mind. This effort, along with a continual focus on maximizing the commercial value of the frac treatments, led to treatment volumes growing significantly over time. By 1980, frac jobs using over 100,000 gallons were common, and very large treatments of ~1,000,000 gallons were sometimes occurring. Treatment volumes continued to grow throughout the 1980s, 1990s, and into the early 2,000s, with most frac designs incorporating relatively expensive high viscosity fluid systems. These fluid systems were designed to suspend the frac sand as it was being pumped so that it would not settle out, but rather would be carried far into the fracture so the fracture would be propped open deep into the reservoir.

By the mid-2000s, oil and gas shale drilling was growing rapidly. Shale frac designs deviated from the historic frac design approach in several significant ways:

- The viscosity of the base fluid would not be raised, so no viscosifiers / gelling agents were added.
- Because viscosity was low, enhanced sand suspension was lost. As a result, the frac jobs needed to be pumped in high turbulent flow (i.e., at much higher pumping flow rates). Use of polyacrylamide-based friction reducers (FR) to reduce the treating pressures of the frac jobs grew exponentially.
- The size of the frac sand being pumped became smaller due to lower terminal settling velocity and ability to carry it farther into the fracture before settling out.
- Well completions increasingly moved into a "manufacturing mode" where the same frac design was pumped on each job. Operational efficiency (amount of time to pump each frac job) became a primary focus.
- Correlations were seen between larger frac job sizes and higher well productivity, leading to another large uptick in treatment volumes.

Today, shale frac job sizes have grown, along with wellbore lengths and number of frac stages per well, such that tens of millions of gallons of water may be used for the completion of the wells on a single drilling pad. As the demand for larger and larger volumes of water grew, a number of issues became problematic and critical:

- In some areas, access to the necessary volumes for the frac jobs became increasingly difficult to find.
- The cost of sourcing these large volumes of fresh became significantly large.
- The cost of disposing of these large volumes of water during flowback after the frac job – always a concern in the past – now became extremely high.
- As a result, recycling and reuse of the previously-used frac water and produced water became a necessity.
- Rising TDS levels resulting from recycling may cause a reduction in efficacy of certain frac fluid components, such as FR. In some cases dilution with additional fresh water to reduce the TDS below a particular threshold may solve the issue, while in other cases a change in FR chemistry may be required.
- Recycling and reusing frac water and produced water ultimately means dealing with all of the challenges of effective water treatment: the need to clean up brine water containing high TDS and high TSS, at times along with dissolved iron, residual oil, residual chemicals, and/or contamination with bacteria.

The number and size of frac jobs pumped annually is expected to continue to grow in the coming years, which means that the water volumes required to make up the frac fluid will continue to increase. Effective treatment and cleaning of recycled frac and produced water for reuse in frac treatments will not only remain a critical aspect of the frac job execution for years to come, but it will be a necessity and required enabler for economic and social viability of the drilling and completion of new oil and gas wells.



## A golden age for shale plays and wastewater recycling

Given that the process of unconventional development, including hydraulic fracturing of shale for oil & gas production in the U.S., is equal to about 65% of total U.S. output, there is no doubt that we are in a golden age for shale plays (within the industry, hydraulic fracturing and the created fractures are known as frac'ing and fracs). The rise of North American shale oil & gas production has brought game changing predictions about supply and demand, and with it, key players with technologies and expertise to unlock previously inaccessible shale resources.<sup>6</sup> The Independent Petroleum Association of America (IPAA) informs us that hydraulic fracturing has been safely used in the United States since 1947 and more than 1.7 million U.S. wells have been completed using the frac'ing process. Indeed, the EPA has stated that unconventional oil and natural gas plays a key role in our nation's clean energy future.<sup>7</sup>

However, oil and gas production obtained from shale plays uses a lot of water! Depending on the play, a well may require from 2 to 5 million gallons or more before completion, of which 80-90% is used for fracturing and only 10-20% will be typically required for drilling, and other purposes.<sup>8</sup> That is a lot of frac wastewater for potential disposal, and although the EPA advises us there are approximately 144,000 underground injection (disposal) wells for produced water (PW) disposal, some practices can possibly create problems. If injection volumes into disposal wells result in injection pressures that exceed the frac gradient of the injection formation, microfractures can be created that grow vertically into other formations that lie above or below the injection zone. For shallow injection wells, this could include formations that contain potable groundwater, resulting in risks of contamination to shallow groundwater aquifers. Another potential effect of over-injection is the creation of localized micro earthquakes being felt at the surface. With these potential negative impacts, it is clear that effective management of produced wastewater is critically important to ensure positive environmental, social, and governance (ESG) impacts result instead. Adequate numbers of local injection wells must exist and be available to ensure that wastewater disposal injection pressures stay well below formation frac gradients.

Additionally, note that during the sequential oil or gas recovery process, PW emerges as an associated byproduct, containing mainly formation water (FW) and a small portion of frac fluids as flowback. As an example, in the Permian Basin, the PW to oil ratio (PWOR) of shale wells is around three, and for all U.S. plays on average, over 90% of the PW is naturally occurring FW and connate/interstitial water. That is a lot of frac wastewater for potential disposal, and although the EPA advises us there are approximately 180,000 underground injection wells for produced water (PW) injection, some practices can possibly create problems. Currently, the preferred method for disposal of produced water is through permitted Class II water Injection wells, of which 20% are salt water disposal wells and 80% are wells that are enhanced oil recovery (EOR) injection wells. These EOR injection wells include waterflood injection wells (i.e., injection of water to drive oil in the reservoir to producing wells), steam injection wells (to thermally thin and drive viscous oils), and water alternating gas (WAG) injection wells or simultaneous water and gas (SWAG) injections wells (both are techniques to improve the sweep efficiency of waterfloods or gas floods). The alternative to disposal of frac fluids is wastewater capture, treatment, and reuse – for new frac jobs, irrigation, cooling water, or other purposes. This recycling practice has been growing year over year in output volumes. However, in view of the continuing global importance of oil & gas, produced by both conventional and unconventional means, and the need to move closer to a water-secure and net-zero world, it is important during new well development and production to aim to use even less fresh water and associated chemistries. Thus, in the oil & gas industry, it is also necessary to recover, treat, and reuse as much PW, FW, and flowback frac fluids and blends as possible.

### "Water, Water, Everywhere, Nor Any Drop to Drink"

*Rhyme of the Ancient Mariner,  
by Coleridge.*

### The Three R's of Water: Reuse, Recycle, Reclaim

This water reuse, recycle, reclaim focus is of significant business interest to both large and small service companies in the oil & gas and water treatment chemical/equipment fields. These firms tend to operate in several specialist niche sectors

and geographies within the global oil & gas support services market, and may offer separation processes, **such as oil/water separation, evaporative water recovery, or wastewater clarification.** Specific performance chemicals "packages" may be required, to perhaps include *demulsifiers* (treaters, droppers, and hybrids, etc. to destabilize/ break/ flocculate/ coalesce water-in-oil emulsions), *reverse demulsifiers* (to break oil-in-water emulsions), *reverse emulsion breakers* (REB), to break complex water-in-oil-in-water (W/O/W) emulsions; and also, *gas hydrate inhibitors, surfactants, antifoams, coagulants, flocculants, precipitants, piping corrosion inhibitors, and antisclents.*

Prior to more recent history, chemistries for slickwater generation, proppant support, and some limited water treatment for scale, corrosion, microbiological, and/or general fouling inhibition, were typically primarily focused on treating a wide range of fresh waters, with perhaps less emphasis being given to treating the scaling tendencies of re-injected (and usually diluted) recycled brines. This focus is changing, and more applications expertise is often now available for managing the native reservoir brines that will be produced in the future. Service companies offer expertise in working with their arsenals of complex (and now usually more eco-friendly) chemistries and formulations, in order to modify produced brines for reuse as frac fluid bases. Some service firms may also be active with remedial stimulation of existing producing wells - which traditionally has been a smaller focus for business development opportunities, but is expected to grow in the future. Similarly, growth is also expected for novel or "green" production chemistries, and their application in optimizing repurposed brines and other industrial waters for reuse.

However, it is a mantra that consideration of the formation rock surfaces and mineralogy is very important and must always be a primary consideration when formulating new chemical treatment products. Nearly everything injected into a well is foreign to it, so there is a need to fully understand the likely impact of fluid constituents on the rock and its associated environment. This means that a comprehensive analysis of all fluid interactions with the formation rock and its environment is the first need. It is well understood that produced water quality



varies from play to play, and no single technology exists that is best for treating all produced waters in all operating areas, such that it can be recovered for blending or direct reuse. More than this, operators understand that to produce a laboratory analysis of water quality and contaminants is not particularly difficult, but its interpretation and what this ultimately means in terms of slick water and other frac fluid chemistries can be challenging. The question of how best to implement any specific frac job using fresh or recycled water, and precisely what type of processes may eventually be required to treat the volumes of produced water that are ultimately evolved thereby implementing the three R's of water - reuse, recycle, reclaim - are altogether more critical and arduous tasks to perform. Firstly, what chemicals are present in the frac fluid?

Frac fluids potentially contain a wide range of additive chemistry products that vary in composition from play to play, such that each additive is itself a formulation of performance chemistries, collectively providing a task-specific component of an overall fracturing fluid program. Beyond the addition of primary ingredients, such as, say 0.2-2.0% of KCl or substitute in the base water, 5-15% or so of fracturing acid employed (usually HCl), and the many tons of varying size, shape, and strength of crystalline silica sands, or other ceramic proppant (of typically, 0.1 to 0.2 mm diameter), the total formulated performance additive packs may comprise perhaps 0.3 -0.75% by volume (3,000-7,500 mg/L, or ppm) of the base frac fluid.

Chemistry additive components for hydraulic fracturing fluids may include some or all of the following materials:

**1. Surfactant:** Used to reduce oil/water surface tension, such as a PEG methyl ether, or similar.

**2. Gelling agent:** Typically, guar gum or a derivatized guar-based polymer such as hydroxypropyl guar (HPG), carboxymethyl hydroxypropyl guar (CMHPG). Other polymers that may be used include hydroxyethyl cellulose (HEC) and xanthan gum. In all of these cases the purpose of the gelling agent is to increase the frac fluid viscosity and help support and carry the proppant. Non-derivatized guar gum is used in the vast majority of water-based frac jobs requiring significant viscosity. Other types of

gelling agents include those for oil-based frac fluids, such as phosphate ester surfactants (e.g. dialkyl phosphoric ester) – or phosphorus free gelling agents, may be used to recover or enhance production output.

### 3. Gelling agent cross-linker:

Typically zirconium, titanium, or borate-based. These create or improve the polymer network and system viscosity. Uncrosslinked guar-based polymers (commonly called "linear gels") may become thinner with an increase in temperature, so a cross-linker can aid viscosity stabilization.

### 4. Slickwater friction-reducer (FR):

Fracturing fluids need sufficient viscosity to create and open a fracture, but must also have a low friction coefficient. Linear gels typically generate 12 – 18 centipoises (cPs) of viscosity, where crosslinked gels can generate viscosities of 500 – 4,000 cPs or more. For many unconventional shale formations, however, low viscosities of only 1-5 centipoises (cPs) may be all that is required and desired, although in some cases a High Viscosity Friction Reducer (HVFR) may be used to generate viscosities in the 8-13cPs range. In either case, FR or HVFR yield relatively low frac fluid viscosities. Because shale frac designs show a preference for low viscosities, the terminal settling velocity of the frac sand particles is relatively high, and results in the frac sand settling out quickly in the typical shale frac design. Since it is desirable to achieve a higher propped frac length (that is, to pump the frac sand grains farther into the fracture from the wellbore before settling out), the frac fluid pumping rate must be very high (typically 80-140 bpm) on shale frac jobs in order to achieve adequate propped frac length. At these levels of pumping rates, friction pressure becomes high and friction reducers are necessary to lower the frac job pumping pressure. In some cases a lightly gelled linear guar is used, but FR and HVFR are generally preferred because they are able to lower the friction pressure to a greater degree at a lower cost. FR and HVFR can lower the friction pressure by 60-80%, depending on the water salinity and other chemical presence. FR and HVFR chemistry are typically based

on polyacrylamide (PAM) or PAM/AM copolymers.

**5. Live breaker:** Ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] and other oxidizers break the polymer network and reduces the viscosity of a fracturing fluid (ideally) following the end of each frac stage to help flow the well back. The breaker oxidation reaction speeds up significantly with increased temperature and increased breaker concentrations, so designing an optimized breaker schedule for the specifics of each frac job is desirable.

### 6. Encapsulated breaker:

To ensure the breaker does not reduce frac fluid viscosity too early, encapsulated breaker can be used. Encapsulated breaker consists of a time-release coating or encapsulation of ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] that results in a slower release of the oxidizing breaker. This allows the designed concentration of oxidizer to reach the tip of the fracture at full strength before releasing, so the entire fracture sees a uniform viscosity degradation after completion of the frac job.

**7. Corrosion inhibitor:** Typically, long-chain ethoxylated fatty acid alkylamine film formers, used to reduce the corrosion resulting from acids being pumped down steel casing and tubing (pipes) that make up oil and gas wells.

**8. Scale inhibitor:** Typically, a copolymer and/or a standard phosphonate, or perhaps a DETA phosphonate, as deemed suitable for management of alkaline earth salts and scales such as calcium carbonate, barium sulfate, etc.

**9. Iron inhibitor:** Perhaps control here might also be served by the scale inhibitor/dispersant, or via a water soluble EDTA, gluconate, terpolymer, or alternatively, by imidazoline film adsorption. In combination with pH control (keeping the solution pH at less than 5), a viable approach can be to use iron inhibitors to prevent oxidation of ferrous iron (Fe+2) to its ferric (Fe+3) form - ferrous iron does not precipitate below a pH of 8.5, but ferric iron (Fe+3) forms precipitates at pH of 3.5 or above.



**10. pH buffer:** Used to control the pH of a solution. Perhaps a simple chemistry such as hydronium ion/conjugate base (e.g. a citric acid-phosphate mix), or perhaps the use of a methane/ethane sulfonic acid chemistry.

**11. Biocide:** Used to kill bacteria that is present or can grow in surface tank and systems, or downhole in producing wells. Typically a non-oxidizer gluteraldehyde, quat, or isothiazoline blend.

**12. Demulsifier:** Perhaps an EO block copolymer, ethoxylated alkylphenol, or di-epoxide (all of appropriate hydrophilic-lipophilic balance, HLB), in, say, a methanol or HAN solvent.

As discussed earlier, following frac jobs, *produced water* containing both *formation water* and *flowback water* is most seen, with the proportion of formation water increasing over time. It is common to find that the amount of frac fluid volume recovered to be very low, with a significant amount of the injected volume being “lost” to uptake/absorption forms of inhibition and/or other mechanisms in the formation. We know that produced formation waters are highly variable within and between shale formations. We also understand that sometimes sampling problems and limitations of some analytical test methods can occur, which adds to problems to be solved.

Table 1, shown below is an example of typical analytical ranges of some commonly found parameters in raw produced water samples. Table 2 also shows a produced water analysis, but this time with a review of analytical constituents and key saturation parameters, as calculated using French Creek *ion association modeling* software. Results are indicative of which contaminants, dissolved minerals, and potential downstream problems may need to be reviewed when treated produced waters are reused as a fracfluid, or for other purposes such as drilling, cooling, or irrigation water.

- Note that inorganic and wet chemistry tests on produced waters can be affected by very high solids content and other shale matrix complexities.
- Few volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) are regularly detected in produced formation waters. However, when they are seen, benzene, toluene, and xylenes (BTX) are the most common VOCs found, and phenols and pyridene are the most common SVOCs.
- Concentrations of barium and strontium salts tend to rise and fall but generally correlate with total dissolved solids (TDS) results. Chloride represents the most abundant anion.

- Concentrations of these various analytical parameters appear to increase with time following hydraulic fracturing activities, and remain at high concentrations in the produced formation water from operating wells in each shale formation.<sup>10</sup>

### Separation technologies and other treatment considerations in water recycling

Considering the current water recycling position, most recent R&D work, technical reports, and promotional documents essentially say the same thing: i.e., recycling O & G produced water for reuse in new frac operations or other water uses (e.g. irrigation, purple pipes, toilet flushing, drinking/potable, etc.), is a viable process and usefully saves freshwater, transport costs, and waste! The question then becomes one of identifying future uses of treated reclaimed water, and then adjusting one or more standard equipment treatment technologies or process trains (and selective water treatment chemistries) to precisely match needs. Going forward, a better understanding of the variabilities in production brines and matching them with appropriate performance chemistries will likely be a bigger focus.

Some useful related comments extracted from cited papers and reports on this subject are provided below:

1. *Ten years ago ExxonMobil affiliate XTO Energy teamed up with a major oil field services company to test the feasibility of reusing produced water for new frac'ing operations. Real world tests confirmed that with minimal treatment, the fluid used in these wells could successfully fracture the rock, and carry sand into the fractures to hold them open, even when based on 100% produced water, saving fresh water, money, and wasted truck trips.*<sup>11</sup>

2. *According to the Texas Water Development Board, in areas of Texas where freshwater is scarce, the water-intensive nature of hydraulic fracturing could be a cause for concern. Some frac wells require 10 million gallons of water or more. Isn't there a way to recycle and reuse this water? Frac fluids combine water with proprietary mixes of chemicals, and are unsuitable for reuse without treatment. "There are chemicals, oil droplets, rock fragments, polymers and a bunch of gunk you need to get*

**Table 1: Example of typical analytical ranges for constituents of produced water across plays**

Raw Produced Water samples, reflecting typical analytical ranges of some commonly found parameters		
Parameter	Units	Range of results
pH	-	4.0 – 7.0
Electrical conductivity	µS/cm	Not possible due to oil
Calcium	mg/L Ca	500 – 35,000
Magnesium	mg/L Mg	500 – 4,500
Chloride	mg/L Cl	20,000 – 165,000
Sodium Na	mg/L Na	22,000 – 70,000
Potassium	mg/L K	1,250 – 1,750
Strontium	mg/L Sr	60 – 2,400
Boron	mg/L Bo	20 – 30
Barium	mg/L Ba	1 – 7
Iron	mg/L Fe	0.5 – 35
Zinc	mg/L Zn	0 – 5
Total dissolved solids	mg/L TDS	45,000 – 275,000
Turbidity	Neph. TU	80 – 250
Total suspended solids	mg/L TSS	1,000 – 12,000



# DownHole SAT™ Water Analysis Report



## SYSTEM IDENTIFICATION

Sample 1  
Lab Tech: Ernest Jack  
Field Tech: Joseph Bear

Sample ID#: 669  
ID: 04201988  
Sample Date: 03-20-2014 at 1436  
Report Date: 03-20-2014

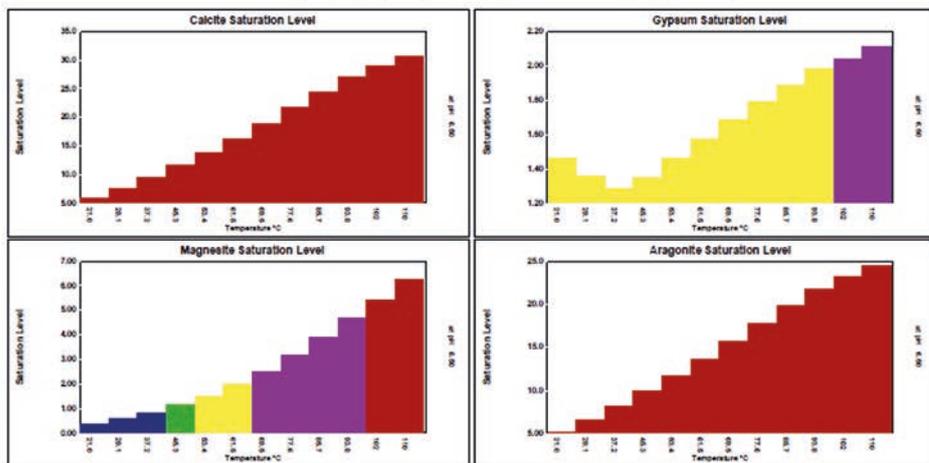
## WATER CHEMISTRY

CATIONS		ANIONS	
Calcium(as Ca)	6230	Chloride(as Cl)	45800
Magnesium(as Mg)	474.00	Sulfate(as SO <sub>4</sub> )	1860
Barium(as Ba)	0.00	Bromine(as Br)	0.00
Strontium(as Sr)	67.30	Acidity(as CaCO <sub>3</sub> )	129.69
Sodium(as Na)	22000	"M" Alkalinity(as CaCO <sub>3</sub> )	795.00
Potassium(as K)	1370	"P" Alkalinity(as CaCO <sub>3</sub> )	0.00
Lithium(as Li)	0.00	Silica(as SiO <sub>2</sub> )	0.00
Iron(as Fe)	0.600	Phosphate(as PO <sub>4</sub> )	0.00
Ammonia(as NH <sub>3</sub> )	0.00	H <sub>2</sub> S (as H <sub>2</sub> S)	0.00
Aluminum(as Al)	0.00	Fluoride(as F)	0.00
Manganese(as Mn)	0.700	Nitrate(as NO <sub>3</sub> )	0.00
Zinc(as Zn)	0.00	Boron(as B)	0.00
Lead(as Pb)	0.00		
PARAMETERS		Temperature(°C)	20.00
		Sample pH	7.45

## SCALE AND CORROSION POTENTIAL

Temp. (°C)	Press. (atm)	Calcite CaCO <sub>3</sub>	Anhydrite CaSO <sub>4</sub>	Gypsum CaSO <sub>4</sub> ·2H <sub>2</sub> O	Berite BaSO <sub>4</sub>	Celestite SrSO <sub>4</sub>	Siderite FeCO <sub>3</sub>	Mackawite FeS	CO <sub>2</sub> (mpv)	pCO <sub>2</sub> (atm)								
21.00	0.00	5.91	0.121	0.928	-28.53	1.46	132.39	0.00	-0.0457	0.557	-33.74	0.675	-0.0532	0.00	-0.555	0.0873	0.0655	
29.09	0.00	7.61	0.147	0.930	-26.85	1.36	107.41	0.00	-0.0658	0.543	-35.50	0.965	-0.00484	0.00	-0.563	0.120	0.0655	
37.18	0.00	9.50	0.173	0.975	-9.12	1.29	88.13	0.00	-0.0902	0.543	-35.39	1.33	0.0383	0.00	-0.572	0.123	0.0655	
45.27	0.00	11.53	0.197	1.06	19.92	1.25	99.86	0.00	-0.119	0.548	-34.57	1.77	0.0769	0.00	-0.581	0.0818	0.0655	
53.36	0.00	13.80	0.222	1.20	55.67	1.46	119.60	0.00	-0.156	0.551	-34.03	2.31	0.113	0.00	-0.591	0.0274	0.0655	
61.45	0.00	16.26	0.248	1.40	93.93	1.57	135.36	0.00	-0.203	0.552	-33.80	2.96	0.147	0.00	-0.602	0.105	0.0655	
69.55	0.00	18.89	0.274	1.69	131.47	1.68	148.12	0.00	-0.261	0.551	-33.87	3.71	0.178	0.00	-0.613	0.109	0.0655	
77.64	0.00	21.60	0.300	2.08	166.11	1.79	158.59	0.00	-0.333	0.547	-34.21	4.57	0.207	0.00	-0.626	0.113	0.0655	
85.73	0.00	24.31	0.326	2.63	196.66	1.88	167.35	0.00	-0.422	0.542	-34.82	5.50	0.232	0.00	-0.639	0.0674	0.0655	
93.82	0.00	26.88	0.350	3.39	222.69	1.98	174.83	0.00	-0.531	0.535	-35.70	6.48	0.254	0.00	-0.654	0.0452	0.0655	
101.91	0.0714	28.83	0.378	4.40	247.53	2.03	182.05	0.00	-0.675	0.519	-37.96	7.36	0.272	0.00	-0.676	0.0580	0.0702	
110.00	0.415	30.65	0.397	5.67	266.14	2.11	187.99	0.00	-0.842	0.508	-39.56	8.22	0.283	0.00	-0.694	0.0826	0.0927	
		Lbs per 1000 Barrels	xSAT	Lbs per 1000 Barrels	xSAT	Lbs per 1000 Barrels	xSAT	Lbs per 1000 Barrels	xSAT	Lbs per 1000 Barrels	xSAT	Lbs per 1000 Barrels	xSAT	Lbs per 1000 Barrels	xSAT	Lbs per 1000 Barrels	xSAT	Lbs per 1000 Barrels

Saturation Levels (xSAT) are the ratio of ion activity to solubility, e.g., (Ca)(CO<sub>3</sub>)/K<sub>sp</sub>. pCO<sub>2</sub> (atm) is the partial pressure of CO<sub>2</sub> in the gas phase. Lbs/1000 Barrels scale is the quantity of precipitation (or dissolution) required to instantaneously bring the water to equilibrium.



**Table 2: Example of a produced water analytical constituents review (courtesy French Creek Software)<sup>9</sup>**

rid of," says Dr. Jean-Philippe Nicot, senior research scientist with the Bureau of Economic Geology at the University of Texas at Austin. "Also, you may have collected chemicals that might not be compatible with the chemicals injected into the water for your frac operation, and therefore it might not work." And because of its potential toxicity to water-borne organisms, frac water cannot simply be disposed of in surface waters.<sup>12</sup>

3. In 2014, Apache Corporation (Texas) treated and recycled more than 10 million barrels of produced water," says Cooper, "which was then used in the company's hydraulic fracturing operations. These efforts reduced the company's road use by more than 80,000 truck trips."<sup>12</sup>

4. The study shows that brine water possesses all the characteristics required for effective frac'ing: easy preparation, rapid hydration, low fluid loss, good proppant transport capacity, low pipe friction, and effective recovery from the reservoir. Unlike fresh water, salt water does not restrict oil flow because of an osmotic imbalance that results in clay swelling. Simply put, salt water is good for frac'ing and any statements otherwise are unfounded.<sup>13</sup>

5. Why does the oil industry, continue to operate on the assumption that water with high levels of TDS is unsuitable for frac'ing? The perceived understanding has always been that salty water prevents the proper hydration of the crosslink-gel and

friction reducers, but as this study indicates - salt is clearly not the issue. Is there something else that would prevent a proper hydration of guar gum in the water? The real reason that the oil industry prefers to use fresh water for frac'ing is simply because it is cheap and clean, completely justifiable when trying to run a business. In essence, it is the low count of Total Suspended Solids (TSS) in aquifer water that makes the gelling hydration possible, not the absence of salt. The fact is, that TSS in the form of colloidal particles are very small in size (0.001 to 1 micron), yet very large in surface area. This structure makes colloids abrasive to friction inducers, negatively impacting the rheology of crosslinked gels. Where the oil industry has long-operated on the notion that TDS is the bottleneck in widespread frac water reuse, the study shows that TSS is the real culprit. The study recounts that at 99% TSS removal, the produced water was successfully blended into a crosslinked-gel-based frac fluid suitable for hydraulic fracturing.<sup>13</sup>

Third party opinions on treatments, as stated above, tend to focus on TSS and its removal being the key requirement, and whilst the authors of this paper are in agreement that total TSS removal is a good first step, the need to separate oil, oily sludges, and hydrocarbons from water is also required in order to produce clean brines. If WW treatment is restricted to TSS alone, the PW is likely to be undertreated!

Consider the following WW treatment notes to support our view:

- a. Hydrocarbons in produced water will cause issues with salt-tolerant FR chemistries.
- b. Also, in some regions and plays, it is necessary to control sulfur compounds (as, say, with geo-thermal brines).
- c. Additionally, what must be considered is the role of additive chemistries to inhibit potential scale, corrosion, and deposition problems - initiated by alkaline earth metals (i.e. Ca, Mg, Sr, Ba, Ra) and/or some of the transition metals (i.e. Cu, Fe, V, Co, Mn, Ni, Cr, Ti, etc.).



d. High silica, in either colloidal or reactive forms, can present additional problems – depending on brine pH, temperature, magnesium content, etc. How do we treat for silica control?

For some plays, produced water (PW) quality may be such that 100% can be directly reused without further treatment, (i.e. those with lower salt content, minimal TSS and low hydrocarbon content) – except, perhaps, for adding a biocide and changing out the FR in the “slickwater package”, for a more expensive, but salt-tolerant, friction reducer (STFR) chemistry. Under these conditions, there is no expectation for a reduction in well performance.

Novel, high viscosity STFR chemistries (HVFR) are now offered by any number of service companies, that can tolerate in excess of 200,000 mg/L brine TDS. Chemistries tend to be based on new types of very high molecular weight (2-30 Million MW), multivalent surfactant co-ter-polymers, in anionic, non-ionic, and cationic forms. An example is a reaction product formed from, say, a cationic monomer, e.g. [3-(methacryloylamino propyl)trimethylammonium chloride, with a non-ionic monomer, e.g. N-vinyl formamide, and a carboxylic monomer, e.g. maleic acid metal salt.<sup>14</sup>

### Water treatment equipment options and processes for production fluids and complex brines

Where PW treatment is required, process equipment options for treating PW and other WW are commonly available in the market, from the most basic, low-cost “standard treatments” to sophisticated, high-cost technologies that may include zero liquid discharge (ZLD). However, with the use of an effective and optimal treatment process, PW disposal volumes as wastewater may be reduced by perhaps 80-90%. Some service companies’ offer fully-integrated mobile WW treatment system trains, incorporating large reaction or frac tanks and other equipment that can treat perhaps 50,000 bbl/day of formation/flowback water. These systems typically use conventional separation technologies, such as API separators and dissolved air flotation (DAF) - to demulsify and separate oil, grit, and sludges from water. Also, coagulation and flocculation techniques with a clarifier are required for the removal of most or all total suspended solids (TSS), and perhaps these systems will also provide some

targeted precipitation of minerals such as iron salts - which form part of the total dissolved solids (TDS).

Examples of “standard” wastewater process treatments are given below – most are aimed primarily at TSS reduction or removal, but some treatments are offered specifically for oil and oily sludge removal, TDS reduction (or total elimination – as in ZLD), and also disinfection, destruction of VOCs and other types of organics, and removal of disinfection by-products.

#### 1. Sedimentation and clarification:

A basic technology that relies on some particulates in water eventually settling out naturally, or being aided by the use of inorganic chemical combinations (typically iron or aluminum based), and organic coagulation and flocculation chemistries, mainly alums and polyacrylamide (PAM). These chemistries can reduce the settlement time, and provide an improved settled sludge, with improved clarification of the supernatant fluid (i.e. less TSS).

**2. Filtration:** Systems may use back-washable multimedia, sand, disc, or bag/sock filters. Where the fluid contains organics, a granular activated carbon (GAC) filter may be preferable/required after the media filter, to remove VOCs or other organics.

**3. Chemical precipitation:** With the correct precipitant and pH (usually determined by field trials), this separation technology can be used to precipitate either specific metals and minerals, or a range of contaminants. Clarification or filtration is required to remove the resulting precipitates.

**4. Electro-coagulation (EC):** EC is an electro-kinetic technique with over a 100 year history, most often used in mineral mining operations and WW treatments - including oily-waters and metal plating waste. EC typically has Fe or Al alloy electrodes which, under the influence of a DC electric current, create metal salts that act as precipitants, coagulants and flocculants, which are used to remove transition/heavy metals, and/or other polluting chemistries, such as Cr, As, Se, and pesticides. EC is a form of electrophoretic deposition (i.e. deposition of charged particles in a fluid or gel under the influence of an electric field).

**5. Dissolved air flotation (DAF):** Treatment equipment systems may also

include variants such as dissolved gas flotation (DGF), – using N<sub>2</sub>, or induced air flotation (IAF). The objective is to separate oil or particulates, which rise, and can be skimmed off from clean water. DAF may be preceded by API tanks or lamella systems!

#### 6. Evaporation and thermal distillation systems:

There are several technologies that can potentially be employed, including single and multi-effect, or multi-stage thermal or mechanical evaporators. These separation technologies are very effective in producing a low TDS, clean and purified water, but often at significant cost. An example is the mechanical vapor recompression distillation process, which can, typically, recover in excess of 90% of inflow without the need for pretreatment to remove alkaline earth and transition metals that may be present. Such systems may also incorporate a steam stripper to remove light-end hydrocarbons. Other evaporative technologies include MSF and MEV.

#### 7. Zero liquid discharge technologies

**(ZLD):** ZLD involves a combination of technologies that ultimately result in a zero liquid waste discharge. Equipment employed is commonly a combination of a brine concentrator, evaporator, and crystallizer. Pretreatment is almost always required to first remove oil, TSS, and some scale-forming contributors to TDS. Ultimately, solid salt crystals/powder and high purity water are the only outputs, but these outputs come at a high capital and thermal heating cost.

#### 8. Advanced oxidation processes

**(AOP):** Sometimes known as super-oxidation, there are various types of systems in the market, and these are now commonly employed as a tertiary treatment in drinking water processes to breakdown pesticides, volatiles, and other complex organics in water, and to also reduce chlorine disinfection by-products. The most common process uses a combination of UV light and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or ozone (O<sub>3</sub>) to generate highly reactive, oxidative hydroxyl radicals. In the frac/PW market, there are vendors who provide this type of technology mounted on mobile systems for direct site treatments. These systems incorporate a series of steps that may also include the provision of ozone, acoustic and hydrodynamic cavitation, and electro-chemical processes.



## Water chemistry, and water management of reuse production fluids and complex brines

The O&G industry uses a lot of water and operators may work with production fluids having a high water cut, in the oil, gas and formation fluid mixture; so understanding the quality, consistency, and overall composition of the various waters and mixtures involved is important. Regarding the chemistry and physics of water, note that a water molecule is dipolar with a distorted or bent shape, and these polar forces draw water molecules together (cohesion), such that the oxygen in each water molecule forms a bond with hydrogen atoms from other molecules. This is an electrostatic attractive force, termed *ahydrogen* bond. This type of molecular bond holds the liquid water molecules together. Within the water molecules' tetrahedral shape we find that each water molecule is hydrogen bonded to four other water molecules – with lots of empty space within the liquid water 3-dimensional structure, which allows for the solvent water to accept a wide range and quantity of dissolved solute ions – which is why water is an excellent solvent.

Water's capability of solvating and housing very many different solute molecules is evident in treating hydraulic fluids and PW, evidenced by the high concentration of salts present in the PW. While water may not technically be a universal solvent, it does dissolve more substances than any other liquid. Note that this solubilizing effect can lead to problems, such as unwanted reactions, the incorporation of biological material, salts with reverse solubility (that quickly precipitate on heating), and strongly ionizable salts that can only be removed by reverse osmosis (RO), distillation, or expensive evaporative processes.

The rationale for discussing concepts of self-ionization of water, its solvation, amphoteric, amphiprotic, and acid-base behavior, etc., is that the properties of water give rise to the fact that water is perhaps the most common solvent for precipitation, oxidation/reduction (redox), and acid-base reactions. Note that, some of these reactions commonly occur in dynamic industrial waters, such as cooling water, process water, wastewater, reuse, hydraulic frac fluids, and PW; and these results may be difficult to control.

In view of water's chemistry and an anticipated need to aim for reuse of PW

where possible, to reduce freshwater requirements, it is probably necessary to first consider what types of WW treatment and options described earlier are offered by equipment OEMs and O&G service companies.

1. What treatment processes can work for us and match our needs?
2. Can any of the various standard equipment processes eliminate the need for chemistries (such as biocides, iron and sulfur precipitants, and scale/corrosion inhibitors)– at least on a temporary basis?
3. Are the chemistries critical primary additives, or only needed as water quality "polishers"?

Depending on any specific water under consideration, other factors will determine whether some of these equipment processes will prove useful and cost-effective. For example, thermal distillation, ZLD, or AOP processes are typically used for producing high purity water and may be too expensive. Some equipment technologies offered to the water-reuse market sector may seem to be "overkill" and are probably not required, especially if we have a light-brine PW that simply needs TSS and some oil removed to produce a clean brine that can be easily blended into a hydraulic fluid base. Similarly, **membrane technologies** such as *reverse osmosis* (RO) or *electro-chemical deionization* (EDI) are not likely required for most recovered brines, unless ultimately reused for cooling water makeup, irrigation water, purple pipes, or toilet flushing, etc. Even so, it may be more useful to use *microfiltration* (MF) and/or *ultrafiltration* (UF) with damage resistant PVDS or PES membranes. These may prove to be extremely useful "clean-up" processes, in guaranteeing the removal of all TSS. Note that UF has the added benefit of removing all bacteria and viruses, thus providing an alternative disinfection route.

Consider that one or more of these physical processes, supported by "polishing" chemical treatments, **only** become necessary if the future reuse of a water source under consideration demands it. Thus, what treatment steps are really required, and what is a reasonable quality standard for a clean brine?

1. To consider what treatment steps

are required, note that common salts used in the preparation of simple brine systems include sodium chloride, calcium chloride, and potassium chloride. More complex brine systems may contain zinc, bromide, silica, or iodine salts. These complex brines are generally corrosive and more costly to treat in terms of fluid chemistry components and the up-front need to anticipate potential operational problems (such as various forms of pitting corrosion). Brines often have complex chemistries with wide variabilities and constituent ion concentrations. What is their chemistry? What concerns do we have? Concerns may include mineral and biological contaminant *residence times* and *crystal induction times*. Also, we need to consider *common ion association models*, and *hydrate formation nucleation kinetics*. What actions are required by water treatment practitioners when confronted with more complex brine water chemistries?

2. As noted above, many gaseous and mineral impurities commonly found in production brines and other brine sources are generally corrosive. Salts typically present include inorganics, such as  $MgCl_2$ ,  $CaCl_2$ ,  $NaCl$ , and- at higher temperatures, will hydrolyze to some degree forming oxides and HCl, an acid gas that condenses in water to form hydrochloric acid, and which can be extremely corrosive to common steels and other metals. (Note that  $NaCl$  is more resistant to hydrolysis at lower temperatures.) Desalting processes, plus the use of inhibitors such as amines and ammonia can be employed to neutralize or may originate from various sources. It forms weak corrosive acids that can result in corrosion products such as siderite ( $FeCO_3$ ).

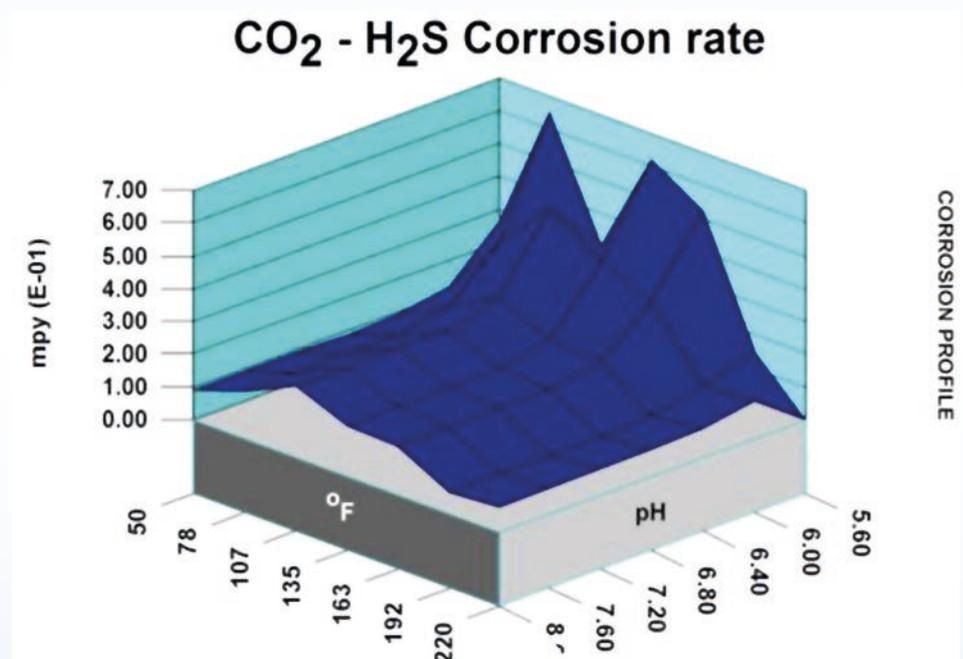
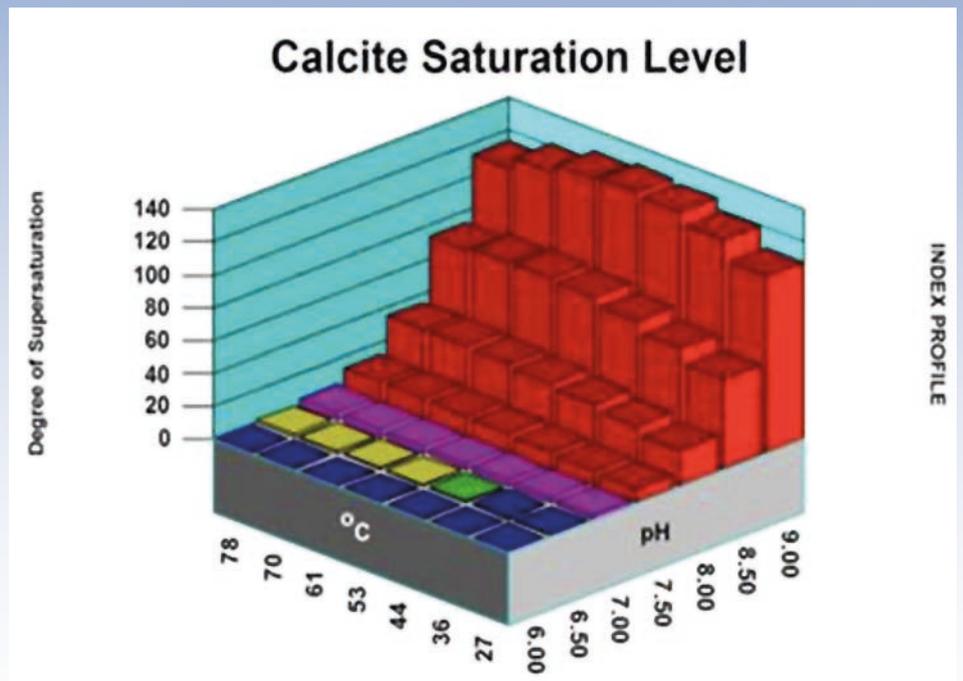
3. Sulfur compounds, in the form of corrosive sulfides (e.g.  $H_2S$ ), sulfates, and mercaptans, are almost always present to some degree. Effective control of sulfur chemistry corrosion processes and corroded metal cleanup (or at least its minimization) may be affected by using high-chrome steels in critical process areas, or by the use of inhibitor chemistries such as *tetrakis(hydroxymethyl) phosphonium sulfate* (THPS) or *2-(decylthio) ethanamine hydrochloride* (DETA).

Note that both THPS and DETA chemistries can also be used as bio-dispersants for control of biofilm formation. In their EPA registered form, THPS and DETA are both extremely effective microbiocides for control of sulfate reducing bacteria (SRB's), and other sessile and planktonic microorganisms contributing to problems of microbial induced/influenced corrosion (MIC).

4. Note also that scaling risks are compounded by rapid *nucleation rates* and the degree of dissolved mineral *supersaturation* and both of these factors are variables with negative effects linked to longer residence times, inverse salt solubilities, and higher temperatures. Thus, we sometimes see a decrease in solubility of undesirable ionic precipitates over time, and these may develop at some point beyond supersaturation concentrations. When they are produced, it is commonly by the addition to the solution of a soluble compound (from another ingredient) having an ion in common with the supersaturated precipitate (*i.e. the common ion effect*). This solubility change leads to an increase in actual precipitation and deposition, and beyond localized nucleation times, severe mineral salt scaling may occur (*i.e. salts of Ca, Mg, Sr, Ba, etc.*).

5. Thus, in considering potential scale and corrosion control chemistries (and also antifoulants and dispersants), we have to consider among other factors, the degree of risk of scaling as indicated by saturation index (SI) calculations (e.g. Langelier, Ryznar, Puckorius, Stiff & Davis, etc.). Typically, oilfield WT software is much more useful in providing accurate and comprehensive diagnoses and advice, as compared to these simple SI formulae. As an example of what can be modeled to examine scaling and corrosion risks, see examples of French Creek's *Downhole SAT* in Tables 3 & 4.<sup>9</sup>

Until fairly recently, there has been limited PW recycling in some shale plays. However, as treatment technologies have improved and the scale of operations have grown, it now can be more cost effective to recycle PW than to dispose of it in SWD wells. The financial rationale for the recycling of PW as make-up water for fracturing fluids will continue to improve because, at present in some



**Tables 3 & 4: Modeling waterside chemistry risks using French Creek oilfield simulation software**

plays, produced water volumes are 200-400% in excess of the annual completion source-water demand, thus offering significant opportunities for water reuse.

This brings us back to the question of what is a reasonable quality standard for a clean brine? A useful minimum specification table for reusing clean brine as recycled PW is shown below as Table 5. The table has been devised by a team from NM State College of Engineering, with support from NGL Water Solutions – a water midstream treatment business unit of NGL Energy Partners.<sup>15</sup>

**A guide to organic scale and corrosion control additives for more complex brine water chemistries<sup>16</sup>**

Rules of thumb tell us there are several primary functional organic chemical groups that act as scale and corrosion control additives (and more) in aqueous environments. Today, the focus on key functional group chemistries is often based on **phosphonates/ amino-phosphonates, maleates/ succinates or homo/co/ter-acrylate polymers**, although, there are other chemistries, such as: *iso- and polyiso-propenylphosphonic acid (IPPA, PIPPA)*, which are reaction products of



**Table 5: Common Clean Brine Minimum Specification for Reusing Recycled Produced Water (PW)**

Parameter	Minimum Specification
Salinity	Reported after treatment
pH	6.0 – 8.0
Oxidation reduction potential (ORP)	>350 mV
Turbidity	<5mg/L (approx. 25 NTU)
Oil	<30 ppm - no sheen
Hydrogen sulfide (H2S)	Non-detectable
Particle size	Filter <25 micron

both polymer and phosphonate, and various acrylate/ maleic/ phosphonate/ sulfonate polymer combinations. Also, there are chelants, green chemistries, azoles, imidazolines, long chain fatty acid amines, surfactants, esters, and vapor phase corrosion inhibitors (VpCI). Formulations for any specific range of problems generally require a combination of additives drawn from two or three, or more of these functional categories.

Rules of thumb also advise that each individual well formulated chemistry program selected will typically not be used in any moving body of water under examination (such as recirculating cooling water or drilling water) in concentrations exceeding 3-5 mg/L total "actives" concentration, depending on the degree of supersaturation, scaling species induction time, and/or nucleation rates. There will likely be a mix of chemicals employed under these conditions, and the total "actives" concentration of all chemistries will seldom exceed 15-20 mg/L, but more typically will be present in the body of water at a concentration of 10-15 mg/L, in order to meet both technical and financial considerations.

**NB: Induction time** is the time period between the moment a constant supersaturation is created and scale forming crystals are detected, whereas **nucleation rate** describes how many scaling crystal nuclei of critical size form on a substrate per unit area and unit time. Induction time and nucleation rate are important criteria for chemistry application rates, and rates for these various additives will vary based on the specifics of any of a wide variety of industrial water treatment, oil field, and refinery applications. For example, such an additives mix may be used in industrial water system at, say, 12-15 mg/L total actives. However, the same mix can be used as an RO antiscalent/dispersant program, at only 3-4 mg/L total actives. Additionally, the same mix

may be successfully used as a scale inhibitor/dispersant for power-plant condenser cooling, but at only 100-150 ppb. Such a low concentration is possible because exposure to the hot condenser unit may be required for only 6-7 seconds, whereas the scaling crystal nucleation time available may be 10-12 seconds.

The primary types of chemistries employed are shown in Table 6, and the relative properties of phosphonates are shown in Table 7.

#### Some of the basic properties of the various phosphonates are as follows:

1. Sequestration and chelation
2. Threshold effect and scale inhibition
3. Deflocculation and dispersion
4. Good hydrolytic stability
5. Corrosion inhibition and/or synergism with other corrosion inhibitors

**Table 6: The three primary polymeric functional groups**

#### Three Primary Polymeric Functional Groups

- Carboxylates (acrylates, maleates)
- Sulfonates (AMPS, Sulfonated Styrene, other specialty)
- Non-ionics (acrylamide and derivatives, hydrophobes...)
  - *Carboxylates*
    - o Provide general purpose functionality
    - o Typical backbone
    - o Good for dispersion, CaCO<sub>3</sub>, CaSO<sub>4</sub>
  - *Sulfonates*
    - o Typically for stabilization of phosphate, iron, and zinc
    - o Add electrolyte stability
  - *Non-ionics*
    - o Extend functionality to include a broader range of solids
    - o Can change polymer configuration properties
    - o Can be effective for stabilization similar to sulfonates

6. Formulatory compatibility with most or all other additives in the formulatory mix

#### Some commonly used scale and control additive chemistries are listed below:

1. AA/AMPS polymer: e.g. Acumer 2000
2. AA/AMPS/PHOS polymer: e.g. Unichem 134
3. AA/AMPS/TBA terpolymer: e.g. Acumer 3100
4. ATMP phosphonate: e.g. Dequest 2000
5. HEDP phosphonate: e.g. Dequest 2010
6. HPA phosphonate corrosion inhibitor: e.g. Belcor 575
7. PAA acrylate: e.g. AR-900A
8. PAP amino phosphonate: e.g. Multicor 400
9. PBTC phosphonate: e.g. Phos 9
10. PCA polymeric dispersant: e.g. Unisperse 124
11. PMA maleic scale inhibitor: e.g. Belclene 200,
12. TTTATH: triazine based corrosion inhibitor: e.g. Belcor 590
13. *N-tallow, 1,3-diaminopropane*, corrosion inhibitor: e.g. Duomeen T

**Table 7: The relative properties of phosphonates**

RELATIVE PROPERTIES OF PHOSPHONATES							
Property	ATMP	HEDP	PBTC	DTPMP	PAPEMP	EDTMP	BHMT
CaCO inhibition	Exc.	Exc.	Exc.	V. Good	Exc.	Exc.	Exc.
CaSO <sub>4</sub> inhibition	Good	Poor	V. Good	V. Good	Exc.	Exc.	Exc.
BaSO <sub>4</sub> inhibition	Poor	Good	N/A	Good	Good	Exc.	Good
Sequestration	Good	Good	Good	Exc.	V. Good	V. Good	V. Good
Calcium compatibility	Good	Poor	Exc.	Good	Exc.	Exc.	V. Good
Chlorine stability	Poor	Okay	Exc.	Poor	Poor	Okay	Poor
Iron control	Good	V. Good	V. Good	V. Good	Good	V. Good	V. Good
Steel corrosion inhibition	Exc.	V. Good	V. Good	V. Good	Good	Good	Good
Stain removal	Good	Good	Good	V. Good	V. Good	V. Good	V. Good
Deflocculation	Okay	Good	Good	Okay	Good	Good	Good

**Some commonly used chelants chemistries are listed below:**

1. Amine carboxylate (EDTA type)
2. EDTA (Ethylenediaminetetraacetic Acid)
3. NTA (Nitrilotriacetic Acid)
4. DETPA (Diethylenetriamine-pentaacetic Acid)
5. HEDTA (N-Hydroxyethylethylenediaminetriacetic Acid)
6. Natural types (Low strength / Low cost)
7. Citric acid
8. Gluconates
9. Polyphosphates - not hydrolytically stable
10. TEA – For specific applications
11. Silicate – not a true chelant

**Some commonly used supporting microbiocide chemistries are listed below:**

1. NaOCl, 12.5%: aka bleach
2. Stabilized chlorine, 1.5%: e.g. Justeq 07
3. NaBr, 40%: e.g. Bromide Plus
4. Stabilized HOBr, 10.1%: e.g. BromMax

5. BCDMH 32% Br/Cl: e.g. Halogene T30
6. BCDMH/TCCA: e.g. Bromblend 99
7. Isothiazolin, 1.5%: e.g. Kathon WT
8. Gluteraldehyde, 15%: e.g. Aquacar 515
9. DBNPA, 20%: e.g. BioBrom C-103L
10. Polyquat, 60%: e.g. WSCP
11. TBZ, 4%: e.g. Bellacide 325 (Italmatch/BWA)
12. THPS, 25%: e.g. Tollcide PS
13. EO/PO BCP biodispersant: e.g. as manufactured by Italmatch/WST, BASF, DOW/Du Pont
14. Quat ammonium chloride: e.g. Conlen Surfactant CST 8195 (Lamberti Group)

**Some commonly used additional supporting chemistries are listed below:**

1. TTA copper corrosion inhibitor: e.g. Wintrol T-50Na
2. Na Nitrite: Corrosion inhibitor
3. Na Silicate: Corrosion inhibitor
4. Na Borate: pH buffer
5. Tannin/Lignin mixes: Scale/corrosion inhibitors, and dispersants

6. Zn as 25% ZnCl<sub>2</sub>: Corrosion inhibitor

7. Mo as 50% Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O: Corrosion inhibitor

8. H<sub>3</sub>PO<sub>4</sub> (75%) Phosphoric acid

9. SHMP/TSP/TKPP Phosphates: scale/corrosion inhibitors

10. TBTPC biocide: e.g. BWA Bellacide 355

**Miscellaneous supporting notes -phosphonates:**

A phosphonate, such as HEDP or PBTC, is generally essential for calcium carbonate control and to disperse iron and silt. Straight phosphonic acids and phosphonates include ATMP, HPA (HPCA), HEDP, and PBTC. They are commonly used and branded. Thus, for example, Belcor 575 is *hydroxyphosphonoacetic acid*, and Bayhibit AM is a brand of PBTC. HEDP and PBTC have become the defacto multi-functional inhibitor standards for calcium carbonate, iron, and silt, although, as stated elsewhere in this text, HEDP has very poor calcium tolerance. "Calcium tolerance" describes the ability of a chemical to resist complexation with calcium, and so avoid the risk of calcium phosphonate precipitation, it needs to be fed directly into a main flow line using a quill. Note that the poor calcium tolerance of the phosphonates can be suppressed by the addition of an AA/SA copolymer, thus keeping the phosphonate totally active in solution.

Because each of the phosphonates exhibit subtle (or sometimes not so subtle) changes in effectiveness for different contaminants, under different waterside conditions, it is common to blend them. For example, HEDP/ATMP is a very decent scale and corrosion inhibitor blend. HEDP and PBTC also function as useful corrosion inhibitors, by forming calcium carbonate/phosphonate complexes at the metal water interface, although amino phosphonates (such as ATMP) typically perform better as corrosion inhibitors. ATMP is a decent, low-cost, general purpose, scale and corrosion inhibitor, but can be uneconomic in the presence of significant iron. Standard phosphonates perform well up to 100x calcite saturation levels, and under these circumstances appear to be more efficient for calcium carbonate than are most regular AA polymers. Additional notes are presented as bullet



points:

- Examples of calcium tolerance are as follows: A scale of calcium tolerance was shown to be #9 for polyacrylate, through #17 for HEDP, #2 for AMP, #75 for #HPA, #100 for PBTC, #530 for PMA, and #1,640 for the SA/AA copolymer. It is likely that the calcium tolerance value for ter-polymers is much greater, probably about #5,000! HPA is a very good steel corrosion inhibitor and functions by a self-limiting corrosion process, and so, is good for soft water (where calcium is limited). But it may need higher feed rates (i.e. >5 ppm actives). It is not halogen stable, but this negative can be ameliorated by use of MEA in the formulation.
- HPA, because of its excellent solubility, stability, and corrosion inhibition, should also be present across the treating spectrum.
- HPA has scale-control properties, and is a good solubilizer for Fe and Mn. DETA phosphonate (aka Acid-diethylenetriaminepenta (methylene phosphonic acid, DETPMP) is good, general purpose oil and gas applications scale inhibitor. It is useful as a corrosion inhibitor for Al. Also, it has a high sequestration value, making it valuable for chelating Fe, Mn, and Cu. It exhibits good thermal tolerance ability, and excellent hydrolytic and thermal stability.
- PAPEMP is a good example of a multi-functional phosphonate, exhibiting excellent scale-control performance at very high calcite saturation levels. It is also good for iron stabilization, sulfates, silica, and silicate deposit control. Also, being an amino-phosphonate, it is an effective corrosion inhibitor.
- For Ba/Sr in oil & gas, we may need to use *Bis(hexamethylene triamine penta (methylene phosphonic acid (BHMTMP or BHMT), or Hexa-methylene diamine tetra methylene phosphonate (HMDTMP or HDTMPA)*. These are highly efficient chelating agents and have a good effect on calcium carbonate and barium sulfate (barite) scales. Usually available as partly neutralized salts.
- Note that barite solubility increases with temperature (as opposed to the inverse temperature solubility

of calcium carbonate). Also barite solubility is relatively pH independent and lower than that of calcium carbonate.

- Celestite ( $\text{SrSO}_4$ ) solubility decreases with temperature, is relatively pH dependent, and solubility is higher than calcium carbonate. Most barite scales will contain some strontium within the crystal lattice, and barite and celestite are typically associated with other types of oilfield scales.
- Note that barite solubility increases with temperature (as opposed to the inverse temperature solubility of calcium carbonate). Also barite solubility is relatively pH independent and lower than that of calcium carbonate.
- Celestite ( $\text{SrSO}_4$ ) solubility decreases with temperature, is also relatively pH dependent, and its solubility is higher than calcium carbonate. Most barite scales will contain some strontium within the crystal lattice, and barite and celestite are typically associated with other types of scales in oilfields.
- Polyaminophosphonates (PAP) are a developing group of blended phosphonates that offer even more multi-functionality than PAPEMP.
- The merits of PAPEMP for calcium carbonate dispersion under stress indicate that the strong (negative) correlation with calcium carbonate saturation is due, at least in part, to the generation of a (thin) protective film of calcium carbonate. Good corrosion rates are obtained with PAPEMP at saturations as low as 50 times calcium carbonate, while excellent corrosion rates are obtained above 100 times  $\text{CaCO}_3$  saturation.

#### Miscellaneous supporting notes – polymeric chemistries, including polyacrylates and maleics:

Polyacrylic acids (PAA), polyacrylates, and polymethacrylates (PMA – not to be confused with polymaleic acid chemistries, which are often also termed PMA's) are widely employed as dispersants and scale inhibitors in cooling water, RO systems, and many other applications. These chemicals can be employed either on their own as lower-cost chemistries, as components of more complex chemical reaction

blends to produce a multitude of various co- and ter-polymers, or in formulations as physical blends – often as a low cost backup support to a more complex, more selective, and more expensive formulated chemistry. The most popular PAA's and PMA's are those with molecular weights ranging from 2,000 to 10,000. E.g. Lubrizol K752 (which is a brand name for a 2000 MW polyacrylic acid), and Lubrizol K732 (which is a 5,000 MW PAA). Note that the 2,000 -2600 MW homopolymers are decent scale control agents for HVAC, RO, and can be used in sugar evaporators, especially if blended with PMA (polymaleic acid – sometimes termed hydrolyzed PMA, or HPMA) or HEDP. 4,500 MW homoacrylate polymers are good dispersants for  $\text{CaCO}_3$ , silt, and iron, under normal lower-stress conditions, as the backbone molecule tends to "curl" at high temperatures. Blending a 2000 MW and 4500 MW PAA provides for synergy and increased scope of application. (2000 MW polyacrylic acid/acrylate is a good scale inhibitor for light duty. A 4500-5500 MW PAA is a good dispersant, and blending the two provides a wider range of application.

Hydrolyzed polymaleic acid (HPMA) and its salts are low molecular weight solvent-based polymerides, with an average molecular weight of perhaps 500-900, depending on the production method. This chemistry is soluble in water, and has high chemical and thermal stability (the decomposition temperature is above 330°C.) HPMA has a significant scaling threshold effect at high temperatures and pH, and is suitable for use in high alkalinity water systems or built with other chemistries. HPMA has good scale inhibition against carbonate and phosphate scales under high temperatures with effective contact time as long as 80-100 hours. Due to its good scale inhibition and high-temperature tolerance properties, polymaleic acid chemistries are widely used in thermal desalination plants, low-and medium-pressure boilers, crude oil evaporation, pipelines, and industrial circulating cool water systems. HPMA has a good corrosion inhibition effect when used together with a zinc salt. Its limitation is the low molecular weight aspect of its character, as this means that whilst the chemical is a superb scale inhibitor, it is a very poor dispersant, and usually needs the addition of a suitable dispersant, such as a PAA (for lower stress situations) or PCA (for higher stress conditions.) Note that polymaleic acid is typically more cost effective for calcium carbonate



scale control than the best of the more common polyacrylic acid based products - by a high factor. The charge density at the maleic anhydride group is more intense than PAA, allowing for better crystal distortion. This blending approach is matched by evidence that most multi-functional formulas are versatile and forgiving, with various ingredients able to cover for one another. Additional comments regarding polymaleic acid and maleates, including PMA, AA/MA, and SS/MA notes that they are excellent scale control additives, but tend to be limited in their dispersive effect. E.g. Belclene 200 is a brand of PMA, and Belclene 283 is a maleic terpolymer. Provides for much better dispersion. Use with 4500 MW PAA! Finally, the author has successfully used PMA as an antiscalent for MSF evaporators in the Middle East, hardness stabilization for water-storage tanks in the African Kalahari Desert, and sugar evaporators in Central America! It is a great antiscalent, but lacks good dispersive powers due to a low MW. Additional notes are presented as bullet points:

- AMPS based copolymers (e.g. AA/SA) and ter-polymers have high calcium tolerances, and their presence in a formula often causes a major improvement in the calcium tolerance of any phosphonates present, and also of homo-polymers such as polyacrylate and polymaleate.
- It has been found that a terpolymer typically inhibits precipitation of calcium HEDP much more effectively than do co-polymers. This superiority extends to other co-polymers and phosphonates, and persists as temperature, pH and hardness increase. The homo-polymers have no proven appreciable influence on phosphonate stability.
- AMPS copolymers have been found to be excellent dispersants for calcium phosphate when no iron is present. We might then ask under what conditions the higher price the ter-polymers is justified? As an example of this, experiments have shown 10 mg/L of the co-polymer AA/SA-25 is required to achieve 90% inhibition of phosphate precipitation (when no contaminants were present), while only 7.5 mg/L of the terpolymer AA/SA/SS is required. (I.e. a 25% reduction in product usage).
- Where iron content is low, the

co-polymers perform just about as well as the ter-polymers for calcium phosphate. One report has found ter-polymers to be almost twice as effective as the co-polymers in the presence of 1.0 mg/L of iron. These tests showed more significant change when iron was increased to 2.5 mg/L, the ter-polymer then becoming three times as effective. Copolymers have been found to be superior to the homo-polymer (polyacrylate).

- Ter-polymers are more expensive but are highly effective for dispersing phosphate and phosphonate complexes, as well as larger concentrations of iron, zinc, and silt.
- While phosphonates inhibit the formation of crystals (via threshold and chelation mechanisms), polymers distort them (by crystal modification), preventing their further growth, and then disperse them. The homopolymers are excellent lower-cost control agents for calcium carbonate, silt, and iron under "normal" conditions, and their recommended dosage is less than that of copolymers or terpolymers. When raw material prices are factored in, this difference becomes even greater. There is, however, evidence that the dispersive advantage for homopolymers does not extend to calcium phosphate, or to large quantities of iron.
- Copolymers and terpolymers, include: SS/MA, AA/AM, AA/SA, AA/COPS, AA/HPA, AA/AMPS, AA/SA/NI, AA/SA/SS, and PBS/AM. E.g. Betz Dianodic polymer is an acrylic acid/hydroxypropylacrylate, Versa TL4 is a sodium SS/MA, Calgon TRC 233 is a 60/40 AA/AMPS, Acumer 3100 is a strong brand for AA/SA/NI, and Alco Versaflex ONE is a co-polymer. This group of polymers has a range of properties too wide for blanket recommendations, and individual polymer performance strongly depends upon specific polymer architectures.
- AA/SA or AA/AMPS extend the calcium tolerance of phosphonates, especially HEDP.
- AA/HPA was the original dispersant for the Betz Dianodic stabilized phosphate programs. Note: Globally, *stabilized phosphate/sulfuric acid* and *alkaline phosphate/dispersant*

programs are still the first choice of cooling water treatment in developing countries.

- AA/SA/SS (ionic) terpolymer performs significantly better at preventing calcium phosphate precipitation than copolymers such as (neutral) AA/AM.
- AA/SA/SS also exhibits better tolerance to metal ions (e.g. Fe, Mn, Al, Cu, Zn) than AA/SA (even though AA/SA is a good iron oxide dispersant because it is not affected by the presence of calcium – unlike PAA homopolymer).
- Carboxylates, *phosphinocarboxylates* (PCA), and *phosphoncarboxylates* (POCA) are BWA chemistries. For example, Belclene 494 is a POCA, Belclene 161 and Unisperse 124, are both brands of PCA, and Bricorr 288 is a *phosphonated oligomer*.
- PCA is regarded as an excellent, thermally stable dispersant for use in steam boilers, but is also a decent calcium carbonate scale inhibitor.
- Bricorr 288 is a phosphonate reaction product corrosion inhibitor, and alternative to HPA, but our experience is that it often performs better in closed loops than in open systems, and thus, is a good alternative to Belclene 590 (which is itself, an organic replacement for nitrite).
- Nalco's *phosphonosuccinate oligomer* is an alternative to Bricorr 288. Succinates are similar to maleates.

#### **Miscellaneous supporting notes – other chemistries:**

- Azoles protect non-ferrous metals and also prevent metallic contamination. Examples include TTA, BTA, and NaMBT; and are selected for corrosion control of copper and brasses. For example, Wintrol B-40Na is a 40% sodium BTA solution.
- TTA is normally the first choice, but it is not very soluble, necessitating incorporation in, mostly, strongly alkaline inhibitor blended formulations.
- BTA is more soluble, but price



and overall effectiveness may be a deterrent.

- NaMBT is more suitable for closed loops. Products are typically employed to provide from 1 to 2.5 mg/L active azole in the water system – sometimes a little more. Higher concentrations: up to 25-30 mg/L actives are good inhibitors for multi-metal systems and provide disinfection.
- Silica can also represent a problem area. Acumer 5000 and Versaflex Si are standard inhibitors. Also, the use of polyetheramine (e.g. Huntsman Jeffamine M-2070), as silica colloid stabilizers) with Carbosperse K752 or K798 (as dispersants for the stabilized silica).
- Zinc, having strong cathodic functionality and synergism with other inhibitors, is a welcome addition in highly corrosive settings.
- Phosphates are well established components for corrosion inhibition but have serious solubility limits at high pH levels.
- Some experts suggest all formulas should, ideally, contain PBTC, HPA, azole, and terpolymer because of their individual effectiveness, their versatility, and their overall synergism.

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