

Seawater-Based Fracturing Fluid: A Review

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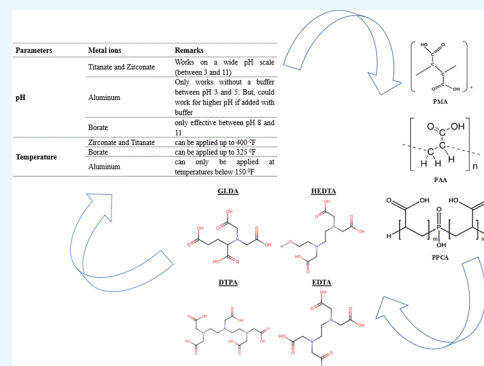
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ABSTRACT: Hydraulic fracturing uses a large amount of fresh water for its operation; conventional wells can consume up to 200 000 gallons of water, while unconventional wells could consume up to 16 million gallons. However, the world's fresh water supply is rapidly depleting, making this a critical and growing problem. Freshwater shortages during large-scale hydraulic fracturing in regions that lack water, such as the Arabian Peninsula and offshore operations, need to be addressed. One of the ways to address this problem is to substitute fresh water with seawater, which is a sustainable, cheap, and technically sufficient fluid that can be utilized as a fracturing fluid. However, its high salinity caused by the multitude of ions in it could induce several problems, such as scaling and precipitation. This, in turn, could potentially affect the viscosity and rheology of the fluid. There are a variety of additives that can be used to lessen the effects of the various ions found in seawater. This review explains the mechanisms of different additives (e.g., polymers, surfactants, chelating agents, cross-linkers, scale inhibitors, gel stabilizers, and foams), how they interact with seawater, and the related implications in order to address the above challenges and develop a sustainable and compatible seawater-based fracturing fluid. This review also describes several previous technologies and works that have treated seawater in order to produce a fluid that is stable at higher temperatures, that has a considerably reduced scaling propensity, and that has utilized a stable polymer network to efficiently carry proppant downhole. In addition, some of these previous works included field testing to evaluate the performance of the seawater-based fracturing fluid.



INTRODUCTION

Hydraulic fracturing is a well-known stimulation technology that is continuously being improved. It can be modified to reduce the flow-path resistance in a variety of geologic contexts, from source rocks to reservoirs, thus enabling, enhancing, speeding up, or (in some cases) restoring production. Since its viability as a technique for extracting hydrocarbons was first recognized in the mid-1940s, hydraulic fracturing has become an industry standard. Over the past seven decades, improvements in fracturing technology and techniques have allowed for significant increases in production, especially in low-permeability reservoirs and source rocks.¹

During fracturing, the requirements for proppant transport and fracture propagation are inherently at odds with one another. The length and complexity of the fracture network and the transport of the proppant inside the network must be simultaneously optimized for obtaining the best fracturing results.² The success of a hydraulic fracturing treatment is highly dependent on the quality of the fracturing fluid system employed.³ Hydraulic fracturing designs must take the viscosity of the fluid into account. To create long cracks, the fracturing fluid must settle gradually enough to carry the proppant. Low fluid loss, minimal pressure losses during transport via the tubing and fractures, and the ability to continue the flow after proppant placement are all necessary.^{4,5} In addition, it needs to be suitable

for use with formation fluids.⁶ In order to prevent any screenout during the treatment, it is also crucial that the fluid is resistant to shear and heat.⁷ There are a variety of water-based fracturing fluids available, including viscoelastic surfactants (VESs), cross-linked fluids, and slick water fluids. Cross-linking and emulsification are both possible with oil-based fracturing fluids.⁸ Some selected fracturing fluids and their qualitative summaries are provided in [Table 1](#).

The proppant transport capacity and distribution efficiency of cross-linked gels are quite high. High pumping pressures are required, and the gel has a destructive effect, which are both drawbacks. Slick water is less expensive to produce than cross-linked fluid and has less of an adverse effect on its surroundings when it is pumped. However, its transport capacity is reduced, and the proppant is not distributed very well.⁹ Foam fluids use less water than slick water and cause less damage to the formation while transporting the proppant. The use of high-effective viscosity fluids (bubbling liquids) and foams can help

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Table 1. Qualitative Fracturing Fluid Selection Chart, Adapted and Modified from Montgomery, 2013 (ref 8) (Copyright (2013, IntechOpen))^a

fluid system	prop. pack KFW	low pump pressure	viscosity				compatibility					safety and environmentally friendly	total
			prop. transport	stable	life	breaking	formation fluid	fluid recovery	fluid loss	ease of mixing	cost		
water frac ^b	5	5	1	3	3	5	3	4	1	5	5	4	44
linear gel ^c	3	5	3	3	3	4	3	4	2	5	4	5	44
linear gel ^d	5	5	3	3	3	4	3	4	2	5	4	5	46
borat Cross-link ^c	3	3	5	5	5	3	4	3	5	4	3	5	48
delayed borate Cross-link ^c	3	3	5	5	5	3	4	3	5	3	3	5	47
delayed metallic Cross-link ^e	3	3	5	2	2	3	4	3	5	3	3	4	40
delayed metallic XCross-link ^f	3	3	5	2	2	3	4	3	5	3	3	4	40
VES ^g	5	3	5	4	4	2	1	3	2	2	1	5	37
nitrogen foam	5	2	5	3	3	5	4	4	5	2	1	3	42
CO ₂ foams	5	2	5	3	3	5	4	5	5	2	1	2	42
gelled propane	5	3	4	4	3	4	5	4	4	2	1	1	40
poly emulsions (K1)	4	1	5	5	5	4	4	3	5	2	3	2	43
lease crude	2	3	2	5	5	5	5	3	2	5	5	1	43

^aNote: qualitative rate of 1–5, where 1 is poor, 3 is moderate, and 5 is excellent. ^bUses polyacrylamide (PAA) as a friction reducer. ^cUses guar (hydroxypropyl guar (HPG) or carboxymethyl hydroxypropyl guar (CMHPG)) as the gelling agent. ^dUses hydroxyethyl cellulose (HEC) or carboxymethyl hydroxyethyl cellulose (CMHEC) as the gelling agent. ^eUses titanium or zirconium cross-linker for the guar, HPG, and CMHPG gelling agents. ^fUses titanium or zirconium cross-linker for the CMHEC gelling agent. ^gUses a viscoelastic surfactant (VES) as the gelling agent.

avoid surface damage to the fracture with less water. When reservoir temperatures are high, however, they have poor proppant suspension and dispersion.^{10–12} Other fluids like gels and polymer-based fluids, which may damage the fracture surface but lead to fracture propagation that is more perpendicular to the flow than in the direction of the flow, are also used to carry proppant.¹³

Selecting the right fluid system for propping fracturing treatment follows the same decision-making framework as with viscosity⁸ and continues to meet the following factors: it should be safe (offer little risk to on-site workers), environmentally friendly (have as many “green” components as possible), a breaker (the fluid must “break” to a low viscosity so that it may flow back and be cleaned up after), cost-effective (the fluid cannot be too expensive, otherwise the expense of treatment will be too high), compatible (the fluid must not affect the mineralogy of the formation or the formation fluids), and be able to be cleaned up. To avoid water blocks, it is important that the fluid does not alter the relative permeability of the formation or damage the fracture conductivity of the fracture; this is especially important for low-pressure wells or those that produce exceptionally dry gas. Even under extreme conditions, the fluid system must be easily mixed. In addition, an ideal fluid should have a fluid loss flexibility.

Fresh water from the surface and subsurface is typically used to make fracturing fluid. Clay stabilizers must be added to the pumped water to protect the formation clays. Water can also precipitate on an inorganic scale around the wellbore. Water can generate severe emulsions that obstruct emulsions. Tight gas wells also report water obstruction. After treatment, only 10–30% of the pumped water flows back, with the rest being blocked in clays or pores due to high capillary pressures. Obtaining fresh water has become difficult in some fields due to the high water transportation costs from the source to the wellsite, as well as rising limits on freshwater supply.¹⁴ Conventional wells use 200 000 gallons of water for hydraulic fracturing, while

unconventional wells can use up to 16 million gallons.^{15–19} For example, fracturing shale and tight sandstone formations often require more than 1 million gallons (3700 m³) of water per well.²⁰ This method uses a lot of water, damages the formation, and restricts future savings. Therefore, it is vital to examine alternatives to water-based fracturing fluids that support the preservation of water and encourage sustainable growth. Waterless hydraulic fracturing procedures can reduce or eliminate water use.¹⁵ It has become essential to find ways to optimize hydraulic fracturing operations in order to utilize less fresh water and more green additives.

One possible sustainable option is to use seawater instead of fresh water. However, formation damage and viscosity degradation may occur if seawater is used. One of the main issues with employing seawater as a fracturing fluid is that the divalent ions present in water sources, such as calcium and magnesium, tend to precipitate out with hydroxide ions under high pH conditions to lower the pH of the fluid.²¹ When comparing the same formulations between seawater and fresh water, it is clear that fluid instability increases with temperature. Polymers are known to precipitate out of solution once they reach their cloud point, as evidenced by numerous case studies.¹⁹ Salts have the potential to alter the cloud point of polyelectrolytes by shielding the electrostatic interactions between the charged groups. The cloud point in ionic water (such as seawater) appears to be around 300 °F, and fluid exposure at this temperature gives insufficient rheological stability for sufficient proppant movement in conventional fluid systems.

Because of the high concentration of dissolved particles in seawater, the rheological performance of gelling agents is drastically reduced. Hydrogen bonding between the polymer's hydroxyl (OH) groups and the surrounding water molecules is responsible for the hydration of the gelling agents in water. Incorporating water molecules into the polymer via this interaction creates a strong polymer network. Proppant can be

transported downhole and into the fracture network via the cross-linking mechanism, which takes place when cross-linker molecules (such as borate or metal)^{19,22,23} engage with chemical moieties on numerous polymer strands. Because the cations in seawater disrupt the hydrogen bonds between the polymer and water, the fluids have a much lower viscosity. The hydration of the polymer can be fully prevented by excessive concentrations of particular ions.

Although difficulties have been encountered in the past when attempting to create fracturing fluids from nonfresh water sources like seawater, some researchers and experiments have been successful under certain conditions of total dissolved solids (TDS) and temperature. There are a variety of additives that can be used to lessen the effects of the various ions found in seawater. Fracturing fluids can contain a wide variety of chemicals, such as gelling agents, cross-linkers, breakers, surfactants, scale inhibitors, corrosion inhibitors, clay stabilizers, biocides/bactericides, fluid loss inhibitors, chelating agents, pH modifiers, and acids, which can be made from either fresh water or seawater. In order to prevent scale from forming, optimized seawater-based fracturing fluids have been formulated such that neither the addition of additives nor the blending of the fracturing fluid filtrate with formation brines would cause any precipitation of scale.²⁴

In order to address these problems, it is crucial to develop technologies that can reliably treat seawater (to obtain a fluid that is stable at higher temperatures and has a significantly reduced scaling tendency) and to develop a fluid with this treated seawater that offers a stable elastic polymer network to effectively deliver proppant downhole. Seawater-based fracturing fluids could save millions of gallons of fresh water while also lowering the cost of hydraulic fracturing applications. Furthermore, because of the high salt concentration of seawater, the formation damage caused by the swelling of clay when fresh water is used can be avoided. The challenges of developing a seawater-based fracturing fluid is described in the following section.

SEAWATER-BASED FRACTURING FLUID CHALLENGES

Seawater-based fracturing fluid provides a potential solution for water management. The use of seawater as a fracturing fluid in petroleum applications, specifically hydraulic fracturing, is technically possible. However, there are several challenges and considerations associated with this approach. In order for seawater to be used as a replacement for fresh water in hydraulic fracturing without compromising safety or effectiveness, its treatment process must remove or reduce contaminants such as particulates, heavy metals, and dissolved salts to acceptable levels.

Seawater contains a high concentration of salts and minerals that can be corrosive to the equipment and infrastructure used in hydraulic fracturing operations.^{25–28} Specialized materials and coatings are required to mitigate corrosion issues. Seawater also has a high content of dissolved inorganic salts, such as calcium and magnesium, which can cause scaling issues and affect the development or reduce the conductivity of the fractures. The ions also slow polymer hydration, which reduces the fracture fluid's viscosity and gel–hydrocarbon stability.²⁹ Scaling occurs when these minerals precipitate and form deposits on the wellbore, fractures, and production equipment. Scale precipitation caused by the interaction of seawater and formation water is another major concern when considering fracturing with

seawater. Sulfate scales are formed primarily in seawater by the mixing of two incompatible liquids, such as the mixing of seawater with its high concentration of sulfate ions and formation water with its high concentration of barium, calcium, and strontium ions.³⁰

In order to overcome the obstacles associated with using fracturing fluid made from seawater, it is necessary to first comprehend the composition of seawater-based fluid. The parts of the various oceans of the world that typically display oil and gas activity are summed up here.³¹ Because hypersaline conditions brought on by rapid evaporation are common in the Arabian Gulf, Arabian seawater has the highest main ion level of any sea at 54 000 mg/L. This has become a major consideration for developing seawater-based fluid for this region.²⁸ The average sulfate content worldwide is approximately 2900 mg/L, with the Arabian Gulf having the highest concentration of the ions at 4020 mg/L, compared to ion concentrations of 1400 mg/L and 2500 mg/L in offshore Angola and the South China Sea, respectively.³¹

Unlike with fresh water, it is critical to examine several variables and chemical qualities that influence the fracturing fluid developmental process for seawater. Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , and SO_4^- ions are the primary contributors to the salinity of seawater. Each of the salt ions in seawater has the potential to detract from the fracturing fluid's effectiveness. The cross-linking properties of guar-derivative fracturing fluids can be affected by the presence of Ca^{2+} , Mg^{2+} , and SO_4^- due to the production of solid precipitates and chemical interference with cross-linking sites.^{28,32} Divalent cations like Ca^{2+} and Mg^{2+} have an effect on the viscosity and stability of fracturing fluids that are based on saline water. If the saline water system lacks divalent ions, then monovalent ions will lower the viscosity of the fluid. Ca^{2+} and Mg^{2+} ions lower the viscosity of seawater by decreasing polymer hydration. These ions may neutralize the effects of many additives, including gel breakers and pH control agents.²⁹ At a pH >10, Ca^{2+} and Mg^{2+} can precipitate, thus decreasing the viscosity and cross-linking while allowing for the formation of a variety of scales. Therefore, it is important to regulate the pH or employ scale inhibitors if a high pH is required. It is also important to keep a close eye on the fluid's thermal stability. Maintaining stability at high temperatures requires that the surroundings have a high pH.^{7,21,33–35} In comparison, Na^+ and K^+ are commonly employed in fracturing fluid systems due to their low cost and minimal formation damage. In addition, K^+ is widely used as an antishrink additive in the oil industry.³⁶

Formation water and seawater are expected to create barium sulfate, calcium sulfate, and strontium sulfate scales at 300 °F.³⁰ The sulfate in seawater has an effect on ion pairs due to its high concentration. The electrostatic attraction between the charged ions in sulfate allows it to form ion pairs with strontium, calcium, and magnesium. Half of the sulfate in the ocean is in the form of free ions that can link up with other molecules.³⁷ Another challenge for seawater-based fracturing fluid is the hydration process, where the viscosity is built up using guar gum to create the whole fracturing fluid. Because of its high salt content, seawater affects the viscosity accumulation in a different way. This results in a high ionic strength, which has a negative impact on the reservoir and the fluid's rheology and can harm the formation.³⁸

It is important to note that seawater-based fracturing fluids can be improved by either adapting existing fracturing fluids or creating a new fracturing fluid that can efficiently control polymer hydration, cross-linking, additive compatibility, and

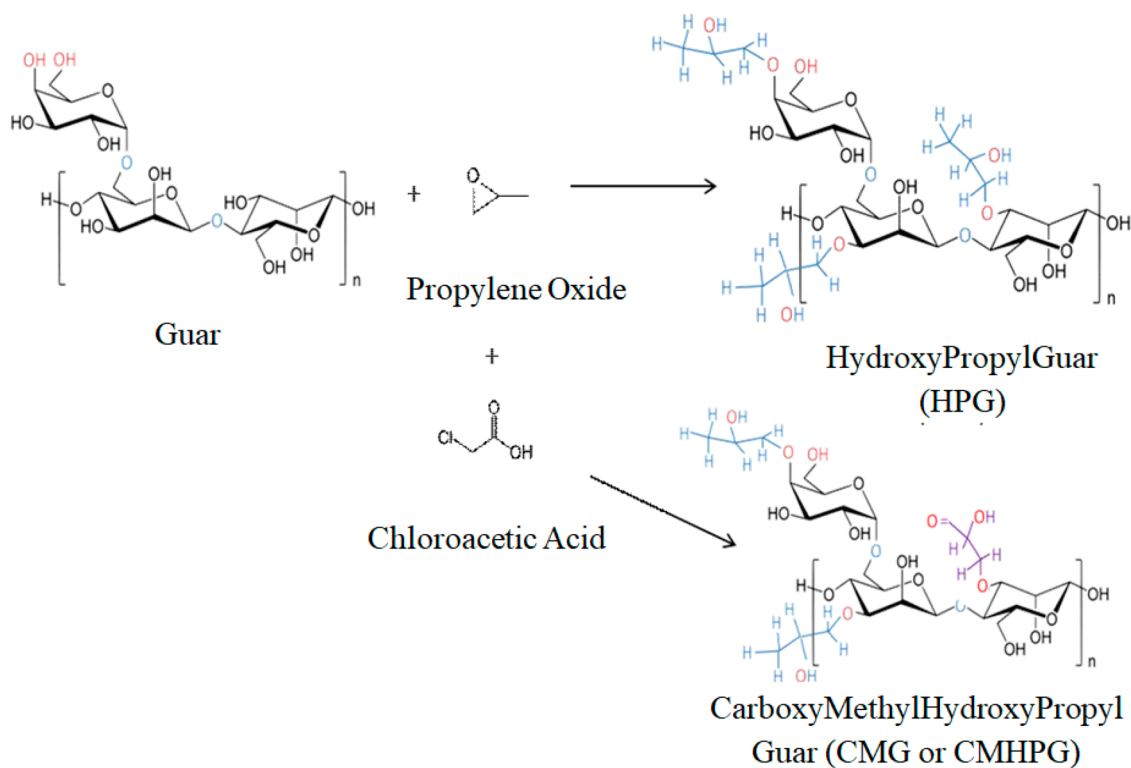


Figure 1. Formulation of HPG, CMG, and CMHPG from guar, adapted and modified from Montgomery, 2013.⁸ Copyright (2013, IntechOpen).

breaking performance within the intended temperature range. Another issue is bacteria, as seawater contains a diverse range of microorganisms including bacteria. One of the most significant concerns related to bacteria in seawater-based fracturing fluids is their potential for biodegradation. Bacteria can break down organic compounds present in fracturing fluid including polymers.

Depending on the design parameters of the fracturing fluid, additives such as bactericides, gel stabilizers, and breakers can be added to the base gel. The presence of bacteria in seawater, which hosts a wide variety of microorganisms, poses another problem. Biodegradation is a major issue that has been linked to microorganisms in seawater-based fracturing fluids. The organic chemicals in the fracturing fluid, such as polymers and chemical additives, can be degraded by bacteria. Additionally, biofilms or microbial mats can grow in the wellbore and fracture network when bacteria are present. Biofilms have the potential to impede fluid circulation within a reservoir by decreasing the permeability and obstructing flow routes. As a result, production rates may drop and pumping pressures may rise. Agents are often added to keep the pH of the fluid within the desired range; ultimately, a cross-linked fluid is generated by combining a cross-linker with a suitable pH additive to stabilize the cross-linking in the desired pH range, thus resulting in a high viscosity. In the next section, we will discuss the role that each chemical additive plays in making seawater a compatible fracturing fluid, starting with the polymers and surfactant.

Besides the use of additives, another technique that can be used is nanofiltration. Before injecting the fluid into the reservoir, seawater can be nanofiltered to remove impurities before being used in the fracturing process. Researchers have shared several field applications of nanofiltration.^{38,39} While the results reveal that the formation brine is compatible with nanofiltration technology, the necessary equipment and facilities

take up a lot of room. This presents an additional challenge for locations with little available space, such as those located offshore. Therefore, despite the difficulties, treating raw seawater appears to be a better option.

■ POLYMERS AND SURFACTANT COMPATIBILITY WITH SEAWATER FLUID

By adjusting the fracture half-length, fracture width, and fracture and reservoir permeabilities, an optimal dimensionless fracture conductivity can be achieved during the design phase of a fracture. For these conditions to hold, the fluid must be capable of carrying the proppant with low velocity settling, low fluid loss, and low formation damage.⁴⁰ Polymers are used in fracturing fluids to keep the proppants in place, help provide the fracture width, keep the fluid from leaking out of the formation, and reduce the friction pressure in the tubular goods. Most fracturing fluids use polymers made from guar gum and cellulosic derivatives. The content and purity of a polymer determine the conformation that it takes in solution. The viscosity, thermal stability, and shear rate behavior of the cross-linked material could change as a result.⁴¹

Different thickeners allow for the separation of the seawater-based fracturing fluid system into two primary groups. Synthetic polymer fracturing fluid systems fall into the first group; in these systems, a modified polyacrylamide polymer is used as a thickener. High-valence metal ions are particularly problematic for this fracturing fluid system because of the low salt-resistant COO⁻ ion that is generated by the hydrolysis reaction of acylamino. Systems that use guar gum or its modified products as a thickener make up more than 90% of all fracturing fluid thickeners.⁴² Both the polymer and the cross-linking gel are notoriously challenging to break down. Reservoir damage can occur when a cross-linker's polymer reacts with precipitation produced by the cross-linker's high-valence metal ions.

Furthermore, synthetic polymers are more expensive than synthetic gum. The second type of fracturing fluid system employs a thickener known as a viscoelastic surfactant (VES). VESs are highly sensitive to iron. It is easy to make and works well for achieving continuous mixing on offshore platforms because it may be created with seawater straight from the source.⁴² Other features of this fracturing fluid system are that it breaks automatically in the presence of oil, it leaves no residue after breaking, and it flows back easily due to its low interfacial tension. The negative effect that the high-valence cations in seawater have on cross-linking is a major issue for this setup. Seawater has a far higher salinity than fresh water. High concentrations of cations bind to the polymer branches of guar gum, limiting the thickener's ability to swell in water and reducing the efficiency of subsequent cross-linking.

The polymer guar gum, characterized by its high molecular weight, long chains, and intermolecular hydrogen bonding, is widely used as a gelling agent. Guar gum has an insoluble residue between 10 and 14%,¹⁵ depending on the purity of the gum and the separation technique. By limiting the fracturing efficiency, these residues impede the flow within fissures. The oil sector typically uses hydroxypropyl guar (HPG) more than any other guar derivative. Carboxymethyl hydroxypropyl (CMHPG) guar, in contrast, is the most popular option for fracturing because it efficiently hydrates and leaves behind little to no residue.^{35,43,44} Pads, whether conventionally cross-linked or unconventionally linear, are formed when polymers are hydrated in water. Slurry is injected into the formation from these pads, which initiates the fracture and allows for adequate leak-off, ensuring that less fluid is wasted during the process.^{35,43} The chemical structures of HPG and CMHPG, which are formulated from guar,⁸ are shown in Figure 1.

The amount of insoluble residue in guar gum varies up to 14%, depending on the gum purity and isolation method used. These residues cause damage to the proppant pack and formation, lowering the efficiency of hydraulic fracturing. Guar is often chemically synthesized to lessen its amount of insoluble residue. Guar can be converted into hydroxyethyl guar (HEG), hydroxypropyl guar (HPG), and carboxymethyl guar (CMG) through alkaline treatment with an oxide, propylene oxide, and chloroacetic acid, respectively. Carboxymethyl hydroxypropyl guar (CMHPG) is another version of the guar gum polymer that has also proven useful.⁴⁵

The process by which polymer chains absorb water and change from being tightly coiled to more spread-out and relaxed is known as hydration. This happens when water molecules interact with the functional groups of the polymer. Viscosity is used to measure hydration, and a stable viscosity is thought to be the most hydrated state. With all other factors being equal, the only thing to worry about in terms of hydration is how long it takes. Seawater requires significantly more time to obtain 100% hydration than fresh water.³⁴ In order to increase the viscosity, the polymer (gelling agent) must be hydrated in water. Guar gum and its derivatives, HPG and CMHPG, typically hydrate better in water when in slightly acidic conditions (pH = 6–6.5).³⁴ Other polymers, such as carboxymethyl cellulose (CMC), xanthan gum (XG), hydroxyethyl cellulose (HEC), and synthetic polymers, may have differing hydration requirements.^{34,46,47} The effect of pH on the hydration of CMC, XG, and HEC is pH-dependent.^{48,49} The swelling behavior of succinoglycan carboxymethyl cellulose (SG/CMC) hydrogels is pH-dependent, and the viscosity of CMC and HEC is also

affected by the pH.⁴⁸ CMC and HEC are also compatible with synthetic surfactants.⁵⁰

Seawater-based fracturing fluids and fresh-water-based fracturing fluids have been compared when used with HPG and CMHPG.³⁴ The results demonstrated that the use of both polymers with seawater results in a slight delay in full hydration. Stability conditions can be met with fluids based on seawater, with CMHPG being more stable than HPG. HPG has the same viscosity in both seawater and fresh water. At a lower pH in both types of water, CMHPG has demonstrated a slightly higher viscosity.³⁴ Because HPG is a nonionic polymer, it dissolves in seawater. In this situation, guar can form an insoluble precipitate when it is exposed to high salt concentrations. As an anionic derivative, CMHPG is also impacted by excessive water salinity. This is because the electrostatic repulsion of anionic groups causes the polymer chains to become less entangled.²⁰ The two types of guar gum polymers were compared in a previous study for developing a seawater-based fracturing fluid; it was found that the highest hydration of HPG in seawater occurs in an acidic medium with a maximum viscosity of 47 cP at a pH of 5.³⁴ In the laboratory, however, at ambient temperature (68 °F) and a pH of 6, seawater with the same polymer concentration had a viscosity of 43 cP. CMHPG viscosity in seawater ranges from 42 to 47 cP at a pH of 5 to 8. The greatest viscosity was found in a neutral medium (pH = 7). The viscosity was 41 cP in the laboratory test at ambient temperature (68 °F) and a pH of 6. At a lower pH, CMHPG showed a slightly higher viscosity.²⁸

Molecules having a hydrophilic headgroup and a hydrophobic tail, known as surfactants or amphiphiles, are physically dissymmetric and possess a wide range of self-assembly tendencies in the bulk phase. Micelles, nanoribbons, and vesicles, among other aggregates, can develop in semidilute solutions in a wide variety of shapes and sizes.^{51,52} Surfactants could be used as additives to make a seawater-based fluid. Because of electrostatic attraction, high salinity causes micelles to change from highly viscoelastic worm shapes to low-viscoelastic layered forms.⁵³ However, it also weakens the repulsion between micelles that are shaped like worms. Both of these factors reduce the efficacy of the clean fracturing fluid. Micelles with a wormlike shape may withstand the electrostatic force of inorganic salts in seawater due to the noncovalent binding of *N*-carboxystearamido methanesulfonic acid (MSA) and cetyltrimethylammonium bromide (CTAB) molecules. The self-assembled structure of the MSA/CTAB mixed system transforms from wormlike micelles to spherical micelles in response to changes in pH, which accounts for its exceptional rheological responsiveness.^{53,54} The electrostatic effect of the inorganic salts of seawater is likewise resisted by this structure.

Switchable amine-based surfactants (e.g., Duomeen TTM, Ethoduomeen T13, and Ethomeen C12) have recently received a lot of attention, as they exhibit both nonionic and cationic characteristics, depending on the pH of the solution.⁵⁵ In seawater, Armovis (a VES) has been shown to be soluble and exhibit viscoelastic wormlike micelles.⁵⁶ Duomeen TTM is thermally and chemically stable at high salinity (22% total dissolved solids), high temperature (248 °F), and low pH (4) conditions for up to 30 days.⁵⁷ The use of an Agilent 1100 high-performance liquid chromatograph in conjunction with an evaporative light scattering detector corroborated these results. With 0.4 wt % CMC of Duomeen TTM, the experiments could reach 248 °F and 3400 psi.⁵⁸ However, in regard to the impact of surfactant concentration (0.05–1 wt %) on foam viscosity at 248

°F and 3400 psi, the foam viscosity did not significantly improve above a surfactant concentration of 0.5 wt %.

Armovis can generate highly temperature-stable foams. It is applicable for the in situ diversion used in the HCl acidizing of carbonate reservoirs. In high salinity, Armovis surfactant molecules elongate into rodlike micelles that form a cross-linked gel structure, thus giving viscosity to the fluid, and that are resistant to thermal degradation over time at temperatures <350 °F. It has been found that 0.1 wt % CMC of Armovis dissolves in brine at 229 903 ppm, while the optimum concentration for the CMC is 0.3 wt % at 176 °F.⁵⁹ The chemical structures of these two surfactants are listed in Table 2.

Table 2. Duomeen TTM and Armovis VES Structures and Their Chemical Types

Structure	Surfactant	Surfactant type
	Duomeen TTM (Trimethyl diamine)	Hybrid between cationic/nonionic ⁶⁰
	Armovis VES	Zwitterionic ⁶⁰

Some of the surfactants that have been developed for use in seawater-based fracturing fluids include fatty methyl ester sulfonates (FMES) and sulfonic Gemini zwitterionic viscoelastic surfactants. FMES-based fracturing fluid has greater salt and shear resistance due to the presence of numerous hydrophilic groups and branching structures.³⁶ FMES has a great viscosity increasing capacity thanks to its long carbon chain structure. Thus, FMES is an excellent viscoelastic surfactant for making fracturing fluid out of seawater. A Gemini zwitterionic viscoelastic surfactant has also been synthesized. The Gemini zwitterionic viscoelastic surfactant, termed VES-S, can have its viscoelasticity improved by the addition of salt due to a tightening of its network structure.⁶¹ When compared to cationic Gemini surfactants, VES-S was discovered to be a salt-tolerant viscoelastic surfactant. At moderate NaCl concentrations, phase separation was found to occur in solutions containing a cationic Gemini surfactant, and the viscosity declined significantly.

Co-surfactants are sometimes included in cross-linked polymer formulations. Methods for increasing the viscosity of a fluid can involve providing a fluid containing a thickening amount of a cross-linked polymer, adding a viscoelastic surfactant to the fluid at a given concentration, controlling the fluid to a specified temperature, and defining the fluid's viscosity profile as a function of the concentration and temperature.⁶²

The additives that are employed have an impact on the decision between using a polymer or a surfactant. In order to optimize the rheology of the fluid, it is crucial to assess the compatibility of the polymers and surfactants with other additives. Chelating agents, another chemical additive, are explored in the following section for their effects on seawater fluid.

■ CHELATING AGENTS EFFECTS ON SEAWATER FLUID

The viscosity of the fluid is increased by using water-soluble polymers. Under the high salinity and high temperature conditions that are observed in most reservoirs, most polymers and surfactants break down.⁶³ Chelating agents are introduced as unconventional fluids to address these breakdown issues because of their distinct properties, low costs, and eco-friendliness.^{29,64–66} During chelation, ions and molecules are chemically bonded to metal ions. To form a chelating agent, two or more different coordinate bonds must be developed between a central atom and a ligand with multiple bonds. Many names are used for these chemicals, such as “chelants”, “chelators”, “chelating agents”, and “sequestering agents”. They are mostly organic compounds. Chemicals such as ethylenediaminetetraacetic acid (EDTA), diethylenetriamine pentaacetate acid (DTPA), ethanolic phosphotungstic acid (EPTA), L-glutamic acid, N,N-diacetic acid (GLDA), and hydroxyethyl ethylenediamine triacetic acid (HEDTA) are all examples of chelating agents that are utilized in the industry.⁶⁷ However, among these chemicals, only GLDA breaks at high temperatures without the aid of breakers, as it is the only compound to exhibit breaking behavior at a pH of 12 and temperatures higher than room temperature.⁶⁸ The chemical structures of some of the chelating agents are shown in Figure 2.

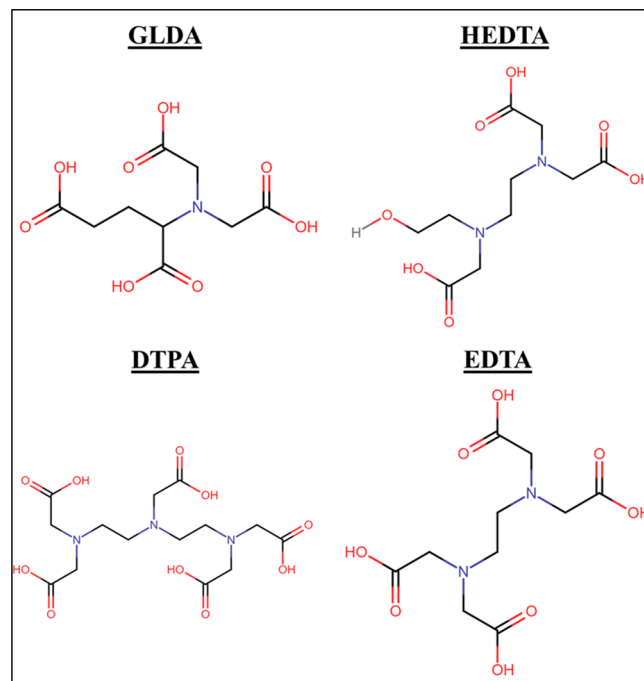


Figure 2. Chemical structures of GLDA, HEDTA, DTPA, and EDTA.

GLDA is environmentally friendly and more resistant to high temperatures and salinity.^{65,66,69} Additionally, it has the ability to increase the viscosity of the stimulation fluid. An environmentally friendly stimulation fluid has been developed by adding GLDA to polymeric gel solutions.⁷⁰ The results showed that GLDA improved the stability and viscosity of the gel solution. Additionally, another stimulation fluid was created by combining GLDA with a polymeric gel solutions. In this experiment, GLDA increased the gel solution's stability and

viscosity. At a low shear rate ($100\text{--}500\text{ s}^{-1}$), the addition of 15 wt % GLDA was able to raise the foam viscosity by 15 cP.⁶⁵

Chelating chemicals have been recommended to be added to fracturing fluids in order to improve the consistency of excessively saline fracturing fluids.⁷¹ This technique produces fracturing fluids with greater stability.⁶⁸ EDTA and sodium gluconate, however, have the effect of lessening the viscosity.⁷² A decrease in the pH or the possibility of the chelating chemicals binding with the boron cross-linker have been proposed as explanations for this phenomenon.^{73,74} Additionally, the GLDA pH level may affect the polymer hydration rate, leading to behavior that varies with time.⁶⁷ The use of chelating agents is an approach that appears to have potential. Using a chelating agent and a sulfate scale inhibitor in conjunction with one another may be a feasible alternative to the practice of employing seawater as a fracturing fluid.⁶⁴

Seawater salt ions changes the way the CMHPG polymer moves. When GLDA was added to solutions of magnesium chloride and calcium chloride, the viscosity went up. Because the viscosity of both solutions changed when GLDA was added, these findings demonstrate that sulfate ions regulate the seawater rheology.⁴⁵ The chelating agent GLDA has been studied for its potential to lessen corrosion in foamed acidic fluids made from nitrogen dioxide (N_2) and carbon dioxide (CO_2), to increase fluid stability, and to lessen environmental effects.⁷⁵ The results showed that GLDA helped the foamed fluid become more stable and, it increased its viscosity. The generated viscosities ranged from ~ 5 to ~ 25 cP throughout a broad shear speed range. Higher shear rates reduced the viscosity in general without affecting the foam quality. Corrosion inhibitor-containing fluid systems also have reduced viscosities. The most consistent and relatively high viscosity values have been achieved with 1% surfactant, 15% GLDA, and 0% corrosion inhibitor.⁷⁵ It was determined that N_2 had a foam height and half-life of 182.8 mm and 16.5 min, respectively, while CO_2 had a foam height and half-life of 77.4 mm and 2.16 min, respectively. Corrosion inhibitors had the largest negative impact on the half-life of the CO_2 foamed fluid, but they were still detrimental overall. In addition, the tested fluid systems were able to be studied and used as dependable stimulating fluid systems at temperatures up to $300\text{ }^\circ\text{F}$.⁷⁵

At high pH values, the chelating agent EDTA is available in several forms, including sodium salt (Na_4EDTA), ammonium salt (NH_4EDTA), and potassium salt (K_4EDTA).^{76,77} Compared to the ammonium and sodium salts, potassium salt is more difficult to come by. As a result of its greater stability in acidic conditions compared to potassium and ammonium salts, sodium salt has found widespread use in the oil and gas industries.⁷⁶ To determine whether chelating chemicals could improve oil recovery, two core flooding tests were conducted. One used only seawater, and the other used a 5% Na_4EDTA solution diluted in seawater.⁷⁸ Using fresh water as a dilution basis, the efficiency of EDTA resulted in an increase of 3% in original oil in place (OOIP) at 1 wt % and a 5% increase at 2 wt %. More importantly, oil recovery increased from 12% excess recovery to 15% OOIP at 5 wt % after being diluted with seawater. Seawater affected EDTA because its salts absorbed some of the chemical. Seawater had no effect on EDTA at higher concentrations (5 wt %) because EDTA is able to handle and tolerate more salts than those found in seawater. EDTA is ineffective against rock degradation at quantities below ~ 1 wt % because it can only dissolve the salts found in seawater.⁷⁸ This

experiment showed that EDTA could be one of the chelating agents that is compatible with seawater.

In comparison to fresh water, the reaction rate slows when seawater is added to DTPA and may necessitate the use of more DTPA.⁷⁹ In comparison to 15 wt % HCl with 3 wt % corrosion inhibitors, DTPA showed a very low corrosion rate of 0.0034 g/cm^2 without the addition of corrosion inhibitors; the industry maximum is 0.0244 g/cm^2 in 6 h.⁷⁹ While the reaction of the chelating agent DTPA with calcite is shown to be surface reaction limited in fresh water, it was discovered to be mass transfer limited in seawater.

In the presence of multivalent cations, such as calcium and magnesium, in seawater, the polymer degrades. It has been found that adding 5% HEDTA to the solution increases the polymer viscosity but has no effect on the polymer break time.⁷⁶ The chelating agent HEDTA chelated the multivalent cations from seawater and removed their effect on the polymer viscosity, which aided the polymer stability and maintained the viscosity until breakdown.

Chelating agents have also been tested in seawater. They form soluble complexes with the divalent species and protect them from hydroxide ions and other chemicals that could precipitate them and harm the proppant's conductivity. Chelating agents have also been shown to increase heat stability, preserve fracture conductivity, buffer the pH, and control fluid loss. In addition, the cross-link delay time is maintained, and the fluid's preparation is simplified by the addition of a chelate. Chelating agents work well on borate cross-linkers compared to metallic ones. By adding a chelating agent to a borate cross-linked fracturing fluid, the heat stability of the seawater fluid increases, leading to a higher cross-linking efficiency.²⁹ In contrast to traditional fracturing fluids, chelating agents do not exhibit noticeable viscosity buildup or performance. Moreover, due to the large amount of shear required in a fracturing treatment, the use of chelating compounds as viscosifiers in fracturing fluids is prohibitively expensive. Other additives such as scale inhibitors (SIs) could be used as a substitute for chelating agents to develop seawater-based fracturing fluid. SIs have been successfully used to prevent the creation of distinct scales. They serve as chelating agents to generate a soluble complex, as threshold inhibitors to prevent the formation of supercritical nuclei, or as scale crystal retarders.^{16,27,80} Scale inhibitors are explained later in this review.

Cross-linkers, another chemical additive, are discussed in the following section, as they play a crucial role in increasing the viscosity of fracturing fluid.

■ CROSS-LINKER PERFORMANCE ON SEAWATER FLUID

Cross-linkers are utilized to increase a fracturing fluid's elasticity and viscosity without increasing the polymer content.⁴⁵ The fluid's characteristics shift from being viscous to being viscoelastic as a result of its change in elasticity. The thermal stability of fracturing fluids may be affected by a number of linkages, but two of the most important are the polymer backbone bonds and the cross-linker-to-polymer links.⁸¹ When compared to a linear gel, a cross-linked polymer is more harmful to formations but has more viscosity and proppant-carrying capacity.⁴⁴ Borate, titanium, zircon, and aluminum ions are used to join together polymers that dissolve in water. Cross-links are formed when the guar's galactose side chains react with their OH pairs. Cross-linking improves the rheological properties of a polymer. However, cross-linking agents are limited in what kinds

of polymers they can connect because of their pH and temperature ranges.⁴⁰

Buffers are used with polymers to ensure that the pH is optimal for polymer hydration. When the ideal pH is reached, a polymer achieves the highest possible viscosity.^{8,82} Fracture fluid buffers typically consist of a combination of weak acids and weak bases, with the ratios of these ingredients being adjusted to obtain the required pH. The high-temperature viscosity of biopolymer solutions is positively correlated with basicity. Buffer, polymer, and gel stabilizer mixtures have been tested as potential gel stabilizers for high temperatures (>250 °F).⁸² The ideal pH for stability was chosen as the pH of the base fluid. Multiple transition metal cross-linkers were used on the optimized base fluid to find the best one. The results showed that higher pH levels are associated with more consistent viscosity. Amines, carbonate/bicarbonate solutions, hydroxide, and acetate/acetic acid solutions are all examples of buffers.⁸ Boron, titanium, zirconium, and aluminum are some of the most common cross-linkers used in guar gum polymers; the specific cross-linker that is utilized depends on the final product's pH, temperature, and polymer type. Table 3 shows a list of the most important features of cross-linkers that are often used based on their optimum pH and temperature.

Table 3. Metal Ions and Their Optimum pH and Temperature

parameter	metal ions	remarks
pH	titanate and zirconate	works on a wide pH scale (between 3 and 11)
	aluminum	only works without a buffer between a pH of 3 and 5, but could work for a higher pH if added with a buffer
	borate	only effective between a pH of 8 and 11
temperature	zirconate and titanate	can be applied up to 400 °F
	borate	can be applied up to 325 °F
	aluminum	can only be applied at temperatures below 150 °F

By forming links between polymer chains, cross-linkers like borate or metal compounds like zirconium (Zr) and titanium (Ti) compounds transform a linear fluid into a cross-linked fluid with enhanced gel viscosity and high-temperature stability. Cross-linked fluids work better than linear fluids, even though the polymer concentration does not have to be raised. For example, cross-linked fluids can hold and move proppant particles better than their non-cross-linked counterparts with the same amount of polymer.²¹

Most fluids used in fracturing are guar fluids that are cross-linked with borate. Borate cross-linked fluid acts like a shear-thinning fluid, which experiences a decrease in viscosity as the shear velocity increases due to the polymer coil alignments.⁸³ Borate cross-linked guar fluids work best in an environment with a high pH of 8 or above.⁴⁰ Seawater, which is rich with divalent cations such as calcium and magnesium ions, is less stable at high temperatures because the ions precipitate out at a high pH, depleting the buffers and lowering the fluid's pH. For this reason, borate cross-linked fluids are typically only utilized with fresh water in wells hotter than ~200 °F. To make borate cross-linked seawater fluid work well at high temperatures, the addition of scale inhibitors to seawater prevents scale formation.^{3,84} Using

seawater as a borate cross-linked fracturing fluid also has advantages, as high salt levels may prevent clay damage.³¹

The acid–base equilibrium of boric acid and borate ions is disrupted by any acidic or alkaline component that may be present in the fracturing gel.³¹ At particular pH levels, acids, bases, breakers, surfactants, and inorganic cations can precipitate out, thereby providing all possible representations of such components. The temperature of the solution is ultimately determined by the concentration of borate ions. As a result, it is essential that the pH levels of all the components of the fluid are kept in proper balance.³¹

Precipitation in the pH range of borate cross-linking necessitates chemical adjustments, such as the inclusion of scale inhibitors, as the presence of other ions in seawater and forming brines may affect the borate ion equilibrium. Low fluid pH results in a borate gel with a much lower viscosity because the borate ions in the gel are unable to maintain an equilibrium concentration high enough for cross-linking.^{31,42}

In a previous experiment, guar gum was modified to increase its solubility and swelling capacity in concentrated potassium formate (CHKO₂) brine; then, a tertiary release cross-linking approach was used to make a boron/zirconium composite cross-linker.⁸⁵ Above 140 °F, the boron ions were slowly released, strengthening the gel against sand intrusion. Cross-linking activity from a complexed zirconium ion commenced at temperatures >284 °F, and the resulting bond was significantly stronger than that created with boron ions. The CHKO₂-weighted fracturing fluid created with the composite cross-linker showed excellent performance in static filtration loss and formation damage, as well as the capacity to preserve a high viscosity at 320 °F. In another study, an organic zirconium cross-linker with seawater compatibility was evaluated.⁸⁶ The gel for fracturing was made by combining a CMHPG fluid based on seawater with an organic zirconium cross-linker. Fourier transform infrared (FT-IR) and ultraviolet–visible (UV–vis) spectroscopy analyses confirmed that the ligands successfully bonded to the zirconium ions.⁸⁶

In yet another study, a fracturing fluid was manufactured with a stable operating temperature of 350 °F at 30 lb/1000 gal by mixing CMHPG with synthetic polymers (AA-AM-AMPS).⁸¹ The cross-linker–polymer strength was able to be maintained at temperatures exceeding 350 °F by using a zirconium cross-linker that reacted slowly. To further protect the cross-linker–polymer bond at temperatures exceeding 350 °F, an external cross-linking delay additive (a sugar alcohol derivative) can be utilized. Sodium thiosulfate is more stable at temperatures above 350 °F. However, the properties of acetic acid and pH-neutralizing acetate diminish significantly above 350 °F. It was found that at a pH of 5 and a temperature of 300 °F, the thermal stability of a 40 lb/1000 gal pure CMHPG fracturing fluid system did not improve due to the addition of sodium thiosulfate.⁸¹

Developing a successful seawater-based fracturing fluid will depend on the choice of cross-linker, especially if the fluid is intended to have a high viscosity. When selecting a cross-linker for a seawater-based fluid, the strength of the cross-linker's bond with the polymer and the cross-linker's compatibility with scale inhibitors will be of primary importance. The following section discusses scaling inhibitors, as these compounds are a critical component in preventing scale caused by seawater ions.

SCALE INHIBITORS

Scaling is accelerated by the high salinity of seawater-based fracturing fluids. Unlike seawater, fresh water does not cause

scaling problems in fracturing fluids. Sulfate scales form in seawater when two incompatible waters mix together, such as the mixing of seawater (containing a high concentration of sulfate ions) and formation water (containing a high concentration of barium, calcium, and strontium ions).³⁰

Scale is formed through two crystallization mechanisms: surface crystallization and bulk crystallization. Scaling is a hybrid of these two systems.^{87–89} Different nucleation mechanisms lead to crystallization at the surface and in the bulk of a material. Scaling combines elements of both of these systems.⁹⁰ In contrast to bulk crystallization, which is the outcome of homogeneous nucleation mechanisms, surface crystallization is the consequence of a variety of different types of nucleation. The different stages of scale formation are described as follows:⁹¹

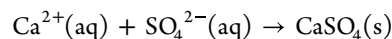
- **Aggregation**
Ion pairs are formed when cations and anions in a solution, such as Ca^{2+} and CO_3^{2-} or SO_4^{2-} , collide and reach supersaturation levels. They then form microaggregates, which serve as miniature crystal centers, embryos, and micronuclei.
- **Nucleation**
These microaggregates play an important role in the formation of microcrystals by acting as the nucleation points for the crystals. At somewhat higher saturation ratios, it is possible for nucleation to occur on the substrate, and it is also possible that it might form in the bulk fluid.
- **Crystal growth**
Depositional microcrystals are formed when the microcrystals formed in the solution agglomerate or are absorbed onto a solid surface, where they grow into larger microcrystals that then fuse together to produce depositional microcrystals.
- **Agglomeration**
Scales begin to form on the surface of the formed microcrystals as a result of the continued adsorption of additional scaling ions in the solution. These transform into deposits as they grow.

Many types of scales can be prevented from forming with the use of scale inhibitors. There are a few different types of scale inhibitors, such as chelating compounds that create a soluble complex, threshold inhibitors that stop supercritical nuclei from forming, and growth retarders for scale crystals. In general, scale inhibitors can be broken down into these three categories: chelating agents, threshold inhibitors, and retarders of the scale crystal growth.^{92–94} In order to lessen the amount of calcium sulfate that precipitates, many different kinds of calcium sulfate inhibitors, including polyphosphates, organophosphorus compounds, and polymeric inhibitors, have been used. In order to successfully produce a high-temperature seawater-based fracturing fluid, it is essential for the metal cross-linkers and the scale inhibitors to be compatible with one another. Mineral salt precipitation exists in a variety of forms known as scales. Calcium carbonate (CaCO_3) or calcite and Group 2 sulfates, such as barium sulfate (BaSO_4) or barite, calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or gypsum, and strontium sulfate (SrSO_4) or celestite, are common scales that form in oil fields.^{92,95,96} It has also been observed that several common scale inhibitors have the inherent capacity to chelate the zirconate ions of the cross-linker.¹⁶ Several possible scale types that may be present when preparing seawater as a fracturing fluid are listed in Table 4.

Table 4. Several Scale Types Related to Seawater-Based Fracturing Fluid and Their Reactions

scale type	reaction
calcium carbonate	$\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CaCO}_3(\text{s})$
sulfate	$\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$
	$\text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{CaSO}_4(\text{s})$
	$\text{Sr}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{SrSO}_4(\text{s})$
	$\text{Mg}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{MgSO}_4(\text{s})$
sulfide	$\text{Fe}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightarrow \text{FeS}(\text{s})$
iron	$\text{Fe}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{FeCO}_3(\text{s})$
	$4\text{Fe}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{Fe}(\text{OH})_3(\text{s})$

Sulfates are abundant in seawater (usually in concentrations >1000 ppm),³¹ while divalent ions like calcium and magnesium are abundant in formation water. Thus, when both brines come into contact, an insoluble calcium sulfate scale forms. At bottomhole conditions, where the solubility limit decreases as the solution temperature increases, calcium sulfate has a higher potential for scaling. This temperature range is >104 °F.⁹⁷



At 300 °F, calcium sulfate scale precipitation is strong, so SIs must be included when seawater is utilized.¹⁶ Several types of calcium sulfate scale inhibitors, such as polyphosphates, organophosphorus substances, and polymeric inhibitors, have been used to lessen calcium sulfate precipitation. Polyphosphate scale inhibitors, such as sodium hexametaphosphate (HMP) (NaPO_3)₆, have limited applications in the oilfield industry due to their tolerance for high calcium concentrations.^{98–101} Organophosphorus chemicals are another kind of calcium sulfate scale inhibitor. Phosphonates and phosphate esters are the two most common forms that are used in oilfield settings. Phosphate esters have a lower thermal stability than phosphonates and can only be utilized up to 200 °F with few practical uses.^{16,102,103} For example, triethanolamine phosphate (a phosphate ester) can only be used up to 176 °F before it begins to hydrolyze. In comparison, phosphonate-based calcium sulfate scale inhibitors have been shown to be effective in numerous studies, especially when the scaling index is high.^{103–105} Notably, if the saturation index is less than 1.0, hexamethylenediamine tetra(methylene phosphonic acid) (HDTMP) is the most effective inhibitor for calcium sulfate scaling.^{80,106,107}

The most commonly used phosphonate-based inhibitors are 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCa) and 1-hydroxyethane-1,1-diphosphonic acid (HEDP). Phosphate inhibition can be improved by adding an amine group, which increases the metal-binding capacity of the phosphonate-based molecule.¹⁰⁰ Aminophosphonates such as amino tris(methylene phosphonic acid) (ATMP), ethylenediamine tetra(methylene phosphonic acid) (EDTMP), and diethylenetriamine penta(methylene phosphonic acid) (DTPMP or DETPMP) are examples. The chemical structures of ATMP, EDTMP, DTPMP, and HEDP are shown in Figure 3.

Polymeric inhibitors have been widely used alongside phosphate- and phosphonate-based medicines. Several other types of functional groups are used in the synthesis of these inhibitors. These include poly(maleic acid) (PMA), poly(acrylic acid) (PAA), and polyphosphino carboxylic acid (PPCA). Polymeric inhibitors can be constructed from a single type of monomer (homopolymer) or from a combination of several monomers (copolymer and terpolymer). This class of scale

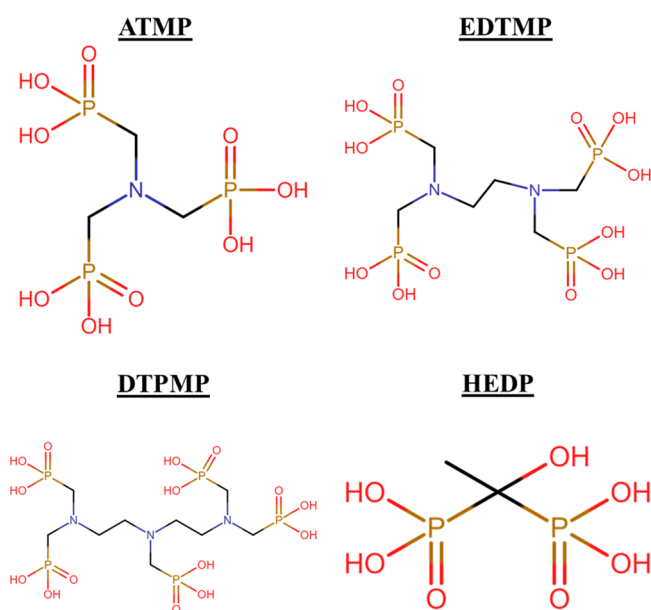


Figure 3. Chemical structures of several phosphonate-based scale inhibitors.

inhibitor has greater temperature stability and tolerance for calcium ions.^{100,101,104,105,108} The chemical structures of several polymeric scale inhibitors are shown in Figure 4.

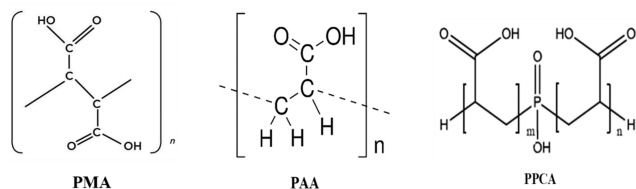
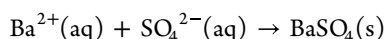


Figure 4. Chemical structures of several polymeric scale inhibitors.

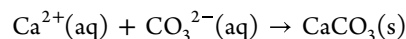
Almubarak et al. conducted an experiment with a high-temperature seawater-based fracturing fluid that showed the application of two scale inhibitors at 3 and 0.5 gpt (gallons per 1000 gallons) prevented calcium sulfate scaling in seawater and formation brine mixes at 250 and 300 °F.¹⁶

Other scaling issues that occur from sulfate scaling are with barium sulfate (BaSO_4), which is a serious concern in most production areas across the world (e.g., the North Sea, West Africa, offshore Brazil, and the Gulf of Mexico).^{31,109,110} Because of their strong reactivity, barium cations produce a barium sulfate deposit wherever sulfate ions are present. This deposit has the lowest solubility of any mineral scale and is resistant to acid treatment.^{111–113} Phosphonate or polymeric scale inhibitors are the most commonly used SIs to inhibit the formation of barium sulfate. In addition, the synergistic effect of mixing two (or more) SIs for improved scale inhibition efficacy can be employed.¹¹⁴



When formation water and seawater interact at a temperature of 302 °F, barium sulfate and calcium sulfate scales are expected to form.¹⁰⁷ Shaw et al. conducted a phosphate–phosphate synergistic test.¹¹⁴ diethylenetriamine penta(methylene phosphonic acid), or DETPMP (a commonly used “traditional” pentaphosphonate SI), was evaluated synergistically with four

additional phosphonate products: HMTMPMP (a long carbon chain pentaphosphonate), EDTMPA (a tetraphosphonate), HMDP (a long carbon chain tetraphosphonate), and HEDP (a long carbon chain diphosphonate). All four outcomes demonstrated that using all four SI combinations provided a synergistic benefit.¹¹⁴ In another study, it was found that within the production facility of an oil and gas asset located in the North Sea, a significant amount of CaSO_4 and BaSO_4 scale accumulated over time.²⁷ Six scale inhibitors were tested: an amine-based polymer, sulfonate-based polymers, an acrylic-based polymer, a phosphonate-based SI, and a maleic-based polymer. According to dynamic loop tests, the phosphonate-based SI showed the best performance on CaSO_4 and BaSO_4 co-deposition under the test conditions.²⁷ The amine-based polymer and the phosphonate-based SIs displayed good environmental qualities while also demonstrating good performance through the traditional scale laboratory screening tests.²⁷ Another study stated that DETPMP nearly totally inhibited calcium sulfate (with an inhibition efficiency of 100% at a DETPMP concentration of 10 ppm); however, the CaSO_4 inhibition efficiency dropped when trace amounts of chelants were present.¹⁰⁴



CaCO_3 precipitation can be effectively inhibited by using polyamino polyether methylene phosphonate (PAPEMP).^{102,103} In one study, an eco-friendly scale inhibitor for use with seawater in offshore areas was studied, and it was found that a mixture of the linear carboxymethyl β -cyclodextrin-epichlorohydrin polymer and the citric acid-dopamine-epichlorohydrin polymer showed promise. At an inhibitor concentration of 19.2 mg/L ($\text{Ca}^{2+} = \text{CO}_3^{2-} = 2400$ mg/L, $\text{Ca}^{2+} = \text{SO}_4^{2-} = 800$ mg/L), the polymer mixture had an excellent scale inhibition efficiency of 94.6% against CaCO_3 and 92.5% against CaSO_4 .¹¹⁵ Diethylenetriamine penta(methylene phosphonic acid) (DTPMP) is another type of phosphonate inhibitor that is often used, as discussed previously. When DTPMP is completely ionized, it has an anion charge of 10. Calcium carbonate scaling can be reduced by as much as 98.2% when DTPMP is used at a concentration of 10 ppm.¹¹⁶

■ GEL STABILIZERS EFFECTS ON SEAWATER FLUID

To prevent the chemical breakdown of polymer solutions, gel stabilizers are often used. The gel stabilizers that are used in fracturing fluids include methanol, triethanolamine (TEA), and several inorganic sulfur compounds.⁸ While some stabilizers assist by stopping the chemical breakdown process, many of them also interfere with the cross-linking mechanism. TEA and sulfur-containing stabilizers provide various benefits over methanol, which is flammable, poisonous, and expensive.⁸ TEA maintains the fluid's viscosity as the temperature increases. According to Yang et al., mixing the fracturing fluid with a cross-linking agent utilizing the triethanolamine zirconium complex as an ultrahigh temperature cross-linking agent could be a viable option for obtaining high-temperature resistance. It was found that the shear viscosity of a fracturing fluid system increased to over 200 mPa s after 90 min of shearing and to over 130 mPa s after 120 min of shearing at 446 °F and 100 s^{-1} .¹¹⁷ Common inorganic sulfur stabilizers that are used in the petroleum industry include metal-based compounds, such as iron sulfide (FeS), zinc oxide (ZnO), and manganese dioxide (MnO_2).

Oxygen scavengers, high-temperature stabilizers, and buffers can be used in the stabilizer package. This stabilizer package can then be added to the polymer to provide it with high-temperature shear resilience in order to reduce the problem of shear and temperature degradation.

It is important to degrade the polymer that is injected. Biodegradable polymers are a class of synthetic or natural polymers that have the ability to decompose or degrade in the environment, primarily through natural biological processes, into nontoxic and environmentally friendly substances.^{118–120} For nonbiodegradable polymers, the injected polymer can be broken up using a breaker so that it can flow back and be cleaned. The breaker effects on seawater fluid is explained in the following section.

■ BREAKERS EFFECTS ON SEAWATER FLUID

The molecular weight of a polymer must be drastically decreased for complete breakdown to occur. High temperatures, high pH levels, and high salt concentrations typically deactivate or denature enzyme gel breakers. Enzymes are recommended for use in fracturing fluids to degrade gelling polymers.¹²¹ Enzymes work to break down polymers into ever smaller pieces, which immediately translates to less wear and tear on the proppant pack, fracture face, and formation as a whole. Furthermore, enzymes are specific to a given bond and do not react with any other polymeric additions. The use of gel permeation chromatography (GPC) has been suggested for the investigation of polymer-gel breakers. Optimizing the time, temperature, gel breaker concentration, and polymer loading based on the results of GPC testing can assist in the evaluation of each gel breaker used in field treatments.¹⁶

Unlike enzymes, which are pH-dependent, oxidizers are temperature- and salt-dependent. Oxidizing breakers based on chlorine (CBO) allow for temperature regulation between 200 and 300 °F.¹²² However, for temperatures <200 °F, such high-temperature oxidizing breakers need to be enhanced by chemical activators (CAs) and chemical intensifiers (CIs). While activated, CBO may dissolve gels in fresh water containing 2% KCl. However, a greater concentration of CBO and CA, in addition to a CI, is required to dissolve gels in seawater.³¹ Meanwhile, for the Zr cross-linker zirconium oxychloride, acetic acid and triethanolamine can be mixed together to make the Zr cross-linking agent. At high temperatures, this cross-linker can make the substance thicker, thus taking a longer time to break.^{8,123–126}

Seawater-based fracturing fluid methods that have been shown to work under specific conditions of temperature and shear rate are detailed in the following section.

■ SEAWATER-BASED FRACTURING FLUID DEVELOPMENT

The cloud point in ionic water, such as seawater, appears to be precisely 300 °F,^{32,71,127} and fluid exposure over this temperature gives insufficient rheological stability for sufficient proppant movement in conventional fluid systems.¹⁹ A novel high-temperature fracturing fluid system that is improved with nanoparticles and formulated with untreated seawater for applications up to 300 °F has been created. The fluids, which were made of metal cross-linked polysaccharide polymers, maintained their stability at temperatures as high as 300 °F. The fluid viscosity in a typical test remained over 500 cP at a shear rate of 40 s⁻¹ for at least 60 min at 300 °F.¹²⁸

The rheological effects of a number of additives, such as polymers, GLDA, and a cross-linker, have been investigated by contrasting five different grades of hydroxypropyl guar (HPG) and carboxymethyl hydroxypropyl guar (CMHPG) in seawater.¹²⁹ The results showed that the additives had a significant effect on the rheology of the fluid. The optimal polymer was chosen after hydrating five different polymers (0.6 wt %) with seawater and fresh water. The top-performing polymer was next subjected to experiments involving L-glutamic acid, N,N-diacetic acid (GLDA) concentrations of 1%, 4%, and 8%. The first phase of testing was conducted at 248 °F with a pressure of 500 psi and a shear rate of 100 s⁻¹. The identical formulations were then subjected to a series of temperature ramp tests spanning from 77 to 248 °F. The ramped temperature data showed that the presence of a cross-linker significantly altered the rheology of the fluid in response to even slight variations in the concentration of the chelating agent. It has been found that, compared to higher concentrations of GLDA, viscosities are greater and last longer at lower concentrations.¹²⁹

In order to reduce the scaling propensity during fracturing treatments utilizing seawater-based fluid when combining with high TDS formation water, the nanofiltration (NF) of seawater was introduced.^{38,39} It was discovered that the scaling issues during fracturing with seawater-based fluid may be effectively minimized by combining nanofiltration with the use of scale inhibitors, and it was determined that this combination is suitable for field applications. Nanofiltered seawater has been found to work well with scale inhibitors and is able to maintain its rheological qualities for extended periods of time at temperatures as high as 350 °F.^{19,30} In one study, it was found that no scale inhibitor was needed to produce negligible precipitation in mixtures of NF seawater and formation water. The reduced sulfate concentration of the NF seawater predicted a decrease in precipitates. After 80 min at a shear rate of 100 s⁻¹ and a temperature of 300 °F, the apparent viscosity of the NF seawater-based fracturing fluid dropped to ~200 cP, and after 120 min, it dropped below 100 cP. Because of its fluid stability, it could be used for proppant fracturing.¹³⁰

Nanofiltered (NF) seawater-based fracturing fluid, which is a component of the stabilizer package, confers a number of important benefits. These benefits include the provision of a seawater-based fluid that has a nearly nonexistent scaling propensity as well as strong shear and temperature stability.^{39,131} However, the equipment used for nanofiltration requires a lot of space. This presents an additional difficulty for locations with limited landmass, such as those offshore. Treatment time and energy requirements both increase with nanofiltration as well. Nanofiltration is also more expensive compared to conventional fracturing treatments or the use of additives with raw seawater.

In one study, it was found that sulfate scaling was inhibited in seawater/formation water combinations at 250 and 300 °F when scale inhibitors SI-A and SI-B were added at 3 and 0.5 gal/Mgal, respectively.¹⁶ At 300 °F and a shear rate of 100 s⁻¹, the apparent viscosity of the fracturing fluids made from raw seawater with scale inhibitor SI-B was >200 cP. These liquids were thick enough to reliably transfer and suspend proppant.

In yet another study, South China seawater, the anionic–nonionic viscoelastic surfactant FMES, and sodium chloride were the three components utilized in the creation of an innovative viscoelastic fracturing fluid system. The findings of the experiment indicated that the seawater-based fracturing fluid possessed the right rheology for use in relevant fracturing applications, even when subjected to high temperatures and low

shear rates. This fluid also had low formation damage.³⁶ In the next section, some previous works that have developed seawater-based fracturing fluids and tested them in the field, where they showed a positive result, are discussed.

■ FIELD-SCALE APPLICATION OF SEAWATER AS FRACTURING FLUID

To reduce damage and residue, a seawater-based fracturing fluid was developed with a low-residue polymer cross-linked with zirconium. Specifically, a seawater-based fluid with a pH lower than 10 was created by cross-linking low-residue polysaccharides with zirconate. The seawater-based fluid proved to be more stable at high temperatures compared to HPG fluid. Twenty multistage hydraulic fracturing treatments in three wells in the offshore Romanian Lebăda oil field were completed successfully using this fluid.³³

In another study, raw saltwater was used as part of the fracturing fluid system in Saudi Arabia's Well-A, along with an improved scale inhibitor package.¹³⁰ It was found in the eastern region of Saudi Arabia, namely in the southern portion of the Ghawar anticline formation. Nearly half (47%) of the total fluid that was used in the fracturing procedure was raw seawater treated with a scale inhibitor. To achieve the desired etched pattern on the fracture face, the treatment plan was based on the acid fracturing method, which involves pumping polymer-based pad fluid, emulsified acid, and diverter fluids into the formation in phases. The desired etched half-length was achieved by using a four-stage pumping process. Initial production test results showed gas production at 27 MMSCFD (million standard cubic feet per day) with a flowing wellhead pressure of 1800 psi after the well was shut in for 12 h and then opened for flowback for 3 days.

Well-B was treated using NF seawater fracturing technology to a sandstone formation in Saudi Arabia.¹³⁰ The zone that was treated was sandstone, and the bottomhole temperature was >280 °F because the well was dug vertically. Because Well-B was recompleted with a 7 in. production liner and 4.5 in. tubing, it has a moderate net pay. Perforations that were 2 and 7/8 in. in diameter and 4 shots per foot (SPF) in orientation were used to penetrate the well 30 feet in the direction of the maximum horizontal tension. A preliminary mini-fracturing treatment was carried out prior to the major proppant fracturing treatment. Seawater was nanofiltered with a clay stabilizer and surfactant for the injection stage and step rate test. The magnitude of the friction pressure close to the wellbore was measured with a step-down test. Estimates of the fracture closure pressure and fluid efficiency were derived by examining the calibration injection drop.¹³⁰

At a maximum proppant concentration of 10 lb/gal, 80 262 gal of an NF seawater-based zirconate cross-linked gel and 362 400 lbs of 20/40 high-strength proppant were pumped to create the main fracturing treatment. According to the calibration test results, the treatment plan included a 26% clean pad. Clean-up operations started once the stimulation treatment was finished, and gas rate readings were acquired to calculate the treatment-related output. At a flowing wellhead pressure of 3766 psi, the post-fracture gas rate was 5.6 MMSCFD.

The large-scale sand fracturing operation of South China Sea Well A utilized the fracturing fluid system and a continuous mixing technique was developed.⁴² According to the interpretation of well testing, the formation permeability was around 1 mD and the formation temperature was 170 °F; all of these

characteristics identify Well A as a low-permeability horizontal well. The formula for the 176 °F resistant system was the following: 0.3% HPG + 0.5% FA-17 + 0.6% SC-150 + 0.2% GM7010 (1% clean-up additive, 0.5% breaker). The two-part procedure was successful. The operation utilized continuous mixing equipment to blend the fracturing fluid in real time. The thickener was able to cross-link immediately upon hydration and function effectively. In this operation (mini-fracturing and two-stage main fracturing), 770 m³ of the fracturing fluid was prepared with the constantly mixing machine, significantly reducing the preparation cost and platform space requirements. The well was propped up with 74 t of proppant. Due to a lack of production prior to the fracturing procedure, the pilot well was shut down. The fluid production of Well A stabilized at 20 m³/d after treatment.

In another study, raw saltwater was used as the fracturing fluid in a 16-stage fracturing process.²⁴ The well was finished in an unconventional carbonate reservoir at a temperature of 280 °F, and the formula for the seawater-based fracturing fluid was developed after multiple trials, adjustments, and iterations of the design process.²⁴ The researchers were able to modify the seawater-based fracturing fluids so that they could be used in the field. These fluids were designed to have rheological properties that would allow them to carry and transport proppant under both dynamic and static conditions, despite the difficulty of the direct incompatibility between SIs and metallic cross-linkers. Scale did not form in the final formulations when the fracturing fluid filtrate was combined with different formation brines. Most crucially, they were developed to be utilized in pipes that carried untreated raw seawater without any additional treatment.¹³²

■ RECOMMENDATIONS FOR FURTHER RESEARCH

The main difficulties in developing seawater-based fracturing fluids are the issues of scaling and the compatibility of the additives with each other. Further research is needed to fully understand the effects of combining different additives, such as how the chelating agent could affect the cross-linker. There is still a need for more research regarding the influence of specific scale inhibitors on polymer hydration, as the use of scale inhibitor types becomes an important factor when it comes to specific polymer or surfactant compatibility. Because the ion concentration of seawater may vary depending on location, the use of synthetic seawater in experiments is another avenue to investigate. The synthetic seawater component could depend on the oilfield location. Calcium carbonate scale is produced in large quantities when saltwater is treated with brine from the North Sea, which has a high calcium content. When compared to other regions of the world, the Arabian Gulf has the largest sulfate content, which results in more sulfate precipitation.

Another future research avenue is related to salinity and temperature. The effectiveness of the additions is drastically altered by both salinity and temperature. For example, polymer hydration is sensitive to changes in the temperature and salinity. Salinity also has an effect on the structure and functionality of surfactants. The effectiveness of a scale inhibitor varies with the salinity and temperature of its environment. Likewise, the effectiveness of a cross-linker is affected not only by a fluid's salt content but also by its temperature. Salinity and temperature also have an impact on the chelation process. Several problems that arise in the field call for additional research into the certain salinities and high temperatures. It is also important to think about the shear rates and times required for the fracturing

procedure, as well as how the fluid would not break under those conditions.

Additives made from more environmentally friendly chemicals must also be considered. While concerns about the impact of chemicals on the environment have certainly been a driving factor in the search for a greener alternative, the use of more breakable additives would also help avoid formation damage.

SUMMARY

Despite the previous research and experiments that have studied the development of seawater-based fracturing fluids in order to realize the objective of conserving millions of gallons of fresh water, there is still a need for further research in this area. Some aspects that still need to be researched are the use of scale inhibitors (to prevent scaling), the selection and development of the most effective polymers, chelating agents, and cross-linkers (to meet the required fluid viscosity), and the development of a solution that is suitable for high-temperature conditions. The main challenge for developing seawater-based fracturing fluids is finding solutions for the scaling issues and the fluid resistance to the shear volume that is involved in fracturing treatments. Although we are currently only in the early stages of developing a successful fracturing fluid based on seawater, some studies have already shown the significant potential it has as being a greener way to perform hydraulic fracturing.

This paper offered an overview of seawater-based fracturing fluid, including its usual chemical additions and the existing field research. The goal of this review was to inform readers about the challenges, developments, and benefits of using seawater-based fracturing fluid technology, which might help us save millions of gallons of fresh water. The following are some conclusions that can be drawn:

Saving millions of gallons of fresh water and reducing the cost of hydraulic fracturing can be accomplished by making fracturing fluid out of seawater. The high salt concentrations in seawater also avoid formation damage caused by the swelling of clay.

Scaling is a significant issue that must be considered during fracturing treatments that use seawater-based fluid, as scaling can potentially cause well blockages and reduce the efficiency of the fracturing process.

CaSO₄, BaSO₄, and CaCO₃ were the common scales that form when preparing seawater-based fracturing fluid.

Because of the abundant amount of sulfate ions in seawater, sulfate scale is becoming a major concern for developing seawater-based fracturing fluid.

Phosphate- and phosphonate-based scale inhibitors are the most common scale inhibitors that are used to address calcium scales, while polyacrylic-based scale inhibitors have seen widespread adoption and show resistance at higher temperatures.

When choosing a scale inhibitor, its compatibility with other additives needs to be considered, especially for high-salinity fluids.

Ca²⁺ and Mg²⁺ are the two main ions in seawater that cause precipitation, which leads to a decreased cross-linking ability and viscosity.

GLDA is commonly used over other chelating agents due to its environmental friendliness and stability at high temperatures and salinities.

CMHPG, which is a derivative of HPG, is the most commonly used polymer because it efficiently hydrates and leaves behind little to no residue.

The optimal pH range for several polymers needs to be evaluated in order to obtain the desired hydration.

Inhibitors and gel stabilizers can be used to enhance the rheology of a fluid system.

The combination of additives can vary. Some combination examples include a chelating agent and a cross-linker, a polymer plus a chelating agent plus a cross-linker, or a polymer plus a cross-linker plus a scale inhibitor. However, using fewer chemicals to achieve the desired rheology for stimulation fluids is preferable for both economic and environmental reasons.

Several oil fields in Romania, Saudi Arabia, and the South China Sea have reported successful seawater fracturing operations.

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Notes

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NOMENCLATURE

TDS=total dissolved solids
APCA=aminopoly(carboxylic acid)
NTA=nitrilotriacetic acid
EDTA=ethylenediaminetetraacetic acid
DTPA=diethylenetriamine pentaacetate acid
EPTA=ethanolic phosphotungstic acid
GLDA=L-glutamic acid, N,N-diacetic acid
HEDTA=hydroxyethyl ethylenediamine triacetic acid
SI=scale inhibitor
VES=viscoelastic surfactant
HPG=hydroxypropyl guar
CMHPG=carboxymethyl hydroxypropyl guar
HEG=hydroxyethyl guar
CMG=carboxymethyl guar
MSA=methanesulfonic acid
TEA=triethanol amine
GPC=gel permeation chromatography
NF=nanofiltered
EC=electrocoagulation

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