

Developing the Origin of Raw Materials to Achieve Environmentally Responsible Products without Sacrificing Performance

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Abstract

The oilfield is uniquely positioned to utilize commonly accepted analytical benchmarks to begin to documenting their carbon product management as part of an environmental, social, and governance (ESG) program. Both the origin and fate of many formulated products can be reliably assessed with the use of renewable carbon index (RCI) ([Integrity Biochem 2021](#)) and [OECD 301B](#) Biodegradation protocols. Both techniques can be deployed without sacrificing product performance and proprietary molecular composition. While not new to the scientific community, the combined use of RCI and OECD protocols delivers important information regarding the volume amount and year-to-year trends on the conversion from non-renewable carbon to renewable carbon. This information quantifies the producers efforts to 1) lower the total carbon budget in its consumables, 2) measure efforts to achieve new zero carbon additions, 3) benchmark legacy products with newer “greener” products and 4) compare the product service lifetime to the overall product lifecycle.

In this paper, we discuss means to utilize these type of protocols to assess modernity of carbon in the overall carbon budget in a company’s consumable product lines. Advancing this concept establishes foundational principles on how environmentally responsible supply can be defined. As biotechnology manufacturing advances into long-practiced chemical manufacturing practices, metrics can be readily achieved without sacrificing product performance and limited product availability. This paper will contrast the performance of a few common drilling, completion, and stimulation additives based on their RCI to demonstrate the ability to produce and achieve the performance required in these oilfield applications while advancing ESG goals.

Introduction

The oilfield is responding to its social obligation in many different aspects of its business. One component of its business that remains largely unattended is its management of its consumable raw materials and products. Although the chemical spend for the upstream activity of the oilfield (drilling, cementing, stimulation, completion etc.) ranges from 2% to 20% of the cost of a well, many of the products used to perform this work are manufactured from the petroleum found and

produced from the efforts of these combined phases. According to the US EIA ([EIA 2021](#)) and Visual Capitalist ([Conte 2021](#)), fifteen to twenty percent of every barrel of crude is used for applications not directly related to fuel. This crude oil category of chemical feedstock is the primary source of non-renewable carbon that accretes anthropogenically.

However, the oilfield is working to displace this vast reservoir of non-renewable carbon with sustainable renewable carbon-based products without sacrificing performance and distorting business cost models. In fact, use of renewable carbon products is poised to develop transparent and quantifiable environmental, social, and governance (ESG) metrics that will differentiate individual oilfield chemical supply companies.

Bio-Based Surfactants and RCI in the Oilfield

In 2020, all surfactant consumption in the oilfield exceeded \$1 Billion USD or approximately 2% of the global surfactant market ([Global Market Insights, 2021](#)). However, the relative use of bio-based surfactants, both from fermented and reacted origins, accounted for over \$38 Million USD or nearly 4% of the oilfield surfactant market ([Global Market Insights, 2021](#)). Although this paper will illustrate efforts to increase the use of biosurfactants, the oilfield already has demonstrated a willingness to incorporate these as additives at a relatively high rate.

The oilfield has a strong preference and a long history of utilizing non-ionic and anionic surfactants owing to fluid and rock compatibility and relatively lower toxicity compared to cationic surfactants. Non-ionic surfactants account for approximately 36% of the total oilfield supply ([Global Market Insights, 2021](#)) and a large fraction of this category are ethoxylates derived by petroleum feed stocks. With Compound Annual Growth Rates (CAGR) projected to exceed 4% for the next several years, it’s easy to envision that bio-based and synthetic surfactants will participate in the associated market growth. In fact, large surfactant producers have entered long-term commitments to produce the two largest categories of biosurfactants: rhamnolipids and sophorolipids. This commitment to improve the environmental footprint of all carbon-based products, including biosurfactants, is relatively easy to monitor.

Early Social Responsibility Measures in the Oilfield

The global petroleum industry has made attempts to speak to responsible drilling and completion behavior. Most of its efforts have been made to communicate no harm or no significant harm to the environment. In addition, to routine aquatic toxicity and mobile metal reporting, the industry has incorporated standardized biodegradation into its efforts either as a matter of compliance or transparency. The Organization for Economic Co-Operation and Development (OECD) protocols are a series of testing protocols as a primary tool for these assessments. These tests screen formulated chemical products and additives for relative biodegradability; OECD 301 focuses on biodegradability in an aerobic aqueous system and includes, among other biodegradation tests, [OECD 301-B](#) the CO₂ Evolution also known as the Modified Sturm Test. These tests do inform all stakeholders of the relative lifetimes of a product, both service lifetime and otherwise, but offers little opportunity to quantify the specific origins of the carbon in the products or additives.

A well-accepted analytical technique called Renewable Carbon Index (RCI) can be used to verify the relative use/concentration of non-renewable and renewable carbon in a product portfolio. The RCI has high potential as a measure of sustainability in the oilfield due to the transparently sound scientific principles on which it is based. Renewable carbon can be measured by a well-established protocol ([ASTM D6866](#)) based on radiometric age dating, given the clear contrast in isotopic signatures of modern carbon (<57,000 years) versus geologically derived carbon, i.e., from crude (millions of years). A product's RCI is calculated by dividing the number of carbons derived from renewable sources by the total number of carbons in the product ([Integrity Biochem 2021](#)). This method and results combined with an accuracy of $\pm 1\%$ can be used to, for example, determine the biodiesel blending percentages of retail biodiesel blends in the US ([Reddy et al. 2008](#)).

The classification of renewable and non-renewable carbon materials provides a benchmark to assess the accretion of carbon as found in the subsurface into the modern environment. Note that if the RCI reports the proportion of renewable carbon relative to the total carbon in a product, then as the non-renewable carbon is replaced by renewable carbon, it follows that the accretion rate of geologic-sourced carbon such as carbon dioxide, methane and ethane is slowed.

The following discussions benchmark common legacy products versus new generations of functional additives as formulated with renewable carbon feed stocks. In these comparisons the newer products formulated with renewable carbon are identified as RCI products. [Table 1](#) shows current RCI measurements for this generation of additives as applied in the areas of inhibition, iron control, emulsion prevention, and suspensions. While a few of the RCI additives presented herein measured 100%, others are less; however optimization is an ongoing process to achieve as near 100% RCI as practical.

Performance of RCI Additives for Common Oilfield Applications

In the following sections, RCI additives or products are examined using common laboratory assessments with respect to their potential to achieve essential and acceptable functional effectiveness. The oilfield utilizes surfactants across a very broad range of phases which includes drilling, completion, stimulation, and production. Specifically within these phases, an individual field, well, and/or formation may dictate challenges such as: inhibition of reactive clays, iron control, prevention of emulsions, and stabilizing and enhancing suspensions. These difficulties listed are a very small subset of the plethora of problems, challenges, and risks encountered in well construction. It follows that these often inherent risks are mitigated by engineering the fluids to meliorate anticipated problems and to reduce or eliminate non-desired costs, time lost, or delayed production. The following assessments benchmark several different RCI additives versus traditional legacy type products with respect to the latter's typical application in a fluid as well as concentration.

Inhibitors for Reactive Clays

There are multiple techniques to inhibit reactive clay minerals that are typically encountered when drilling, completing, or re-entering a well with a completion/workover brine ([Gomez et al. 2015](#)). For example, relatively large concentrations of salts in a completion brine reduces the amount of free water whereby the use of less water potentially reduces swelling of reactive clays. If this is not possible or effective, a KCl completion brine, or even dry KCl added to a completion brine, has proven to be effective in drilling many fields, wells, and native formations ([Shenoy et al. 2008](#)). Clay inhibitors can also provide an option when concentration is optimized for effectiveness and cost ([Gomez and Patel 2013](#)).

However, these inhibitors must not only be compatible but environmentally acceptable in the area of use. For example, some quaternary salts and amines are not environmentally acceptable as they fail local required toxicity tests ([Table 2](#)). While some of these additives can achieve water and brine solubility, this does not guarantee they are environmentally acceptable. However some additives can achieve PLONOR approval, specifically in North Sea operations, it is considered the more restrictive process as biodegradability is favored over toxicity ([Preston et al. 2020](#)). However, the enhanced biodegradability of a high RCI additive which functions as a clay inhibitor promotes environmental approval for its use, for example, in water-based mud and/or brines.

An RCI clay inhibitor was assessed using a common technique, Capillary Suction Test (CST), and compared to choline chloride, a quaternary ammonium salt, and KCl. While numerous clay inhibition test methods are available, this CST technique allows rapid and in most assessments, repeatable results.

For this assessment a shale pack was fabricated using bentonite, rev dust, and very fine-grained calcium carbonate with 70% w/w comprising bentonite (i.e., montmorillonite) to function as the reactive clay mineral. The fluids and additives were agitated for five minutes with an overhead mixer then combined with this shale pack and static aged an additional fifteen minutes to promote hydration. For each CST test, each fluid plus the shale pack was agitated for an additional thirty seconds before immediately transferring to the CST cell. The results shown in [Table 3](#) are the average of three runs where the value is typically referenced to tap water, completion brine, or selected inhibitors.

Two different RCI clay inhibitors were assessed ([Table 3](#)), CS1 and CS2, where CS1 has a lower RCI ([Table 1](#)). These inhibitors were combined with tap water. One series of testing shows that 2% v/v CS2 is as effective as 7% w/w KCl or 35% v/v choline chloride for inhibiting this shale pack. The baseline, tap water, averaged 835 secs while 7% KCl and 35% choline chloride averaged 41.6 secs and 16.9 secs, respectively. In comparison, 2% v/v CS2 averaged 10.9 secs. To further, at a concentration of 0.5% v/v, CS2 averaged 38.9 secs, which for this method, equates to the performance of 7% w/w KCl.

A simple static aging assessment at ambient temperature, shows these RCI products are dispersible and soluble in 10.0 lb/gal NaCl as well as 11.0 lb/gal CaCl₂ ([Fig. 1](#)). The increase in turbidity for both, as measured, are negligible.

In summary, the RCI products, CS1 and CS2, perform as effectively as traditional products at a significantly reduced concentration and represent less anthropogenic carbon added to the environment.

Iron Control

Iron control agents function as chelating and/or reducing agents for dissolved iron in oilfield waters and brines. Specifically dissolved ferrous iron as is commingled in formation, flow back, and produced waters to prevent the development of ferric iron phases. In addition, fracturing fluids which typically do not possess sufficient acid thus cannot dissolve iron or iron compounds from the formation or even the equipment in which they are pumped ([Dill and Smolarchuk 1988](#)). Iron control agents, at the least, should prove compatible in a range of waters and brines, function over a relatively broad pH range, and be compatible with other required additives, for example oxygen scavengers. With respect to effective concentration, an iron control agent should complex relatively high concentrations of Fe³⁺ at the lowest functional concentration thereby reducing treatment cost as well as promoting functionality and compatibility of any other required additive(s).

Three RCI iron control additives, designated as IC1, IC2, and IC3 ([Table 1](#)) and two common iron control products, 5% sodium citrate and ethylenediaminetetraacetic acid (EDTA) were compared. [Fig. 2](#) shows their concentration versus iron concentration over a range of 10 to 100 ppm of Fe³⁺. As [Fig. 2](#) shows, at concentrations of 1 gal/1000 gal and less, all three RCI additives will complex 50 ppm Fe³⁺ versus 4.0 to 4.5 gal/1000 gal for sodium citrate and EDTA, respectively. To

further, at concentrations less than 2 gal/1000 gal, all three RCI additives will complex 100 ppm of Fe³⁺ versus 7.0 to 9.0 gal/1000 gal of 5% sodium citrate and EDTA. Thus proving the higher efficiency of the RCI additives.

With respect to compatibility with produced or recycled fracturing/stimulation waters, [Fig. 3](#) shows IC1 as used to dose synthetic brines at a concentration of 1 gal/1000 gal. Their TDS ranges from 10,000 to 250,000 while pH ranges from approximately 3.7 to 7.5 or approximately 3 log units ([Table 4](#)). The multivalent cations range from <10 mg/L or near fresh water to nearly 90,000 mg/L. The cations include Ca²⁺, Mg²⁺, Mn²⁺, Sr²⁺, Ba²⁺, Fe^{2+,3+}, and B³⁺ and serve as a litmus test for potential incompatibility. Furthermore, synthetic Brine L is formulated to simulate a produced brine from the Marcellus, approximates 200,000 mg/L TDS with ≥200 mg/L iron, thus the orange color in [Fig. 3](#). IC1 exhibits complete solubility in all of these brines.

Non-Emulsifiers

To briefly clarify between a non-emulsifier or emulsion preventer and a demulsifier, it may be necessary to understand and differentiate their functionality ([Luyster et al. 2002](#)). Non-emulsifiers are similar in nature to demulsifiers in that they are surface-active agents. However, demulsifiers are oil soluble, whereas, non-emulsifiers are water and brine soluble for good reason. Both must have the capability to remain in solution. However for a non-emulsifier increasing salt saturation in relatively moderate to high density brines yields lower water activity primarily due to the nature of divalent cation-water hydration complex ([Foxenberg et al. 1998](#)). If a non-emulsifier cannot remain in solution as the brine penetrates deeper into the formation, its ability to prevent an emulsion will be reduced. If only partially soluble or dispersible, it will likely adsorb onto the surfaces of formation grains, further weakening its ability to prevent emulsions. Another essential characteristic of a non-emulsifier is strong attraction to the potential crude-brine interface. To be effective, the non-emulsifier must be able to compete against large odds for its place at a potential interface. It will likely compete with asphaltenes, resins, cresols, phenols and organic acids. In addition metallic salts, silt and clay-sized particles, and even salts can all function as emulsifiers. In summary, a non-emulsifier must be able to: disrupt and/or prevent the formation of an interface, flocculate crude droplets, and promote their coalescence in the water phase such that they evolve into the crude phase. These advantageous functions are used for benchmarking and differentiating RCI-type non-emulsifiers.

Two RCI non-emulsifiers, NE1 and NE2 ([Table 1](#)), were first assessed for dispersibility and solubility in three brine types, KCl, NaCl, and CaCl₂. NE2 is specifically blended for high density brines (e.g., divalent brines) and NE1 for less dense or monovalent brines. These products were added at a concentration of 0.75% v/v, which is considered economic in most applications. The results, [Fig. 4](#), show that both RCI-type non-emulsifiers were dispersible and completely soluble in monovalent (NE1) and divalent brine (NE2).

To further assess their performance, a test crude was created using a sweet crude, API gravity 50°, and a heavy bitumen crude with API gravity of approximately 10°. These mixtures were blended at a ratio of 80:20, respectively, whereby the final blend was utilized for the following analyses.

For the second assessment, the NE1 was added to a 3% w/w KCl at a concentration of 0.75% v/v, again considered a cost-effective treatment level in some, if not most, completions. This brine and the aforementioned blended crude were added to test jars at ratios of 25/75, 50/50, and 75/25, percent by volume. In this scenario, this RCI non-emulsifier was assessed for its ability to resolve an interface at varying volumes or interface. The test bottles were then agitated for one minute and placed in a water bath heated to 150°F. The jars were removed for observation at intervals of 1, 5, and 30 minutes. The results are shown in [Fig. 5](#). For each ratio, any interface was resolved in five minutes and only minor amounts of crude remained, i.e., non-coalesced. After 30 minutes, nearly all the crude coalesced from the brine phase into the crude and a sharp interface was evident; thus proving the functionality as a non-emulsifier.

For the last assessment, the NE2 was added at a concentration of 0.75% v/v to the following brines: 3% KCl, 10.0 lb/gal NaCl, and 11.0 lb/gal CaCl₂. Again, these brines and the blended crude were added to test jars at a ratio of 50/50, percent by volume. In this phase, the NE2 was assessed for its ability to resolve an interface in the CaCl₂ brine as compared to the less dense KCl and NaCl, whereby the CaCl₂ approximated 32% w/w and the NaCl 26.5 % w/w.

The test bottles were then agitated for one minute and placed in a water bath heated to 150°F. The jars were removed for observation at intervals of 1, 5, 15, and 30 minutes. The results are shown in [Fig. 6](#). For the CaCl₂ brine, the interface was resolved relatively rapidly, approximately one minute. Nearly complete coalescence was apparent after 15 minutes where minor amounts of crude remained e.g., non-coalesced. After 30 minutes, nearly all the crude coalesced from the CaCl₂ into the crude leaving a sharp interface. When compared to the other two brines at 30 minutes, interface is evident in both. This result supports, in part, the flexibility of blending this RCI surfactant for specific functionality, high-density brine use.

Dispersants and Modifiers for Suspensions

Liquid suspensions, as used in our industry, are produced to convey concentrated viscosifiers, fluid-loss-control additives, crosslinkers, friction reducers, etc., to name just a few. These systems and their additives are utilized in nearly every phase of the oilfield industry. The ability to concentrate functional additives or products, and combinations thereof, yields less containers, packaging, and transport. A suspension is typically blended to mitigate separation and gelation whereby the functional additives remain inert during blending, transportation, as well as under relatively broad static conditions or environments. A quality suspension will retain these parameters such that they promote ease of use at the wellsite. For example, a suspension that remains homogeneous will flow or pour out of its container leaving no residuals. To further, once the suspension is commingled or pumped with the

desired fluid, the suspended additives/products react or yield quickly, to enhance water-wetting, friction reduction, or viscosity such that the operation continues without delay or equipment problems.

Additives typically incorporated into aqueous-based suspensions enable and promote these desired parameters, indirectly or directly, and are referred to as viscosity modifiers or dispersants. Such additives, can be derived from ethoxylated alcohols, alkylphenol ethoxylates, styrenes, bentonite-type clays, acrylic polymers, or linear polymers, to name a few. The RCI values for a majority of the aforementioned are either relatively low or zero if the product is sourced entirely from non-RCI chemistries.

However, bio-based surfactants, as utilized to enhance viscosity, dispersibility, and/or wettability, carries a bio-based composition greater than 90%. Even as the typical use concentration for these type of additives is often less than 2% w/w, they are readily biodegradable, exhibit water/brine solubility that is near complete, and compatibility with alcohol-type surfactants.

As an example of assessing dispersibility and suspension, two aqueous-based crosslinked suspensions used for fracturing were compared against two base fluids – one using 2% w/w KCl and the other 32% w/w KHCO₂. One set used a common non-RCI type with the other set an RCI type, DS1 ([Table 1](#)), both non-ionic and both at a concentration of 1% w/w ([Table 5](#)). Viscosity was measured at three shear rates at temperatures ranging from 22 to 27°C, initially after mixing and after static aging for 16 hours. The results shows comparable viscosity at all shear rates after mixing and elevated viscosity, especially at the low shear rates, 0.0636 sec⁻¹, after static aging. In this simulation, the use of DS1 improved the low shear rate approximately 3x in the 2% KCl base and 1.5x in the 32% KHCO₂ base fluid. Once again proving the performance of the RCI-type bio-surfactant against a comparable surfactant with a higher RCI value.

Summary and Conclusions

These results strongly suggest that this new generation of bio-based fluid additives can simultaneously deliver performance and reduced non-renewable carbon footprint for the oilfield. The first benefit to utilizing products with higher RCI is that an accepted tool is awaiting the oilfield and its stakeholders to report annual improvements in the carbon budget of its supply chain. With respect to the test methods and materials and fluids utilized, the following conclusions are proposed for this generation of RCI additives:

- RCI clay stabilizers are soluble in monovalent and divalent brines and exhibit performance equivalent to 7% w/w KCl at a concentration of 2% v/v.
- RCI iron control agents demonstrated solubility in synthetic brines up to 250,000 TDS and over a pH range from 3.7 to 7.5. At concentrations up to 2 gal/1000 gal, these agents complex more ferric iron than 5% v/v sodium citrate or EDTA.

- RCI-type non-emulsifiers can be custom formulated for use in relatively high-density brines, CaCl_2 , as well as less saturated brines such as KCl and NaCl. These emulsifiers exhibited the ability to resolve a potential interface as well as promote coalescence of an 80/20 sweet/bitumen crude blend from the brine phase into this crude.
- An RCI-type surfactant enhanced viscosity of aqueous crosslinker suspensions at three shear rates, especially the 0.0636 sec^{-1} shear rate, after static aging. In this simulation, the shear rate values increased 3x in a 2% KCl base and 1.5x in a 32% KHCO_2 base versus a non RCI surfactant.
- RCI-type surfactant performance is comparable to non-RCI as a dispersant/viscosity modifier in concentrated liquid suspensions.
- The use of RCI-type additives, especially when manufactured to yield higher RCI values, not only reduces ancient carbon, but also replenishes the modern carbon pool, and creates additives that are inherently biodegradable.

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Nomenclature

<i>CAGR</i>	= Compound Annual Growth Rate
<i>EIA</i>	= Energy Information Administration
<i>ESG</i>	= Environmental, Social, and Governance
<i>gpt</i>	= gallon per thousand
<i>TDS</i>	= Total Dissolved Solids
<i>v/v</i>	= percent by volume
<i>w/w</i>	= percent by weight

References

- ASTM D6866-21: Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis. 2021. (January 15, 2021). Available from www.Techstreet.com
- Conte, N. 2021. "What's Made from a Barrel of Oil." Online publication by Visual Capitalist, September 14, 2021. <https://www.visualcapitalist.com/whats-made-barrel-of-oil/>
- Dill, W. and Smolarchuk, P. 1988. "Iron Control in Fracturing and Acidizing Operations." *Journal of Canadian Petroleum Technology*, vol. 27, no. 3 (May-June 1988). PETSOC-88-03-08. <https://doi.org/10.2118/88-03-08>
- EIA. 2021. "Oil and Petroleum Products Explained – Refining Crude Oil." (July 26, 2021). <https://www.eia.gov/energyexplained/oil-and-petroleum-products/refining-crude-oil.php>
- Foxenberg, W.E., Ali, S.A., Ke, M., Shelby, D.C., and Burman, J.W. 1998. "Eliminate Formation Damage Caused by High-Density Completion-Fluid/Crude-Oil Emulsion." SPE International Symposium and Exhibition on Formation Damage, Lafayette, Louisiana, February 18-19, 1998. SPE-39444-MS. www.doi.org/10.2118/39444-MS
- Global Market Insights Inc., 2021. "Global Oilfield Surfactants Market Anticipated to Exceed \$1.3 Billion by 2027, says Global Market Insights Inc., (Jan. 21, 2021). Report ID: GMI4583. <https://www.prnewswire.com/news-releases/oilfield-surfactants-market-anticipated-to-exceed-1-3-billion-by-2027--says-global-market-insights-inc-301211597.html>
- Gomez, S., Ke, M., and Patel, A. 2015. "Selection and Application of Organic Clay Inhibitors for Completion Fluids." SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, April 13-15, 2015. SPE-173731-MS. <https://doi.org/10.2118/173731-MS>
- Gomez, S., and Patel, A. 2013. "Shale Inhibition: What Works?" SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, April 8-10, 2013. SPE-164108-MS. <https://doi.org/10.2118/164108-MS>
- Integrity Biochem 2021. "Measuring Sustainability." Online Sustainability webpage by Integrity Biochem, 2021. <https://www.integritybiochem.com/sustainability>
- Luyster, M.R., Hebert, P., Ali, S.A., Kippie, D.P., and Carboni, J.A. 2002. "Asphaltic Crudes and High Density Brines: A Potentially Lethal Combination" SPE International Symposium and Exhibition on Formation Damage, Lafayette, Louisiana, February 20-21, 2002. SPE-73732-MS. <https://doi.org/10.2118/73732-MS>
- OECD. 1992. "Test No. 301: Ready Biodegradability." in: *OECD Guidelines for the Testing of Chemicals, Section 3*, OECD Publishing, Paris. <https://doi.org/10.1787/9789264070349-en>
- Preston, M., Deville, J., Miller, J., and Burrows, K. 2020. "Environmentally Acceptable Shale Inhibitors for High Performance Water-Base Muds" International Petroleum Technology Conference, Dhahran, Saudi Arabia, January 13-15, 2020. IPTC-19902-MS. <https://doi.org/10.2523/IPTC-19902-MS>
- Reddy, C.M., Demello, J.A., Carmichael, C.A., Peacock, E.E., Xu, L., and Arey, S. 2008. "Determination of Biodiesel Blending Percentages Using Natural Abundance Radiocarbon Analysis: Testing the Accuracy of Retail Biodiesel Blends." *Environmental Science & Technology*, vol. 42, no. 7 (February 27, 2008) 2476-2482. <https://doi.org/10.1021/es071814j>
- Shenoy, S., Gilmore, T., Twynam, A. J., Patel, A., Mason, S., Kubala, G., Vidick, B., and M. Parlar. "Guidelines for Shale Inhibition during Openhole Gravel Packing with Water-Based Fluids." *SPE Drilling & Completions*, vol. 23, no. 2 (June 2008) 80-87. <https://doi.org/10.2118/103156-PA>

Table 1 – Approximate RCI Values		
Product Reference	Function	Renewable Carbon Index (RCI)
CS1	Clay stabilizer/inhibitor	73.8 %
CS2		7.1 %
IC1	Iron control	100.0 %
IC2		100.0 %
IC3		100.0 %
NE1	Non-emulsifier	47.0 %
NE2		Indeterminate
DS1	Dispersant	89.8 %

Table 2 – Selected Toxicity of Common Additives for Reactive Clay Minerals					
Type	Example	Concentration	Test	Result	Score
Inorganic Chlorides (salts)	Sodium Chloride	20%	LC 50	175,000 – 250,000	Pass
	Potassium Chloride	2%	LC 50	170,000 – 180,000	Pass
Quaternary Ammonium Salt	Choline Chloride	7 lb/bbl	LC 50	>500,000 ppm SPP	Pass
			Microtox® ¹	90%	Pass
	Tetra Methyl Ammonium Chloride	7 lb/bbl	LC 50	< 10,000	Fail
		2%	Microtox	<10%	Fail
Oligocationic Amine	Amphoteric	7 lb/bbl	LC 50	>500,000 ppm SPP	Pass
		6%	Microtox	92%	Pass
Polycationic Amine	PHPA	7 lb/bbl	LC 50	>500,000 ppm SPP	Pass
		3%	Microtox	32%	Fail
Triethanolamine Methy Chloride		7 lb/bbl	LC 50	>500,000 ppm SPP	Pass
		2%	Microtox	31%	Fail

Table 3 – Comparison of Clay Inhibition Effectiveness Using Capillary Suction Test								
Concentration (% v/v)	Capillary Suction Test Results (sec)							
	CS1	CS2	2% w/w KCl	7% v/v KCl	3% v/v KCl	2% v/v KCl	20% v/v Choline Chloride	35% v/v Choline Chloride
100	-	-	-	12.4	17.2	37.5	-	-
2.00	44.3	10.9	41.6	-	-	-	40.0	16.9
1.00	-	26.2	106.7	-	-	-	295.1	41.4
0.75	-	38.9	140.5	-	-	-	619.2	128.5
0.50	-	123.1	-	-	-	-	-	408.9
Control, Tap Water: 835 seconds								

¹ MICROTOX is a registered trademark of Microbics Corporation.

Table 4 – Selected Properties of Synthetic Brines

Synthetic Brine	Density (lb/gal)	pH	Total Dissolved Solids (mg/L)	Total Multivalent Cations (mg/L)	Cations
A	9.81	3.7 - 4.1	250,000	17,000	Ca ²⁺ , Mg ²⁺ , Sr ²⁺ , Ba ²⁺ , Fe ^{2+,3+} , B ³⁺
B	9.52	4.0 - 4.5	200,000	17,000	Ca ²⁺ , Mg ²⁺ , Sr ²⁺ , Ba ²⁺ , Fe ^{2+,3+} , B ³⁺
C	8.94	4.3 - 5.3	100,000	10,000	Ca ²⁺ , Mg ²⁺ , Sr ²⁺ , Ba ²⁺ , Fe ^{2+,3+} , B ³⁺
D	8.94	4.7 - 5.7	100,000	5,000	Ca ²⁺ , Mg ²⁺ , Sr ²⁺ , Ba ²⁺ , Fe ^{2+,3+} , B ³⁺
E	8.45	4.9 - 6.0	14,000	<50	Ca ²⁺ , Mg ²⁺ , Fe ^{2+,3+}
F	8.42	6.5 – 7.5	10,000	<10	Ca ²⁺ , Mg ²⁺ , Fe ^{2+,3+}
G	8.85	6.1 – 7.3	84,000	1,800	Ca ²⁺ , Mg ²⁺ , Fe ^{2+,3+}
L	9.90	5.4 – 5.8	203,000	88,500 –88,900	Ca ²⁺ , Mg ²⁺ , Sr ²⁺ , Ba ²⁺ , Fe ^{2+,3+} , Mn ²⁺

Table 5 – Aqueous-Based Crosslinker Suspensions

Suspension Names:	Base - 2% w/w KCl		Base 32% w/w KHCO ₂	
	Non-ionic Non-RCI	Non-ionic DS1	Non-ionic Non-RCI	Non-ionic DS1
Initial Measurements				
0.3-rpm (0.0636 sec⁻¹)*	53,789	59,500	63,986	45,800
20-rpm (4.24 sec⁻¹)*	1,848	1,830	1812	2,190
300-rpm (511 sec⁻¹) Dial Reading	120	91	228	176
Temperature °C	22.4	26.7	24.4	26.7
Static Aged Measurements and Observations				
0.3-rpm (0.0636 sec⁻¹)*	17,390	49,600	20,796	32,300
20-rpm (4.24 sec⁻¹)*	1848	2,322	2,620	2,292
300-rpm (511 sec⁻¹) Dial Reading	122	101	169	196
Temperature, °C	24.4	24.4	25.5	24.4
Visual Observations	No separation or gelation. Fluid pourable	No separation or gelation. Fluid pourable	No separation or gelation. Fluid pourable	No separation or gelation. Fluid pourable

* 0.3- and 20-rpm readings using a Brookfield rheometer with a No. 2 LV and a No.3 LV, respectively.

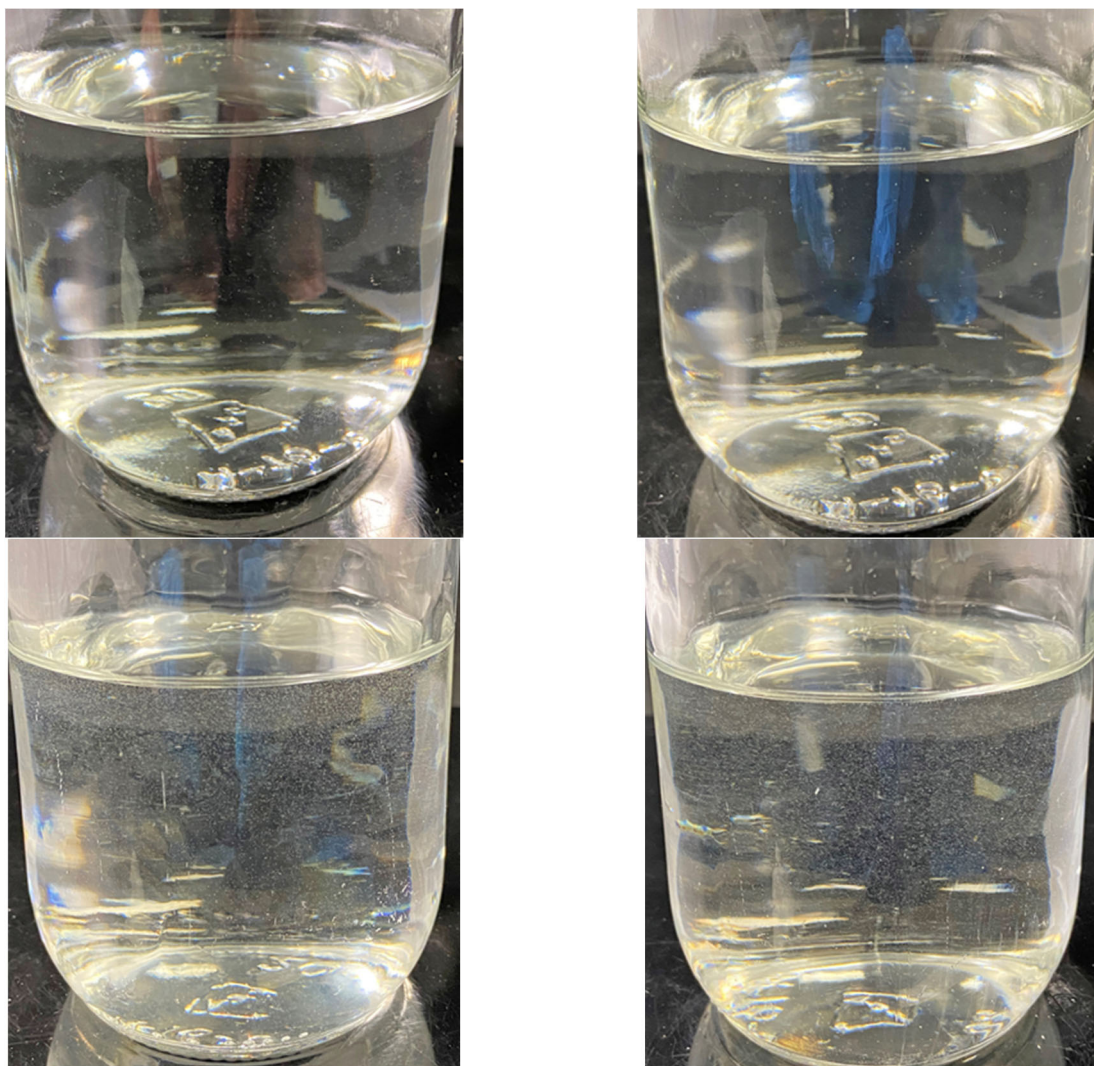


Figure 1 – Images on top, left to right, show 10.0 lb/gal NaCl without CS1 and with 1% v/v CS1. The NTU increased from 0.7 to 0.8. Images on bottom, left to right, show an 11.0 lb/gal CaCl₂ without CS1 and with 1% v/v CS1. The NTU increased from 2.3 to 2.7.

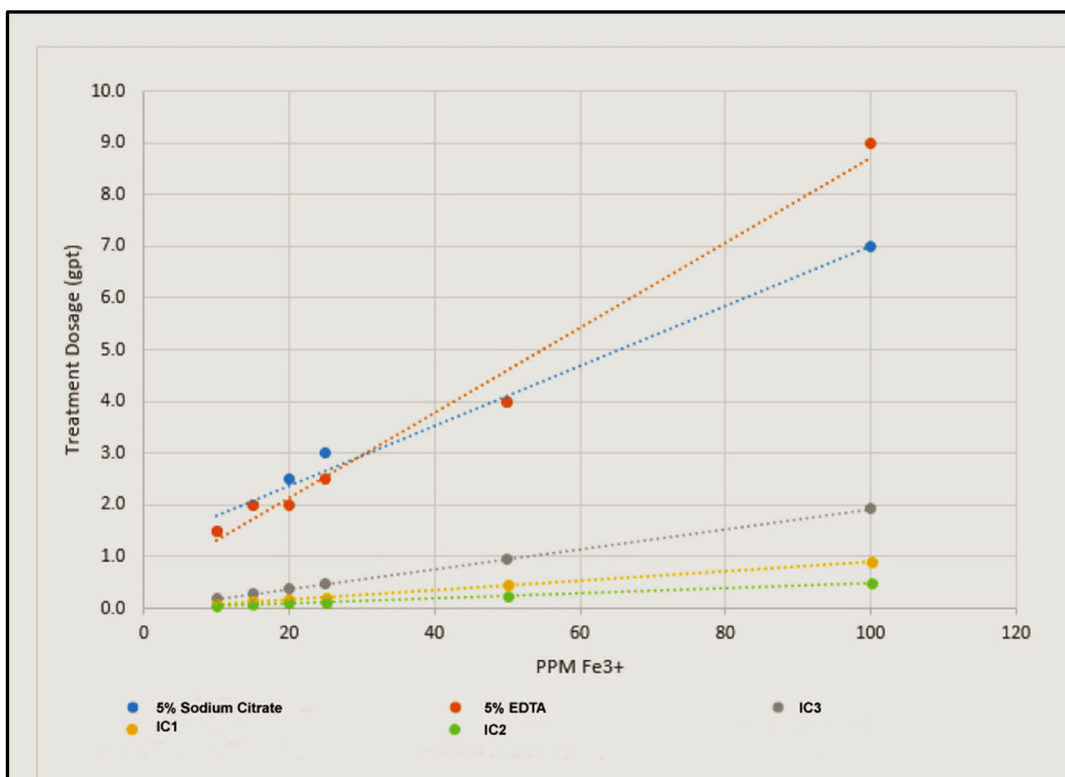


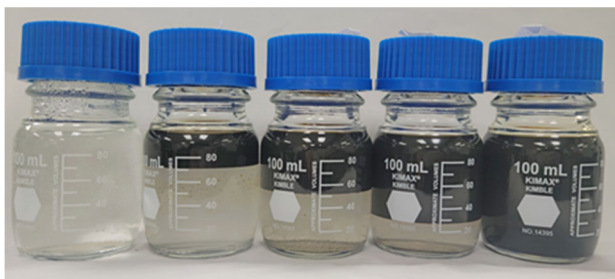
Figure 2 – Iron control efficacy of three RCI additives, IC1, IC2, and IC3 as compared to 5% sodium citrate and 5% EDTA over a range of 10 to 100 ppm Fe³⁺. Less than 1 gal/1000 gal of all three RCI additives will complex 50 ppm of Fe³⁺ versus 4 to 4.5 gal/1000 gal of sodium citrate or EDTA. Less than 2 gal/1000 gal of all three RCI additives will complex 100 ppm of Fe³⁺ versus 7 to 9 gal/1000 gal sodium citrate or EDTA, respectively.



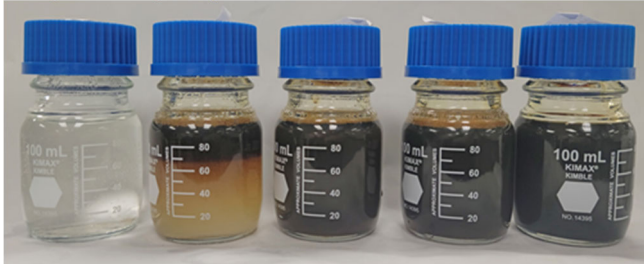
Figure 3 – Digital image showing synthetic brines as described in Table 3, left to right, Brine A, B, C, D, E, F, G, and L, after addition of IC1 at a concentration of 1 gal/1000 gal brine.



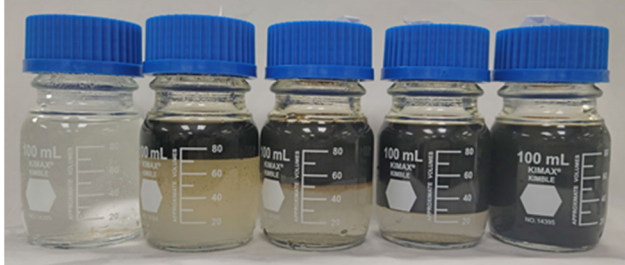
Figure 4 – Digital images showing 2% w/w KCl, 26% w/w NaCl, and 32% w/w CaCl_2 after the addition of 0.75% v/v NE1 (top). As NE1 is formulated for less dense brines, complete solubility is evident in the two monovalent brines on the left while incomplete solubility is evident upon addition to the CaCl_2 (thin white layer - jar on right). NE2 (bottom) which is formulated for higher density brines, is shown in the same three brines however more complete solubility is evident in the 32% CaCl_2 .



Digital image showing test jars, 3% KCl with NE1, at ambient before agitating



Digital image showing test jars, 3% KCl with NE1, immediately after agitating



Digital image showing test jars, 3% KCl with NE1, after 1 minute of static aging at 150°F



Digital image showing test jars, 3% KCl with NE1, after 5 minutes of static aging at 150°F

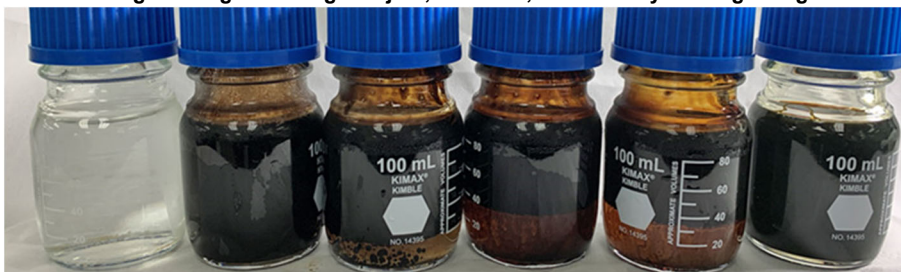


Digital image showing test jars, 3% KCl with NE1, after 30 minutes of static aging at 150°F

Figure 5 – Digital images left to right: 3% w/w KCl control, 75% KCl/25% crude, 50% KCl/50% crude, 25% KCl/75% crude, and 100% crude. Images from top to bottom show a time lapse from initial to 30 minutes whereby jars were removed from a water bath with temperature at 150°F. NE1 was added at 0.75% v/v to the 3% KCl.



Digital image showing test jars, with NE2, immediately after agitating



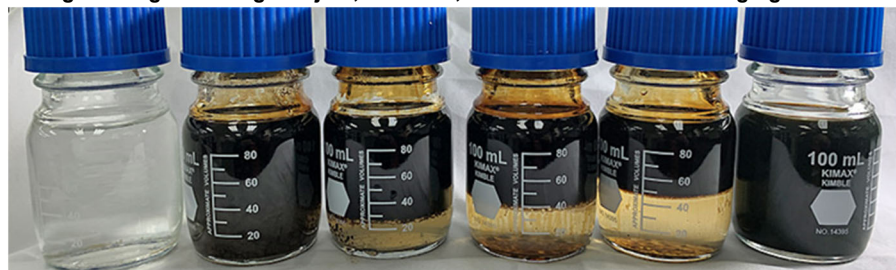
Digital image showing test jars, with NE2, after 1 minute of static aging at 150°F



Digital image showing test jars, with NE2 after 5 minutes of static aging at 150°F



Digital image showing test jars, with NE2, after 15 minutes of static aging at 150°F



Digital image showing test jars, with NE2, after 30 minutes of static aging at 150°F

Figure 6 – Digital images left to right: Control (100% untreated tap water), 50% tap water/50% crude, 50% 3%KCl/50% crude, 50% 26%NaCl/50% crude, 50% 32%CaCl₂/50% crude, and 100% crude. Images from top to bottom show a time lapse from after agitation to 1 minute, 5 minutes, 15 minutes, and 30 minutes whereby jars were removed from a water bath with temperature 150°F. NE2 was added to each brine at 0.75% v/v. NE2 exhibits a clean break of the crude from the 32% CaCl₂.