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Oilfield Corrosion & Corrosion Inhibitors

The "real" cause and effect!

EXECUTIVE SUMMARY

Oilfield corrosion is a reality. It damages tubulars and vessels. And it is so taken for granted in today's oilfield operations that we almost naturally turn to the oilfield chemical companies to mitigate it through the application of oilfield chemical corrosion inhibitors.

Is this the right approach? Are chemicals the best approach? Are there any significant side effects of applying chemical corrosion inhibitors? If so, what are they and what are their affects? And finally, what are our options?

In many oilfield operations these and other corrosion related questions go unasked. Let's face it, few oilfield operators, engineers, supervisors, or managers are knowledgeable about corrosion, corrosion inhibitors, or oilfield chemistry. So, it's just easier just to put it all in the hands of the local oilfield chemical company and let them deal with it.

This paper explains the reasoning supporting the minimization of corrosion inhibitors in order to reduce the offsetting and growing volumes of 1) off-spec crude created by the emulsions resulting from the addition of chemical corrosion inhibitors, and 2) inverse emulsions, oil wetted solids, and oil, and grease concentrations, in produced water which accumulate in the bottoms of water storage tanks and carry over to become plugging agents in injection and disposal wells.

This paper explains how oilfield corrosion inhibitors often negatively affect oil quality, create emulsions, deter water quality, and add dramatically to injection/disposal well plugging, and more importantly, what to do about it!

OILFIELD CORROSION – MACRO VIEW

Corrosion is common in oilfield operations. It is generally galvanic or bacteria in nature. In galvanic corrosion a chemical reaction between steel and the produced water causes the loss of steel, often is small cells. In bacterial corrosion the bacteria generate highly corrosive by-products by virtue of their metabolism which then react with steel to cause metal loss, or corrosion.

Both of these are often dealt with chemically. The chemicals used are normally quite effective at slowing or stopping the corrosion. So, when viewed on this basis, the chemical control of *corrosion is generally successful. This is the macro view … focused only on the corrosion cause and effect.*

OILFIELD CORROSION – MICRO VIEW

The micro view of chemical corrosion control through the use of oilfield chemicals is quite different. It looks beyond the obvious and focuses on the overall effects of these chemicals. Since this view is not widely known, it is the unique purpose of this paper to help the reader gain a broader appreciation of the overall affects of these treating chemicals in the typical day-to-day operation of an oil property.

In the typical lease operation, the producing wells may experience tubing leaks or rod parts attributed to corrosion. These often lead to the conclusion that a down-hole corrosion inhibitor is justified. There are three traditional ways to accomplish this:

1. *BATCH TREATMENT: A chemical treating truck (aka "Shot Truck") can pump a few quarts of a corrosion inhibitor down the annulus of the producing well followed by a few barrels of "flush water" to help carry the corrosion inhibitor to the bottom of the well. The more fluid there is over the pump, the more the volume of flush water. This is a periodic "one-shot" treatment. The normal treatment rate is one-half to one quart for each 100 barrels of water produced daily times the number of days between treatments.*
2. *CONTINUOUS INJECTION: A chemical feed pump can be installed at the wellhead. A small by-pass line can be installed between the flow line and the casing to circulate produced fluids back downhole. The chemical pump will continuously inject the desired quantity of corrosion inhibitor into the by-pass stream which will carry the corrosion inhibitor downhole. The normal injection rate is one-half to one quart of corrosion inhibitor per 100 barrels of water produced daily.*
3. *BATCH AND CIRCULATE: This is similar to the "batch treatment" described above, except that once the dosage is reduced by 50% and is pumped down the annulus. In addition to this reduced treating volume the entire flow of the well is also by-passed from the flow line to the casing. Ideally, the recirculation of all produced fluids continues for the equivalent of three displacement volumes of the tubing string, after which the production is turned back into the flow line. This is by far the efficient method where the concentrated corrosion inhibitor has three opportunities to adsorb onto the surfaces of the rods and tubing. Extensive field tests have shown that the first circulation results in about 50% of the inhibitor being adsorbed; the second circulation about 30%; and the third about 25% leaving the rods and tubing 95+% protected for longer periods of time than in the first method described above.*

Let's discuss what happens in each case.

BATCH TREATING: When a corrosion inhibitor is batch treated down a well bore its instantaneous concentration is very high. While it may average 1 qt./100 bbls., if the treatment occurs once a week the instantaneous dosage is seven times the average. If the treatment is twice *a month, the instantaneous concentration is fourteen times the average. Treatment dosage rates of one quart per 100 barrels is roughly 60 parts per million by volume (ppmv). Weekly treatments increase this to 420 ppmv. By-weekly treatments increase this to 840 ppmv. These high instantaneous concentrations of the treating chemical have offsetting effects. In fact, the difference between average and actual dosage concentration is often quite deleterious to both oil and water quality.*

CONTINUOUS INJECTION: When a corrosion inhibitor is continuously injected down the annulus of a well, the instantaneous concentration may be quite small (i.e.: 60 ppmv). However, depending on the volume of fluid over the downhome pump (FOP), which is always oil, the inhibitor may be either concentrated or diluted by the FOP. It may be completely absorbed and concentrated in the oil layer in the FOP column because of its relative solubility in oil. Or, when the fluid level in the annulus is right at the pump intake, the inhibitor will be pumped up the tubing string in nearly the same concentration as it was when it was pumped into the annulus at the surface. At the 60 ppmv concentration level there is so little interaction between the steel surfaces and the chemical inhibitor mixture that only minimal surfactant cleaning can occur, and only minimal adsorption of the inhibitor concentrate can or does take place. This is, however, typically adequate to replace previously applied inhibitors that have been worn off by rod-to-tubing contact, or by fluid flow erosion. So, to be effective with continuous injection, the entire tubing string and flow line must first be treated with a high concentration dose of the corrosion inhibitor. This is usually accomplished by periodically batching a very high concentration down the annulus to assure the rods, tubing, and flow line are completely coated with corrosion inhibitor. It must also occur whenever the well is being pulled, so all tubing and rods are run back into the well through a layer of concentrated corrosion inhibitor.

Yet again, these high instantaneous concentrations of the treating chemical have offsetting effects. In fact, the difference between average daily and actual batch treating dosage concentrations is always quite deleterious to both oil and water quality.

BATCH TREATING: In all batch treating applications the concentrations of the inhibitor package are much higher than the 60 ppmv. In fact, the instantaneous concentrations at any interval can approach 100% (1,000,000 ppmv)! So again, the difference between average daily and actual batch treating dosage concentrations has a hugely negative effect on both oil and water quality.

In order to learn why this happens to oil and water quality during these applications it helps to understand the chemistry of corrosion chemicals.

THE CHEMISTRY OF CORROSION INIBITORS

Corrosion inhibitors are a blend of semi-soluble or insoluble high molecular weight long-chain organic compounds. The most common are derivatives of refinery amine reactor bottoms. These residue products are thick and heavy, so they are first mixed with a staged blend of mutual solvents. In the final stage the thick mix is diluted sufficiently to render them suitable to be dispersed into a carrier liquid, often an inexpensive high aromatic solvent, so they are suitable for use in oilfield *operations. An anionic surface-active agent (aka: surfactant, or "soap") is added to the final blend so that when the corrosion inhibitor final blend is applied the surfactant cleans the surface of the steel. This "cleaning" is critical to the effectiveness of the inhibitor, allowing the actual corrosion inhibitor concentrate to attach the surface of the cleaned steel. As corrosion cells are cleaned by the surfactant, the anionic inhibitor fraction of the mix can then adsorb onto the highly cationic surface of the steel, isolating the steel from the passing water as if it were painted. This is why the Navy paints the hulls of its ships. When contact between the steel surface and the water ceases, so does all galvanic corrosion.*

Clearly, the surfactant plays a big role in the effectiveness of any corrosion inhibitor. It is necessary, and performs a very useful purpose … at least from a corrosion mitigation perspective. This is the micro view mentioned above.

However, when we take a broader (macro) view of the water and oil chemistry as they are affected by corrosion treatment, we may begin to see that solving the corrosion problem can create an even more serious and more costly set of problems. So, let's focus on that macro view.

CAUSE AND EFFECT

The role of the surfactants used in blended corrosion inhibitors is to clean the steel surfaces of corrosion cells. To do this the surfactant concentration must be sufficient to emulsify any oil or break up any layer of wax, scale, bacteria, sand, or silt attached or adjacent to the steel surface. The surfactants chosen are extremely effective at doing this; thus, the success of the applied corrosion inhibitor in the first place. However, when the surfactant interacts with the fluid stream to emulsify the oil and solids in the mix, this emulsion of oil and suspended solids of various types has a very negative affect on both overall oil and water quality.

As the surfactant breaks up oil droplets and disperses suspended solids, they all become such small droplets or particles that they no longer readily separate from the produced fluid. They become what we identify as "basic sediment and water", or BS&W.

Downstream of the well we typically separate oil, water, and sediment in vessels and tanks. While these can be very effective, when we create these stable emulsions, separation often suffers, and with it, operating efficiency. In the oil phase, emulsions are usually small droplets of water nucleated around a very small solids particle, and surrounded by a layer of oily residue. Because the oily residue is a mixture consisting of produced oil it tends to stay suspended in the crude oil phase. However, the mixture also contains the water wetting surfactant from the corrosion inhibitor, so the inner layer of the oily film surrounding the water droplet stays soluble or dispersed in the water droplet. When these droplets are smaller than 30 microns, they cease to separate, and stay suspended in the oil phase and take much longer to separate; often longer than the typical treating/storage facility has available. When they are smaller than 1 micron, they NEVER separate. As this concentration of BS&W increases, oil buyers penalize oil producers by lowering the price they pay for the crude oil. This decline in oil quality is the most direct cause and effect, but it is not the only cause and effect at play! Over the course of a year this may cost the producer

1-5% of their oil revenue. In a 30 barrel of oil per day well where oil is valued at $40/barrel, this translates to between $4,380 and $21,900 each year, averaging $13,140 annually.

In addition, the oil emulsified in the produced water is also lost! Experience has shown that this typically amounts to a 1-2% loss of oil, costing the 30BOPD oil producer an additional $4,380 to $8,760, averaging $6,570 each year.

Just as Joy dishwater soap emulsifies all oil and grease when we wash dishes at home, the surfactants used in oilfield chemicals emulsify oil and suspended solids in the produced water. Water that may have appeared crystal clear before a corrosion treatment may look like chocolate milk after the treatment. The "chocolate milk" color is mostly emulsified crude oil in very small droplets. And, every droplet of that oil suspended in the produced water stream is one more drop of oil that will not be sold to the oil buyer. Instead, it will be swept through the production treating and storage facilities, and will eventually be injected into a deep-water injection or disposal well where it will adsorb onto the surface of the formation rock and fill the tiny pore spaces between them until the well no longer take the water at an acceptable rete.

At this point, the injection/disposal well must be cleaned out. This may be necessary annually! It is a complex and costly exercise, rarely costing less than $150,000, and often exceeding $300,000 per cleanout, and averaging over $225,000 annually.

So, when we combine the costs of applying a corrosion control chemical to a producing well, the overall effect may be to mitigate one rod part, or one tubing leak, but it may also result in a BS&W, lost oil, and a disposal well cleanout cost which can easily exceed $240,000, not counting the cost of the chemical corrosion inhibitor!

Clearly, we should all take a hard look at the cause-and-effect relationship of applying corrosion inhibitors before we simply assume that doing so is the right approach.

CONCLUSIONS

It can be truthfully said that the oil industry is plagued by a myriad of paradigms. The most prevalent is the answer to the question "Why?" … "Because we've always done it that way!"

Let's face it. We've always accepted the near-automatic cause-and-effect relationship between downhole corrosion and our decision to apply a chemical corrosion inhibitor wherever we see corrosion. While we may still choose to take that approach, we might ask ourselves, "Are we doing this because we've always done it this way?", or "Should we look at the problem of corrosion in light of the broader picture with cause and the effect in mind?".

Clearly, when corrosion costs us too much we should treat for it and suffer the consequences. But, when it doesn't, we should learn to suffer with the occasional rod part or tubing leak, and resist the temptation to fall into another old paradigm.

ABOUT THE AUTHOR

Bill Ball is the founder and owner of Breakthrough Engenuity LLC. He enjoys a distinguished career as an inventor, holding 20 US patents in the field of oilfield separation equipment. Bill is a life-member of the National Association of Corrosion Engineers, and of the Society of Petroleum Engineers. His hands-on oilfield experience and career portfolio make him one a valuable industry resource.

After his university studies Bill launched his career in a 1,000,000 b/d oilfield waterflood operation where he was responsible for the evaluation and performance improvement of all surface facilities and the effective application of all oilfield chemicals. He was recruited into the field of oilfield chemistry and was instrumental in building what became one of the largest oilfield chemical companies, Baker Hughes. He sent many of his days crawling through process equipment, gaining knowledge, experimenting with equipment designs, chemicals, application methods, and making improvements. His hands-on experience has advanced the technologies necessary to improve process equipment efficiencies across the board.

In the early years Bill learned what works, and what doesn't! In the decades since he has given back to the industry by developing and perfecting systems reflected in his 21 patents and hundreds of facility designs. The result is a unique approach; one at Breakthrough Engenuity LLC, "Where Engineering meets Ingenuity!"

Bill's efforts continue to innovate improvements like the patented combination free water knockout-heater treater in one vessel called KOTREAT®. Through the use of highly efficient internals, KOTREAT® has become is a game changer. Another example of Bill's ingenious innovation is the MorOil™ system. MorOil™ is a patented system designed to condense the valuable C4+ hydrocarbon liquids from hot produced natural gas streams and generate a new stream of cash flow in the form of NGLs where every 10°F temperature drop captures another 50% of the C5+ natural gas as liquid fractions!

And yet another innovation is the L-POD® System. This patented system marries 21^{st} *century AI with the IoT to produce a fully automated, self-managed crude oil dehydration system. Using the most advanced components and artificial intelligence available, the L-POD® automatically reduces the BS&W concentration of off-spec crude oils to below the 0.1% level (that's 99.9% oil purity!), eliminating all rejects!*

These are just a few of Breakthrough Engenuity's unique contributions.

Today, Breakthrough Engenuity is one of the industry's leading low-cost engineering and design firms. We specialize developing designs for the industry's most efficient high and low pressure, two and three-phase heated and unheated separators, and we provide cost-effective general engineering services for most other oilfield process needs.

Now, more than ever, Breakthrough Engenuity can be found in every sector of the oil and gas industry, adding cash flow to operators and efficiency to their operations. We're a full-service engineering firm. We pledge to meet and exceed every client's expectations.

CONTACT US

*Call Bill Ball at **Breakthrough Engenuity** (Where Engineering meets Ingenuity) for assistance. You can reach Bill on his cell phone at 918-231-9698 seven days a week.*