MATCHING CORROSION NEEDS OF ROD-PUMPED OIL WELL SYSTEMS WITH SPECIAL PROPERTIES OF CORROSION INHIBITORS

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INTRODUCTION

Recent estimates indicate that oil producers will spend about $750 million in 1977 to replace tubing rods, pumps, etc. because of corrosion. While down time caused by the need to replace corroded equipment will not necessarily result in permanent loss of production, it certainly does result in lack of ability to produce oil *now* when we need it. To compound the problem, we will also import more than 40 percent of our petroleum needs in 1977. Thus, in addition to the out-of-pocket costs of replacements, oil producers also suffer from reduced income when wells are not producing.

An obvious remedy is to prevent the corrosion. Not so obvious is how. Using corrosion-resistant materials is one approach, but the expense of exotic metals could exceed the cost of replacing conventional corroded equipment. Proper design can reduce corrosion, and corrosion allowance can be included in the design. Neither is totally satisfactory, but each will extend the time before replacement will be required. Production practices such as slowing pumping rates to reduce rod stress and complete exclusion of oxygen in annular spaces, especially wells with low fluid levels, help alleviate corrosion problems. Since the combined effects of corrosion and wear are greater than just the sum of both if each occurs alone, rubbing parts (rods and tubing) and solids entrained in fluids should be avoided. Corrosion can also be slowed by changing the corrosivity of the fluids by removing corrodents (H_2S, CO_2 or oxygen) or by altering the pH. Sometimes one or more of these can reduce corrosion to acceptable levels. Where they will not, *corrosion inhibitors* are used. For optimum effect (lowest cost) corrosion inhibitors have been developed to exhibit a wide variety of properties that enable them to prevent corrosion under a variety of production practices and equipment configurations.

Corrosion inhibitors that are used to prevent corrosion in rod-type oil wells do so by adsorbing onto metal or metallic corrosion products such as iron sulfides, carbonates, oxides, and scales. They can prevent corrosion when as little as a monolayer of inhibitor molecules are adsorbed on the surfaces that would otherwise be exposed to the water that is necessary for corrosion reactions to proceed. In essence, one end of the inhibitor molecule adsorbs and the other end sticks out from the surface to repel the water. There are several important fundamental aspects of chemistry and physics that determine both the rates of adsorbtion and the quantities adsorbed. Second, there are also several important characteristics of inhibitor mixtures that influence these functions. And third, there are several physical factors related to equipment, production practice, and variables in the corrosive environment itself that affect the adsorption and subsequent corrosion protection.

ROD PUMPED SYSTEM VARIABLES

Corrosion-environment variables are those that affect the severity of the corrosion, while the mechanical factors affect the practices and inhibitor characteristics that are required to prevent corrosion in a specific corrosive environment. Factors affecting corrosivity are pH, temperature, electrolyte concentration, electrolyte composition, concentration of corrodents, kind of corrodents (H_2S, CO_2, organic acids, oxygen), velocities, scaling or deposits, and the oil-to-water ratio. Mechanical factors are stress levels (pumping rate), consideration is that it has been possible to make better corrosion inhibitors when ingredients and ingredient ratios tend to promote oil solubility. One of the reasons for this is that higher molecular-weight organic molecules of the type that make good corrosion inhibitors tend to be oil soluble and the higher molecular-weight materials provide both thicker and more persistent films after adsorption onto metal and metallic corrosion-product surfaces. On the other hand, very often some of the properties such as high detergency are more important than film persistency, and water-soluble inhibitors generally provide the best detergency. Adsorption and film formation can occur in either oil or water solutions, but it takes time. The time required for film formation, at constant composition, is important. For example, at very high water-to-oil ratios a product in the oil phase may simply not be in contact with parts of the system long enough in passing through to form protective films.

Solids affect both corrosion rates and control practices in many ways. It has been established that the combined effect of corrosion and wear are greater than the sum of each if each occurred alone. Put another way, if a given system would lose 30 thousands metal loss from wear when no corrosion was occurring or 30 thousands loss from corrosion when no wear was occurring, the same system would lose more than 60 thousands loss during an equal time period when both the corrosion and the wear occur simultaneously. Formation solids (sand in particular) contribute to the wear, but solids from any source are troublesome. Another effect of finely divided solids is that they present a large surface area for inhibitors to adsorb onto instead of the metal surfaces they are supposed to protect. And a third effect is that accelerated, localized corrosion occurs beneath solids, and in particular, beneath sulfide deposits.

Temperature affects corrosion directly because chemical and electrochemical reaction rates rise with increasing temperature, but there are indirect effects as well. Solubilities of acidic gas (and oxygen) in the liquid phases are lowered as the temperature rises. Scaling can occur when increasing temperature drives off a portion of one of these (CO_2) from water solution. The form that corrosion products take can be affected by temperature, often in unpredictable ways. All of these affect both the rate and the form that corrosion takes in a specific producing well as well as the chemical and application requirements for control.

Small changes in the pH can exert large effects on corrosion. Hydrogen-ion concentration is related to the concentration of acidic gases in solution, which inturn is related to pressure, temperature, and the concentrations of other materials such as salts, organic acids, and inorganic acids. The lower the pH goes, the more corrosive a system becomes. Whereas, the pH of a specific system containing CO_2 may be 6-7 at atmospheric pressure, it could be as low as 3-4 under high pressure. Thus, corrosion rates can vary widely from one part of a system to another. Temperature, pressure, and concentration of acidic gases are all interrelated and affect both the properties and the concentration of corrosion inhibitors required for control.

The stress level built into rods by metallurgical treatment to obtain mechanical strength affects failure from both general and localized corrosion. Most troublesome is the sudden failure by fracture produced by stress-corrosion cracking whether caused primarily by sulfide or high stresses produced by high pumping rates, load, or both. Corrosion inhibitors can prevent this kind of failure, but most of the time they must be used at concentration levels too high to be practical (5-10 times normal).

Similarly, galvanic effects often produce rapid failures near the junction of metals different in strength, composition, or both. Some pump parts (balls and seats) are necessarily made from harder metals than other parts. Thus, pumps sometimes fail when the remainder of a specific rod-pumped well is under good corrosion control.

The presence of a casing annulus packer severely limits both the kind of inhibitor and the method of application.

Downstream facilities are often affected by corrosion programs. Notable is the emulsion treating. Oils that are easily emulsified and emulsion treating systems that are barely adequate require both special inhibitors and special treating procedures.

The fluid level in the annulus of a rod pumped oil well often dictates which inhibitor properties are necessary, how treatment must be done, and the effectiveness of the corrosion control. The amount of fluids being produced affects both the method and frequency of treatment.

PROPERTIES OF INHIBITORS

The solubility of inhibitors varies widely, and the significance and importance of solubility in applications are often misunderstood. The solubility affects the transport of inhibitors in a very significant way. That is, an oil-soluble inhibitor will be presented to the metal surface by the oil and a water soluble by the water. Sounds simple, but it is not. Inhibitors can be made from materials that are basically oil soluble, but put into water solvent. When these are placed in an oil and water system, often almost all of the inhibitor will wind up in the oil. Similarly, water-soluble inhibitor components can be placed in oil solvents and wind up in the water in the produced fluids. Finally, both water-soluble and oil-soluble components can be incorporated into a single formulation that can be placed in either oil or water solvent systems. In the latter case, both the produced oil and water could contain inhibitor. In short, the terms "oil soluble," "water soluble- "oil soluble-water dispersible," and "water soluble-oil dispersible" cannot be used to predict the actual transport except in a single-phase system (all oil or all water). The actual oil-to-water partition is just too complicated to predict accurately in two-phase systems without determining the partition in the well fluids in question. It is clear that the solubility question does have a major influence on whether a given corrosion inhibitor will be presented to all of the corroding surfaces in rod pumped oil wells.

Surfactant properties of corrosion inhibitors vary with the type of inhibitor, and extra surfactants are often added to obtain more detergency, solids-dispersing capability, or both. Water-soluble inhibitors tend to be more surface active but oil-soluble inhibitors can be formulated with added surfactant to approach the properties of the water solubles.

Most film-forming corrosion inhibitors used in rod-pumped oil wells are effective against most of the common corrodents found in rod-pumped oil wells, but some are much more effective in the presence of one corrodent (i.e. CO_2 or H_2S) than another. Some are not effective at all in the presence of oxygen, and a few are most effective in only a narrow pH range. Thus, combination systems, in addition to being more corrosive in their own right, make the selection of corrosion inhibitors more difficult. There are only a very few inhibitors that could prevent the corrosion in a system containing CO_2, H_2S, and oxygen at a pH of 4.

The "temperature" properties of corrosion inhibitors must be discussed from two view points. The first is the temperature range in which a given inhibitor will prevent corrosion. The second is how stable the inhibitor is to degradation at high temperature. Some inhibitors will prevent corrosion only up to about 150° F, others will to 250° F, and only a handful will to 350° F. There are perhaps only two that are effective to 500° F. Many inhibitors contain several ingredients that can and do form polymeric materials when the temperature exceeds some value specific for that mixture. Such polymers are often very difficult to remove.

Some inhibitor molecules have little effect on the emulsion characteristics of oil and water while others have large effect. Very small amounts of emulsion-preventing chemicals are incorporated into some inhibitor formulations to prevent the natural tendency of the inhibitor molecules to cause emulsions. Some of these inhibitors not only do not cause emulsions but instead they can assist in the actual separation of oil from water.

The question of inhibitor film persistency is very important. It is related to both the molecular weights of the inhibitors and their solubilities. Most of the inhibitors that exhibit long-term film persistency are those which have high molecular weights and those which exhibit limited solubility in either oil or water. Generally, water-soluble inhibitors have low molecular weights and exhibit short film persistency.

The density of corrosion inhibitors can determine where the bulk of the chemical goes and how long it is available within the system. Inhibitors have been formulated to weigh as much as 12 lbs/gal to fall through liquid columns.

Lubricity can play an important role in rod-pumped wells where rod wear is a problem. Some inhibitors are also excellent lubricants.

Though some properties of corrosion inhibitors are indeed mutually exclusive, some products are truly multipurpose. There is at least one product that prevents corrosion due to H_2S, CO_2, *and* materials of construction, solids, and production practices that affect the ability to place a given fluid or chemical in contact with all surfaces in the system. Among the latter is the fluid level in the annulus of a rod pumped well.

In order for an inhibitor to work in an actual system, it must often possess additional characteristics aside from its basic protective film-formation capability. For a specific system, an inhibitor may need additional ingredients to assist the actual filming ingredients to function, or it may just have to be in the right form (oil soluble, water soluble, etc.). The most important concept to understand is that, for an inhibitor to prevent corrosion, it must get to the surface it is supposed to protect and it must be able to win out over other substances that are competing with it for the metal surfaces (scale, paraffin, corrosion products, water, and dissolved substances in the water or oil).

The properties of inhibitors that influence performance in rod-pumped oil wells are solubilities, surface activity or detergency, relative effectiveness in the presence of the common corrodents (CO_2, H_2S, organic acids) or specific pH ranges, relative effectiveness at specific temperature ranges, chemical stability of the inhibitor versus temperature, effect on emulsification characteristics of the produced fluids, film persistency, density of the inhibitor formulation, and inclusion of other chemical products to prevent other problems such as scale, paraffin, etc. Some of these properties are mutually exclusive, and this by itself prevents the formulation of a universally applicable corrosion inhibitor. For example, it is easier to put together inhibitors that are effective in the presence of only one of the corrodents. It is also easier to make an inhibitor that is more effective within a narrow pH range. It is impossible to make a product that will aid in preventing emulsion and at the same time be a good detergent to remove deposits that may be aggravating the corrosion.

The first step one must take when approaching any corrosion problem is to secure a thorough analysis of the problem by asking the questions.

1. What kind of corrosion is it? Sweet? Sour? What pH range?
2. Where is the corrosion most severe? Downhole? In the pump? On the rods? In the flowline?
3. What form is it taking? General? Pits? Stress corrosion - craking of rods? Beneath deposits?
4. What are the equipment parameters that will affect either the properties the inhibitor must posses or the method of treating?
5. Is the corrosion severe enough to justify the cost of treatment?

In short, one must gather all available information on controlling variables in order to have the best chance to match the needs of the system with an inhibitor that possesses as many of the needed characteristics as possible.

Thus, to select the inhibitor most likely to perform best in a given rod pumped well, we need to do the following.

1. Survey the system itself to determine:
   A. the type and severity of the corrosion.
   B. the mechanical aspects of the system.
   C. special needs of the system such as deposit control or control of emulsions, etc.
2. Screen likely candidate inhibitors by lab tests for the following.
   A. corrosion performance in field fluids.
   B. emulsions.
   C. solubilities.
   D. compatibilities with other chemicals in use.

   It should be noted that the lab-screening step is often omitted because local field-performance data may already be available on the inhibitors to be used.

3. Evaluate the best inhibitor as determined by the fit of data from survey, lab tests, and known properties of candidate inhibitors in the field itself. The objectives are to select both inhibitor and method of application that will protect the system from corrosion at the lowest cost and provide uninterrupted production.

The oil-to-water ratio is important in the selection of corrosion inhibitors for rod pumped oil wells, but not always in the most obvious way. At first glance, it seems logical to assume that water-soluble corrosion inhibitors should be used when more water than oil is produced. The actual rule is far from being that simple. An important *oxygen*, prevents scaling, removes solids, and prevents paraffin deposition. Other inhibitors have been developed to kill bacteria, scavenge oxygen, remove deposits, and prevent scale while controlling corrosion. Finally, inhibitors are made up as concentrates for very corrosive systems or dilute to permit easier injection into systems requiring low concentrations of inhibitor for control. Some concentrated inhibitors are effective enough to require only a few ounces (cupful) per week for control of some wells. Distribution of one cupful would require dilution prior to using if concentrated inhibitor were used for these wells. Wells that produce larger quantities of fluids often require both the most effective inhibitors available and the most concentrated form of that inhibitor.

SELECTION

The objectives of the method of treatment are to get the corrosion inhibitor to all the surfaces in the system subject to corrosion at a concentration that prevents corrosion and alleviates other problems associated with production of crude oil. Thus, if the corrosion is severe, high concentrations of corrosion inhibitor may be required. High concentration could cause emulsions if the wrong inhibitor is selected. The frequency of treatment must be tailored to the film persistency characteristics of the inhibitor that may have been selected because of some other requirement. It often happens that one property of the inhibitor dictates the treating method. At other time, the mechanics of the system dictate the treating method, and this in turn selects the inhibitor.

Rod-pumped oil wells that do not pump off, that do not contain casing annulus packers, and which contain 200-400 fluid column in the annuli above the pump intakes are easiest to treat for corrosion. Almost any inhibitor that will prevent the corrosion from the corrodents and fluid system can be used, because the wides varity of treating methods can be used. The fluids in the annulus can act as a reservoir for an inhibitor so it feeds in continuously even when the inhibitor is injected only periodically. Feed can be continuously with flush, batch with circulation, batch without circulation, squeeze, or tubing displacement. Feed concentration can be high or low, depending on other considerations; the inhibitor can actually be selected on the basis of other properties such as detergency, emulsion characteristics, and combination products with other chemical functions such as scale or paraffin.

Rod-pumped wells that are kept pumped down are more difficult to treat for several reasons. First, they often pump off and pull in oxygen through leaky casing valves. Second, there is little if any reservoir for chemicals to feed into the pump intake over any extended period between treatments. The result is that inhibitor selection is limited to the very persistent inhibitors if periodic-batch treatment is used or dilute inhibitors if a continuous-injection method of treating is selected. Alternately for the latter, continuous injection followed by produced fluids flush can be used for non-persistent inhibitors feed. Often the high return of inhibitor after periodic batch dictates the use of a non-emulsifying inhibitor formulation.

The rod-pumped oil wells that are most difficult to treat are those with several hundred to several thousand feet of fluid standing in the annuli above the pump intake. Often the produced fluids volumes are high, requiring large quantities of inhibitor; it is difficult to get the inhibitor to the pump intake. It would be ridiculous to inject an oil-soluble inhibitor into the annulus without circulation to get it to the pump intake and expect any benefit at all.

Sometimes circulation is not feasible, the fluids are too corrosive for a low-persistence inhibitor, and the well cannot be squeezed because of the possibility of formation damage. In this case, very few inhibitors are available with the properties required for treating these wells. Weighted inhibitors are useful here but the weighting agents lower the amount of active inhibitor ingredients.

To treat these high fluid level problem wells, techniques have been developed in which highly concentrated inhibitors exhibiting good film persistency and other properties as required are emulsified into produced water and the well is treated with the emulsion. Part of the inhibitor is released to the oil on the way down to the pump intake for continuous feed between treatments but most falls all the way to the pump to be produced. Filming is accomplished just as well from the produced water and inhibitor emulsion as it would be from either water or oil solution.

The time required to establish protective inhibitor films is determined by several things. Among these is the nature of the inhibitor itself. Another is the concentration in solution. If an oil-soluble inhibitor in a well producing more water than oil is to be used, the concentration in the oil must be high enough to film during the shorter contact time the oil will have than the water throughout the system.

There is no cutoff water-to-oil ratio, but it is conceivable that at very high water ratios oil may almost never contact some surfaces. In this case, a water soluble inhibitor must be used.

Solids in suspension raise the inhibitor dosage requirement because they adsorb large quantities of inhibitor. Solids that are deposited require detergent properties in the corrosion inhibitor formulation. This is particularly true of sulfide- and oxygen-containing systems because corrosion will be more severe beneath the deposits in these systems.

Pitting systems require special properties. It has not been well defined, but some inhibitors are much better than others in preventing pitting. Sometimes it is the detergency property. Other times it is for unknown reason. The rule is to observe the effect of candidate inhibitors instead of attempting to predict which will reduce pitting.

To establish the best corrosion treatment for a rod pumped oil well, we list all of the well parameters that influence the corrosion, list all of the other effects the corrosion program will have on the system, list the most desirable treating method from both economic and logistic points of view, and list the properties of corrosion inhibitors most likely to perform under the combined effect of conditions and treating method desired. If the desired treating method is incompatible with one or more desired inhibitor properties, then the decision must be made which is more important. The actual selection of the inhibitor to use should be the one with most of the desired properties. If all of the above are included in the selection process, the likelihood for the most economic and trouble-free corrosion control is very good.