Corrosion Inhibitors in Subsurface Equipment

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Introduction

Successful corrosion control in producing oil wells depends upon two indispensable factors: 1. The inhibitor must be capable of controlling the corrosion, and 2. The inhibitor must be applied on a rigid schedule and in a manner which will insure that it comes into contact with all surfaces to be protected.

Corrosion In Oil Wells

The corrosion which gives us most of our trouble is that due to acid substances which are dissolved in the brine in the producing reservoir. These acids are hydrogen sulfide (sour gas), carbon dioxide (the principal destroyer of subsurface equipment), and organic acids (such as the acetic acid which is present in vinegar). Steel immersed in systems which contain acidic brines and oils will be dissolved at a rate which depends mainly upon the following factors:

1. The pH of the brine

The pH is a direct measure of the "acidity" of a solution, the lower the pH, the more potentially corrosive the system. It is dependent, among other factors, upon the concentration of acidic substances in the produced brine. Since both hydrogen sulfide and carbon dioxide are gases, wells which produce these substances will tend to be more corrosive at high pressures. This is true because gases are more soluble in the brine at high pressure. Incidentally, here is partial explanation of why some wells are more corrosive at bottom hole conditions than they are at the surface.

Some of the other materials which are dissolved in oil field brines act as "buffers." These substances will not be discussed here except to state that they permit quantities of acidic substances to be dissolved in brine without a substantial decrease in the pH. These materials are mentioned at this time simply to demonstrate another reason why two wells, both of which contain high concentrations of acidic gases, may differ widely in their corrosiveness—the one which is well "buffered" will tend to be less corrosive than the other, all other conditions remaining the same.

2. The temperature

As a very general working rule, it is often assumed that a rise in temperature of roughly 20 degrees F. will double the rate of a chemical reaction. Again, other variables the same, a high temperature well will corrode more rapidly than a cooler well. Here, too, is another factor which may cause bottom-hole equipment in a given well to corrode more rapidly than the cooler surface equipment.

3. Composition of the crude oils

Crude oils are extremely complex mixtures. Other than hydrocarbons, crude oil contains organic compounds of sulfur, oxygen, and nitrogen. These compounds possess inhibiting characteristics themselves, and dependent upon the type and quantity present, an oil will itself possess certain protective properties. Many wells which produce high concentrations of acids are not corrosive owing to the natural protective ability of the produced oil.

4. Water-oil ratio

Consider for a moment a well, the oil of which possesses a given tendency to wet the subsurface equipment. When that well is new, and is making a relatively low quantity of water, it is often true that the natural film-forming agents and oil-wetting agents in the crude will prevent corrosion from occuring, assuming the oil film to be non-corrosive. As the reservoir becomes depleted, water production generally increases substantially, and a point will be reached where the volume of water is so great that purely by virtue of its mass, that water will overpower the limited natural oil-wetting ability of the crude, and the tubing, rods, and pump will convert from inhibited oil-wet surfaces to brine-wet surfaces. At this time, the well becomes corrosive, and requires that additional inhibitor and wetting agent be added from the outside in order that protection can again be established. This phenomenon is well understood, and studies in many oil fields have progressed to the point where the operator knows in advance at what water-oil ratio his wells will start corroding.

Mechanism of Corrosion Inhibition in Oil Wells

The above discussion shows that it is the action of acids dissolved in water which brings about the greatest loss of steel equipment in oil wells. With this background, it becomes obvious that corrosion can be controlled by any process which will prevent the acid-bearing brine from coming into contact with the surfaces to be protected. The semi-polar organic corrosion inhibitors are able to perform this function to various degrees. The degree to which these molecules are able to reduce corrosion is dependent upon several factors, which are outlined below.

1. Nature of film formed by molecules

A semi-polar corrosion inhibitor has one or more polar groups within the molecule. These groups possess the ability to absorb onto a metal surface, and dependent partially upon the magnitude of this polarity is the tenacity with which the molecule sticks. The tighter the adhesion, or absorption, the longer the film—life of an inhibitor will be. This means not only better protection, but also that treatment can be made at intervals of several days, for the protective film will not come off to any appreciable extent with that length of time. Actually, the polar group is an unbalanced electric force field which permanently exists within the molecule, and this force field induces an opposite field in the surface of a metal with resultant attraction between the molecule and the surface. There are a number of ways known to the chemist to impart this polarity to organic molecules. One of the primary objects of his research is to increase the magnitude of this property.

The organic semi-polar molecules may be thought of as molecules of oil or hydrocarbons, into which the chemist places atoms of sulphur, nitrogen, oxygen, or other electronegative atoms. These confer upon the molecule at the spot in which they are located, polar properties. The geometric shape of the hydrocarbon portion of this molecule can be almost unlimited. The hydrocarbon portion of some semi-polar molecules may be in the shape of a straight rod; or, it may have one or more branches like the limbs of a tree. The chemist must be careful to place the polar groups in these structures at locations near the outside of the molecule so that the polar group can move into close proximity to the surface upon which it is to absorb. Otherwise, the polar group may be buried deep within the hydrocarbon portion of a highly branched chain, and its effect will be shielded from the metal surface. Thus, the research chemist not only seeks ways to make groups of maximum polarity, but he strives to place these groups within the molecule in such locations that they can exert a maximum effect upon the surface to be protected.

2. The extent of oil-wetting conferred upon the oil by the semi-polar molecules.

All organic inhibitors possess one or more polar groups as stated above, and the remainder of the molecule is a non-polar hydrocarbon residue. This residue is identical in composition to oil, or produced hydrocarbons. It is consequently miscible with, or in other words, soluble in, the oil phase. To assume a simple picture of an inhibitor film on metal, consider the polar groups attached to the steel surface, and the hydrocarbon residues projecting outward from the surface of the metal into the produced fluids. Because these hydrocarbon residues are oil-like, they will attract produced oil to themselves with the result that in addition to an inhibitor film next to the protected surface, an additional film of produced oil will exist on the outer surface of the inhibitor film. This is an added advantage, when it is remembered that the corroding agents are in the water. We have both a layer of inhibitor and a layer of oil between the metal surface and the corroding phase, brine.

The above phenomenon is in a sense related to oil-wetting, but when we speak of oil-wetting we refer primarily to a somewhat different idea. In most corrosive oil-wells, metal surfaces are water-wet. We must add agents to the system which will reverse this situation, and render the metal surfaces oil-wet and water-repellent. By oil-wetting agents, we mean chemical substances which confer upon the oil in the system the ability to displace water from the metal surfaces and coat these in turn with an oil film.

There are numerous reasons why oil-wetting is important. One lies in the fact that at every instant of time, inhibitor molecules are being lost from the protective film which they form on steel. This is partially a result of erosion by the produced fluids. However, the principal cause is the thermal energy of the absorbed molecules themselves. These are in constant motion—partly of the molecules as a whole, partly as oscillations and vibrations of various portions of the molecule with respect to one another. This motion causes a molecule to "jump off" the metal surface every now and then.

It is therefore necessary to periodically repair the inhibitory film by replacing the lost molecules. Remembering that an inhibitor film consists of a water-repellent (hydrophobic) outer surface which maintains a transitory oil film on top of itself, it is at once apparent that the film cannot be efficiently repaired if the that phase is repelled by the residual inhibitor film.

By contrast, when the mending inhibitor is soluble in oil, and especially when that inhibitor enhances the ability of the oil phase to wet the surface, oil containing dissolved inhibitor will spread out over the remaining film residue and will give the fresh inhibitor maximum time and proximity to the surface which are so necessary for efficient film repair.

Good oil-wetting characteristics are also important in the establishment of a protective film in a well not previously treated. It is easy to see that even a partial film in a well which has been formerly treated will be quite oil-wet. However, when establishing a film on a new surface, it is actually necessary to displace water with oil. By similar reasoning, it will be seen that oil-wetting properties will permit use of smaller quantities of inhibitor for the mending of partially desorbed films, for more of the inhibitor will have time to find its way to the metal surface prior to being produced out into the stock tank simply because of the better contact of the inhibitor-bearing oil with the surfaces to be protected. Also, in very high water-oil ratio wells, the oil which carries the inhibitor is relatively small in volume, and consequently will need excellent spreading powers in order to coat the down-hole metal surfaces with fresh inhibitor.

Importance of Uniform Treating Schedule

It is customary to treat wells at intervals of several days. Assuming that all of the inhibitor at each injection is immediately flushed to the bottom of the hole and is produced up the tubing within a short period of time, then the protective film must be established during this time interval. Once the inhibitor has passed out of well, the inhibitor film starts a continuous desorption which does not end until the next injection of chemical. If chemical treatment is performed at intervals such that the film is still in good condition, a very minimum of inhibitor will be required in order to obtain excellent oil wetting, and consequently, high efficiency of repair to the film. The result is a structure which does not corrode, even during part of the time, and further, a large reduction in the quantity of chemical required.

In the event that one or more treatments are missed, and the film residue is scanty, the normal treating volume which has been maintaining protection on the regular treating schedule will be insufficient to restore a protective film—the pipe will be water wet and corroding. Skipping a few treatments, and then resumption of the regular treating amount and schedule may result in a corroding well even during the following period. It will be necessary to resort to a high slug treatment before the film can be reestablished.

The interval between treatments is limited not only by the tenacity of the film formed, but also by another characteristic of organic inhibitors—all semi-polar inhibitors possess inherent tendencies to aggravate brine-oil emulsions. This undersirable occurrence is especially prevalent with initial heavy slugs in wells when first treated. In some cases, heavy treatments at fairly long intervals have been substituted for light treatments at more frequent periods, and increases in BS and W have been noted.

The most necessary part of a good treating program is thorough flushing of inhibitor by well fluids. The best way to demonstrate this fact is by actual case history. On February 1, 1953, a selected group of more than 500 sour wells in the state of Kansas were set aside for special study. These wells had been treated with very good success for several years prior to February 1, 1953, and it was considered that maximum results and minimum treatments had been established. The purpose of our project, however, was to determine if more precise treating practices could not achieve better results. On February 1, 1953 treatment in all the wells was cut exactly in half. At the same time, a four weeks schooling program for the pumpers of the involved leases was held in the field, where the importance of routine treatments and thorough flushing of product was emphasized. On February 1, 1954, a survey of all well failures attributable to corrosion during the controlled twelve-month test showed that well failure had decreased by 35 percent during that period in spite of the fact that the quantity of inhibitor used was just one-half of what had been previously used and that the equipment was another year older, which as explained later, tends to increase equipment failures.

The following is an incident which was encountered by one of our field men and illustrates an extreme in poor operating practice. A large lease in Kansas was divided by a highway. Very low corrosion failures were noted on one pumper's half of the lease, while 2 and 3 workover units were always on location across the highway. Our field engineer, when calling upon the man beset with troubles, asked how his inhibitor injection program was faring. The pumper, in all sincerity, was very frank in stating that he was unable to get his inhibitor program on a routine schedule, because his time was consumed almost entirely by workover jobs. Our man explained that the pulling jobs were an evil caused solely by the fact that he did not have his inhibitor program under way. The pumper had lived so close to his problem that he had failed to realize this rather obvious fact. Our man and the pumper then spent several days together, and the importance of treating was clearly demonstrated. Today, the pumper who had no time for inhibitor injections, now has nothing to do but gauge his tanks and treat his wells.

In the remaining time, we would like to try and clear up a common misunderstanding regarding the manner in which equipment corrodes with time. This misunderstanding has led many to believe that a given corrosion inhibitor will work in a well for a period of perhaps several months, and then it becomes ineffective in that well. In other cases, an operator has changed products and observed that well failures were more frequent with the product last used. This information alone is no criterion that the former product was superior to the one last used.

The Bureau of Standards conducted an immense project which required nearly 15 years to complete. The project was to determine the manner in which various soils corroded mild steel pipe. Thousands of piece of pipe of different diameters and lengths were buried in many types of soil, and certain numbers of these were dug up each year and examined for corrosion. This work proved very decisively that the following relationship holds for any structure which is corroding at a constant, unchanging rate.

cumulative failures equal k (age of equipment) to n-th power, where n is greater than l. This is a parabolic curve symmetrical with the vertical coordinate.

In order to clarify this phenomenon, let us consider a very severely corrosive well in West Texas, in which new rods were experiencing about 3 failures per week at the end of a 20 week period. These data are represented approximately by the equation,

cumulative rod failures equal 0.1 x (age of rod) to 2.14 power.

These data are summarized in Figure 1.

One inhibitor was used throughout the test, and we can assume that the corrosion rate was fairly constant during the entire 10-week period. This extreme example demonstrates clearly that the frequency of failures constantly increases with time. Nearly 3 weeks elapsed before the first rod failure occurred. Providing that failures versus time is a linear curve, we should then expect but one failure to occur between the 6th and 9th weeks. Figure 1 shows, however, that at the end of 9 weeks, 8.6 failures had occurred, while at the end of 6 weeks, 4.6 failures had occurred. The difference of 4 failures is the number which occured during the three week interval between the 6th and 9th weeks. Suppose now that at some period of time following the third week and prior to the sixth week, the operator had changed from one inhibitor to another, and to keep the picture simple, assume that the second inhibitor was exactly as effective as the first. Then we would have obtained the same curve as shown in Figure 1. However, if we did not know that these failures are a parabolic function of the time the equipment has been in service, we would assume that the second inhibitor was much less effective than the first—an unjust conclusion.

In addition to the above relationship, we must remember that curves such as Figure 1 can only be obtained from a large number of case histories which well give us a statistical trend. Pulling jobs in a single well will be quite erratic in general and will not show a uniform increase with time.

Therefore, it is clear that to correctly evaluate any corrosion mitigation program, it is essential to conduct controlled tests in a large number of wells over a period of time sufficient to give a definite, continuous trend—generally a period of several months. The accumulation of such large amounts of data can be analyzed mathematically in order to determine an equation such as (1) for different methods of corrosion control. Differences in the exponent of time is the true measure of differences in corrosion control programs.

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