Corrosion Inhibition In The Permian Basin - 1960

By HENRY FISCHER
Norcor Chemical Company

THE NATURE OF INHIBITORS

To provide an avenue for a discussion of the use of organic film-forming inhibitors in Permian Basin oilfield remedial practice, it is necessary to provide a brief review of what this classification of inhibitor is, the intent of application, and the manner in which it has been used in the past.

A film-forming inhibitor is, in general, a compound or mixture of specialized organic chemicals, wetting agents, and solvents. The active agents most generally incorporated into organic inhibitors are compounds of nitrogen designated as amines. Some amine groups have an affinity or polarity toward metal surfaces; the resulting phenomenon is a plating out or filming effect. The prevalent opinion is that the amines will form a monomolecular film on a metal surface, rendering a protective shield against the attack of corrosive fluids.

A modification of filming of amines is enhanced by the presence of hydrocarbon molecules on the nitrogen atom. When special wetting additives are mixed with a basic inhibitor formulation, the oil-wetting characteristic is improved. Inasmuch as the basic active inhibitor is most usually oil soluble, the addition of preferential wetting agents tend to render the inhibitor water dispersible, thus affording improved distribution of inhibitor through both the oil and water phases of produced fluid.

As a matter of record, the first appreciable use of a film-forming inhibitor, as such, in the oil field was found in the practice of injecting formaldehyde into the well annulus. Although effective to a degree in the inhibition of corrosion caused by hydrogen sulfide attack, the use of formaldehyde was gradually discontinued due to its toxicity and the formation of objectionable precipitates upon contact with corrosive well fluids.

Late in 1949 and in 1950, the first amine-blended inhibitors were formulated. Although primitive as compared to current formulations, these first inhibitors found widespread acceptance in the control of hydrogen sulfide attack.

Since these early developments in the field of corrosion inhibition, intensive research has gone into the precise formulation and careful selection of inhibitors to perform specific services. Whereas the first organic inhibitors were straight oil-soluble compounds, research with wetting phenomena has led to the development of water dispersible mixtures. Through special manufacturing processes, true water-soluble inhibitors have become available for the mitigation of sour fluid attack in water systems.

PRACTICE, PAST AND PRESENT

Methods used by field personnel in the application of inhibitors have varied with well conditions, general maintenance programming, and the availability of trained personnel. In the past, continuous injection of the liquid inhibitor by means of a chemical pump has been used, the normal practice being the injection of the chemical by increments into the casing annulus, whereupon it will fall to the fluid zone and be produced back up the tubing with production fluids and so contact the metal surfaces of equipment. The major objection to the use of continuous chemical injection is that an appreciable amount of inhibitor will fail to descend to fluid level due to evaporation of solvents and the adherence of the inhibitor to the well pipe. In the case of a well having a high fluid level in the annulus, the inhibitor will tend to remain in the fluid instead of descending down the hole.

The most popular practice of treating in the last ten years has been the slugging of a specified quantity of inhibitor into the annulus and then recirculating up the tubing and back down the annulus by means of the oil well pump. The chemical is introduced into the annulus by means of a well head lubricator. The amount of inhibitor used, and the circulating time have been variable among operators. In the past, it has not been a general practice to properly evaluate the amount of inhibitor and circulation time necessary to produce the most effective and economic inhibitor protection.

Histories of the treatment of pumping wells in west Texas have shown differences in practice varying from injecting the inhibitor daily to injecting it once or twice a week, with circulation periods from five minutes to several hours. The major objection to the slugging or batch type treatment is the time consumed in the effective circulation of well fluids for the greatest placement of inhibitor film on subsurface equipment.

Pellets and Sticks

An early innovation to inhibitor batch treating was the use of film-forming inhibitors manufactured as pellets. The active inhibitor is mixed with an inert weighting material, such as a compound of barium, and pressed into pellet form. The use of pellets has eliminated circulating time. When batched into the casing annulus, pellets fall to the bottom of the well where they dissolve gradually in well fluids and are produced back up the tubing. When correctly applied, this method provides satisfactory protection of bottom hole equipment.

Pellets were first used in flowing wells and gas wells where packers prevented circulation. Later they became popular in areas where pump corrosion problems were extreme. A decided advantage of pellet application is in the treatment of wells with high fluid levels in the annulus, or in wells that flow periodically through the casing. In such instances, the pellets can be lubricated down the annulus with produced fluids, even where a small amount of casing pressure is present.

In the last few years, disadvantages of treating with pellets have become evident. The pellets will sometimes bridge between the tubing and the casing in a crooked hole, or operators have found that pellets can be drawn into the pump if it is located at the bottom of the well where the pellets accumulate. Misuse also occurs when the pellets are introduced into a pumping well that has several feet of static fluid below the pump and perforations, where a lack of fluid movement prevents their effective solubility in well fluids. Another critical point has been the poor protection afforded by pellets to vapor space corrosion in the annular void of the well.

Some producers, however, have found that with careful application pellets can offer satisfactory protection, particularly where liquid inhibitors are used to augment pellet treatment.

Inhibitor manufactured in the form of a stick found utility much in the manner of pellets: facility of application where the mechanics of the well prohibited treatment with liquid. The normal practice for stick application is to introduce it into the tubing-head by means of a special lubricating device. Inhibitor manufacturers and producing companies have felt that sticks should be suitable for use in gas distillate, flowing and gas-lift wells. However, objections to their use have been voiced.

Sticks have been found bridged in the tubing, impairing production flow. Weighting materials and wax, sometimes used as a bonding agent, will form deposits in the well chokes and surface treating equipment. Also, many operators fear that the sticks never completely migrate to the bottom of the tubing in deep wells. Field personnel in many instances have shown a dislike for injecting sticks where very high well-head pressures are involved.

It can be noted that very few inhibitor sticks are currently being used in the Permian Basin area; but on the Gulf Coast of Texas and Louisiana, operators have reported adequate protection through the correct use of sticks.

Other special methods for inhibitor treatment used in production practices have been: side well chemical injectors, tubing displacement with high concentrations of inhibitor mixed with stock tank oil, and special wire line dumping devices. The many methods that are in use have depended largely upon the nature of well conditions, the type of inhibitor being used (oil-soluble, oil soluble-water dispersible, etc.), and the special objectives of the particular corrosion mitigation program.

Special emphasis must always be placed on the mechanics of the well being treated, i. e., single or dual completion, presence of a packer, type of lifting equipment, water, oil and gas ratios, bottom hole temperatures and pressures, height of fluid leg in the annular space, open hole or perforated completion, previous well treatment (fracturing, shooting, acidizing, etc.), the use of other chemicals in the well, such as breakers, which might influence the film persistency of the inhibitor, etc.

During 1959, a new outlook emerged in remedial programs involving the use of chemical inhibitors. A closer look has been taken at the economics of inhibitor treating and this new interest has paid particular attention to the formulation of inhibitors and their methods of use. During 1960, the manufacturers of chemical inhibitors may expect a closer inspection of the utility of their products and intensified investigation of new treating methods directed toward more effective treating programs.

NEW METHODS

Field

In the past several months, operating companies have emphasized corrosion remedial programs and have, in many cases, appointed special personnel to evaluate and recommend treatment policy in the field. The research personnel of major oil companies have been oriented toward more liaison with field personnel handling treatment programs. This general trend will continue in 1960 and the subsequent result can only be more effective and more economic methods.

There have been many reasons for poor chemical treatment programs in the past several years. Paramount among these has been the lack of skilled personnel both by the chemical manufacturers and the operators, to study and supervise maintenance programs. Also, testing methods have been inadequate, resulting in the misapplication of chemicals designed to perform specific tasks. There have been times when lack of sufficient production personnel in the field, particularly in extremely corrosive areas requiring close attention, has resulted in poor or inadequate treatment.

This year we will see chemical manufacturers sending skilled representatives into the field, trained to properly estimate their products and capable of making objective and honest recommendations for their use. There will be a greater emphasis by major oil operators on the selection and training of personnel to supervise more comprehensive and efficient studies of specific corrosion problems.

Where batch treatment of inhibitor is now being used, there will be a more careful measure of the type and amount of inhibitor to be injected, and a more precise consideration of the circulation time required for proper batch treating. Some major firms have already improved their batch treating methods by appointing a single person to be responsible for the treatment of all corrosive wells in a particular field or area.

In general, this program entails providing this individual with a tank-mounted truck in which he carries a large volume of inhibitor and makes a routine check and treatment of each well.

Inhibitor Squeeze

A very new and interesting development in west Texas has been the introduction of the inhibitor squeeze. This method of well treatment has been in use for some time on deep wells in the Gulf Coast area, but is just now finding possible application in the shallower corrosive oil wells of west Texas. The principle of inhibitor squeeze is to inject a large volume of highly inhibited oil into the well and displace it by overflush into the producing zone. The supposed result is to provide protection by (1) the placement of inhibitor in the formation to be entrained in formation fluids and gradually returned to the surface by normal production methods, thus affording a slow and continuous treatment of subsurface equipment and (2) the exposure of subsurface equipment to a high concentration of inhibitor, providing a long-lasting and tenacious inhibitor film.

It may be noted that there is considerable conjecture as to which of these factors contributes most to the life of inhibitor squeeze. The current popular opinion is that exposure of the metal surfaces to high concentrations of inhibitor is the paramount factor in optimum protection. This can be refuted, however, by certain flim-persistency tests conducted by laboratory methods which quarrel with any extended film life concept. Interesting data have been gathered related to the slow return of inhibitor from producing zones, referred to as "feed-back", and various attempts have been made to measure the effectiveness of feed-back. At this time, the most popular measurement is by the quantitative analysis of amines present in well fluids following treatment.

Other attempts at measurement have been made, and, at the present, some interesting work is being done with the use of radioactive tracers. It has been noted that in a squeeze application of inhibitor, where great quantities of overflush have been used, and the well has been shut in for a substantial period of time, amine counts have run consistently higher than baseline measurements.

The heavy overflush of the inhibited oil and the shutin time can accomplish two things: (1) a more positive and extensive displacement of inhibitor into the producing zone and (2) a more thorough wetting of the formation with inhibitor due to the presence of surfactants incorporated with inhibitor.

Testing

Concurrent with new treating practices is the development of new field testing methods. The most efficient index of well treatment performance is in well workover frequency due to corrosion failures. This, however, is not the most economic method of evaluating a treating program. The field testing method which has been most popular since the advent of oil well inhibitor treatments, has been the well-head or flow line coupon index.

This method is, in brief, the exposure of small steel coupons to well fluids over a given period of time and an analysis of the effects of corrosive fluids by weight loss. This weight loss is usually computed in terms of mils penetration per year. The coupon survey does not always present a true profile, either of rate of corrosion or per cent of inhibition.

For example, the positioning of coupons at the surface in the flow line will not give a representative profile of corrosive conditions existing at the pump, where temperatures, pressures, fluid velocities, and fatigue factors are manifest. Coupon surveys, however, still remain the most inexpensive method of evaluating inhibitor treatment and do have statistical value when programmed over a great number of wells. These data are significant if properly evaluated.

Another method of checking the effectiveness of inhibitor treatment is the determination of iron present in produced waters. In sweet corrosive systems, corrosion products can be introduced into produced waters as soluble iron. By making checks following treatment, the iron determination method often provides an excellent profile of inhibition.

There is a fallacy in the use of iron analysis in west Texas waters, primarily where high concentrations of hydrogen sulfide are present. The reaction product of hydrogen sulfide and iron is iron sulfide, which is not water soluble. The iron sulfide may quite possibly be produced back in surges with well fluids or may remain intact as a scale on the surfaces of the equipment. Random water samples thus taken will, as a rule, not contain representative amounts of iron. It might be mentioned here that in an initial treatment with inhibitor, great quantities of iron sulfide may be produced with well fluids, which would lead untrained personnel to believe that corrosion rates had been accelerated. However, the fact is that the wetting agents incorporated in the inhibitor are, in effect, detergents which tend to dislodge and wash out accumulations of iron sulfide scale present in the system.

Particularly applicable to inhibitor squeezing methods is the use of bottom hole coupons. Such coupons might be run into the hole with equipment and positioned where optimum corrosion factors may occur. Typical of this type of coupon is a flat metal panel of such dimensions as to allow easy placement at the bottom of the well by a special fastening device. Another representative coupon test of downhole conditions is the use of rod subs positioned in the string above the pump. Rod subs can be carefully weighed to fractions of ounces and the corrosion rate determined by reweighing after exposure for a fixed time interval.

The caliper survey has proved useful for determining corrosion in tubular goods, but this type of evaluation is not always accurate. If there are deposits of scale present in the tubing, the caliper will show an irregular profile which could be misconstrued as pitting. Also the caliper tool can damage any protective coating or lining which has been applied to the tubing, as well as cause damage to the metal itself, creating points of fatigue.

Research

During 1960, improved laboratory methods will be devised for the proper evaluation of inhibitors for particular application. At present, there are a number of laboratory evaluation methods which can be classified both as static and dynamic tests.

Briefly, a static test is a quick index of relationship between a metal surface and its corrosive environment, or between a metal surface and a film-forming inhibitor. Under the heading of static test, we can gather the most popular: (1) the drop size ratio test, (2) the copper ion test and (3) the bottle test.

The drop size ratio test is designed to measure the wetting effects of an oil soluble inhibitor in a water environment. There are many variations of the drop size ratio test, including one recent method which measures the adherence of residual water to a metal surface which has been preferentially oil-wetted.

The copper ion test measures the temporary effectiveness of a film-forming inhibitor to resist the plating of copper on a steel surface immersed in a copper sulfate solution. It is controversial whether the copper ion test is more truly a measurement of the oil-wetting of a surface or a true determination of inhibitor filming.

The static bottle test involves the exposure of an inhibited steel surface to a corrosive fluid for a given period of time without turbulence or agitation with a subsequent computation of weight loss due to attack.

The dynamic tests are varied and generally are, in effect, an effort to duplicate producing well conditions. These tests involve exposing a steel surface to oil and corrosive brines with turbulence and agitation as a factor. Bottom hole temperatures, and, in some instances, bottom hole pressures are incorporated in the testing procedure. The mechanics used in the dynamic test are generally in the form of revolving wheels, turbulence through line systems, etc. For all practical purposes, the dynamic testing methods are inherently relative to field application.

The problems which will be encountered in determining the reliability of various laboratory test methods lie not in the mechanics of the methods, but rather in the basic concept of what an inhibitor is supposed to do. For example, a high degree of wetting found in one inhibitor may appear ideal when subjected to one type of evaluation but prove ineffective when evaluated by another method.

Briefly, it can be stated that although oil-wetting of a metal surface is highly desirable, it may prove to be undesirable if film persistency is an objective, inasmuch as wetting agents acting as detergents may hinder the placement of a tenacious inhibitor film. In other words, one inhibitor may appear to have excellent characteristics in terms of one type of test, and fail completely when evaluated by another test using identical corrosive fluids.

At this time, it appears to be prerequisite that an inhibitor perform well on some or other specific laboratory test method before it can be approved for use in the field; but it must be kept in mind that an inhibitor manufacturer who has provided himself with an alert technical group can formulate, blend and compound any inhibitor to pass just about any test, although that inhibitor may fail in providing protection of equipment in the field.

NEW STANDARDS

This year in the Permian Basin, there will be a concerted effort toward the standardization of testing methods which will result in more efficient and effective protection from corrosion.

The year of 1960 will find manufacturers and users of inhibitors drawing closer together toward more reliable testing and application methods. With all of us taking a closer look at economics, we will see less waste of chemicals in the field through improved batch treating methods and squeezing, and advances made in the formulation of inhibitors toward greater film persistency for extended inhibitor life.