Control of Oil Field Corrosion by the Use of Inhibitors

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The loss of subsurface equipment due to corrosion became fully appreciated as an economic factor in the production of crude oil and gas about 1944. Up to that time, corrosion losses, while recognized, were accepted as a necessary part of production costs. Some wells required replacement of sucker rods every two to three weeks. Tubing failures in as short a time as two to three months were not uncommon. The short life of these items obscured the recognition of casing corrosion as a serious problem. About this time, it was established that hydrogen sulfide was the principal agent causing rod breaks but as late as 1945 the causative agent of condensate well corrosion was generally unknown.

In 1945, the introduction of formaldehyde as a specific inhibitor for hydrogen sulfide corrosion, spurred various companies to initiate studies aimed at solving downhole oil and gas well corrosion problems. Many chemicals were offered as inhibitors, some of which are still in use today. The results of the work on sulfidic corrosion problems served to stimulate work which has resulted in the generally successful use of inhibittors for most oil and gas production corrosion problems.

MECHANISM OF INHIBITOR ACTION

Inhibitors are materials which, when added in small amounts to a corrosive environment of a metal or alloy, effectively decrease the corrosion rate. This is accomplished by affecting the reaction at either the anode or the cathode of the corrosion cell. To better visualize the manner in which this is accomplished, a review of the simplified equation[1] describing the steady state corrosion rate may be helpful.

$$E_R = E_A + E_{IRi} + E_{IRe}$$

Where E = Total reversible EMF of the couple

E = Anodic polarization = sum of (1) concentration polarization at anode, (2) possible anodic overvoltage and (3) IR drop through films which may cover anodic areas.

E_C = Cathodic polarization = sum of (1) concentration polarization, (2) cathodic overvoltage and (3) IR drop through films.

E_{IRi} = Product of current flowing and resistance of electrolyte between cathode and anode.

E_{IRe} = Product of current flowing and resistance of metal between cathode and anode areas. Re is generally very small; hence, IRe may be neglected in most cases.

The dissipative terms E_A, and E_C and E_{IRi} are functions of current density. If the major factor is E_A, the cell is considered to be under anodic control; if E_C, it is under cathodic control. Inhibitors function by changing one or more of the factors, i.e., E_A or E_C and have very little effect on E_{IRi}. If the material alters E_A it is said to be an anodic inhibitor; if E_C it is a cathodic inhibitor.

Alkali metal hydroxides, chromates, phosphates, silicates and carbonates are examples of anodic inhibitors. These materials form or maintain films which increase anodic polarization. Since the mechanism is one of film formation substantially at the anode, incomplete coverage results in a decrease in anode area without a corresponding change in the cathode area. Thus the cell will continue to operate at nearly the same driving force and intensity, but penetration at the anode will be increased due to higher current density at local areas. Thus anodic inhibitors may increase the penetration rate if their concentration is inadequate.

Those materials, i.e., calcium in water systems, which slow down the cathodic reaction are called cathodic inhibitors. These materials are believed to congregate at and shield the cathodic metal areas. Since metal does not go in solution at the cathode, incomplete coverage of this area does not increase the corrosion intensity; therefore, as a general rule, cathodic inhibitors are considered safe at any concentration.

Most inhibitors used in oil wells are organic materials. The compounds are not clearly anodic or cathodic based on selective adsorption. It is postulated by Hackerman[2] that the adsorption may be viewed as general in character involving both physical and chemical forces. Regardless of the forces involved the inhibitors form barriers of varying effectiveness. It is further postulated that chemisorption of the compound inhibits corrosion by an energy as well as a material barrier.

Work by our laboratory using radioactive tagged amine-acid salt inhibitor has shown that the inhibitor film is not a static film like a protective coating. Over a long period of time during which inhibition was maintained, the density (thickness of inhibitor film) changed. Some evidence showed that "active" areas on the metal surface shifted from site to site, causing a redistribution of the inhibitor.

The organic inhibitors may be affixed to the metal in a multi-layer or monolayer and conceivably might increase the corrosion under certain conditions. Evidence from both laboratory and field use has shown that in certain cases excessive inhibitor can produce a relative ineffective barrier. Work with a specific amine type material has shown that overtreatment can result in the formation of film capable of holding considerable water in a tight emulsion. Such a film offers little or no protection to the metal substrate.

From the above it becomes apparent that inhibitors function through their ability to form films on metal. Whether these films prevent corrosion by simple mechanical barriers or through energy redistribution is still open to question. The controlling mechanism probably depends, at least in part, on the chemical nature of the inhibitor, i.e., its ability to chemisorb to metal surfaces.

Since a film forming mechanism is involved, it is obvious that for most efficient treatment consideration should be given to the metal to be protected. Since most of the metal in oil field use is carbon steel, this discussion will be confined to that metal. Many of the inhibitors in use for oil and gas well protection are amine salts. These materials have the ability to readily adsorb to most solid surfaces. Thus they will "coat" or adsorb onto corrosion products, metal surfaces or suspended solid particles in the flow stream. It is therefore apparent that for an inhibitor to function it must be able to "see" clean metal. Fortunately most of the amine salt compounds exhibit detergent properties and can, with time, remove such corrosion or loose mill scales as might be present on the metal. Obviously, maximum obtainable inhibition will not be achieved during this descaling period.

An inhibitor film can be described in terms of degree of protection and film life. The degree of protection obtained by the use of a specific compound is, to a large extent, determined by its molecular structure. This is basically a problem of the formulators and little can be done by field techniques to affect this property.

Film life is affected by several factors, which are to some extent under field control: fluid velocity, volume and concentration of inhibitor used per treatment, temperature of the system, type of substrate available for adsorbtion of the inhibitor and length of time the inhibitor is in contact with the metal and composition of the fluid system.

Previous work[3] has shown that film life is inversely related to fluid velocity. In accelerated laboratory tests using the same corrosive system and inhibitor, at a velocity of 1.0 ft/sec. film life was 20 hrs; doubling the velocity, the film life was only 2.5 hrs. Per cent inhibition during film life was the same in both cases. It was also shown that changing the water-oil ratio from 100/0 to 50/50 increased film if by a factor of 7 for an oil soluble material.

Other work in this laboratory has shown that for certain amine type inhibitors a 5-7 per cent concentration of material in oil is the optimum for establishment of effective films.

It has been observed that the amine-acid salts adsorb strongly to an iron sulfide substrate. This is not to infer that the materials will not function efficiently in other systems such as sweet condensate wells. It may, however, explain why some of these inhibitors provide relatively less effective inhibition in oxygen corrosion systems than where H^2S is the corroding agent.

Field use has shown that these same amine-acid salts will protect against oxygen corrosion when they are continuously present in the system. Thus the method of treatment may vary depending on the controlling mechanism of the corrosion attack.

METHODS OF USE

The treating methods that have been devised for field use are generally dictated by the mechanics of well completion rather than good corrosion control techniques. This situation has to some extent been responsible for the development of the various treating methods now in use.

A basic change has taken place in inhibitor treatment over the last few years. Originally the purpose was to treat the fluids in a system; that is, maintain a supply of inhibitor in the fluids at all times sufficient to control corrosion. It will be seen that an equally effective method is to treat the metal. This procedure uses infrequent slugs or batches of inhibitor to coat the metal with little regard for carrying inhibitor in the fluid. Combinations of the two methods are also used. The best treating method to use is obviously the one which gives maximum protection with the least cost.

Substantially, continuous treatment is obtained, in the case of wells, by daily injection of inhibitor solution after an initial heavy treatment. The initial heavy treatment serves to penetrate scales which are generally present on the metal surface and initiate film formation. The subsequent smaller daily injections continue to remove foreign material from the metal surfaces and replace the film that has been lost by solubility effects and abrasion. Due to the volume of fluids contained in the annulus, inhibitor is continuously produced in the annulus, inhibitor is treatment is involved, this technique is useable only where the necessary manipulation of wellhead equipment is extremely simple. Thus the technique is generally used on low pressure shallow pumping wells or where automatic injection equipment can be justified.

Batch or Slug treatment of wells has in many cases proved more economical and efficient than continuous treatment. In this technique, the weekly or monthly requirement of inhibitor, based on continuous treatment, is injected in the well in one batch. The success of this treatment is dependent upon obtaining the optimum amount of inhibitor for best film formation. The inhibitor film life must be at least equal to the time between treatments. Generally, after the system is brought under control, the total volume of inhibitor will be less than the total that would be required for continuous treatment. Labor cost for injection is also reduced. Time between treatments can be determined by corrosion test coupon techniques or in some cases by analysis of the produced fluids for soluble iron. In some cases the time between treatments has been as long as six to eight weeks. In terms of both manpower and chemical cost this method often proves to be a very economical treating procedure.

The squeeze treatment is a relatively new technique. In this method a large volume of inhibitor solution, 10 - 30 bbl, is pumped down the tubing and in some cases displaced into the formation. Satisfactory protection for periods as long as 12 months has been reported. The interval between treatment is determined by corrosion coupon data or analysis of the produced fluids for corrosion products.

Inhibitors in solid forms have been successfully used in many cases. The advantage of this technique is the relative ease with which the chemical can be transported to the bottom of the well through a long fluid column. The melting point and solubility of the solid binder can be formulated to allow controlled release of the inhibitor under bottom hole pressure.

It is apparent that the successful use of inhibitors depends upon transporting the chemical to the metal surface in amounts sufficient to form a tough film. Once formed, this film must be kept in repair by periodic additions of chemical. Generally, the most attractive way to use inhibitors is based on the premise of treating the metal surface instead of the fluids in the system.

Costs of inhibitor treatments vary with the system to be protected. In H_2S wells it has been reported[4] that the cost of such a program averages $13.50 per well per month. Cost of corrosion in the same wells has been shown[4] to be an average of $50.00 per well per month. For condensate well corrosion the cost was estimated to be $4.27 MMcf; cost of inhibition is less than $1.00/MMcf.

There are many good inhibitors available for field use for primary production. Most inhibitor failures in the field can be traced to some form of misapplication. Typical examples would be lack of sufficient inhibitor used, failure to allow time for the system to clean up and for an inhibitor film to deposit. Another failure would be selection of the wrong material, that is, water soluble or oil dispersible, for the system under treatment. Failures in the field, then, could be summed up to being due to unsufficient inhibitor or failure to transport the inhibitor to the metal surface.

An important factor to consider in field use of inhibitor is the presence of active ingredients in the material. While most inhibitors are of the same general type, active ingredient content may vary from 15 to 40 per cent. Obviously, economics dictate that the customer obtain the most active material for dollars spent.

It should not be construed that inhibitors are necessarily the most economic method of corrosion prevention. In many systems, while the use of inhibitors will give adequate corrosion control the use of the material may be more expensive in the life of the project than coatings or more resistant materials. This is a problem that should be thoroughly investigated by the field enginee whenever an inhibitor program is planned.

REFERENCES

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