DIAGNOSIS AND INHIBITION OF CORROSION FATIGUE AND OXYGEN INFLUENCED CORROSION — TWO PARTICULARLY PAINFUL OILFIELD CORROSION PROBLEMS

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ABSTRACT

In the effort to raise more hydrocarbons to the surface, production practices have evolved which aggravate certain corrosion related problems. One of these problems, corrosion fatigue, is usually associated with rod pumped wells because it has a stress component plus a corrosion component; as wells are pumped harder, stresses are higher and corrosion fatigue becomes more prevalent. Another of the problems becoming more frequent is an indirect result of both harder pumping and depletion of gas pressure in oil reservoirs, and a direct result of certain stimulation methods; oxygen can enter production fluids and alter the mechanism of corrosion in oilfield fluids. This paper outlines diagnosis of these two problems and describes their control with corrosion inhibitors.

INTRODUCTION

The best practice when dealing with corrosion fatigue is to keep stresses as low as possible, handle strings properly, and control corrosion. When considering oxygen corrosion in oilfield fluids, a good practice is to prevent contact of oxygen with fluids and remove it completely if it does. In today's conditions, these are still preferred practices but are compromised with increasing frequency. In these situations, use of corrosion inhibitors specially designed for the specific conditions can greatly extend the useful life of steel production equipment.

Corrosion fatigue cracks can be triggered by corrosion pits, mechanical nicks, metal defects, or stress concentration due to improper string make-up or operation. In many situations, cracks start without perceptible stress concentrators. Corrosion is under control as indicated by coupons and/or downhole steel, yet strings are parting. These breaks may be the result of high lifting or pounding stress, or of high strength steels in fluids that have become sour so hydrogen embrittlement becomes a factor, or a combination of both. The facts that: Rod wells are pumped faster to get more production with a given unit; more wells are operated in a fluid or gas pound condition; more production is sour; all contribute to the problem. Corrosion inhibitors designed by considering the fundamentals of corrosion fatigue can control the practical problem as will be shown later.

Oxygen can contact production fluids because of air leaks into negative pressure well annuli or gas gathering systems, or during surface handling of oilfield waters when gas blanketing is imperfect. These are direct and indirect consequences of less gas pressure in oil wells. Sometimes oxygen (air) entry is unavoidable, for example, air to sustain firefloods, air in drill fluids, and aerated surface water use. Corrosion problems due to the former reasons are more subtle since they usually begin gradually. Systems that have been historically under good corrosion control can gradually begin showing damage since very small amounts of oxygen can significantly change corrosion and corrosion inhibitor mechanisms. Location of air leaks into the annulus of a producing well is often impossible. In water handling systems oxygen can be partially reacted with natural reducing agents (e.g., sulfide) and exist as an intermediate.[1] In this state, oxygen will not react with oxygen scavengers nor register by the usual oxygen analysis techniques, yet it has a strong influence on corrosion and inhibitor mechanisms. In most of the above cases, it is advantageous to be able to inhibit corrosion in the presence of oxygen or its derivative.

DIAGNOSTIC TOOLS

Until recently diagnosis and control of both problems was difficult. Only pulling records, failure samples, and corrosion coupons or probes were available for diagnosis and frequently these do not directly point to the cause. One tool developed in the last few years is called a Potentiodyne Analyzer. It is a self-contained, portable instrument that potentiodynamically polarizes test electrodes in field systems; the polarization curves thus produced show the corrosion character of the system.[2] Information given by these tests include general (average) corrosion rate, penetration rates in corrosion pits, and oxygen entry possibilities. Test timing can be coordinated with corrosion inhibitor treatments to evaluate inhibitor performance. Particular emphasis is placed on pit growth rate measurement since most oilfield corrosion is pitting rather than uniform thinning. Oxygen effect measurement is also quite important. Both will be discussed in more detail shortly.

Another useful tool recently available to our research is an electrochemical hydrogen detection probe. Operating principles will not be discussed here since a similar laboratory probe is described in a previous paper.[3] Briefly, it measures corrosion generated hydrogen atoms that migrate through a steel probe wall into an internal cavity containing electrodes. It is more sensitive than pressure type hydrogen probes and much easier to install and operate than vacuum hydrogen probes. Recent research has pointed out the importance of hydrogen-in-steel to corrosion fatigue properties[4], therefore, electrochemical hydrogen probes mounted in oil well flowlines are important to the understanding of corrosion fatigue.

Another tool available to oilfield corrosion where corrosion fatigue is a consideration is stress analysis of sucker rod strings. API calculation or dynamometer determination of maximum and minimum lifting stresses certainly isn't new.[5] Minimum to maximum rate determines the maximum allowable stress before strictly mechanical fatigue can proceed. The only new facet of the picture is quantification of the contribution of pound; either gas or fluid pound adds stress to a rod string and so must be considered. Pound is, in simple terms, an impact of the lowering pump plunger with the gas/liquid interface inside the pump. Stress imparted to the rod string at the point of impact is a function of the speed of impact and not relative masses.[6]

Pounding can therefore be quantified by knowing the percentage of plunger fill and the stroke length/speed of the unit. We can simplify by assuming that motion at the pump is a triangular ramp rather than sinusoidal, and that displacement at bottom is the same as at top. neither of these assumptions compromise accuracy beyond experimental scatter. Therefore, we have:

Stroke Length x Stroke Speed x (1-Fraction of Chamber Fill) x 8 = Impact Speed
if impact is above the stroke midpoint;

Stroke Length x Stroke Speed x (Fraction of Chamber Fill) x 8 = Impact Speed
if impact is below the stroke midpoint.

Fraction of fill can be obtained by comparing the actual production of a tight pump to the API theoretical displacement calculation. It is possible to convert impact speed to stress and to use pulse speeds plus attenuation in the rod string so that a stress value can be added to maximum and subtracted from minumum. However, the calculation isn't simple, and an added factor of rod buckle and subsequent rod-to-tubing drag cannot be quantified. Hence, the impact value is left as an inches-per-minute speed and evaluated empirically. For example, when fluid pound is involved (clean-cut gas/liquid interface), the maximum allowable speed is about 2,000 in/min.. A well with low rod lifting stresses could tolerate a higher speed before experiencing significant damage due to fluid pound but 2,000 is a median value. For gas pound situations, the interface is not as distinct, impact is not as severe, so speeds of up to 3,500 in/min. can commonly be tolerated.

CORROSION FATIGUE

The detailed mechanism of corrosion fatigue will not be dealt with here but in essence involves three measurable parameters. The stress parameter includes normal lifting stresses plus any pounding stress plus any bending stress, all modified by stress riser effects of corrosion pits, mechanical nicks, or make-up deviations. The corrosion parameter involves uniform thinning plus stress-rising pit formation plus corrosion on fresh metal in the growing crack. Hydrogen dissolved in the steel is the third parameter and has as its source hydrogen ions discharged during the corrosion process. Two general rules concerning hydogen penetration into oilfield steels are; first, a greater amount of corrosion generated hydrogen atoms enter steel when sulfide is in the corrosive environment; and second, the harder (greater tensile strength) the steel, the more prominent the effect of hydrogen on physical properties. A corrosion inhibitor has been designed which can modify the surface film, even in the presence of sulfide, so that less hydrogen enters the steel. When stress and corrosion are in a reasonable range, lowering hydrogen entry can have a large influence on corrosion fatigue, even when the steel in question is a medium strength such as is found in API Class "C" sucker rods.

Table 1 shows data from five wells to illustrate this point. Corrosion as measured by the Potentiodyne was acceptable; experience has shown that pit growth rates that average less than 25 MPY during the treatment cycle represent adequate corrosion control in a rod pumped well. Lifting and pounding stresses were optimum under existing conditions. These wells show a significant decrease in string failures using both "C" class and "D" class (higher strength) rods in both sweet and sour production when changing to a hydrogen-entry corrosion inhibitor. All rod strings were the same before and during the test periods with only broken rods being replaced.

Electrochemical hydrogen entry probes were placed in the flowlines of two of the test wells and readings in μ amps averaged during the treatment cycles. The wells with hydrogen probes show a factor of two higher hydrogen readings on a conventional inhibitor than on the restricted hydrogen entry inhibitor, Inhibitor "D". Experience has shown that for the size of probe used, 16 in.^{2} (103 cm^2) of corroding area, probe readings should be less than 9.5 μ amps for acceptable life of Class "C" rods. API Class "D" rods can tolerate less. Highly stressed strings of any strength level can tolerate less and conversely, low stressed strings can tolerate more. Our experience is not wide enough yet to quantify these effects. Data on Wells S3 and K7 does clearly show the influence of hydrogen, however, when other factors are fixed. The third condition of the K7 well illustrates the influence gas pound can have when other factors are essentially constant.

Inhibitor D is an oil soluble, water dispersible inhibitor that has about the same general corrosion inhibition properties as conventional oilfield inhibitors. It has components new to oilfield inhibitors which modify the steel surface film so that less corrosion generated hydrogen enters the steel. Less hydrogen in the steel means that corrosion fatigue cracks do not propogate as readily, which in turn means less frequent corrosion fatigue failure no matter what initiates the cracks.

OXYGEN INFLUENCED CORROSION

Oilfield corrosion inhibitors function by incorporating into a thin corrosion product layer on the metal surface.[7] Certain molecules can adsorb and incorporate in specific kinds of corrosion product films. Once oxygen or any other oxidant contacts the surface film, chemical changes occur in the film so that the same molecules no longer incorporate effectively. Only a small amount of oxidizing power is required since the films can be quite reactive and few molecules are involved in the thin surface film. The task then is to locate new kinds of inhibitor molecules which will incorporate into a partially oxidized surface in the presence of salts, sulfides, and carbonates commonly found in oilfield corrosion environments.

Only brief mention will be made here about the laboratory tests which led to inhibitor molecules effective under partially oxidized conditions. Corrosion tests in the lab were designed using electrochemical techniques to give desired surface film properties and to show trends consistent with field experience. On the basis of these tests, three blends of molecules having desirable properties were selected for field testing; one, a water soluble inhibitor for corrosion in sweet or sour systems that contact air; two, an oil soluble/water dispersible for sour systems that contact air, and three, an oil soluble/water dispersible for sweet systems that contact air. Different functionality is required whether the air contaminated system is sweet or if it is sour; these functionalities can be combined in a water soluble formulation, they cannot in an oil soluble formulation.

In field systems, a Potentiodyne is most helpful in diagnosing oxygen influenced corrosion problems. As mentioned earlier, an average measured pit rate in excess of 25 MPY for systems subject to alternating stress, in excess of 35 MPY for others, represents inadequate corrosion control. The reason for the inadequate control may be insufficient amount of inhibitor or failure of the inhibitor to reach the metal surface, but another possibility is oxygen contamination of the fluid. Oxygen influenced corrosion damage is usually worse in crevice areas such as in pumps and adjacent to threaded areas. It is frequently worse near the point oxygen first enters production fluids. Since only a small amount of oxygen is soluble at the point of fluid entry, oxygen is frequently consumed by corrosion or other oxidation processes as it moves away from the entry point. In producing wells this usually means corrosion damage at lower portions of the well and less in upper sections. In sweet production, oxygen may survive to the top; in sour wells, oxygen is usually in the form of a sulfide/oxygen intermediate toward the top.

If Potentiodyne tests show that the inhibitor isn't functioning properly and there is a current arrest on the cathodic half reaction, oxygen is likely to be the problem. Figure 1 shows a typical set of polarization curves generated by the Potentiodyne; the cathodic curve exhibits such an arrest, termed a diffusion limited area. When an oxidizing agent is present in limited concentration, a diffusion limited current shows up for the maximum arrival rate of that reactant to the cathodic electrode.[2] A clean electrode (fresh or anodically defilmed) is required for this test since inhibitor films can slow cathodic kinetics. Oxygen or its derivative is responsible for these arrests in near neutral pH (5-9) systems since it is the only possible strong oxidant in production systems. Other oxidants are possible only if they have been intentionally added; for example, chlorine might be added in surface handling systems to control bacteria.

It is fundamentally possible to relate the arrest current to a concentration of oxygen. However, several parameters would need to be determined to make the conversion in each case. Many of these would require considerable experimenting to measure. Partly for this reason the value of current at the arrest point has been related empirically to inhibitor requirements. Another reason for not converting is that oxygen in a sour system may be in a sulfide/oxygen intermediate at the measurement point, so it is no longer oxygen yet it can effect corrosion reactions. Experience has shown that a system which gives a diffusion current higher than 0.2 ma on unfilmed standard sized (9 cm^2) electrodes will not experience adequate corrosion control with conventional corrosion inhibitors. Diffusion currents from 0.1 to 0.2 ma are in a marginal range and anything lower can be controlled conventionally. For the sake of defining a range, diffusion currents in oilfield fluids do not commonly exceed 10 ma. When equilibrated electrodes are anodically defilmed before making cathodic diffusion limiting current determinations, a factor must be applied to account for the relative defilmed area. So, this test measures not concentration, but effect of oxygen on the corrosion reaction.

Table 2 shows results of field tests of new inhibitors in systems diagnosed to have some degree of an oxygen problem by the above tests. Four types of systems are included, sour and sweet waters, and sour and sweet production. In the first two types, a water soluble inhibitor was desirable, and in the second two, an oil soluble/water dispersible was desirable. All types show significant improvement after changing to the new oxygen-influenced-corrosion inhibitors. All of these tests were begun using existing steel with only corrosion damaged parts being replaced. Economic savings are appreciable in each case; repair and replacement costs are saved, plus production interruptions are minimized. Similar results have been obtained in other hydraulic and injection waters; submersible, rod pumped, and gas lift wells making supply water, secondary recovery oil production, carbon dioxide flood production, and fire flood production.

SUMMARY

Conditions exist in the oilfield which are not the most desirable from a corrosion standpoint. Some of these can and should be corrected; some cannot, however, because of physical, chemical, economical, or practical reasons. In general, the trend is to encounter these situations more frequently, especially in the cases of corrosion fatigue and oxygen influenced corrosion. This paper has shown that these problems can now be diagnosed and can be controlled by new inhibitors which have been designed along basic mechanistic principles.

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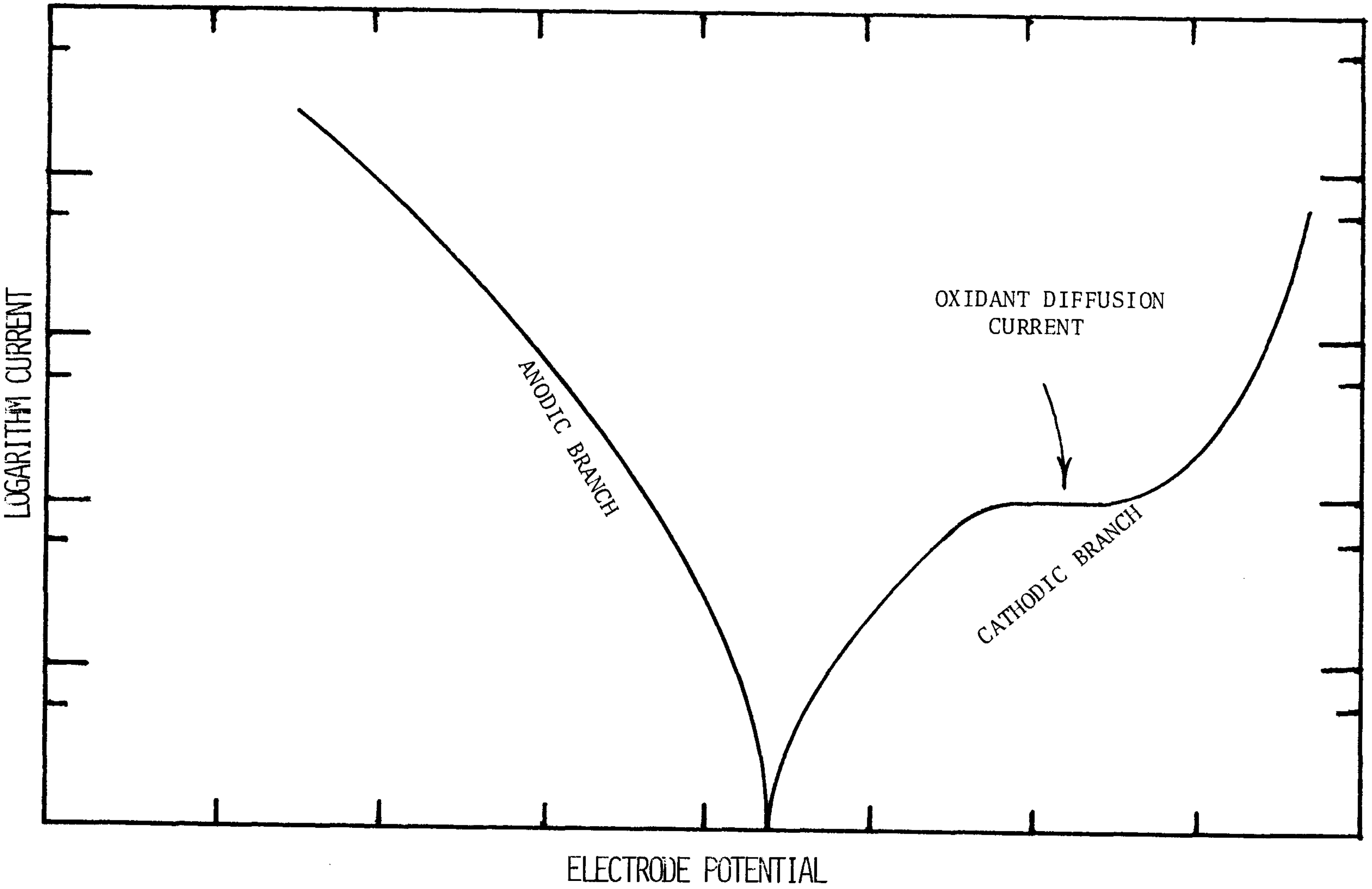

FIGURE 1—TYPICAL POLARIZATION CURVES FOR STEEL IN OILFIELD BRINE CONTAINING DISSOLVED OXYGEN

TABLE 1—FAILURE PARAMETERS IN ROD PUMPED OIL WELLS

Well	API Rod Class	Inhibitor	Production Character	Potentiodyne Pit Rates MPY	Lifting Stress		Pound		Average Hydrogen Current u Amps	Rod String Failures Per Year
					Max PSI	Min	Type,	Impact Speed		
H4	D	A	Sour	12	25,100	3,000	F.P.	Near 0		10
H4	D	D	Sour	14	25,100	3,000	F.P.	Near 0		0
G2	D	B	Sweet	5	27,300	3,200	G.P.	2,700		3
G2	D	D	Sweet	4	27,300	3,200	G.P.	2,700		0
G3	C	B	Sweet	8	26,900	3,500	G.P.	Near 0		4
G3	C	D	Sweet	5	26,900	3,500	G.P.	Near 0		0
S3	C	C	Sour	8	25,100	4,200	F.P.	450	11	15
S3	C	D	Sour	9	25,100	4,200	F.P.	450	6	2
K7	C	C	Sour	13	19,500	4,700	G.P.	4,200	18	15
K7	C	D	Sour	13	19,500	4,700	G.P.	4,200	8	2
K7	C	D	Sour	14	18,500	5,800	G.P.	2,100	7	0

TABLE 2—INHIBITION OF OXYGEN INFLUENCED OILFIELD CORROSION

System	General Nature	Previous Treatment	Previous Results	Reason For Oxygen	Present Treatment	Present Results
Hydraulic power water on 10 wells	Sweet	Scavenger and Inhibitor E	50 leaks per year	Entry in transfer and/or storage/ uncertain	Scavenger and Inhibitor F	4 leaks per year
Mixed water Injection water	Sour	Scavenger and Inhibitor G	10 leaks per month	Oxygen tied in intermediate	Only Inh. F	0.8 leaks per month
Two rod pumped oil wells	Sweet	Inhibitor H	Rod life 3-4 mos. 36 rod and pump pulls/year	Negative pressure casing gas gathering	Inhibitor I	Rod life 12 mos.+: 2 pump pulls/year
Three rod pumped oil wells	Sour	Inhibitor J	36 corrosion pulls/ yr.	Negative pressure in annulus	Inhibitor K	3 corrosion pulls/yr.

Inhibitors E and G are conventional water soluble —
Inhibitors H and J are conventional oil soluble/water dispersible --
Inhibitor F is new water soluble —
Inhibitor I and K are new oil soluble/water dispersible