Field Application of Laboratory Corrosion Inhibitor Test Data

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INTRODUCTION

In order to select the appropriate inhibitor for a given application, two outstanding pieces of information need to be known. They are: "How much corrosion will occur in a given length of time under the specified conditions?" and "How much corrosion can be accepted?" The amount of corrosion that will occur in a given length of time can be determined by running a test which will duplicate the desired conditions; but, the amount of corrosion that is acceptable is somewhat arbitrary. In this paper, an attempt will be made to give the reader an understanding of how tests are run to determine the amount of corrosion that will occur and to help develop a feel for the amount of corrosion that can be accepted. However, before going further, we should review the fundamental definitions of "corrosion" and "inhibition".

BASIC CORROSION THEORY

Corrosion has been defined as the chemical interaction of a metal or alloy with its environment. Thus, for our purposes, it is the destruction of oilfield tubular goods by acid. But, the definition may be carried further by adding that corrosion involves the shift of an element from a high energy state to a lower energy state. The elements in a piece of metal have been supplied with energy to get them to their present state. This energy will be lost spontaneously and the elements will return to a lower energy state, their so-called "natural state". The speed at which this energy is lost will depend upon the environment. Thus, corrosion products slowly form on a piece of steel in air; whereas the steel dissolves rapidly in acid. The dissolution of iron in acid may be illustrated as in Fig. 1. The H^+ units shown here represent hydrogen ions in the acid. The Fe^{2+} units represent iron going into solution. The iron goes into solution at some site on the metal surface known as the anode. In order for iron to go from a neutral atom to a positively-charged ion, it must lose two negatively charged particles — i.e., electrons. These electrons migrate through the metal to a site called the cathode. There they unite with two hydrogen ions to form a molecule of hydrogen gas. This process may be represented by two equations, one for the anodic reaction, and one for the cathodic reaction:

$$Fe^\circ \rightarrow Fe^{2+} + 2e^- \quad \text{Anode}$$

$$2H^+ + 2e^- \rightarrow H_2\uparrow \quad \text{Cathode}$$

These equations may be combined to form the general equation for the over-all process:

$$2H^+ + Fe^\circ \rightarrow Fe^{2+} + H_2\uparrow$$

The diagram shows the anodic and cathodic sites to be separated by some distance. In reality, they will probably be very close together, as little as one atomic distance.

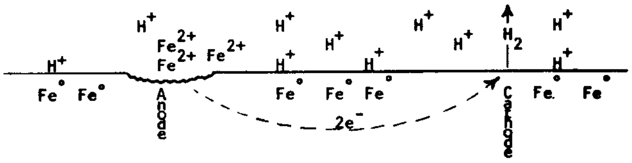

FIGURE 1. — Dissolution of Iron in Acid.

On a piece of metal with a uniform surface, there is a continual shifting of the anodic and cathodic sites and the surface is uniformly corroded. If something keeps these sites from shifting or causes them to be concentrated in one area, then uneven corrosion or pitting results. The rate of the corrosion process is governed by the rate of the anodic and cathodic processes and the rate of each of these depends upon the rate of the other. If one or both of these processes can be slowed down or stopped, then we have inhibition — and any material which will do this may be called an inhibitor.

Inhibitors for acid corrosion are usually organic or inorganic compounds or mixtures that are dispersed in the acid solution. When the acid contacts a metal surface, these materials adsorb on that surface and slow the corrosion process. If the material adsorbs preferentially on anodic areas, it is termed an anodic inhibitor; if it adsorbs on cathodic areas, it is termed a cathodic inhibitor; and if it adsorbs on the entire surface, it is a general inhibitor.

HOW WEIGHT-LOSS CORROSION TESTS ARE RUN

Corrosion tests are most frequently run by a weight-loss method. This involves inserting a preweighed metal coupon in the inhibited acid and bringing this combination to the desired test temperature for a given length of time. When the desired time interval has passed, the coupon is removed, scrubbed with a brush and soap to remove any corrosion products, rinsed, dried, and weighed. From the weight-loss, the corrosion in lb/sq ft is calculated for that time period.

A corrosion test which has meaning must duplicate the desired conditions as closely as possible. Oilfield metals should be used for testing. Different metals, and even different grades of steel, will show large variations in corrosion rates. In a given grade of steel, variations in corrosion may be caused by variations in the constituents used for alloying purposes or by different heat treatments. There are variations in the alloying elements because different manufacturers have different specifications for the chemistry of the steel. When the entire length of pipe does not receive the same heat treatment, the resulting variation causes non-uniform corrosion to occur. Untreated upsets will cause the familiar "ringworm" corrosion.

WHAT WEIGHT-LOSS AND PENETRATION NUMBERS MEAN

Corrosion rates are given either as a weight-loss rate or a penetration rate. The most frequently used weight-loss units are lb/sq ft/time, where the time is the actual length of time for which the test was run. A few years ago, the units lb/sq ft/day were frequently used. The use of these units often involved the extrapolation of short-term test data to 24 hours. This assumes a linear relationship between weight-loss and time. However, the usual case is a linear function up to some point where the inhibitor becomes depleted or degraded, then the slope of the curve increases rapidly as shown in Fig. 2. It is for this reason that we should not attach too much significance to extrapolated corrosion rates.

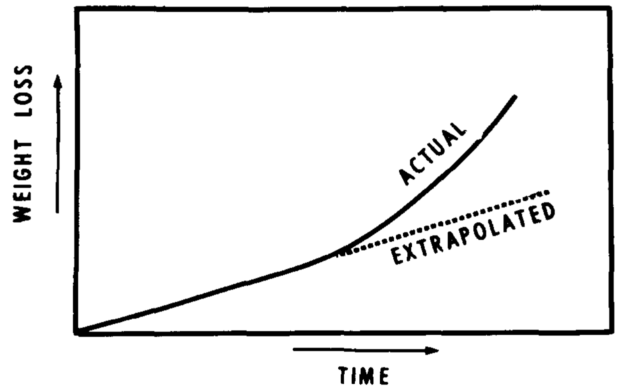

FIGURE 2. — Corrosion Rate as Weight Loss vs Time.

The other frequently used corrosion rate units are the penetration units, usually mils per year, abbreviated MPY. A mil is one-thousandth of an inch. The new instantaneous corrosion-rate measuring instruments give a read-out in mils per year. Once again, in dealing with mils per year, we are often dealing with an extrapolated value. Another disadvantage of using penetration rates is that they imply uniform corrosion.

It may be desired to convert a corrosion rate from one unit to the other. If we wish to convert from lb per sq ft per time to mils per year, the lb per sq ft number is first expressed as lb per sq ft per day, then multiplied by 24.4 to convert to mils per day, and then by 365 to get mils per year. The conversion factor 24.4 is determined by the density of the metal. As an example of this conversion, consider a corrosion rate of .01 lb per sq ft per 16 hours. The conversion to lb per sq ft per day is made by multiplying by 1.5, giving a rate of .015 lb/sq ft/day. Multiplying this by 24.4 yields a mils per day value of 0.36 and multiplying by 365 gives a mils per year value of 134. Likewise, the conversion from mils per year to lb per sq ft per day may be made by multiplying by the inverse of 24.4 x 365 or 1.12 x 10^{-4}.

One bit of significance that is not readily obvious about a weight-loss number is that it serves as an indication of the amount of control that is being exerted over the corrosion process. In general, a high weight-loss indicates that the point has been reached where the inhibitor has ceased to function as it should. When this point is reached, the inhibitor film breaks down and allows corrosion to continue at a rate controlled only by the temperature and acid strength. When the films formed by organic inhibitors fail, the failure tends to be general and there is less likelihood of pitting than is the case with inorganic or arsenic-type inhibitors. Failure of an arsenic film is usually very spotted and pitting results.

There is no set minimum weight-loss that will indicate that the inhibitor has ceased to function properly. This weight-loss will vary with the temperature. High temperature causes higher initial corrosion. Larger weight-losses may occur before all of the inhibitor has been depleted or degraded. Thus, higher weight-losses may result before complete control of the corrosion process has been lost. Figure 3 shows the effect that temperature has on corrosion rates. This diagram shows that, at higher temperatures, the slopes of the curves do not increase until higher weight-losses have been reached.

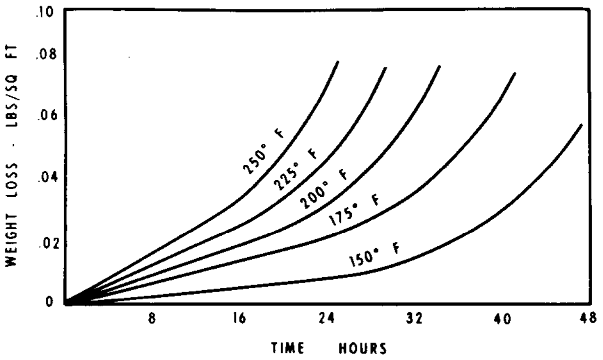

FIGURE 3. — Influence of Temperature on Corrosion Rate as Weight Loss vs Time, 150°F to to 250°F Isotherms.

HOW TO SET CORROSION LIMITS

When acid contacts steel, there will be some corrosion or dissolution of the metal and some weight-loss no matter how well the acid is inhibited. No inhibitor completely stops the corrosion process; however, in most cases, acids can be inhibited so well that only minimal corrosion will occur and there is no particular concern about corrosion damage. But, there will also be cases where the treatment conditions are so severe that high corrosion rates are unavoidable. In these cases, one must be prepared to choose a maximum allowable corrosion rate. About the only way to know what limits must be set is to have in mind a picture of the amount of damage resulting from various amounts of corrosion. Perhaps the best way to form this picture would be to think in terms of reduction of wall thickness of tubing. API Standard 5A lists wall thicknesses ranging from 0.113 in. to 0.375 in. For this discussion, we can pick 0.19 in. wall thickness as being a typical thickness. An allowable reduction in wall thickness is sometimes considered to be 10 per cent. For this example, this would be a penetration value of 1.9 mils or almost 0.08 lb per sq ft. However, visual examination of a specimen that had lost this amount of weight would readily reveal that corrosion had occurred. From experience in running corrosion tests, it is known that 0.05 lb per sq ft weight-loss is about the maximum amount of corrosion that can occur on this type of tubing without being readily apparent upon visual examination. This weight-loss would approximate a reduction in thickness of 1.1 mils or about 6 per cent. Other, lower amounts of weight-loss would not be apparent upon visual inspection; however, if strength reduction and over-all tubing life were important factors, a lower weight-loss might be necessary. A weight-loss of 0.02 lb per sq ft would be equivalent to 0.49 mils or a reduction in thickness of 2.6 per cent; and .01 lb per sq ft weight-loss would be equivalent to 0.24 mils or 1.3 per cent.

Once a corrosion limit has been picked, there are several ways that the treatment may be designed to hold the corrosion under this limit. The time of exposure may be adjusted to keep the corrosion within the limits. The amount of inhibitor can usually be increased to provide better protection. The temperature of the well may be lowered by injecting large volumes of cooling fluid. And, if none of these methods is applicable, a lower concentration of acid or a less-corrosive organic acid may be used.

CONCLUSIONS

By having an understanding of the methods used to determine corrosion rates and the nomenclature used in discussing these rates, one is better able to decide the amount of corrosion that can be tolerated in an acidizing treatment. The amount of corrosion can usually be held to low limits; however, under extremely severe conditions, corrosion may be unavoidably high. When this occurs, it is important that the corrosion be kept within safe limits. This can be more assured by knowing what the safe limits are for the particular conditions.