Corrosion Inhibitor Testing, Field & Laboratory

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PREFACE

It is the purpose of this paper to scrutinize the more common field and laboratory methods of corrosion evaluation. It will be an unbiased evaluation exploiting the advantages and disadvantages of each system

COUPONS

Types of Coupons

Although there is doubt about the validity of coupon results compared to down hole conditions one uses coupons as a guide because of their simplicity of installation and economics. There are numberous types of coupons and many methods by which these coupons are handled; in fact, there are nearly as many different types of coupons as there are ideas in one's mind. For example, a few are

1. single hole
2. two hole
3. rod
4. circular
5. stressed
6. corrosimeter
7. downhole
8. other corrosion media detectors

Single hole coupons are the most commonly used because of their ease in handling and inexpensive construction. They have a large surface area consequently, relative large weight losses result. This type of coupon finds use in low velocity pumping and flowing wells, as well as in static fluid systems in which fluid surging will cause no mechanical damage to the coupon. Also, they are easily manufactured, installed, removed, and analyzed, but, because of the contacting surfaces which tend to set-up oxygen cells or an ideal place in which bacteria may breed they are subject to accelerated corrosion rates at the point of attachment. This disadvantage, of course, results in a higher MPY loss than would otherwise be expected and does not necessarily reflect down hole conditions.

Two hole coupons are constructed in the same inexpensive manner as are the single hole coupons, but another attachment hole is added. The additional rigidness of this construction allows it to be placed in high velocity flowing and pumping wells as well as in the most gentle flowing systems. But, with its larger hold down area, it is even more subject to cell concentration or bacteria breeding than is the preceeding coupon, and the result may be an unrealistic weight loss. This is also a more difficult coupon to handle because of the additional washers and bolts.

The rod type or multi-chuck coupon is used for the same applications and for the same periodic removal as is the circular type, but it is not a stressed coupon. It has the advantages of having a relatively large surface area and is not as subject to cell initiation as other coupons might be.

The circular coupon is an easily constructed coupon that can be "stacked" or rotated for periodic removal and that can be lightly stressed in a static position. It finds application in wells of all types with the exception of high volume gas wells. Further, it is a somewhat easily handled unit; but it has a small surface area which is not always desirable, and it is subject to cell action at the point of contact between the coupon and the washers or gaskets.

Of the four mentioned, the stressed coupon is the least expensive to manufacture and results in a large surface area with a minimum of handling hardships. Again it finds application in all wells with the exception of high volume gas wells, and it has two distinct advantages: (1) it is held in a rigid position with a minimum of contact area, thus the probability of cell formation is reduced; and (2) it may impart a dynamic stress of the coupon.

The corrosimeter is the most expensive coupon type made, and it can be used in most wells. It has the advantage of not being removed from the line for MPY determination; but it is still in the development stage, for there is some question as to the validity of its results. In very sour systems, there have been instances, in the past, where the probe has corroded away before an adequate number of readings could be made.

Down hole coupons are not widely used because of the expense in setting and retrieving the coupons. They are normally run in a gas or mud anchor or set by a wire line above a downhole choke. These coupons are subject to the normal type of damage that would be expected to be encountered in running an object in and out of a hole. However they do, when undamaged, indicate, more accurately, down hole conditions.

Other corrosion media detectors include the caliper, weighted pony rods, the sonoscope, and the very unsophisticated, yet sometimes reliable human eye. The caliper is a relatively expensive tool to run, but it is one of the less complex instruments to use to evaluate down hole conditions. Its results deserve some merit; but its use is restricted because it has so far proven to be a destructive tool to inhibitor films. Recently, however, there are such tools on the market that are advertised as nondestructive. The sonoscope is strictly a qualitative instrument and, as one can surmise, an expensive operation since the objects to be analyzed must be removed from the hole. Weighed pony rods have proven to have some validity in results, but it is cautioned that they must be the same metallurgical value as is the rest of the rod string, or they mean little. Then there is always the human eye, which because of the lack of experience or willful clandestiny, does not always see the true picture. However, it can often times be the most accurate of all corrosion determinants; but because of subjectivity it is being replaced with less vulnerable data collecting devices.

There are many other lesser known corrosion investigating and determining devices, ranging from the simplest concepts to the ultrasophisticated imagination of the human mind. But there is not time to discuss all such "investigators," and that discussion is not the purpose of this paper. Instead, the paper is simply trying to expose the reader to the abundance and nearly nonsensical number of methods used to try and solve a problem, a problem that is now exaggerated to the point of near insolvency, partly because of the great volume of data that cannot be correlated, resulting from this shotgun approach to testing. Each producer or each chemical manufacturer feels that his way is the best way, and consequently various test techniques result.

It is recognized that coupons leave much to be desired, but with some degree of standardization some usable facts could be derived. Examples of variations in testing procedures exist not only in the types of coupons that are available but also in coupon metallurgy and coupon handling. The author will next investigate some of the unrealness involved in these practices.

Coupon Materials

The more commonly used coupons are constructed of AISI or SAE 1010 to 1020 steel which is according to the allowed variations of the standards, metallurgically compounded of given amounts of carbon, manganese, sulphur and phosphorus. These metals are then shaped into the various coupons that are used to attempt to evaluate corrosion rates downhole. The tubing that is normally run into the hole is API J-55, N-80 or more rarely P-105 and special alloys; these all hold within limits of the physical data standardized by the API. The peculiar fact that is obvious here is that the coupon materials have very little, if any, metallurgical significance with regard to the tubing materials.

It is well known that various constituents in metal drastically alter corrosion rates. For example, mild steels often show much less corrosive rates that do those of high carbon and chromium content steels; yet often the reverse is true. Examination of high alloyed tubing in wells show that tubing failures were resulting from intergranular stress corrosion or hydrogen imbrittlement, while the 1020 coupons were indicating a mild general corrosive condition.

Since the four big factors in corrosion environment are time, temperature, stress, and metallurgy, one should try economically and systematically to duplicate them. Why does one insist upon evaluating unstressed 1020 steel against stressed J-55 or N-80? Some say that this evaluation is not necessary because the mild steel is a very good indicator of what is occuring, but this fact is not necessarily true as is evidenced by failures in high alloy tubing with low MPY coupons. One can attempt to duplicate the tubing metallurgy, and he can simulate stress in a coupon by using a holder that can impart stress to the coupon. One has then attempted to duplicate two of the four natural factors in corrosion. The other two variable are known to increase corrosion with an increase in time and temperature, so it is known that if one sustains corrosion with the first two perameters set, he will expect to increase corrosion by extending the last two. However, it seems obvious that one should set some limits on this coupon system to be able to use and understand the data we are gathering.

Coupon Handling

It is realized that all readers are not directly associated with the production of oil and do not delineate the methods of field practices such as determining the place in the flow line where the coupon shall be run or the way to make up the piping to install the rascals. However, some readers are associated with the technicians whose responsibility it is to weigh and handle the coupons. And as in all other aspects of this subject, lack of standardization here has caused a great breech in worthwhile data accumulation.

COUPON MANUFACTURING

Coupon Manufacturing is a starting point for a portion of these uncontained variations. A common method of manufacturing coupons is to shear the metal to the given demensions, but other manufacturers will over-shear the metal, stack a few together, place them in a lathe, and machine them to size, while still others will stamp out the coupons on a punch press. As one can see each method involves a different amount of cold working and stressing of the material which result in assorted physical characteristics of the coupons.

Upon the completion of the forming of the coupons they are blasted with numerous grades of sand, or they are tumbled with a great assortment of abrasives, while still others are worked by a reciprocating table with a variation of abrasives. Different manufactures subject their coupons to these media with varying increments of time. As a result no two coupon manufactures market a coupon of the same physical characteristics.

Coupon Preparation

Preparation of the coupons before and after being emersed in fluid is another facet that lacks any resemblance of standardized procedure. Upon the receiving of the manufactured coupon it is washed and soaked in some organic solvent such as isopropyl alcohol or kerosene or gasoline, etc. Some manufacturers will scrub the coupon lightly; others will attack it with violence; while still others assume that soaking will accomplish the task of cleaning.

After cleaning, the coupon is then weighed and placed in a desiccant or simply placed in a desiccant container until a more oportune time arrives for weighing. Some organizations expend the cleaning operating by placing the coupons in inhibited or uninhibited hydrochloric acid. Of course the exposure time varies greatly as does coupon surface and corrosion rate.

As if initial variations are not wide enough, one really finds variances when he views the final preparation of the coupon for weighing after it has been removed from the fluid stream.

First, the coupon — wrapped in a rag or placed in an envelope, jar, beer can or some other convenient carrying device — is brought into the laboratory from the field; most of these carriers deduct a substantial weight from the coupon because of oxygen exposure or errosion. Second, to remove the residual materials, some technicians will clean the coupon in a variation of organic solvents. Again it is soaked, rubbed, or scrubbed at the technician's will and passion, and all used are types of scrubbing devices: tooth brushes, steel wool, wooden sticks, Ajax cleanser, and finger nails. Then the coupons are dried and placed into an acid of the inhibited or uninhibited variety for any convenient length of time. This time not only is a variable among labs but also with the individual technician in a given laboratory. And, of course, various and grandiose weight losses may occur from this operation. The coupons are removed, washed, scrubbed, dried, then weighed.

It seems rather doubtful that weight losses mean much if the "kid glove" method of handling is compared to the roughneck method. Most producers require (and laboratory personnel do this out of habit) that the coupon be weighed to the fourth decimal place or 1/10 of one milligram. It seems peculiar to weigh to this accuracy when the handling techniques are often so crude that grams, not milligrams, are lost because of poor technique. One can sustain a tenth of a milligram loss simply by breathing upon the coupon or dropping it on the floor. But one can imagine the weight loss incurred when the coupon is scrubbed, rubbed, drubbed or flubbed! It is no wonder that coupons do not reflect the conditions of downhole equipment when all the previous methods are being used for corrosion analysis. One needs some set parameters for this operation.

IRON COUNTS

Perhaps in lieu of coupons as a indicator of downhole corrosion, one should investigate the method of soluble iron determination. Here, again, arguments are numerous both for and against this method. Those of the favorable camp say that this is a method less susceptible to error than are coupons since a single person can perform the test identically each and every time that it is run. It may be run directly in the field and, thereby, assure a fresh sample; nor is there a need to acidize it, a process which can cause variations in iron readings. Also, it is claimed that, if iron is present, it is coming from downhole equipment; and, if the iron counts are being reduced, the equipment is likewise being protected. This group interprets the readings as qualitative analysis and only looks for a downward trend in the counts.

On the other side of the fence there are those who vehemently refuse to accept iron counts as an indicator. They say that there is a possibility that the iron count is a result of normal connate water constituents and that it is not a result of equipment deterioration. They say that altering sampling techniques to the smallest degree will so affect the count that it will be invalid. They also say that if this method is used to determine corrosion in plastic-coated pipe or cement-line pipe, it is not valid because the corrosion is so localized that it will not show, to any marked degree; it is merely indicative of a failure. Also it is felt that iron counts only in the water phase is not telling the whole story. These are not invalid arguments, but they can be tempered with judgment and experience.

If iron counts are to be used as an analyzing factor of corrosion, then what method should be used for this determination: the colorimeter, the spectrometer, or the various titration methods?

Colorimeter Tests

The colorimeter is a relatively accurate instrument that is used in both the field and the laboratory but is more often found in the field because of the ease of set-up, the reduced time to run a test, and the need for less finesse than that of the titration method in performing. The field colorimeter is not an expensive device and, when properly used, is as accurate as the lab colorimeter. The unit is normally a battery operated system that is subject to the inaccuracies of any normal batter-operated unit (deteriorated batteries, momentary voltage drop, and slow-power conversion units). However, this type of unit can be handled in such a manner that it will give surprisingly accurate results.

Some of the more common colorimeteric method of iron determination are:

1. The Thioglycollic method. If run properly it will establish a very stable color that can be read without fear of it deteriorating while being read. It reacts with only ferrous iron and therefore must convert ferric to ferrous, a conversion which is done easily and effectively. It has another advantage: it will not precipitate sulfur as do some of the other colorimeter techniques when an acid is present. Also, it is more accurate in the higher ppm ranges than are most of the meter tests. However, it is subject to typical errors of such an instrument (such as meter accuracy, battery deterioration, energy conversion unit deterioration, etc.). It is also subject to erroneous readings because of contaminated or old solutions and poor execution of the measuring liquids that is involved.
2. The phenanthroline method is perhaps the easiest method of all to run in the field, for it is a direct reading system without the necessity of heating the solution. The phenanthroline method is performed either by using two liquid solutions or by the use of a combination powder. Both methods employ the use of an indicator phenathroline and an acid (oxcylic or citric acid) that when in the presence of iron forms an orange color. The pH of the solution is easily adjusted for more accurate readings of the iron. One disadvantage to this test is that the acid will precipitate sulfur if sulfides are present in large quantities. This test is accurate in the low PPM range and is considered the quickest and most reliable of all such colorimeteric methods.
3. The bipyridine and tipyridine methods are all used in conjunction with the colorimeter, but these methods require more work than does the above. However, the difficulty in performing these tests is that the test solutions must be heated nearly to boiling, then cooled; and of course, these processes involve additional equipment, time, and money. And this method results in an unstable solution in which the color will change if oxygen is present. However it results in more accurate iron concentration readings in the higher ppm range than does the phenanthroline method, and sulfur will not be precipitated because of the presence of sulfides.

Titration Tests

Of the various titration methods available, only two will be discussed here; the versene method and the dichromate method.

The versene system requires an exact technique to accomplish accurately the test. However, when it is properly performed it is accurate between 0.5 ppm and 100 ppm with an accuracy of plus or minus 10 ppm at the upper limits. The pH must be adjusted to the 6 to 7 range (slightly acid) to retain the accurancy of the test. Quite often, if this test is used in the pH ranges normally found in oil field brines, this test will read higher iron ppm than is actually present because versene will pick up calcium very readily and often times before it will iron. However, since this is an ever present problem in oil field brines of a higher count are expected. There is also some speculation about the availability or iron pure versene and the ability to maintain it so. Finally, extreme accuracy is needed in performing this test, and it is not suggested for field use.

The dichromate method of titration for iron is an accurate test at the high ppm ranges of iron because it can be used to determine the iron content directly without dilution errors. However, it is a long and slow method because of the very many steps involved to complete the test. It is suited strictly for laboratory testing and is not conducive to field use.

It should be remembered that these tests are only a cross section of a multitude of tests that are available for iron determinations, and that the other tests are not reviewed because of space limitations. However, the two tests were described briefly to show the variation in testing procedures and the results. Of course all realize that if a single test is used throughout the cycle of gathering information, the results will be relative, and a trend can be established. However, if one method is used in the field and another method is used in the laboratory, it should be understood that, in most cases, the results will not correlate in magnitude, or perhaps even in trend. Also, one must realize that testing methods cannot be changed at random unless one is willing to disregard data previously obtained.

Perhaps one is beginning to realize that the testing techniques are only as accurate as the method, the operator, and, of course, the sample! As has been seen, there is a great discrepancy is test results when the sampling technique is altered, and it is generally agreed that improper sampling techniques result in greater test variation than is normally understood and that these sampling errors must be eliminated before test results are to be considered an accurate guide. But it is not the purpose of this paper to go into sampling techniques; much has already been published on this subject and may be easily obtained.

Again it must realized that a great portion of the money and work that is being consumed to run tests is being wasted because of the inability of the technician to repeat the test, the varying techniques in analyzing in sampling, and the lack of knowledge and experience in data interpretations.

Wheel Test

The Wheel Test is one of the most commonly used devices to evaluate corrosion inhibitors and to establish levels of corrosion. This wheel is regarded by most technicians as a rather crude instrument, and the data gathered from it should be taken lightly. The instrument consists of a disc (with varying diameters among users) which is called the "wheel". To each side and about the periphery of the wheel are clamps so spaced that bottles may be positioned so they will not to touch each other. The wheel is suspended by a shaft running axially through its center-point and is connected to a prime mover by means of a reduction system. The wheel is encased in an insulated, fireproof container in which the temperature is thermostatically controlled. Bottles of various sizes and shapes are filled with various percentages of inhibitor, oil, and water to which odd various shaped coupons are placed; one per bottle. The bottles are then purged with some type of gas and capped, corked, or otherwise sealed, and placed on the wheel. The wheel is then, for a given length of time, rotated at some predetermined speed and at a predetermined temperature. Upon the termination of the test the bottles are uncapped; the coupons are removed and cleaned and weighed. More often than not the data gathered from this type of test will not correlate from one laboratory, or even within the same laboratory. Why is this, one wonders. Some of the variables involved in performing this test should be examined. These basic variables of the wheel are:

1. RPM
2. Temperature
3. Exposure time to inhibitor
4. Exposure time to corrosive media
5. Concentration of inhibitor
6. Water/oil ratios
7. Acid gas used
8. Oil wet or water wet coupon
9. Type of coupon
10. Type of bottle
11. The handling of the equipment and specimens

Quite often laboratories will vary all of the above mentioned items as well as a multitude of physically less significant yet possibly equally important items.

There has been no definite evidence that the RPM of the wheel has any significance in the results obtained when a fixed coupon is used. But this is quite untrue when an unattached coupon is used. Obviously the unattached coupon will strike, with varying impact depending upon the RPM, the walls of the bottle, and cause various weight losses because of erosion characteristics. Presence of an emulsion in bottle will also effect the abuse of coupon by tending to cushion the striking action.

The temperature ranges of these systems vary from 110 F to as high as 200° F. As all realize, temperature is a very important factor in the rate of corrosion, and this rate is greatly accelerated by an increase in temperature. Obviously it is extremely important, when comparing tests, to keep temperatures exact and constant, not relative! And exposure time to both the inhibitor and to the corrosive media must be identical in order to compare results. Some tests call for 2, 12, 18, or 24 hr for inhibitor filming; and they likewise require 12, 24, 48, or 72 hr for exposure to the corrosive media. It is difficult to compare any of the results of tests if they are subject to the operators will in changing exposure times.

The inhibitor concentration also varies in parts per million from 10 to 500,000 ppm, depending on what results one is attempting to obtain. It seems that this is an easy process to follow and duplicate, but one would be surprised at the error that is introduced in the measuring of the inhibitor. For example, if one is using a calibrated pipette, a medical syringe, or an eye dropper to measure the inhibitor, one can effect an error of from 10 to 40 per cent in the ppm, depending on which measuring instrument is used.

Water/oil ratios along with oil or water wet coupons are very important factors. A coupon of the correct metallurgy may show excellent inhibition with water/oil ratios of one magnitude and look terrible if the ratios are changed. Likewise, if the coupon is oil wet it may pass a test, and if it is water wet it may fail the same test or visa-versa.

There is no doubt that the type and metallurgical constituents of the coupon are very important; but, in most cases, they are not considered when running a wheel test or coupons in a well. Certainly there is going to be a different rate of corrosion with a 1018 and a 3140 coupon. And one must not be mislead to believe that the lesser alloyed coupon will show evidence of corrosion much sooner than will the coupon of the higher alloy. This concept is false, and more often than not the carefully alloyed coupons will fail much sooner than will the mild steel, especially when stressed and in the presence of hydrogen sulfide, a condition that is usually the actual one in well tubing.

The types of bottles used are also of interest because they may also foul a test. Because of amine absorbtion into the pores of the coke bottles, it has been considered better technique to destroy the bottles than to attempt to clean them and re-use them. However, many cleaning solutions have been used to attempt to clean bottles such as hot chromic acid, hot caustics, surfactants and hot trichloroethylene, the latter being the only one that exhibits a good cleaning action, although it does not completely rid the bottle of the amine. There have been used other types of bottles that are subject to better cleaning results because of the lack of glass porosity.

Such a bottle is that manufactured by Corning.

The NACE Static Bottle Test is the original test for screening inhibitors, and some of the better inhibitors were developed through the use of this test. It is a rather easy test to perform because the coupon is inhibited and placed in a bottle with varying amounts of water and oil; then the bottle is capped and allowed to stand for seven days. The coupon is then removed, cleaned, and weighed as in previous tests, to determine the MPY loss. This technique has two distinct disadvantages: (1) it is a very cumbersome test because one will have bottles stacked from wall to wall; (2) the results obtained from this test vary as much as do those of the wheel test. Again the variation in procedures are obvious in that many different coupons are used, with different percentages of oil and water, and different handling techniques.

Copper Ion Displacement

Copper Ion Displacement is sometimes used to evaluate inhibitors. The inhibited coupon is exposed to a given concentration of copper sulfate for a given time and if the coupon is not coated with copper it is said to be inhibited. However, film forming amines can be leached by low pH valves which exist in the copper sulfate solution. As the copper sulfate ionizes, the sulfate radical is freed, and thereby, lowers the pH with the resulting copper plating of the coupon. Chemicals can be formulated (such as a polymer) and will not permit this plating to occur, but they are not necessarily good inhibitors. With extensive field experience and the knowledge of the characteristics of the produced crude, one is able to correlate, with good results, the inhibition properties of any film former by using this technique. It is an easy test to perform, but it is often times considered too simple a test in regard to the complexity of oil field production.

Drop Shape Ratio Test

The Drop Shape ratio test is used by some organizations to determine the filming ability of an inhibitor. A drop of inhibitor is added to a given solution, and if the drop exhibits high surface tension and remains in a semi-pherical shape it is considered to be a poor inhibitor. If, however, the drop shows a low surface tension and spreads thinly over an area it is said to have good inhibitor characteristics. However, there are theories now that suggest that this test actually indicates that the reverse is true. That is, if the inhibitor remains in a drop it is a better inhibitor than if it spreads out.

CONCLUSION

There is an abundance of test procedures and techniques and variations of inhibitor testing programs both in the field and in the laboratory. There is nothing more confusing or hindering to a study than to complicate it with unlimited variables. Therefore, in order to pursue inhibitor testing in the field and laboratory for the purpose of controlling corrosion in the oil field, sights should be set on one goal and it should be approached from a given direction. The problem then can be isolated, and with industry wide cooperation most likely solved.