

Corrosion in Waterflood

By H. L. BILHARTZ
Production Profits, Inc.
Dallas, Texas

Corrosion in waterflood is a challenging and important problem. It is challenging because so little is known about it; important because the production of so many barrels of oil rests upon its solution.

It was only a few years ago that speakers covered the subject of oil and gas well corrosion in a single lecture. Not so today. Full day symposiums are devoted to single, specific categories. In one case, a text book has been published covering one phase - Condensate Well Corrosion. The progress made in corrosion technology truly has been amazing. However, the subject for today, Waterflood Corrosion, is still in early stages of development. There are few fundamental principles well defined. The tools of the engineer are limited and frequently reveal confusing and conflicting data. There are no absolute measuring devices. This general lack of knowledge has led to the practice of utilizing criteria and tools developed for other environments; environments that often do not resemble remotely those encountered in waterflood.

It will be the purpose of this lecture to point out the pitfalls of this procedure and to describe techniques that have proved valuable in waterflood studies.

To begin discussion, let us compare secondary recovery by waterflood with primary production. As a generalization it might be stated that reasonable profit can be derived from primary production in spite of what we do, assuming a reasonably good hole drilled into a good oil reservoir. In other words, there is considerable latitude in operations. It is obvious that good engineering can produce more oil for less money; however, it frequently does not make the difference between profit or loss.

On the other hand, waterflooding demands close control from conception to abandonment. Reservoir evaluation and engineering is essential. Likewise, water quality control as a part of the general operating plan must be maintained. This does not mean water quality must be perfect; on the contrary, it must be just good enough to fulfill requirements for a given reservoir. Extra money spent to make it better is wasted. To determine that quality and to achieve that quality at minimum cost is an important problem facing any waterflooder. Corrosion is a factor in this quality; however, it should not be considered alone as a specific problem, rather it must be kept in proper perspective as a part of gathering, transmitting and ultimately injecting the water into an oil sand in the quantity desired and at the time and place it is needed.

Let us explore for a moment the part corrosion can play in this overall problem of water injection. First, it obviously destroys steel equipment. This is the conventionally accepted ramification of corrosion. It is the sole undesirable feature of corrosion in primary production. Second, and less obvious, it produces products of corrosion that plug injection sands. In this case, the destruction of equipment may not be of economic importance, yet to the waterflooder, the corrosion process means limited injection capacity which results in greater operating costs extended over a longer period of time to recover the same amount of oil.

Another comparison between corrosion problems in primary and secondary recovery lies in the respective amounts of steel in contact with corrosion agents. For example, in primary operations, casing, tubing, rods, pumps, Christmas trees of producing wells and flowlines and stock tanks are vulnerable points. All of these are necessary to waterflood. However, a great deal more equipment is necessary. Water

plants, pressure pumps, storage tanks, long high pressure injection lines and finally, subsurface injection well equipment are added points for corrosion in waterflood.

It is evident then that the producer of secondary oil places his physical plant under double jeopardy so far as corrosion is concerned.

The comparison of problems between primary and secondary is still not complete. The actual corrosion processes are greatly aggravated in waterflood. For example, it has been well established that oil in a water-oil system has a natural capacity to wet steel preferentially to water. This oil wetting phenomena provides a degree of corrosion protection until the water-oil ratio exceeds some critical value. In many sweet oil well corrosion problems virtually all corrosion is naturally inhibited until the water cut reaches 50 to 70 per cent.

In waterflood, water cuts are inherently high in producing wells. The normal corrosion problem thus is aggravated. More important, however, is the condition prevailing in injection equipment where oil is removed completely and the brine handled in a separate system under high pressure through long injection lines. It is evident that the corrosion problem is magnified.

This condition contributes to the very low success factor of a popular corrosion prevention technique, i.e., chemical inhibition. Organic inhibitors have been excellent investments in many primary producing problems. Effective concentrations have been well defined for most areas of operation. These concentrations range from 25 to 50 ppm or more in difficult cases. This treatment supplements the oils natural wetting tendency. If the assistance by oil is removed and the water handled as a single phase, what is the logical course to follow so far as inhibitor use is concerned? It would appear that a greater concentration is indicated to replace the original help from the oil. Yet, what is most often done in field practice? The concentration is reduced by a large percentage. The basis for this reduction is not technical. It is a matter of economics. Large volumes of water must be handled to produce a barrel of oil and the economic limit controls the amount of inhibitor that can be used.

The inhibitor illustration is used to exemplify the danger of using procedures developed for one environment in altogether different situations, without having a sound technical basis for the action.

A man well respected in corrosion circles said recently in a talk on corrosion fundamentals, that a major problem of the corrosion engineer today is "unlearning" things that have come to be erroneously accepted as fact. His statement is very true in waterflood studies. Most of us as authors have put into print theories and ideas without emphasizing the limits of our work. Most of us as readers accept literature references without considering the limits implied or stated by the author. This is not a reflection upon the publication of theories. If only proved facts were printed there would be little to read. However, caution is warranted by both readers and writers to maintain a proper factual perspective.

Common Criteria found in Literature:

The cause for frustration to the waterflood corrosion engineer is the general lack of understanding of mechanism and the absence of criteria to diagnose conditions. These factors have naturally led to application of criteria developed

for other systems ranging from primary oil production to municipal water supplies. These criteria, so commonly employed, have been just accurate enough to create confusion and not good enough to provide valid answers.

The first and probably the most misused control tool is the so-called corrosion coupon. Usually one or two small pieces of mild steel are attached to a bull plug or facsimilie (sometimes insulated other times, not) and inserted into the stream of water to be checked. The specimens are generally so arranged as to be parallel to fluid flow. They usually protrude only part way into the water stream. After a short exposure of three to six weeks, they are removed, cleaned of scales and corrosion products and the loss of weight due to corrosion measured. This weight loss is thence computed into a corrosion rate called mils per year (MPY) or inches per year (IPY). The mythical mathematical manipulation assumes that all corrosion is uniformly occurring over the entire exposed surface. It does not consider pitting. When a known environment is being studied, the pitting factor can be corrected by experience data. However, in waterfloods there are usually several mechanisms at work and the mathematical values are difficult to interpret. For example, in some instances, less than 1 MPY does not mean corrosion is minor. By contrast, 20 MPY on short term exposures does not signify serious corrosion in other mechanisms.

Let us assume that these two corrosion processes are occurring simultaneously in a single system. Further assume that coupons are used to measure activity. The 20 MPY mechanism will obviously control the coupon data. This mechanism can be partially controlled by chemical inhibitors so subsequent to treatment, coupon exposures will indicate a marked decrease in corrosion. The other and far more dangerous mechanism is not affected by treatment and is not detected by coupon test. Therefore it continues unnoticed until extensive damage to equipment occurs.

The apparent success indicated by the coupon in the first case has resulted in a false sense of security many times. It has led one major consumer of inhibitors to say "by all methods of evaluation we knew, our treatment was a howling success except we couldn't keep leaks from coming in the line". This has been the experience of many waterflooders.

The second corrosion criteria referred to in the literature is iron content, i.e., the change in soluble iron concentration as the water progresses through the system. It is surprising to note the references where one or two ppm iron change is assigned major significance in defining corrosion. This significance is applied even through conditions in the system would render most of the iron present insoluble. For example, a strong oxidizing (O₂) or a strong reducing (H₂S) environment would confuse the iron criterion except in unusual circumstances.

The third factor often used as a measure of corrosion activity is pH. Usually an acid pH is considered corrosive while a neutral or basic pH is thought to be non-corrosive.

Stability index computed according to the Langelier theory, or a modification thereof, is often used as a corrosion guide. Usually a negative index indicates corrosion while a positive index indicates corrosion while a positive index denotes scale formation. In a sense, these data are good; however, there is one point frequently overlooked: That is the stability index denotes tendency only and in no way reflects capacity. If there is a tendency for water to lay down scale but not capacity, then the deposition will have little economic significance. The same may be said of corrosion.

The salt content is also used as a corrosion index. Many authors say that brines are more corrosive than fresh waters. It will be shown later that factors other than salinity often control the corrosion rate.

Identification of corrosive gases also is used to assess corrosion. For example, oxygen, carbon dioxide, and hydrogen sulfide are looked upon as causative agents. However, rarely do they reflect directly the degree of corrosion.

There are many other so-called criteria referred to in the literature. For the moment let us see how those listed

did or did not define corrosion in actual field cases.

CASE I

This flood is located in the western part of the United States and handles a subsurface brine of approximately 30,000 ppm total solids. The water is handled through a closed system (gas seals) filtered through a diatomaceous earth filter and injected under pressure. The pH is neutral to alkaline and the calculated stability index is normal, ranging from slightly negative to positive with temperature variation. Oxygen and hydrogen sulfide could not be detected by either field or laboratory tests. The iron content was uniform at 3.8 to 4.0 ppm, throughout the system. Insulated coupons revealed less than 1 MPY upon two weeks exposure. Sulfate reducing bacteria were present and active.

With these data, would you prognose a corrosive or non-corrosive system?

Actually, it was very corrosive. The first failure occurred in three months. At the time of this failure, new one foot inspection test spools were installed in the line and inhibitor injection started. The leaks continued until they were occurring throughout the system. Iron contents, coupon exposures and test spool inspections were continued. According to the superficial examination of these data, no corrosion should have occurred. The spools, when inspected by holding up to the sun, revealed no apparent pitting and a good inhibitor film was reported. However, upon closer study, i.e., cleaning the spools with solvent and wire brushing them, pits to 50% penetration were observed in new pipe that had been exposed only to water containing a high concentration of inhibitor.

It is probable that more corrosion observers are trapped by incomplete inspection of pipe samples than for any other cause. The corrosion mechanism in this case was such that the pits were perfectly covered with corrosion products so that they were not discernable upon casual examination. If one thing can be learned from this illustration it should be that the first casual look at pipe samples does not tell the whole story.

CASE II

This flood is in Oklahoma. A closed system, using return brine and fresh alluvial subsurface water is employed. The fresh water contained less than 1,000 ppm total solids and had a pH of approximately 6.7. The stability index ranged from slightly negative to positive as the temperature changed from 41 F to 80 F. There was no hydrogen sulfide or oxygen as free gas. However, there was evidence of air entry when the water wells were pulled heavily. Scales deposited in the fresh water system released hydrogen sulfide upon acidization. Sulfate reducing bacteria were present. There was no correlation of iron content. The variations with time were greater than differences noted as the water progressed through the system. Over 100 coupons were exposed. The corrosion rate was indicated to be less than 1 MPY. The short term exposures revealed no pitting.

The brine or return water used in the system contained 180,000 ppm total solids at a pH of 6.5. There was no hydrogen sulfide or oxygen. Sulfate reducing bacteria were present but less active than in the fresh water system. The stability index was moderately negative. Again, there was no correlation with iron content. Coupons indicated a high corrosion rate (greater than 30 MPY).

With these rather complete data, so far as conventional criteria are concerned, what would you anticipate corrosion-wise? Would the brine be more corrosive than the fresh water? Would inhibitor injection be of value or would corrosion be a problem at all?

This flood is spoken of in the past tense now. Its history is well known. The fresh water was very corrosive. The first failure occurred at twelve months and at eighteen months, several miles of 16" line were abandoned and left in place.

It had no salvage value. After the first few leaks, an inhibitor program was started. It had little or no effect even though the cost exceeded \$115 per day for materials alone.

The brine proved to be moderately corrosive but the majority of leaks were limited to fittings that were subjected to vibration. The leak frequency remained relatively constant and did not get out of hand.

The mixture gave little trouble; however, this injection system was cement lined and all trouble was confined to fittings and collars. The inhibitor apparently had little effect in this regard.

CASE III

This project is in Illinois. It utilized river water and produced return brine. The two waters were mixed in a surface pond and the effluent treated with lime, alum and chlorine. In early life, the mixture contained 13,000 ppm total solids at a controlled pH of 8-9. The oxygen content was high but there was no hydrogen sulfide. Iron content was negligible throughout the system. The stability index was slightly negative. Coupons exposed for two to three weeks indicated 15-30 MPY. Longer exposures revealed a marked reduction in corrosion rate. After one year's operation a section of pipe removed from the system was cleaned and inspected. Pits were measured to a depth of 20% of the wall thickness under tubercle deposits.

After this inspection and with the data given above, what would you recommend? Certainly there is every indication of economic attack. History has proved remedial dollars would have been wasted. No serious trouble was encountered as long as this system was used. The why of this success is a major subject in itself. Let it suffice to say that the "full treatment" performed in textbook style. The short term high corrosion rate indicated by both coupons and pipe sections was to be expected even if the treating program worked perfectly. However, in this type system, the danger lies in not being able to control the leveling off of rate after a short period. Actually, the close technical control necessary is not usually available in the oil field. As a result, case history failures are numerous.

CASE IV

Case III was reported as being unusual in that it successfully employed the "full treatment" plan. Case IV illustrates the normal condition. The project was in the Tri-State area and had almost identical physical factors and chemical treatment to Case III. It was open, fresh water and brine were used as source water, and a pH of 8.7-9 was maintained. Coupon rates were high on short exposure. However, unlike Case III, long term coupon rates were even higher. Also, unlike Case III, the operation proved troublesome. Corrosion was severe.

Why is it that two almost identical systems would perform so differently. The key lies in on-location, day-to-day technical control. Most field operators do not sufficient equipment or technical background to maintain a delicate chemical balance in a complicated system. For this reason, failures in the so-called full treatment systems are more numerous than the successes.

CASE V

Case V is a project in Illinois. A closed system using subsurface water was employed. The deep source well yielded water containing 130,000 ppm total solids. The pH was 6.2 with an iron content ranging from 20-30 ppm. The stability index was very negative ranging from -0.99 at 41 F to -0.56 at 86 F. The water was naturally carbonated with dissolved carbon dioxide. Conventional coupons revealed less than 1 MPY on short and long term exposures.

With these data in hand an engineer could easily be justified in predicting severe attack at least if he were to follow

normal rules set forth in the literature. Yet this system has operated for four years with no penetrations. Very careful checks, including subsurface caliper surveys, have been made periodically.

A great deal of emphasis has been placed on the errors of interpretation in applying criteria of corrosion in waterflood. This emphasis has been supported by case histories. In some spots rather strong statements have been made concerning literature reference. I will undoubtedly be severely criticized by many for dogmatic remarks; however, it is felt that these or similar remarks must be made. Otherwise the waterflooder who of necessity must rely on reference articles will be lulled into a false sense of security because of momentary periods of apparent corrosion control. Likewise, it is quite probable that many technical men can be trapped and placed in embarrassing positions both personally and professionally by some of the claims associated with chemical sales.

Sometimes dogmatic statements are required to offset equivalent dogmatism on the other side. These latter remarks or mythical success stories are usually the ones spread throughout the industry.

So far, this lecture has emphasized the negative side. If it were to stop here, it would have limited value although one might avoid some serious pitfalls in engineering studies. However, to end the lecture in a more positive vein, I want to suggest a method of engineering diagnosis and corrosion definition and control.

First, the engineer must realize the limitations imposed on him by the general lack of well supported scientific knowledge. His tools are limited not only in quality but in number. There are only a few he has to work with from a practical standpoint. Some of them are the very ones most ridiculed in this presentation so far. The difference is the manner in which they are used.

For example, good chemical analysis of the things worked with, the water, scales, deposits, backflow filter samples, and swab samples, comprise a basic starting point. The engineer must know that the tools do not yield absolute measurements. They simply denote trends and he must play the odds. In the water analysis, it is essential that all material in the "sample bottle" precipitated as well as dissolved, be treated as important. From good analytical data can be computed stability index, pH, iron and gas content. Yet all of these accurately determined represent little when used alone. Something else must be added.

The corrosion coupon with all of its limitations is an important tool. However, better data can be obtained if the exposed steel is placed in the system so as to pick up the type of attack most likely to occur. Special, more troublesome and costly installations will pay their way. Even then do not be lulled into false security by no corrosion on coupons. They represent only a part of the engineering analysis.

Corrosion test spools or inspection stations are an important supplement to coupon tests. Caution must be used in assessing significance to the test spool examination. Consider carefully the many things that influence visual attack.

Sulfate reducing bacteria are important to waterflood corrosion mechanisms. Their activity should be measured but their mere presence is no cause for alarm. Usually, attempts to kill all bacteria are fruitless and expensive.

The millipore filtration test is one of the most important diagnostic tools yet developed. Its value does not lie in an absolute measure of water quality. Rather, it provides a method of figuratively tying together data from the other tools such that a reasonably accurate picture can be developed. It is a precise way of measuring suspended solids as those solids exist under in-line conditions.

The engineering tools have been described. One step remains: That is the method of their use and the presentation of the information derived. A single water analysis, millipore run, bacteria activity or any other measurement has little value in itself. The basic tools must be used in a system at each point where the water changes. For example,

at each source water, after treatment, after filters, at injection wells, etc. The amount of work necessary to define conditions in a flood is dependent upon complexity of the water system and not the size. The complexity, in turn, is dependent upon the number of points of water change described above. After quantity measurements have been made, they can be plotted or tabulated so that criteria of water quality is related to the complexity points as the water is traced through the system from its source to its injection. After this is done, one can look at the overall operation from one piece of paper. Subtle trends otherwise undetected take on significance. If water at an injection point is of poor quality, the cause can be traced to its origin. When this is known, it is much simpler to recommend remedial action.

In conclusion, I would like to summarize the important factors of Corrosion in Waterflood:

1. Corrosion is important. The operator places his equipment in double jeopardy. The amount of steel exposed to water is greater and the corrosion problem is aggravated.
2. The causes of corrosion are not clearly defined. New and unexplored mechanisms of attack are

being experienced.

3. The conventional criteria of corrosion diagnosis and control are often misleading. Many literature references will trap the uninitiated.
4. Some corrosion remedial measures commonly used in primary production find little use in waterflood.
5. The basic tools of the engineer must be judiciously used. The engineer must realize that no tool provides an absolute measure of water quality. He must play the trends to get the odds on the side of the operator.
6. The presentation of data is important. All quantitative data resolved to a single sheet of paper showing the water characteristics as they are traced from source to injection is an effective presentation.
7. A water system is dynamic and ever changing. Procedures of control must be altered to conform to new operating conditions.
8. The periodic review of a water system is the key to minimum operating problems. It will allow maximum oil to be produced at minimum cost.