EFFECTIVE OILWELL CORROSION MONITORING USING DISSOLVED MANGANESE IN CONJUNCTION WITH MODERN INSTRUMENTATION AND TECHNIQUES

Rick McCurdy
BJ Chemical Services

ABSTRACT

A considerable amount of money is spent annually on corrosion inhibition programs utilized in the production of crude and natural gas. Consequently, considerable time and effort is placed on monitoring these programs and on searching for the most cost effective, system representative monitoring tool. For many years, dissolved iron was used for corrosion monitoring, though we now realize the many errors of this process, particularly in “sour”, or hydrogen sulfide bearing, production environments. Dissolved manganese has been discussed as a more effective monitoring tool, though early analytical techniques proved this method to be cumbersome with varying degrees of accuracy. This paper revisits the use of dissolved manganese as a corrosion inhibitor monitoring tool with the application of modern techniques and instrumentation.

BACKGROUND

In the beginning of commercial oil production, little concern was placed on how the produced oil interacted with the metals used in the production, transportation and refining process, as many of the early wells were predominantly composed of oil only. As wells aged, they began to produce a salty brine, which contained acid gases such as carbon dioxide (CO_2) and occasionally hydrogen sulfide (H_2S). These brines were often found to be corrosive to the metals they come in contact with and these discoveries often came as the result of failures in the metal pieces themselves. It became imperative that the industry develop an accurate way of monitoring the corrosive nature of these brines and the effectiveness of inhibition programs designed to protect the oil country tubulars from degradation by the produced fluids.

Initially, a focus was placed on testing for the amount of dissolved iron present in the produced brine. This was to be used as an indicator of how much steel was being lost due to corrosion. This monitoring process was desirable as samples were fairly easy to acquire and testing capabilities were improved over the years to where fairly accurate results could be obtained form instruments used in the field. In “sweet”, or non-hydrogen sulfide-bearing reservoirs, dissolved iron or “iron counts” has been used as a fairly successful monitoring tool for quite sometime. Unfortunately, many of the producing oilfields in the United States today are “sour”, meaning produced fluids from these fields contain hydrogen sulfide. In brines containing hydrogen sulfide, dissolved iron very readily reacts with this acid gas to form iron sulfide (FeS) solids. These solids often fall to the bottom of vessels or lines, or stick to pipe walls after having become coated with produced oil. Because of this, the dissolved iron content of sour brines is usually extremely low because of the fact that the iron has already precipitated or it can be extremely high when a large amount of sloughed iron sulfide is caught during the sampling process. Either way is not a true reflection of the corrosive process of the system being sampled.

To improve the oil industry’s ability to determine the corrosive nature of a fluid or to monitor the corrosive rate of an inhibited system, particularly in sour systems, the use of weight-loss coupons were adopted as a preferred method. In this process, pre-weighed metal specimens similar in composition to the metal in the system being monitored are inserted into the system for a period of time. These specimens are generally located in an area that allows for constant contact with the corrosive fluids. Once the specimens are removed from the system and cleaned and re-weighed, calculations can be made that take into effect the type of metal being used, exposed surface area, time exposed and weight-loss to determine the corrosion rate during the exposed time. This rate is often reported in mils per year (mpy) or pounds per square feet per year (lb/ft^2).

One of the advantages of corrosion weight-loss coupons is that they tend to work equally well whether used in sweet or sour systems. However, a downside to using this type of monitoring tool is that they are more labor intensive to use and change-out as compared to simply catching a brine sample for a dissolved iron analysis. Many operators require that a “Lock Out / Tag Out (LO/TO)” procedure be utilized when changing corrosion coupons. Simply stated, LO/TO requires that potential pressure sources up and downstream from the coupon location must be isolated by closing valves and locking these valves in the closed position. Potential energy sources, such as the electric motor on a pump jack, must also be disabled and locked in such a way so as to prevent their energization during the coupon removal and installation process. While critical for protecting the employee involved in the coupon changing process, LO/TO can easily require one hour or more be allotted for the amount of time needed to change out a single coupon location.

An additional hindrance associated with corrosion coupons reflects on the fact that the coupon is only an indication of the corrosion rate where it is installed in the system. Coupons installed in the wellhead of a producing oil or gas well give an accurate representation of the corrosion rate at the wellhead. However, coupons do not reflect the corrosion rate experienced by the metal goods located further downhole where increases in temperature and pressure generally contribute to a higher corrosion rate. A last drawback to weight-loss corrosion coupons is the amount of time that they must be installed in the system to give an accurate depiction of the system’s corrosion rate. While varying from system to system, or application, most coupons are installed in the corrosive environment for 1-3 months.

To eliminate the hindrance of waiting the required amount of time necessary for a corrosion coupon to accurately reflect the system’s corrosive status, many Operators use some form of electrical probe such as ER (electrical resistance), LPR (linear polarization resistance) and PAIR™. These probes can be mounted in a system permanently or in a retractable fashion that facilitates frequent movement from one location to another. The main benefits of these probes are the ability to instantaneously read the corrosion rate of a measured fluid at any time. However, as with coupons, the probe only measures the corrosion rate of the location where it is installed and does not reflect other areas of the system that may have a higher corrosion rate. Probes are also susceptible to fouling from solids, such as iron sulfide in sour systems that bridge the electrodes and render their information useless. Finally, any type of corrosion monitoring probe and the equipment required to gather and calculate the data can increase the cost associated with corrosion monitoring a hundred-fold over the cost of dissolved iron determinations or weight-loss corrosion coupons.

Considering the pros and cons of all of the previously discussed monitoring techniques, the Petroleum Industry had a need for a monitoring tool that possessed the following qualifications:

- Accurate in both sweet and sour systems
- Representative of total system corrosion rate
- Inexpensive
- Not time-extensive

DISCUSSION

Manganese is found in all carbon steel alloys (with the exception of grade H-11) at concentrations ranging from 0.3% to 1.9%. Manganese is critical to iron and steel development due to it’s deoxidizing and alloying properties. In fact, steel manufacturing accounts for the vast majority of manganese used in commercial operations. Manganese behaves much the same way as iron during the corrosion of carbon steel in oilfield brines. Manganese gives up electrons at the anode and manganese ions are carried with the electrolyte (brine). Manganese, however, does have one very important difference with iron. In “sour”, or hydrogen sulfide bearing, brines, manganese, unlike iron, will not usually precipitate until it is present in large quantities, which are seldom seen in oil and gas production.

In the early days of using dissolved iron as a monitoring tool, a baseline of 20 mg/L was established to indicate when a steel system was being adequately protected from corrosion. Since manganese is found in most steel at roughly a 1% concentration and iron is present at 95-98%, we can infer that a well inhibited oilfield system would roughly contain less than 0.2 mg/L of dissolved manganese. If this is the case, accurate monitoring of manganese in treated oilfield systems requires that we have analytical methods that allow for precise determinations in the parts per billion (ppb) range. Methods available for determining manganese are colorimetric spectroscopy, atomic absorption spectroscopy and atomic emission spectroscopy.

Colorimetric Spectroscopy – In colorimetric spectroscopy, manganese present in the fluid sample is reacted with an indicator which produces a color change that is most pronounced at a given wavelength. In a popular, low range procedure, the water sample is treated with ascorbic acid to reduce any oxidized manganese to Mn^{++}. An alkaline – cyanide reagent is then used on the sample to eliminate interference from other metals that may be present in the sample. The sample is then treated with 1-(2-pyridylazo)-2-napthol (PAN) which reacts with manganese to produce an orange colored complex. This procedure is used when the expected concentration of manganese is between 0 and 0.7 mg/L. One of the advantages of this procedure is that it is designed to be run in either field or lab settings. (Note: if the samples are to be taken to the laboratory for analysis, they should be prepared by acidizing with nitric or hydrochloric acid to reduce the pH below 2). Disadvantages of this procedure are low-end accuracy and repeatability, and the inherent hazards and costs associated with disposal of the samples once they have been treated with the alkaline-cyanide reagent and become a "D" listed hazardous waste. The samples must be treated as a hazardous substance as the treated samples will release small quantities of cyanide gas if allowed to come in contact with an acid.

Atomic Absorption Spectroscopy – In atomic absorption spectroscopy (AAS), the sample is converted into a mist and passed through a burner where a light is focused at a specific wavelength for the element being analyzed. The amount of light absorbed in the flame can be compared to a calibration curve and the concentration of the desired atom determined. In the case of manganese, a popular wavelength is 279.5 nanometers (nm) which produces a linear absorption range from 0.02 ppm to 5.0 ppm. To distinguish a main difference between atomic absorption and atomic emission spectroscopy, it should be noted that the flame used in AAS is designed to aid in desolvating and atomizing the sample, and is not intended to excite the atom. Typically, the flame used in AAS is created with either a mixture of acetylene and air, acetylene and oxygen or nitrous oxide and acetylene and produces a temperature range of 2,100-2,800°C. AAS will allow for fairly accurate low-end determinations for manganese, but has one main drawback since most instruments can generally only analyze for one atom at a time. To analyze for other atoms in the same sample, a lamp designated with a wavelength for that particular atom must be installed in place of the previously used lamp. This becomes a time-consuming process when the concentration of several additional elements are desired along with manganese.

Atomic Emission Spectroscopy - In atomic emission spectroscopy (AES), a liquid sample is misted (nebulized) into a plasma energy source that is defined as being an equal mixture of Argon atoms, Argon ions and Argon electrons. The two most common forms of AES are Direct Current Plasma (DCP) and Inductively Coupled Plasma (ICP) spectroscopy. In both types of AES, the temperatures produced in the excitation area of the plasma are of a sufficient nature to cause the atoms in the water sample to become "excited" for a brief instant. In plasma instruments, the accuracy and low end detection capabilities are a direct reflection of the amount of energy available in the excitation area of the plasma. The temperature of the excitation area is a direct expression of this energy. In DCP's, this temperature is around 5,000°C and ICP's provide a greater energy potential with an excitation temperature of 6,000°C.

An atom is considered excited when its electrons temporarily "jump" outward to the next available orbital. Once the excited atoms move out of the excitation area of the plasma, their electrons return to their normal orbitals (or normal states). During this process, ultraviolet radiation (light) is released at wavelengths specific to each atom. By comparing the light emitted at a specific wavelength against a calibration curve for that wavelength, accurate determinations of the concentration of specific atoms can be made.

In older simultaneous instruments, this is accomplished by a lens which focuses this emitted light onto a finally ground grating where the light is then separated into various wavelengths and directed towards numerous photomultipier tube detectors. In newer instruments, a megapixel charge coupled device (CCD) array takes the place of the photomultipier tubes. In a sequential instrument, two servos adjust the grating so that a single specific wavelength is directed to a single photomultiplier tube or analysis of a given element. As soon as the analysis of one element is complete, the servos adjust the grating to the next desired wavelength.

A common wavelength used in detecting manganese in oilfield brines is 257.610 nm. This wavelength has a lower detection limit of 0.003 mg/L (approximately 3 ppb) and has a linear dynamic range from 0.03 to 100 mg/L. This wavelength sees very little interference from other elements with the exception of magnesium (Mg). For every 1,000 mg/L of magnesium in a water sample, a false reading of 0.2 mg/L of manganese will be noted. With this wavelength and a simultaneous instrument or a sequential instrument that is running a method set up to only look for manganese, 60-120 samples per hour can accurately be analyzed. This capability and detection limits make AES clearly the fastest and most accurate method to determine dissolved manganese concentrations; however, the largest drawback to AES is the cost of the instruments themselves as they are very close to an order of magnitude more expensive that AAS and 2 orders of magnitude more expensive than colorimetric instruments.

Table 1 contains a brief summation of the pros and cons of the various methods available for the determination of dissolved manganese.

While dissolved manganese has proven to be very reliable as a monitoring tool, many operators still require some other form of monitoring, whether it is dissolved iron, weight-loss coupons or electrical probes. These other monitoring tools often mirror the data being provided from dissolved manganese. Figure 1 illustrates one such location where dissolved iron, dissolved manganese and corrosion weight-loss coupons were used over a 6-month period. In the graph, dissolved iron is represented by the dotted line and is measured against the left Y-axis. The solid line represents dissolved manganese and the calculated corrosion rates from the weight-loss coupons are shown as solid diamonds with both being measured against the right Y-axis. You will note that the two Y-axes differ by a factor of 100. This is a reflection of the approximate1:100 ratio between manganese and iron in oilfield tubing and rods. If no precipitation of iron or manganese is occurring in a system, we would expect their concentration plots to fall fairly close together when plotted at a 1:100 ratio. When one element (in this case iron) consistently falls below the other, this is an indication that that element is precipitating in the system and is not being reflected accurately in the sampled fluid.

In the example shown in Figure 1, the well in question had a fluctuating fluid level during the first two months and problems were seen in getting the recommended corrosion inhibitor treatment fully circulated in the well. These problems are enumerated by the dissolved manganese values that average 0.7 mg/L for this period and the coupon-indicated corrosion rate of 2.1 mpy. Please note that with one exception, the dissolved iron concentration rarely rose above 20 mg/L. During September, wet weather resulted in the well missing several scheduled corrosion inhibitor batch treatments. Again, the manganese reading of 1.3 mg/L and the calculated coupon corrosion rate of 3.2 mpy reflect this for this period. During the last portion of this data set, an adequate fluid level was maintained in the well and weather permitted all of the scheduled inhibitor batch treatments. This allowed the manganese concentration to be reduced to an average of 0.22 mg/L and the last two recorded coupon corrosion rates to be 0.89 and 0.52 mpy, respectively.

CONCLUSIONS

- Dissolved manganese can be a very effective monitoring tool for monitoring corrosion in oil and gas systems.
- Because of the small amount of fluid required for testing and the small amount of time necessary to collect a sample, many manganese analyses can be performed for the amount of money and time invested in one corrosion weight-loss coupon.
- Based on the most accurate and fastest determinations, the best methods for dissolved manganese are:

  1) Inductively Coupled Plasma Spectroscopy
  2) Direct Current Plasma Spectroscopy
  3) Atomic Absorption Spectroscopy
  4) Colorimetric Spectroscopy

REFERENCES

Eddie C. French, Richard L. Martin, James A. Daugherty, “Corrosion and It’s Inhibition in Oil and Gas Wells”, Reviews on Corrosion Inhibitor Science and Technology, Edited by A. Ramine and P. Labine, NACE, 1963

Charles C. Patton, 1995, *Applied Water Technology*, 2nd Edition, Campbell Petroleum Series.

Capitol Camco, “Alloy % Composition – Carbon Steel”

“Linear Polarization Resistance (LPR) Monitoring”, Metal Samples Corrosion Monitoring Systems, 06 Jan 2006.

John R. Dean (Editor), David J. Ando (Editor), *Atomic Absorption and Plasma Spectroscopy, 2nd Edition,* John Wiley and Sons, April 29, 1997.

Lamotte Company, Individual Test Kits – Manganese, Nov 2005.

Managanese, LR, PAN Method, Method 8149, HACH DR/2010 Spectrophotometer Handbook

NACE Standard RP-0775-99, *Preparation, Installation, Analysis and Removal of Corrosion Coupons in Oilfield Operations,* Revised 1999-06-25, © 1999 NACE International

ACKNOWLEDGEMENTS

The author would like to thank BJ Services Company for the permission and the time to prepare and submit this paper.

Table 1
Comparison of Discussed Oil and Gas Corrosion Monitoring Methods

Dissolved Iron
- *Pros*
  - Easy to sample
  - Relatively inexpensive
  - Long history in Industry
  - Can be field determined
- *Cons*
  - Inaccurate in sour systems

Weight-loss Coupons
- *Pros*
  - Industry accepted
  - Ability to match metallurgy
  - Direct corrosion rate measurement
  - Effective in sweet or sour systems
- *Cons*
  - Only measures corrosion rate of installed location
  - Only provides an average rate over time in system

Electrical Probes
- *Pros*
  - Instant corrosion rate readings
  - Industry accepted
  - Corrosion rates can be remotely sampled and recorded
- *Cons*
  - Only measure corrosion rate at installed location
  - Susceptible to electrode fouling in sour systems
  - More expensive than dissolved iron or coupons

Dissolved Manganese
- *Pros*
  - Easy to sample
  - Can be field determined, but more accurate in lab
  - Reflection of total system corrosion rate
  - No interference from H_2S in sour systems
- *Cons*
  - Not widely accepted in the oil and gas industry
  - Cost of plasma instruments

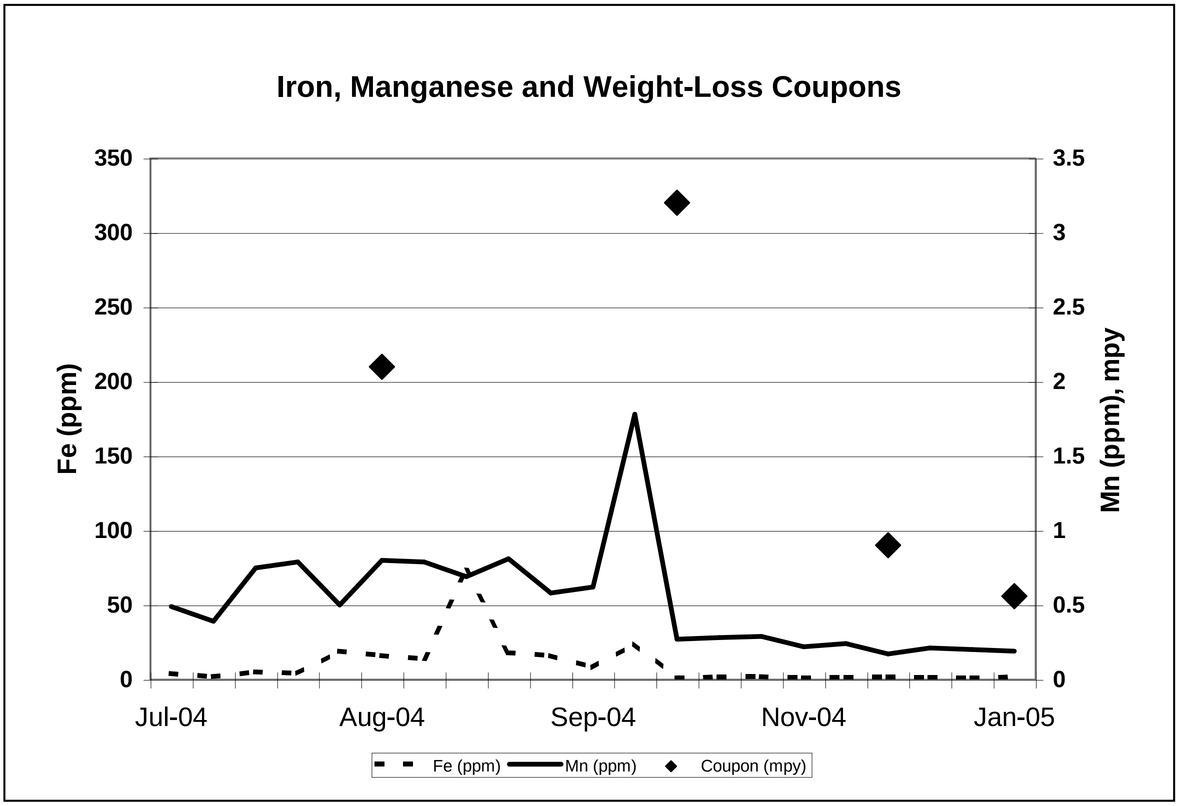
Iron, Manganese and Weight-Loss Coupons
Fe (ppm)
350
300
250
200
150
100
50
0
Mn (ppm), mpy
3.5
3
2.5
2
1.5
1
0.5
0
Jul-04
Aug-04
Sep-04
Nov-04
Jan-05
Fe (ppm)
Mn (ppm)
Coupon (mpy)

Figure 1