

## **APPLICATION OF MULTIELECTRODE ARRAY SENSOR TO STUDY DEWPOINT CORROSION IN HIGH PRESSURE NATURAL GAS PIPELINE ENVIRONMENTS**

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### **ABSTRACT**

Internal corrosion of pipelines occurs where water or other corrosive electrolyte accumulates. This is the basis for Internal Corrosion Direct Assessment (ICDA). Although ICDA focuses on nominally dry gas with episodes of water upset, the well accepted criteria for dry gas (e.g., water less than 112 mg/m<sup>3</sup> or 7 pounds per million standard cubic feet, MMSCF) may be significantly influenced by the presence of bacterial biofilms and hygroscopic solids, such as iron oxide corrosion products and some salts. Therefore, understanding the changes in dew point induced by the presence of these compounds is necessary to better quantify gas quality requirements. The Multielectrode Array Sensor (MAS) probe was used to study the effect of biofilms and corrosion products on corrosion in high pressure gas mixtures. It was found that: (i) the MAS probe is sensitive in detecting localized corrosion in wet gas streams at pipeline pressures; (ii) the corrosion rate is sensitive to gas composition/quality; (iii) the presence of biofilm and corrosion products affected the dew point but the current water content specifications for gas are sufficiently conservative that this decrease in dew point is not a concern; and (iv) the corrosion under the biofilm once initiated at high humidity levels did not decrease even upon decrease of humidity to levels lower than needed to initiate corrosion.

Keywords: Sensor, corrosion, pipeline, carbon dioxide, hydrogen sulfide, biofilm, MIC

## INTRODUCTION

Internal corrosion of pipelines occurs in the presence of water and other constituents, such as carbon dioxide, hydrogen sulfide, and oxygen. Therefore, it is important to determine whether water can accumulate at a given location. This is the conceptual approach used by the dry gas Internal Corrosion Direct Assessment (ICDA). Once potential internal corrosion sites are located, the issues to be addressed include the extent of corrosion, the anticipated rate of corrosion to determine reassessment interval, and any confirmatory assessment that is needed. These issues can be addressed by a combination of corrosion monitoring, inspection, and corrosion rate modeling. The corrosion rates would in part depend on the gas quality i.e. the corrosive constituents in the gas. The interrelationship between these approaches is illustrated in Figure 1.

The ICDA methodology, as applied to nominally dry gas systems, assumes that the water content of the gas is less than the typical tariff limit of 112 mg/m<sup>3</sup> (7 lb/MMSCF). This is considered a reasonably conservative limit, except in cold climates where the water content is set to a lower limit (e.g., 80 mg/m<sup>3</sup> or 5 lb/MMSCF). The dew point associated with various water contents in gas was reviewed in a previous report<sup>1</sup>. The calculated dew point depends slightly on the model used and the composition of the gas mixture<sup>1</sup>, but spans a relatively small range of less than 6°C. For example, for 112 mg/m<sup>3</sup> (7 lb/MMSCF) gas at 3.45 MPa (500 psi) pressure, the dew point ranges from about –8.3°C (17°F) to about –2.3°C (27°F). The relative humidity (RH) of the gas can be calculated as the ratio of the actual water content to the saturation water content. Corrosion occurs when the RH reaches a critical RH at which water condensation occurs. Since the saturation water content for gas at 25°C (77°F) and 3.45 MPa (500 psi) is about 45 lb/MMSCF, the RH corresponding to 7 lb/MMSCF water gas at 25°C (77° F) and 3.45 MPa pressure is 15 percent. For atmospheric corrosion, the rule of thumb is that the critical RH is about 70 percent, suggesting that 7 Lb/MMSCF is a conservative limit from a corrosion perspective. However, it is known that atmospheric corrosion occurs at RH values significantly below 70 percent if there are hygroscopic salts present that can retain water at lower RH<sup>2,3</sup>.

The study presented in this paper evaluates the effect of biofilm and corrosion products on critical RH under natural gas pipeline conditions. A method was devised to monitor corrosion in moist gas mixtures at a pressure of 500 psi. The corrosion due to condensed moisture film was monitored while simultaneously monitoring the RH of the gas phase.

Several methods to measure pipeline internal corrosion rate have been used, including weight-loss coupons, linear polarization resistance probes, electrochemical impedance spectroscopic (EIS) method, electrochemical noise method (EN), and Field Signature Method (FSM) probe. Coupons can be used to measure corrosion under a condensed film, but are not suitable for real-time monitoring and are not sufficiently sensitive. Electrochemical impedance spectroscopy (EIS) can be used to measure changes in corrosion behavior as well as the impedance between electrodes due to moisture condensation. However, the derivation of corrosion rate from impedance spectra can be complicated in many cases involving complex film or corrosion product formation. Electrochemical noise (EN) avoids perturbing the system and the probes may be designed in a coplanar fashion to monitor moisture condensation. However, EN technique, as it is generally employed, is not sensitive to localized corrosion. Furthermore, data interpretation is not simple. The FSM method is non-intrusive

and measures the corrosion of the pipe wall itself, unlike the other methods which measure the corrosion behavior of a steel probe simulating the pipe. However, it is not a tool for monitoring the changes in dew point corrosion dynamically because it involves measuring in pipe wall resistance, which changes gradually over a period of time. The Multielectrode Array Sensor was chosen for this study because it can provide real time measurement of changes in moisture condensation and corrosion and can be designed to operate under high pressures.

## EXPERIMENTAL METHODS

### Construction of Multielectrode Probes

The principles and operation of the MAS probe have been described previously<sup>2-4</sup>. A bundle of fourteen 1-mm diameter metal electrodes of 1018 steel and two platinum electrodes, all insulated from each other, but connected through a network of resistors was fabricated. The probes were potted in epoxy and encased in a stainless steel tube for pressure resistance. It is typically difficult to know *a priori* which area will be anodic and which area will be cathodic. In practice, the differences in microstructures among even nominally identical metal electrodes enable some electrodes to serve predominantly as anodes and others predominantly as cathodes. The smaller the individual electrodes, the more representative they are of the anodic and cathodic sites on the metal. But, if they are too small they may not represent the metallurgy of the actual corroding metal. A resistor was introduced between each steel electrode and a common junction. Electrons from a more corroding electrode (or anodic half-cell) are transported through the resistor connected to the electrode to produce a potential drop. This potential drop was measured with a multi-channel, high-impedance, nano-voltmeter and used to derive the currents. Values of the resistors were selected such that the highest potential drop across the resistors is low enough not to affect the electrochemical processes at the electrode, yet the potentials across the majority resistors were high enough to be reliably measured with the voltage-measuring system. The platinum electrodes enable monitoring the conductivity changes as a result of condensation. It must be noted that the measurement of conductivity on the Pt electrode is only a relative indication of conductivity changes since the cell constant was not calculated. The cell constant is expected to change as the electrolyte layer thickness changes with humidity. Therefore, the measurement of impedance between the platinum electrodes is converted to a “conductivity” on an arbitrary scale. An advantage of the MAS probe is that even in systems where a conductive corrosion product can form between electrodes, shorting two or more electrodes, the measurement resistors can be chosen with a smaller value than that of the corrosion product.

Two MAS probes were first hydrotested in an autoclave at 10.34 MPa (1500 psi) pressure to ensure that they were pressure-tight at the anticipated test pressure of 3.45 MPa (500 psi). They were then immersed in aqueous solution of 1M NaCl + 0.001M NaHCO<sub>3</sub> at ambient temperature and pressure in a glass cell. The cell was then purged with different gases to test the response of the MAS probe system to the varying corrosive conditions. The gas compositions chosen were: 1% CO<sub>2</sub> + Balance N<sub>2</sub> and 1%CO<sub>2</sub> +99-ppm H<sub>2</sub>S+ 0.1% O<sub>2</sub>, and 100% H<sub>2</sub>S. The last mixture was chosen to purposely introduce conductive iron sulfide corrosion products across the electrode surface and determine the effect of electrode shorting.

Following the ambient-pressure tests, the two previously corrosion tested probes were inserted into an inverted type 316L stainless steel test autoclave for the high pressure tests (Figure 5). A high-pressure, relative humidity sensor was also introduced into the autoclave. The autoclave was fitted with ports for entry and exit of gases and for measuring temperature. The humidity of the test gases was varied by mixing dry and wet gas streams into the test autoclave. A part of the gas stream was passed at 500 psi into a type 316L SS autoclave holding deionized water. This wet gas stream was then flowed through the test autoclave. Simultaneously, a dry gas stream was purged directly into the test autoclave. Separate valves on the dry and wet gas streams were used to control their respective

flow rates to control the RH in the test autoclave. The gas then exited the test autoclave through a valve, which was used to reduce the pressure to ambient, and a flow meter to a gas scrubber.

## Corrosion Tests

In the initial series of tests, N<sub>2</sub> was used followed by a gas mixture of N<sub>2</sub> + 1% CO<sub>2</sub> + 0.1% O<sub>2</sub> + 0.01% H<sub>2</sub>S. The latter mixture is well known to cause localized corrosion of carbon steel in slightly alkaline solution. The steel MAS probes were first exposed to either a corrosive solution or a biofilm-forming solution. For the former, the probes were exposed to the 1M NaCl + 0.004M NaHCO<sub>3</sub> solution with 100% H<sub>2</sub>S gas. For the latter, a liquid solution was first inoculated with sulfate-reducing bacteria (SRB) and *Vibrio Natriegen* (slime former) microbes. Once the bacteria reached the log phase growth, the solution was used to grow the bio-film on a MAS probe. A shrinkable Teflon sheath was fitted around the end of the probe forming a small well. The biofilm-forming solution was then placed in this well and corrosion allowed to proceed. Culturing the solution was performed to verify the presence of sulfate reducing bacteria (SRB). The Teflon sheath was then removed, the bulk of the biofilm-forming solution removed, and the probe inserted into an inverted autoclave such that the end of the probe remained facing up. An end-on view of the two probes with biofilm and corrosion products is shown in Figure 3.

To dry these biofilms on the probes at the end of the corrosion cycle, dry gas was purged through the autoclave rapidly. The currents measured from the probe were divided by the nominal area of each probe element and converted to corrosion rate. This method results in two sources of errors: (i) the actual area of corrosion may be smaller than the nominal area and thus would result in an underestimation of penetration rate and (ii) cathodic currents on an electrode are not considered and therefore the calculated corrosion rate may again be an underestimation.

## RESULTS

The effect of changing gas composition on corrosion rate of MAS probe is shown in Figure 4. It can be seen that the gas with only CO<sub>2</sub> showed a high corrosion rate even at ambient pressure and temperature. Visual examination of the end of the electrode confirmed that the penetration was consistent with the measured corrosion rate. The de Waard-Milliams equation<sup>5</sup> would predict a corrosion rate of only 0.05 mm/y for these conditions. However, it must be noted that the corrosion rates calculated by de Waard and Milliams equation represent an overall corrosion rate (averaged over the entire specimen surface) whereas the MAS probe readings represent the local corrosion rates. Furthermore, the corrosion rates measured by the MAS probe are short-term rates. The corrosion rates are expected to decline with time. The aim of this task was not measure the long-term rates, but to determine differences in corrosion rates due to changes in the gas phase. It can also be seen from Figure 4 that the corrosion rates increase considerably when the gas mixture contains H<sub>2</sub>S and O<sub>2</sub>. This is consistent with literature results on the effect of these gas constituents in causing rapid rate of pitting<sup>6,7</sup>. The distribution of current densities amongst the various electrodes in the MAS probe is also shown in Figure 4.

When the CO<sub>2</sub> + H<sub>2</sub>S + O<sub>2</sub> was replaced with 100% H<sub>2</sub>S, significant growth of FeS scale was expected. Although, this condition is not relevant to a natural gas pipeline, it was used as a test of the probe to measure corrosion behavior in the presence of conductive corrosion products. The results are shown in Figure 5. The corrosion rate decreased partly due to the formation of a conductive layer of corrosion products. The resistance between electrodes was measured after removing the electrodes from the solution. The results are shown in Table 1. It can be seen that the average resistance between different electrodes and common point is quite low. The DC resistance was more than 106 ohm prior to the introduction of H<sub>2</sub>S. This explains why the corrosion products affect the measurement of corrosion rate for many of the electrochemical methods as well as the electrical

resistance method. However, when a MAS unit with a smaller resistor (2 to 5 ohms) was used, the measured corrosion rate was about the same as the value measured before the corrosion products were formed (Figure 5). Therefore, unlike the other type of corrosion monitoring methods, the effect of conductive corrosion products on the measured corrosion rate can be minimized by using small coupling resistors in a MAS system. These tests confirmed that the probe was sensitive to changes in the corrosivity of the environment.

The appearance of the electrodes after exposure to 100% H<sub>2</sub>S is shown in Figure 6. The Scanning electron Microscopy – Energy Dispersive Spectroscopy (EDS) analysis of the corrosion products showed it to be predominantly sulfur and iron rich (Table 2). X-ray diffraction of corrosion products showed the presence of Mackinawite (Fe<sub>1+x</sub>S, where x = 0.057-0.064) and Akaganeite ( $\beta$ -FeOOH).

### Tests in High Pressure System

The corrosion rates of the probes covered by the conductive corrosion products or by a biofilm (see Figure 3), when exposed to 100% nitrogen gas with varying RH continued to decrease with time once the RH attained a value close to 70% (Figure 7). This is partly because these corrosion products bridged the electrodes and the apparent corrosion rates decrease with time. Additionally, the iron sulfide films are known to cause a decrease in corrosion rate due to blockage of access of the solution to the steel surface.

For the probe covered by a sulfide corrosion product, when the RH was decreased progressively with pure nitrogen to a value below about 50%, the corrosion rates of the same probes decreased to a less than 0.001 mm/y (0.04 mpy). When the system was relatively dry (RH below about 20%), the nitrogen gas was replaced with a gas mixture containing CO<sub>2</sub> + H<sub>2</sub>S + O<sub>2</sub>. The corrosion rate did not change initially following this replacement, but increased dramatically when the RH increased above about 30% (Figure 8). The conductivity measured between platinum electrodes embedded along with the steel electrodes did not change significantly. Note that the conductivity is not an absolute value because the cell constant is unknown.

The responses of the electrodes covered by abiotic corrosion products (pre-corroded sample) and biofilm are compared in Figure 9. The data covers essentially the same time period as Figure 8. It can be seen that the corrosion rate of the biofilm-covered probes is much higher than that of the corrosion-product covered probe. Both electrodes responded at about the same RH (38 to 45 percent). In both cases, there was an initial increase in corrosion rate followed by a slight drop and a more or less constant corrosion after words.

When the RH is decreased, the corrosion rate does not drop immediately. This is illustrated in Figure 10. The corrosion rate is plotted as a function of RH as the probe is first subjected to an almost saturated gas mixture and then slowly dried. When the humidity decreases from a high value, the corrosion rate decreases slowly, but does not reach a low corrosion rate until the RH decreases to below about 20%. Note that when the RH is cycled at intermediate values between 40 to 70%, the corrosion rate essentially follows in a reversible manner. During the increasing RH scan (from 20%), the corrosion rate suddenly increases when the RH exceeds 39%. This hysteresis in the corrosion rate between decreasing and increasing RH cycles suggests that the corrosion products retain significant amount of moisture and drying is slow. The relationship between conductivity changes (measured on Pt) and corrosion rate of steel probes with a SRB film is shown in Figure 11. The conductivity values are to be considered only as relative values because the cell constant is not known. Significant oscillations in conductivity are observed that may be related to possible changes in the polarization behavior of Pt due to the formation of biofilm. Nevertheless, increased corrosion rate can be associated with increased conductivity due to moisture condensation.

## SUMMARY

The study has shown that

1. The Multielectrode Array Sensor (MAS) probe is a useful tool to study the effect of changing water content in the gas phase and gas composition on corrosion. While the presence of conductive corrosion products bridging the electrode does influence the measured corrosion rate, the effect can be corrected for by the use of appropriate sensing resistance.
2. Experiments with pre-existing mixture of iron sulfide and iron oxide corrosion products have shown that corrosion increases dramatically when the RH increases above 39 percent. Close to room temperature and for 3.45 MPa gas, this RH corresponds to about 336 mg/m<sup>3</sup> (21 lbs/MMSCF) of water in the gas. The increase in corrosion rate in the presence of a biofilm consisting of SRB and slime former also occurs at an RH of about 45%.
3. However, once wetted, the dry out of the corrosion product or biofilm does not occur unless the RH of the gas is below about 20%. The long-term dry out was not evaluated.
4. These findings suggest that the 7 lb/MMSCF (5 lb/MMSCF in colder climates) is conservative for determining if the gas is dry, even in the presence of biofilm and pre-existing corrosion products.
5. The MAS probe was able to function properly at pressures up to 10.34 MPa (1500 psi) and can be used in pipeline internal corrosion monitoring.

## REFERENCES

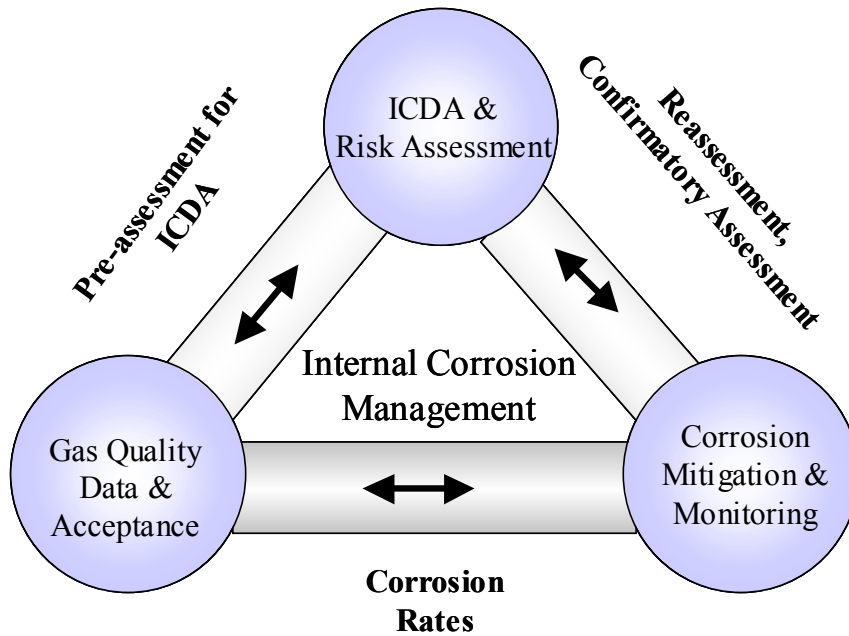
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**Table 1. Electrical resistance measured after exposure to 100% H<sub>2</sub>S in solution**

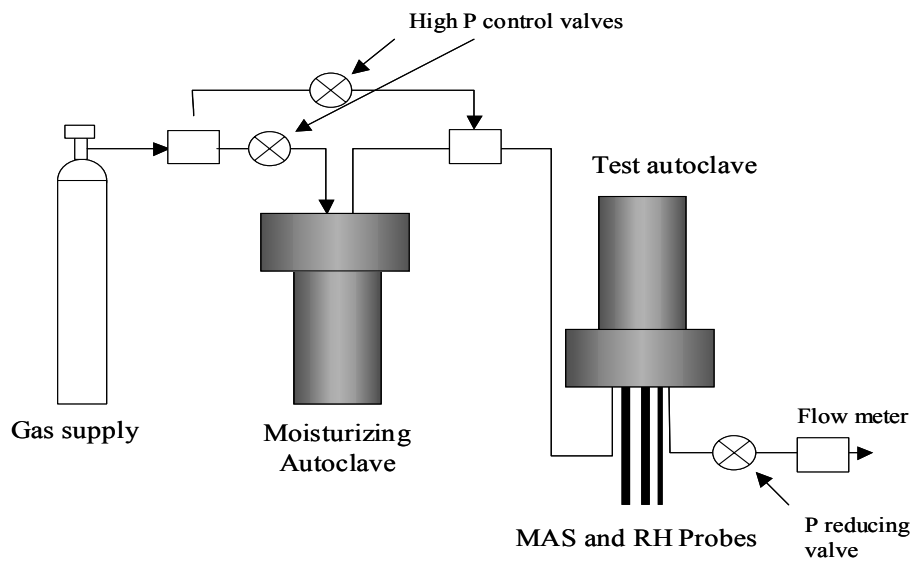
<b>Electrode</b>	<b>Resistance (ohm)</b>		
	<b>Com-to-Electrode</b>	<b>Electrode-To-Com</b>	<b>Average</b>
<b>2</b>	21.8	11.000	16.4
<b>3</b>	17.1	20.000	18.6
<b>4</b>	10.2	10.600	10.4
<b>5</b>	30.4	32.800	31.6
<b>6</b>	11.6	12.400	12.0
<b>7</b>	11.3	12.000	11.7
<b>8</b>	10.2	10.300	10.3
<b>9</b>	33.3	37.700	35.5
<b>10</b>	23.1	24.800	24.0
<b>11</b>	17.8	18.200	18.0
<b>13</b>	29.9	34.400	32.2
<b>14</b>	188.0	195.000	191.5

**Table 2. SEM-EDS analysis on corrosion products on the probe exposed to 100% H<sub>2</sub>S**

<b>Element</b>	<b>Wt. %</b>
Na	8.3
Si	0.91
S	16.48
Cl	5.44
Mn	0.3
Fe	72.67
Al	0.36
Cr	0.18

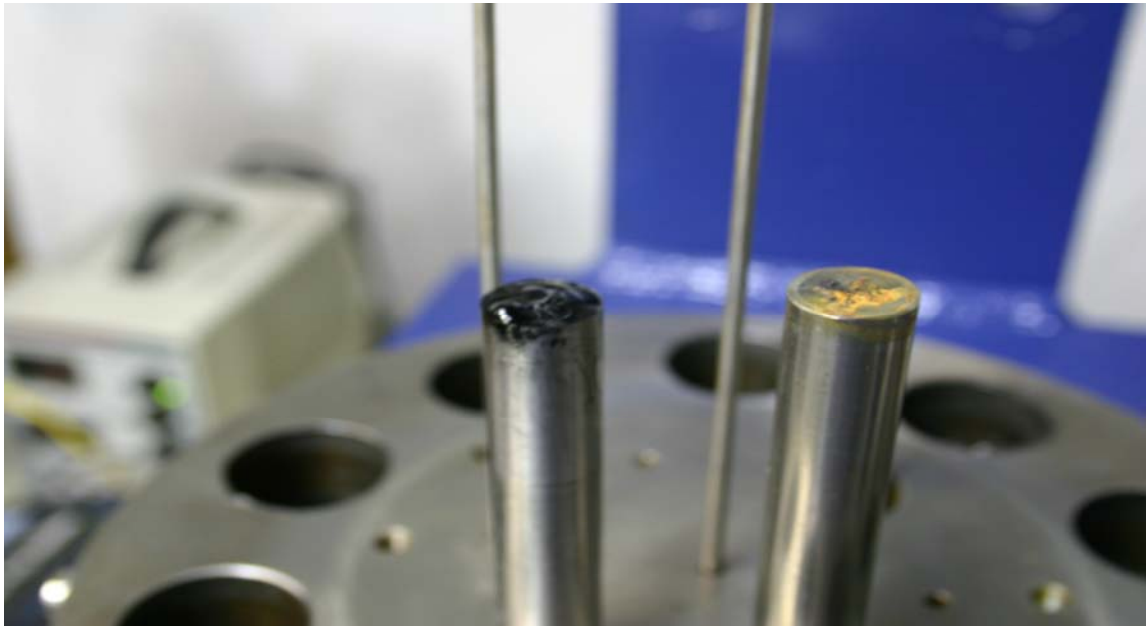


**Figure 1. Schematic view of the interrelationship between the various programs that address internal corrosion management of gas pipelines**

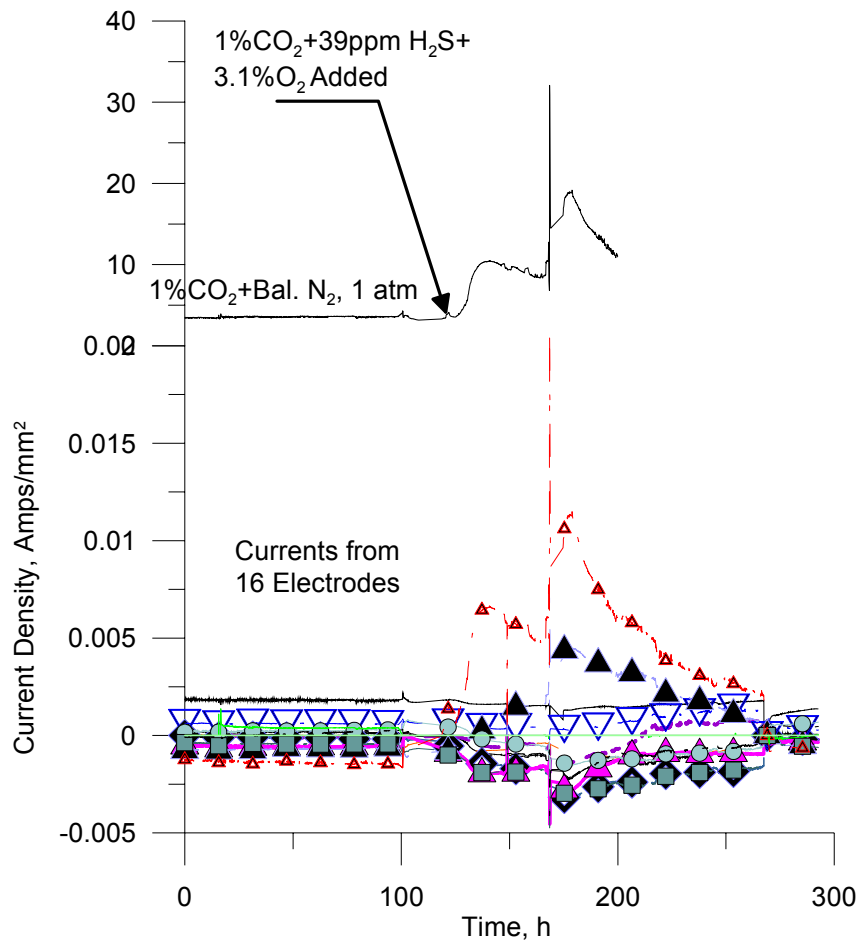


**Figure 2. Overall photo and schematic of the high pressure test showing the MAS system electronics (foreground), the moisturizing autoclave and the test autoclave**

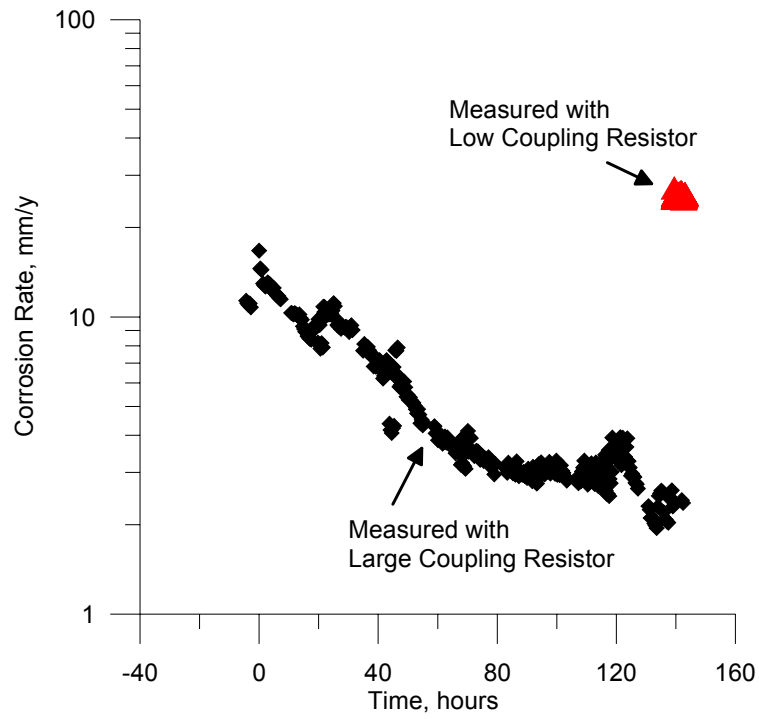




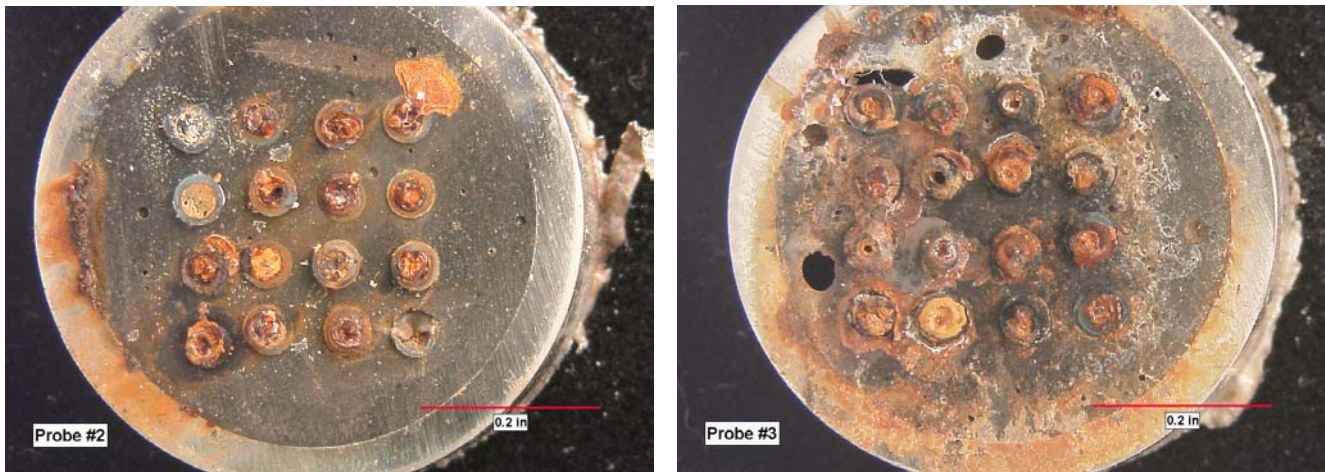
**Figure 3. Two MAS probes, one with a biofilm solution (black) and another with abiotic corrosion product (brown) exposed in the autoclave. Photo was taken prior to the test**



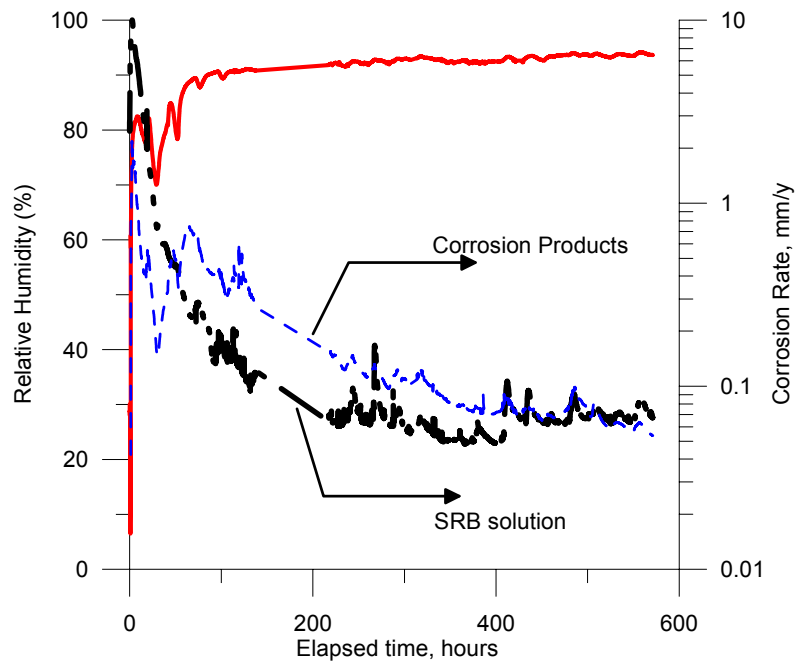
**Figure 4. Effect of gas composition on corrosion rates measured by MAS in a 1M NaCl + 0.001M NaHCO<sub>3</sub> solution. Gases were purged at ambient pressure**



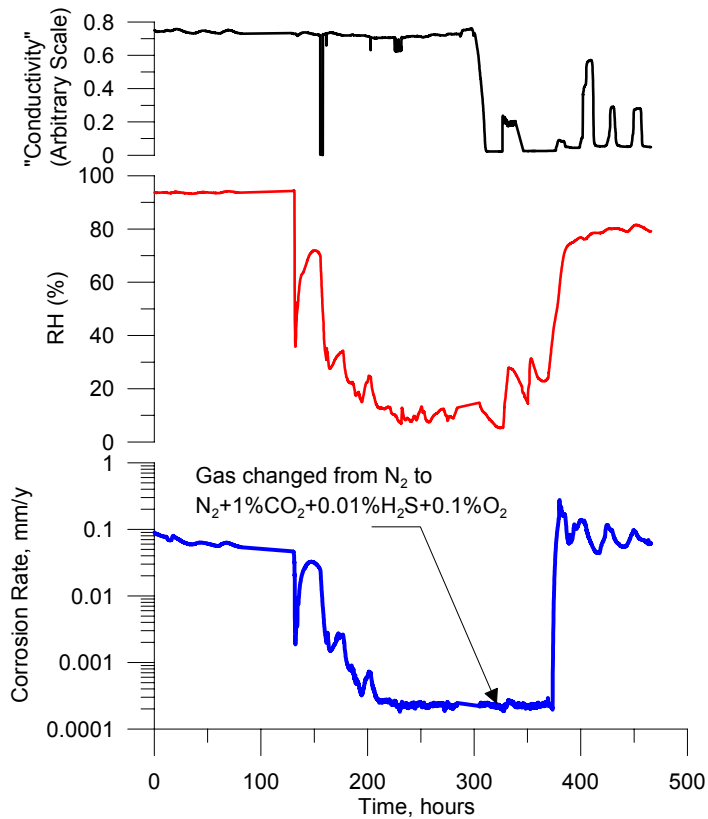
**Figure 5. Effect of the coupling resistor on the carbon steel corrosion rates measured after a thick and conductive FeS was formed in a solution saturated with 100% H<sub>2</sub>S.**



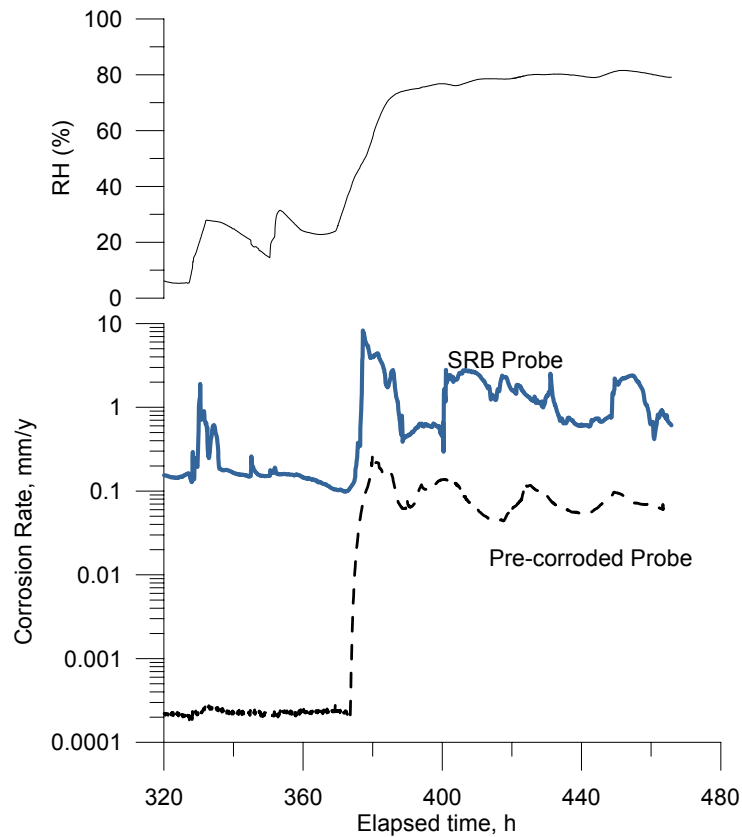
**Figure 6. Probe appearance after in the solution (1M NaCl + 0.004 M NaHCO<sub>3</sub>) saturated with pure H<sub>2</sub>S gas for 7 days. Pitting corrosion was apparent after the corrosion products were removed.**



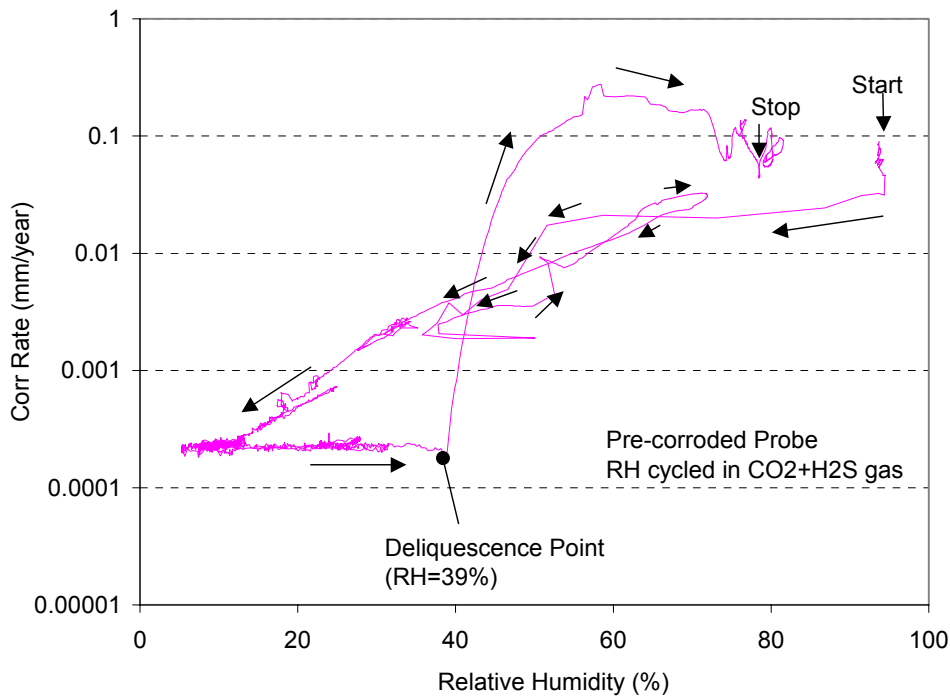
**Figure 7. Localized corrosion rates from the probes covered by a layer of corrosion products and liquid SRB-containing solution exposed to a flow of pure nitrogen gas. Pressure: 500 psi; temperature: 7 to 20°C.**



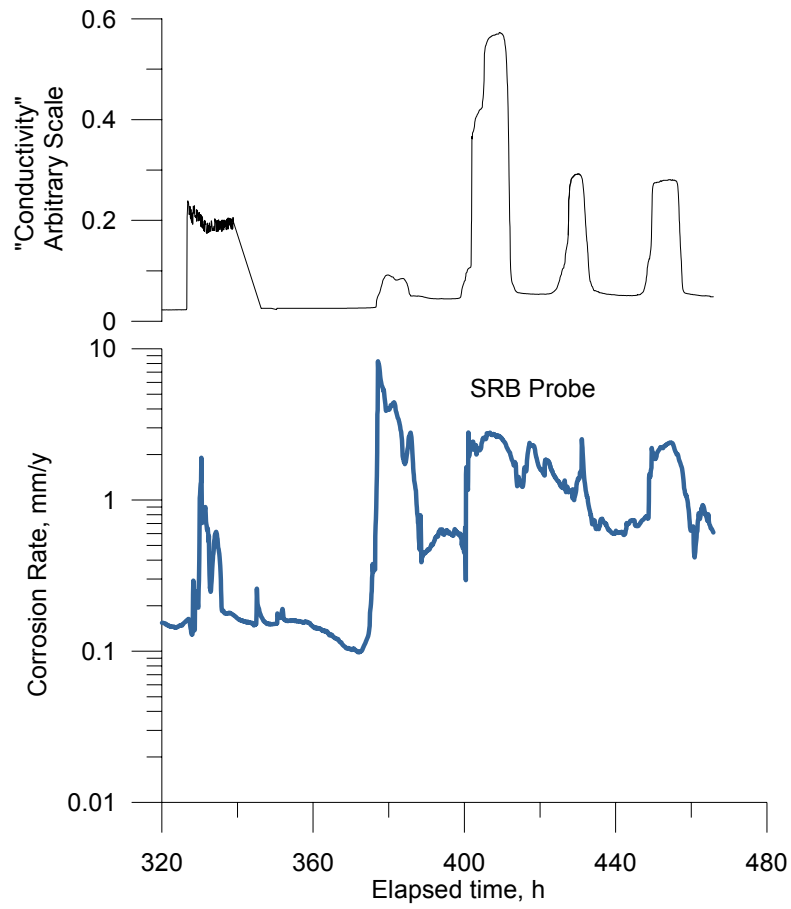
**Figure 8. Localized corrosion rate and the conductivity of the probe covered by corrosion products as a function of relative humidity. Pressure: 500 psi; temperature: 7 to 20°C.**



**Figure 9. Responses of the localized corrosion rates measured from the probes covered by SRB biofilm and by corrosion products to the increase in relative humidity**



**Figure 10. Localized corrosion rate measured from the probes covered by corrosion products as a function of relative humidity. The Arrow in the figures shows the sequence of the test.**



**Figure 11. Localized corrosion rates and the conductivity from the probe covered by SRB biofilm exposed to the  $N_2+1\%CO_2+0.1\%O_2+0.01\%H_2S$  flow during the increase in relative humidity (See Figure 10).**