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Real-Time Monitoring of Carbon Steel Corrosion in Crude Oil and Brine Mixtures Using Coupled Multielectrode Sensors

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ABSTRACT

A real-time coupled multielectrode array sensor was used to measure the non-uniform corrosion of carbon steel material in a crude oil containing different amounts of brine solutions. Parallel immersion tests with carbon steel specimens in the crude oil were also conducted. The measurement results from the sensor and the results from immersion tests show that the crude-brine mixtures were not corrosive if there was no segregated phase of brine or water formed. However, the crude-brine mixture was highly corrosive when a segregated brine phase was present even in a small quantity. The measured results also show that, once initiated by even a small amount of suspended brine particulates, it took a long time for the corrosion to stop after the brine was homogeneously mixed with the crude oil.

Keywords: multielectrode sensor, corrosion monitoring, localized corrosion monitoring, corrosion in crude oil, real-time corrosion sensor, online corrosion monitoring

INTRODUCTION

Coupled multielectrode method has been used to measure corrosion behavior and study the spatiotemporal patterns of electrochemical processes on metal surfaces.[1-4] Coupled multielectrode array sensors (MAS) that give simple indicators, such as localized penetration rate, for non-uniform corrosion based on statistical parameters such as standard deviation of currents or most anodic current from the multiple electrodes have been developed for online and real-time monitoring of non-uniform corrosion, especially localized corrosion such as pitting corrosion and crevice corrosion.[5-25] The MAS technology has been successfully used for online and real-time monitoring of corrosion in concentrated chloride solutions,[7] in simulated cooling water,[6] in simulated sea water with sulfate reducing bacteria[11], under salt deposits in humid air,[14,17] and under paints[21] in laboratories. It was also successfully used in industrial cooling water systems[18] and plant process streams.[16,19] For applications under paints, it effectively detected the defect of the paints and gave real-time indication of the degradation of paints.[21] For applications under salt deposits in humid air,[14] it provided real-time indication of non-uniform corrosion at different relative humidities. In addition, the MAS technology has been demonstrated to be an effective tool in corrosion monitoring under cathodic protection (CP) conditions.[22] It gave real-time indication of the effectiveness of the cathodic protection system. If incorporated into a feed back control unit, it may be used to optimize the cathodic protection potential (or current) so that the potential is just below the protection value for critical components. Tests with the MAS have covered a variety of metals, including carbon steels, aluminum, stainless steels, and nickel-based alloys.

Most crude oils from production environments initially contain contaminants such as tanker salt water, or emulsified salt brine from oilfield formations. Typically, these brines contain dissolved cations such as Na^+, Ca^{2+}, Fe^{2+}, and Mg^{2+} and anions such as Cl^-, SO_4^{2-}, HCO_3^-, and S^{2-}. These can occur in concentrations from 200 ppm up to saturation levels of 300,000 ppm. These contaminants directly influence the corrosivity of a crude oil. Because corrodible surfaces are found throughout the production, transport, and refining equipment, corrosion in crude oil systems is one of the most costly problems facing oil companies.[26] Prior to refining, most bottom sludge and water (known as BS&W) separates and settles naturally in storage tankage. Some emulsified components need to be removed in desalting operations in order to minimize corrosion in the refining process. Desalting typically removes these down to < 10 ppm levels in one or more stages. However, even at these levels, the presence of inorganic chlorides still results in HCl in downstream atmospheric crude tower operations. This paper reports the real-time application of the MAS probe for corrosion monitoring of carbon steel materials in crude-brine mixtures in the laboratory.

In a coupled multielectrode array sensor, multiple miniature electrodes made of materials identical to the engineering component are used as sensing electrodes. The miniature electrodes are coupled together by connecting each of them to a common joint to act as a one-piece of metal[8-10] (Figure 1). In a localized corrosion environment, some of the electrodes simulate the cathodic sites (or less corroding sites) and other electrodes simulate the anodic sites (or more corroding sites) of a one-piece of metal.[9] Because the multiple electrodes are electrically separated by insulators, the anodic currents are forced to flow into the more corroding electrodes and the cathodic currents to flow out of the less or non-corroding electrodes. The resulting electrical currents, as measured from the voltage drop across the small resistors, are used, after statistical treatment, to quantitatively represent localized corrosion rates.[10]

EXPERIMENTAL

The MAS probes are usually made of flush-mounted electrodes. However, preliminary experiments with the crude oil indicated that the flush-mounted probe did not respond to the corrosion in the crude-brine mixtures because the distance among the electrodes was too large, compared with the size of the corrosive brine particulates formed in the two phase system. The electrode-exposed type of multielectrode probe[27] was used in this experiment (Figure 2). The electrodes in Figure 2 were closely packed together so that the distance among the electrodes was as small as possible (<0.3 mm). The probe had 16 electrodes made of Type 1010 carbon steel (UNS G10100) wire (0.5 mm in diameter and approximately 3 mm in exposed length). The surface area of the electrodes in the probe is approximately 0.055 cm^2. The high resolution electronic system and the software has been described previously.[10]

Plate Type 1018 carbon steel (UNS G10180) coupons were used in the immersion test to verify the corrosion signals from the MAS probe. The dimension of the coupons was 5 cm in length, 2.5 cm in width and 0.32 cm in thickness. Typical chemical analyses for the electrode and test coupon materials are shown in Table 1. The selection of the Type 1018 carbon steel material in the immersion test was because of its availability in our laboratory. The small difference in the carbon content between the two types of carbon steel materials (Types 1018 and 1010) is not expected to cause significant difference in corrosion resistance under the test conditions.

The experiment was conducted in a 1-L beaker placed on a magnetic stir. The beaker was initially filled with either desalted crude or mixtures of crude and a brine solution containing 0.5 M NaCl (reagent grade). The temperature was approximately 22 to 24°C through out the experiment. The beaker was open to air; no gas-purging was applied.

RESULTS

Figure 3 shows the response of the non-uniform corrosion currents measured from the electrode-exposed probe made of carbon steel to the addition of a brine solution containing 0.5 M NaCl. The non-uniform corrosion current of the probe in the desalted crude oil was approximately the same as that when the probe was in the air, which is close to the background level of electrical noise signal under the test environment ($<1 \times 10^{-9}$ A). Therefore, the desalted crude oil is not corrosive. When 3.5 mL brine solution was added to the crude oil (615 mL) to form a mixture containing 0.57% (by volume) of brine solution under stirring condition, the corrosion current increased by 3 orders of magnitude in approximately 5 hours. The corrosion current gradually decreased after a peak value of approximately 1 μA was reached.

Figure 4 shows the response of the electrode-exposed carbon steel probe to crude-brine mixtures containing different amounts of brine. During this test, the brine was added to the crude prior to the exposure of the probe and the crude-brine mixture was fully stirred for 2 to 45 minutes (see notes in Figure 4) before the probe was transferred to the crude mixture. In this case, no significant increase in corrosion until the brine content reached 9.87% (by volume). Unlike the previous test, the coupled multielectrode probe showed no significant corrosion in the crude-brine mixture containing 0.57% (by volume) brine. The slight increases in corrosion rate when the probe was changed to the crude-brine mixture containing 1.95% (by volume) brine and to the crude-brine mixture containing 4.8% (by volume) brine were only temporary. The signals returned to their previous values shortly after these changes.

At the end of the test with each crude-brine mixture prior to the transfer of the probe to the mixture containing 9.87% (by volume) brine, no segregated phase of brine was found at the bottom of the glass beaker after the mixture was allowed to settle (without the stirring). Therefore, the mixtures containing up to 4.8% (by volume) brine solutions formed a homogeneous mixture with the crude oil after mixing during the tests.

When the probe was transferred to the well-stirred crude-brine mixture containing 9.87% (by volume) brine solution, the corrosion rate increased sharply, reaching a maximum value of 0.17 μA in 3 hours. Approximately one day after the initial increase, the corrosion rate started to decrease gradually and reached the value prior to the transfer to the 9.87% (by volume) mixture in approximately 6 days (Figure 5). Segregated phase of brine solution was noticed at the bottom of the beaker when the stirring was stopped for a few hours after the addition of the 9.87% brine solution, suggesting that the crude-brine mixture was not homogeneous at the beginning of the test under the stirring conditions. The increase in corrosion rate at the beginning of the test was caused by the brine bubbles in contact with the sensing electrodes. However, at the end of the test with the 9.87% (by volume) mixture, no segregated phase of brine was found at the bottom of the beaker when the stirring was stopped, suggesting that the crude-brine mixture was near homogeneous at the later period of the test. The brine that was initially not fully mixed in the crude-brine mixture was fully dispersed or emulsified sometime during the test.

Figure 6 shows the responses of the electrode-exposed carbon steel probe to air and to a pure brine solution after the probe had been exposed to the crude-brine mixtures and the sensing surface was covered by a thick layer of oil coating. The corrosion rate decreased when it was exposed to air and increased sharply when it was exposed to the pure brine solution. The responses were similar to those observed when the probe was not covered by a coating of crude. Figure 6 demonstrates that the responsiveness of the probe was not retarded after its electrodes were covered by the thick crude coating which may act as an insulating layer.

Total immersion tests were conducted by dipping three Type 1018 carbon steel specimens in: (i) the continuously stirred homogeneous crude-brine mixture containing 9.87% brine (by volume), (ii) a continuously stirred two phase crude-brine mixture containing 12% brine (by volume), and (iii) a stationary pure brine solution covered by floating crude [> 50% (by volume)], respectively. The 9.87% (by volume) crude-brine mixture was initially mixed for 11 days prior to the test (see Figures 4 and 5). The brine solution used in the immersion tests was the same 0.5 M NaCl solution used for the MAS probe test. The stationary crude-brine mixture was not previously stirred. It was observed that the coupon in the stationary pure brine solution started to rust on the second day of immersion. It was also observed that small pits were apparent on the coupon in the non-homogeneous two phase crude-brine mixture containing 12% (by volume) brine on the second day. However, no sign of pitting and rusting were noticed on the coupon in the continuously stirred homogenous crude-brine mixture containing 9.87% (by volume) brine even after the 13th day of exposure. Figure 7 shows the post-test pictures for the coupons. The original machining marks (600 grit) were clearly visible on the coupon that was tested in the homogeneous crude-brine mixture. However, pitting is clearly shown on the surface of the coupon that was tested in the two phase crude-brine mixture. The coupon tested in the pure brine solution exhibited general corrosion. It should be mentioned that the picture for the coupon tested in the homogeneous crude-brine mixture containing 9.87% (by volume) brine were taken 13 days after the exposure, but the pictures for the coupons tested in the two phase crude mixture containing 12% (by volume) brine and in the pure brine solutions were taken 58 days after the exposure. Although no pictures were taken after 13 days after the test for the coupons tested in the two phase mixtures and the pure brine solution, significant pits and rusts were observed on these coupons 13 days after the exposure.

Figure 8 shows the corrosion rate of the coupled multielctrode sensor probe exposed in the same homogeneous crude-brine mixture as the coupon that showed no sign of significant corrosion. The low signal from the coupled multielectrode probe is in agreement with the post test appearance of the carbon steel coupon (Figure 7A).

DISCUSSIONS

No significant corrosion was observed on a carbon steel specimen in the crude oil and brine mixture containing 9.87% (by volume) brine after the brine was homogeneously mixed in the mixture at room temperatures. Therefore, the mixture of crude oil and brine is not corrosive at room temperatures if no segregated phase of brine solution is present, No corrosion was shown from the coupled multielectrode array sensor probe in the same crude-brine mixture either.

However, some results from the coupled multielectrode array probe show that the corrosion rate increased by 3 orders of magnitude when only 0.57% (by volume) of brine solution containing 0.5 M NaCl was added to crude oil under continuously stirred condition (Figure 3), reaching 1 μA. This high signal is close to that observed in the pure brine solution containing 0.5 M NaCl (see Figure 6). Other researchers who conducted experiments with electrode-flush-mount coupled multielectrode probes, which had well-defined surface area for corrosion rate calculation, have shown that the localized corrosion rate of carbon steel in air-saturated simulated seawater (similar to 0.5 M NaCl solution) was from 1 to 3 mm/year (40 to 120 mil/year).[22] The response in Figure 3 was probably due to the contact of the brine particulates with the sensing electrodes during the addition of the brine solution or within the initial time period after the brine addition. When the brine solution was added to the desalted crude oil under the stirring condition, the brine particulates that did not have the time to dissolve may have contacted or been trapped on the surfaces of some of the electrodes of the probe and caused corrosion to the electrodes. Once a corrosion product was formed on the electrodes, the trapped corrosive brine particulates may be retained further by the corrosion products formed on the electrodes. The decreasing trends shown in Figures 3 and 5 after the corrosion reach maximum values are indications probably due to the slowly disappearing of the corrosive brine particulates trapped in the corrosion products on the sensor electrode surface.

The results in Figures 4 and 5 show that for the crude-brine mixtures containing 0.57 to 4.87% brine, a mixing time of 2 to 45 minutes, depending on the content of the brine in the mixture, were enough to homogenously mix the crude-brine mixture and make it not corrosive. When the brine content reached 9.87%, even 45 minutes of mixing were not enough to mix the crude-brine mixture. The low corrosion rates from the coupled multielectrode probe and the immersion test conducted in the crude-brine mixture containing 9.87% (by volume) brine show that the desalted crude oil may be homogeneously mixed with as much as 9.87 % (by volume) brine solutions without forming a separated phase of brine solution after several days of mixing.

CONCLUSIONS

The non-uniform corrosion behavior of carbon steel material in crude oil containing different amount of brine solutions (0.5 M NaCl) was measured using a real-time and online multielectrode array sensor. The measurement results from the sensor and the results from the immersion test show that the crude-brine mixtures were not corrosive if there was no segregated phase of brine or water formed. However, the crude-brine mixture was highly corrosive when a segregated brine phase was present even in a small quantity. The measurement results also show that it took a long time to stop corrosion once it was initiated because the corrosion products may trap the corrosive brine at the corroded sites for a relatively long time.

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TABLE 1

TYPICAL CHEMICAL COMPOSITIONS (WEIGHT PERCENT) OF THE CARBON STEEL WIRES USED IN THE SENSORS AND THE CARBON STEEL COUPONS USED IN THE IMMERSION TESTS

Metals	UNS No.	Fe	Mn	P	S	C
Type 1018	G10180	Bal	0.72	0.008	0.008	0.20
Type 1010	G10100	Bal	0.31	0.04	0.042	0.08
Note: Bal: Balance						

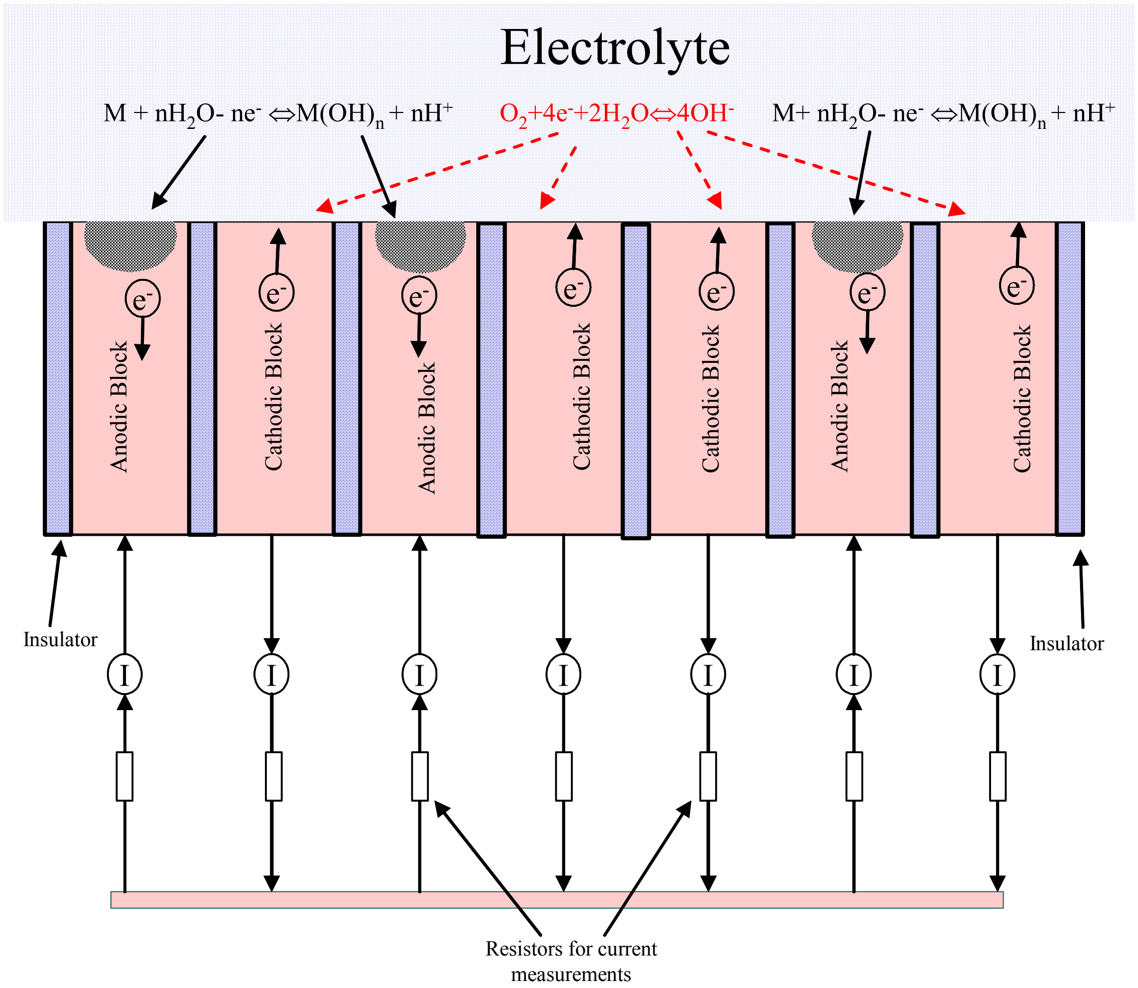


FIGURE 1. Principle of the coupled multielectrode array sensor. The current from or to each electrode, I, was measured by the voltage drop across the resistor between the corresponding electrode and the common coupling joint.

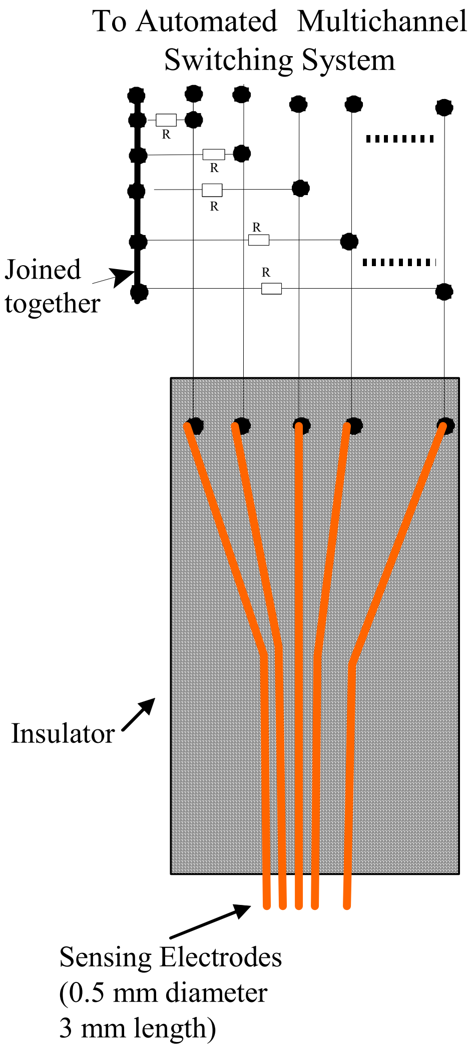


FIGURE 2. Schematic diagram of the coupled multielectrode sensor probe used in the tests

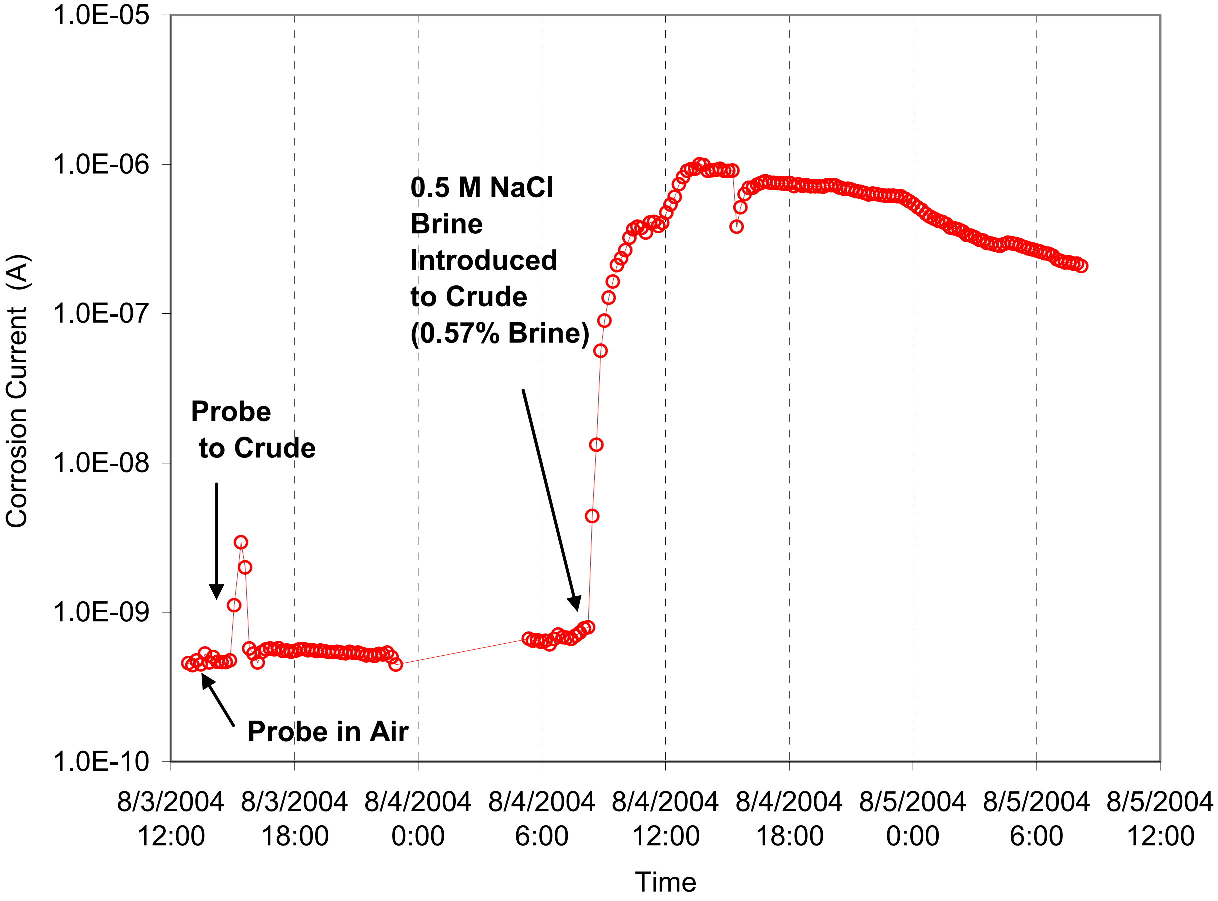


FIGURE 3. Responses of the electrode-exposed carbon steel probe in crude oil to the addition of 0.5 M NaCl brine

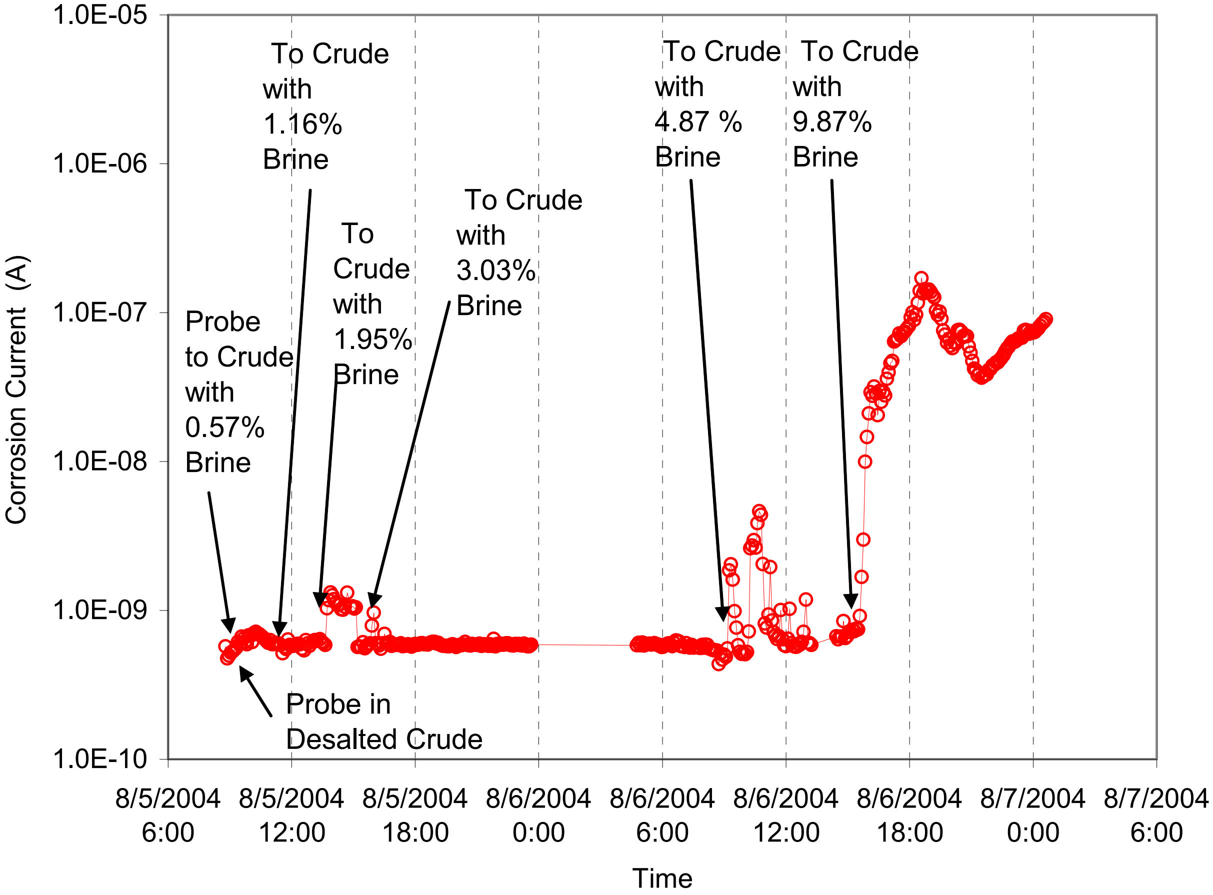


FIGURE 4. Responses of the electrode-exposed carbon steel probe to crude oils containing different amount of 0.5 M NaCl brine solution. Note, the percentage in the figure is the volume percent of the brine solution in the crude-brine mixture.

Note: Before the probe was transferred to a given mixture, the mixture was stirred for at least 2 minutes for the mixtures containing 1.95% or less brine, 5 minutes for the mixtures containing 3.03% or 4.87% brine, and 45 minutes for the mixture containing 9.87% brine solution.

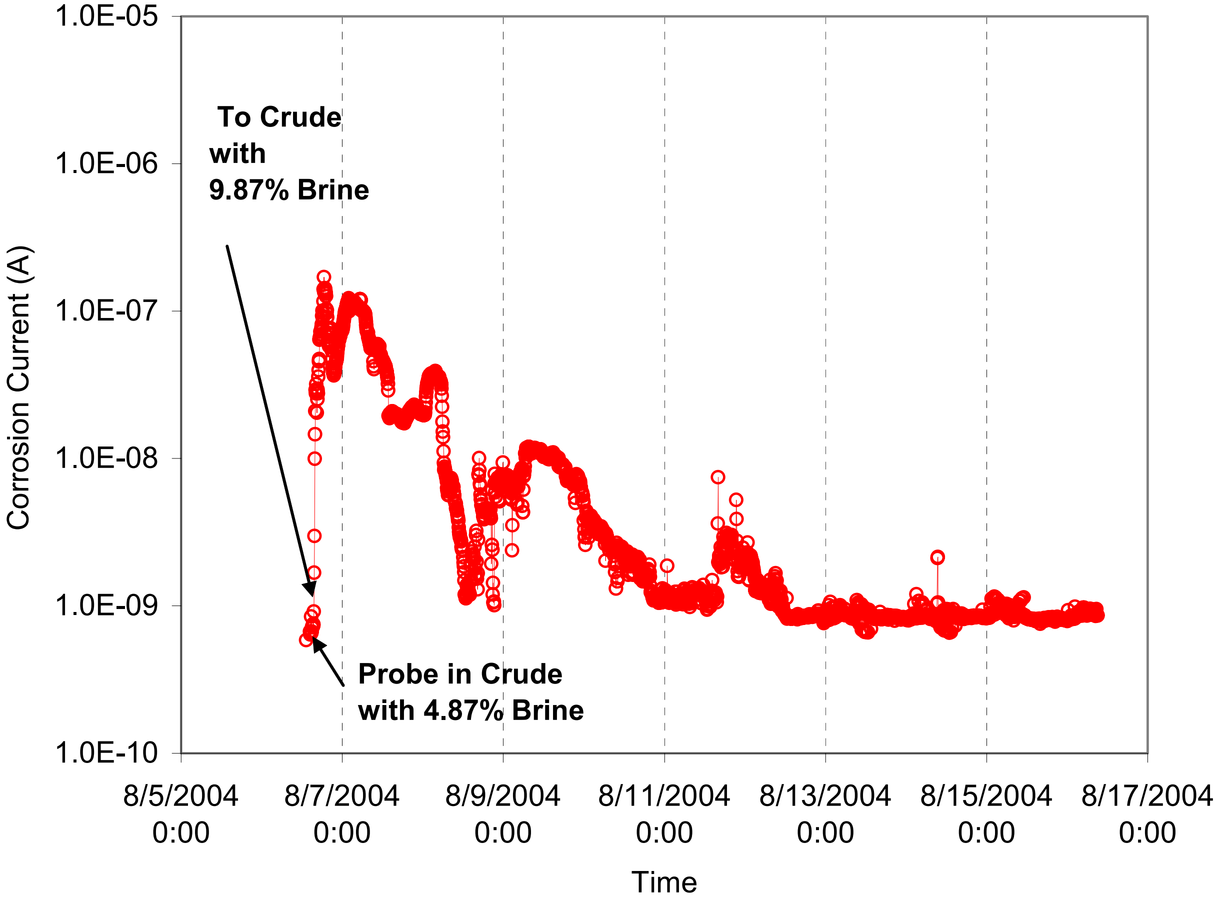


FIGURE 5. Probe signals in a crude-brine mixture containing 9.87% (by volume) brine solution

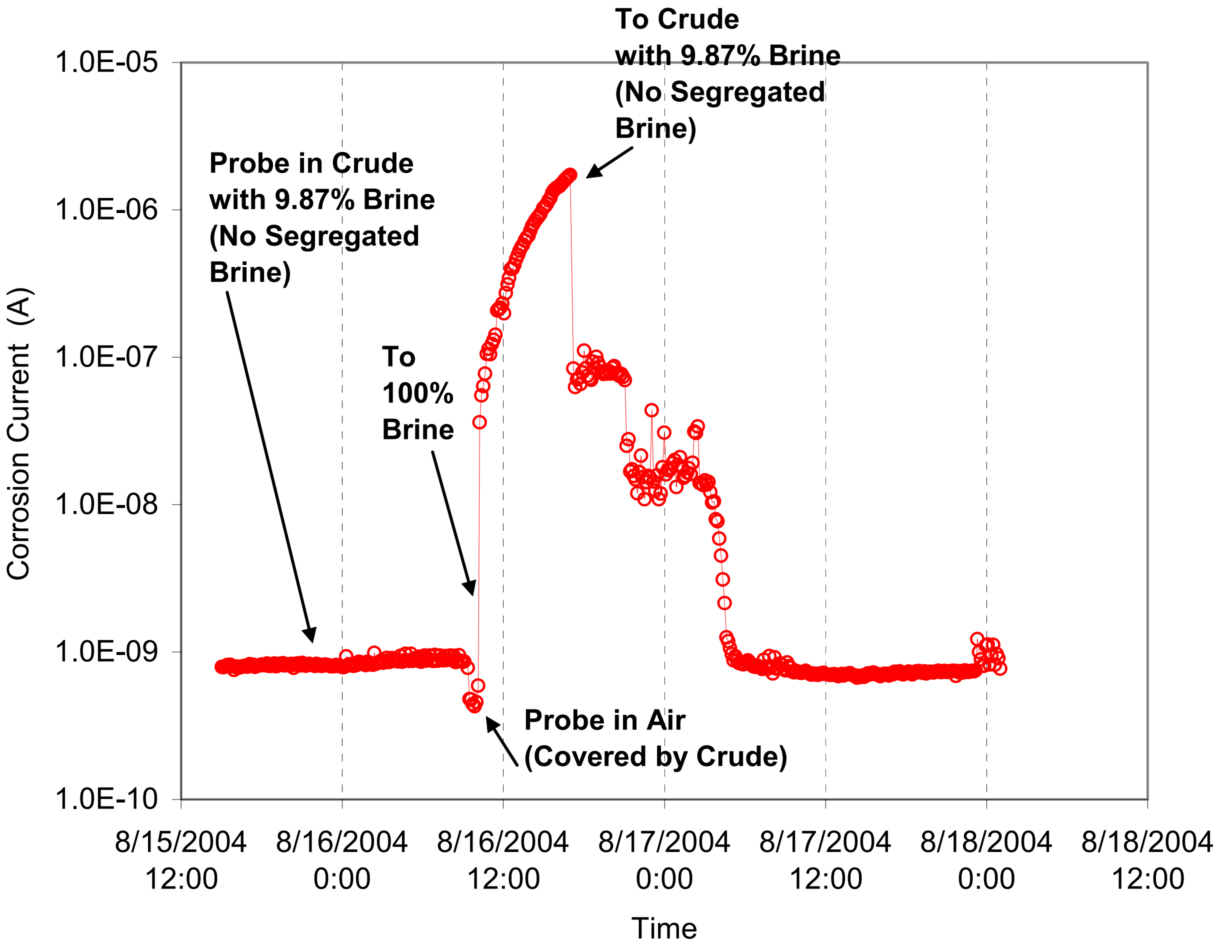
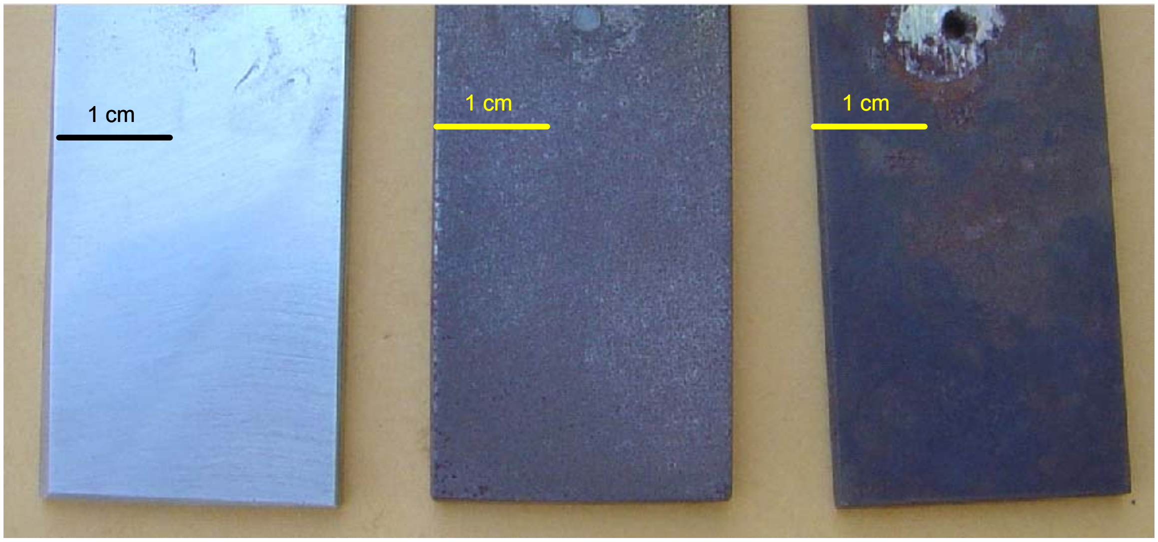


FIGURE 6. Responses of the electrode-exposed carbon steel probe to air and a pure brine solution after the exposure to crude



(A) (B) (C)

FIGURE 7. Post test appearance of carbon steel coupons in a continuously stirred homogeneous crude-brine mixture containing 9.87% (by volume) brine (A), a continuously stirred two phase crude-brine mixture containing 12% (by volume) brine (B), and a stationary pure brine solution covered by floating crude (C).

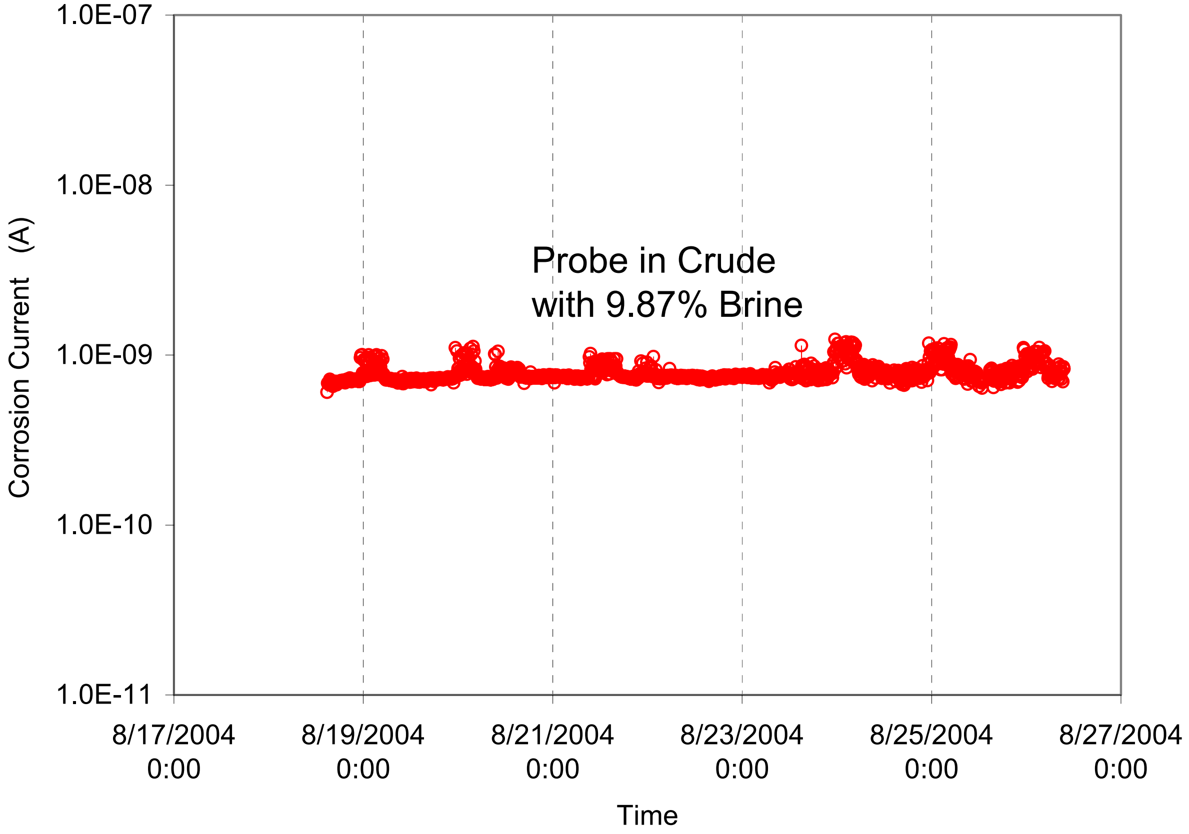


FIGURE 8. Corrosion signal from the MAS probe during the first 9 days of the total immersion test with carbon steel coupons. The crude-brine mixture was initially mixed for 11 days prior to the test (see Figure 5).

FIGURE 1. Principle of the coupled multielectrode array sensor. The current from or to each electrode, I, was measured by the voltage drop across the resistor between the corresponding electrode and the common coupling joint.

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FIGURE 5. Probe signals in a crude-brine mixture containing 9.87% (by volume) brine solution

FIGURE 6. Responses of the electrode-exposed carbon steel probe to air and a pure brine solution after the exposure to crude

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