

Horizontal Rotating Cylinder—A Compact Apparatus for Studying the Effect of Water Wetting on Carbon Dioxide Corrosion of Mild Steel

S. Nešić^{†*} and F. Carroll^{**}

ABSTRACT

Water wetting is a crucial issue in carbon dioxide (CO₂) corrosion of multiphase flow pipelines made from mild steel. This study demonstrates the use of a novel benchtop apparatus, a horizontal rotating cylinder, to study the effect of water wetting on CO₂ corrosion of mild steel in two-phase flow. The setup is similar to a standard rotating cylinder except for its horizontal orientation and the presence of two phases—typically water and oil. The apparatus has been tested by using mass-transfer measurements and CO₂ corrosion measurements in single-phase water flow. CO₂ corrosion measurements were subsequently performed using a water/hexane mixture with water cuts varying between 5% and 50%. While the metal surface was primarily hydrophilic under stagnant conditions, a variety of dynamic water wetting situations was encountered as the water cut and fluid velocity were altered. Threshold velocities were identified at various water cuts when the surface became oil-wet and corrosion stopped.

KEY WORDS: carbon dioxide corrosion, flow, mild steel, pipelines, water wetting

INTRODUCTION

In the open literature, there is only a handful of studies related to the effect of water wetting on car-

bon dioxide (CO₂) corrosion. In a widely used model of CO₂ corrosion,¹ the water wetting effect is accounted for by a binary (0/1) correction factor. This approach is based on two key studies:

- Wicks and Fraser² identified 1 m/s as the minimal velocity for many crude oils to entrain a water phase.
- Lotz, et al.,³ found that in most cases the water cut has to exceed 30% before any water separates out from the oil and wets the steel surface.

On the other hand, there is almost a consensus in the industry that this simple rule-of-thumb is too restrictive and often wrong. It is worth while mentioning some extreme cases to illustrate the point. On one hand, anecdotal evidence suggests that serious CO₂ corrosion was observed in some pipelines with as low as 1% water cut. On the other hand, it also has been reported that in some cases pipelines carrying up to 40% water exhibited little or no corrosion. Flow regime, temperature, crude oil composition, additives, etc., all affect the water wetting in the field; and, clearly at the present, there is no simple universal way of accounting for all these factors. The most reliable approach is still experimentation under conditions that resemble the field as closely as possible.

While accurate field measurements are very difficult and almost prohibitively expensive, even laboratory studies of CO₂ corrosion under multiphase flow conditions are complicated and very costly. They typically involve large-scale multiphase flow corrosion loops and large quantities of working fluids.⁴ In

Submitted for publication November 2001; in revised form, April 2003. Presented as paper no. 02303 at CORROSION/2002, Denver, CO, April 2002.

[†] Corresponding author.

* Department of Mechanical Engineering, The University of Queensland, Brisbane, Qld 4072, Australia. Present address: Institute for Corrosion and Multiphase Flow Technology, Ohio University, 342 West State Street, Athens, OH 45701.

** Department of Mechanical Engineering, The University of Queensland, Brisbane, Qld 4072, Australia.

such large systems, it is not easy to isolate the effect of water wetting and identify its contribution to the overall corrosion rate, which is affected by numerous other factors such as water chemistry, temperature, and the presence of inhibitors, to name just a few key ones.

A good illustration of the latter point is the study by Schmitt and Stradmann,⁵ where the wettability (preferential wetting) of carbon steel (CS) was studied in water at high CO₂ pressure and temperature in the presence of a hydrocarbon phase and with the addition of inhibitors and de-emulsifiers. Even if no realistic flow effects were included, the complexity of this study was formidable. In situ contact angle measurements were made for a sessile and a swimming drop.

Contact angle is defined as the angle (as viewed from the side) where a liquid droplet meets the solid surface. It is a good measure of wettability of a solid surface by that particular liquid in the presence of a surrounding fluid (gas or liquid). When the angle is <90° (measured toward the center of the droplet), this indicates that the liquid has an affinity for the solid surface. In other words, the adhesive forces trying to stretch (enlarge) the contact surface area between the solid and the liquid in the droplet are stronger than the cohesive forces trying to contract the droplet and make it spherical. Vice versa, when the contact angle is >90°, this indicates that the liquid has a lower affinity for the particular solid surface. In the case when the surrounding fluid is another liquid (rather than a gas), the affinity of one liquid is always balanced by the affinity of the other, leading to the notion of preferential wetting (wettability). Most textbooks on the subject of physical chemistry include chapters on contact angle and its relationship with surface tension and preferential wetting.

The information generated in the above-mentioned study of Schmitt and Stradmann⁵ is rather unique and very valuable; however, it is important to keep in mind that the measured static contact angles can be very different from the dynamic contact angles present in flowing multiphase solutions.⁶ There are arguments that at higher flow rates, wettability becomes almost independent from surface properties (static wetting angles) and becomes a strong function of the hydrodynamic parameters,⁷⁻⁸ particularly viscosity.⁹

A technique that enables the study of dynamic contact angles is the so-called dynamic Wilhelmy hanging plate technique.⁶ It amounts to cyclic immersion/withdrawal of a steel plate into/from a stratified multiphase solution, accompanied by force measurement. The technique is well established and can produce accurate measurements of interfacial and surface tensions as well as preferential surface wetting behavior resulting from a cyclic exposure to

different phases. The drawback is that, so far, this technique has been limited to atmospheric pressures and room temperatures as well as extremely low velocities (~10⁻³ m/s).

The present study demonstrates the use of a novel benchtop apparatus—a horizontal rotating cylinder (HRC)—for studying the effect of water wetting on CO₂ corrosion of mild steel in multiphase systems. The setup is similar to a standard rotating cylinder except for its horizontal orientation and the presence of two phases—water and oil. Inside a container, the cylindrical steel sample rotates so that the surface of the steel is cyclically exposed to each of the phases. The proportion of time spent in each phase can be adjusted easily by varying the level of the oil/water interface with respect to the rotating steel sample. It is shown below that this technique, while being relatively cheap, does overcome some of the limitations of the previously mentioned methods. In the first place, the HRC enables testing of preferential wetting under more realistic conditions to cover a broad range of velocities and water cuts. Even if the present proof-of-concept study was conducted under atmospheric pressure and room temperature, and used a pure single-component hydrocarbon phase, the HRC can be adapted easily to cover more realistic water/oil chemistries and to operate at higher temperatures and pressures. In a HRC, a variety of measurement techniques can be used to monitor the wettability as well as the corrosion rate of the steel including visual observation/recording, various optical techniques, and electrochemical and conductivity measurements. With a small additional effort, torque measurements can be made to help quantitatively estimate surface forces that are needed for modeling purposes.

A similar apparatus (HRC) has been used by Mestrovic-Markovic and Matic,¹⁰ who investigated mass transfer, and later by Esmail and Ghannam,¹¹ who investigated film wetting properties in a liquid coating process relevant to a range of traditional and emerging technologies such as coating of photographic films, paper and plates, wire coating, polymer coating, steel galvanizing, and magnetic disk manufacturing. Their study covered gas/liquid systems and aimed at identifying critical filming velocities leading to air bubble entrainment. Another related technique used in the past was the “plunging tape” technique,¹² which could be adapted for the present purpose at a somewhat increased cost.

The present study will not be concerned with the effect on corrosion by the small amounts of water dissolved in the hydrocarbon phase.¹³ The reason is that this effect seems to be important primarily at very low water cuts (<1%). In a recent study, Groysman and Erdman¹⁴ investigated the corrosion of CS in water/petroleum distillate mixtures in the presence of oxygen, related to the transport and storage of finished petroleum products. Low water cuts

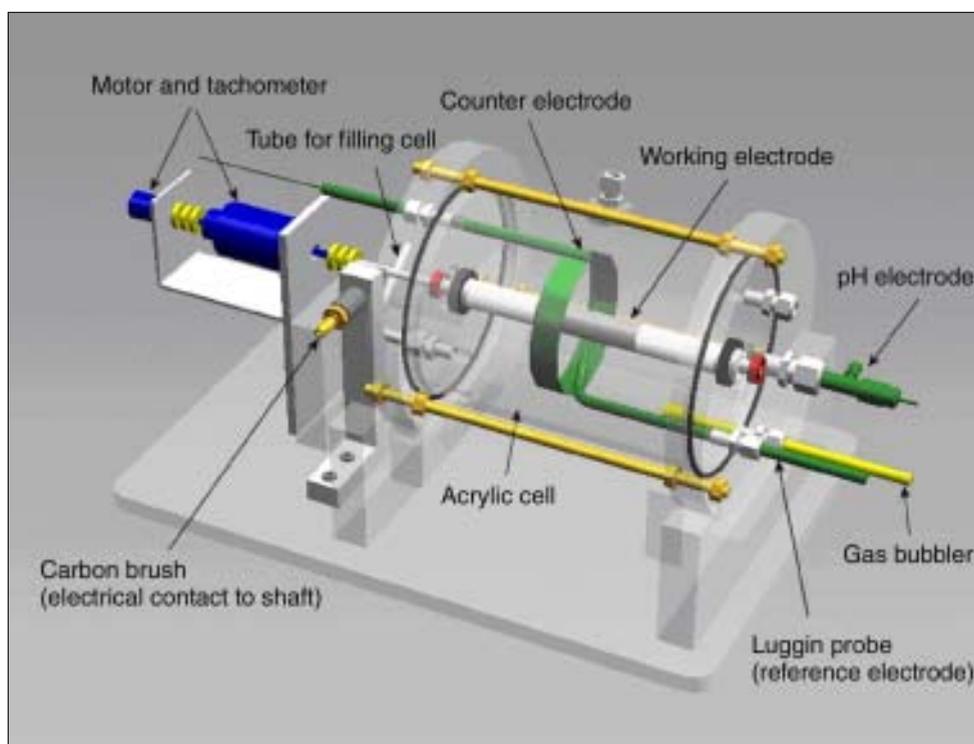


FIGURE 1. Schematic of the HRC test cell.

were used (<5%) with the goal to identify the critical value of water concentration leading to significant corrosion. The tests were done at atmospheric pressure and room temperature using simple agitation of the mixture by a magnetic stirrer. Onset of corrosion at very low water cuts (0.01% to 0.1%) was related to the presence of free water but also to the small quantities of water dissolved in the hydrocarbon phase.¹³

EXPERIMENTAL PROCEDURES

Experiments were carried out in a HRC apparatus. Figure 1 is a CAD representation of the test cell. A cylindrical mild steel test piece, mounted on a horizontal stainless steel shaft (covered with polytetrafluoroethylene [PTFE]), was rotated by a variable-speed 24-V motor, inside a horizontally mounted transparent acrylic cylindrical cell. Fittings on the ends and top of the cell were provided for electrochemical measuring instruments, for gas bubbling equipment, and for filling and emptying the cell.

The electrolyte used was a carbonated water solution, with 1% (wt%) sodium chloride (NaCl) added to aid conductivity. This solution was purged with CO₂ for 30 min before being added to the cell, and then continually while in the cell. The pH was not adjusted during the experiments and was typically at pH 4.1 ± 0.1. The temperature was 25 ± 1°C. The hydrocarbon used was analytical reagent-grade hexane, chosen for its high purity in these initial

laboratory experiments. In the future, other types of hydrocarbons will be tested with a special focus on the effect of additives such as surfactants, scale, and corrosion inhibitors.

The steel electrode was polished with abrasive paper, down to 1000 grit, prior to each experimental run. During and after polishing, the specimen was rinsed with ethanol to minimize any oxidation on the surface. The cylinder was mounted on the shaft and quickly placed into the cell, in a CO₂ environment. The pre-carbonated solution was promptly added, to the desired level, and the cell was topped with the hexane.

Experiments carried out included polarization resistance measurements, potentiodynamic scans, and corrosion potential measurements. All electrochemical measurements were performed using a potentiostat, connected to a personal computer.

Two-phase experiments were done at five different water cuts (volume fractions)—5%, 15%, 30%, and 50% water, and in the water phase alone (100% water cut). At each water cut, a series of polarization resistance experiments were carried out as follows: The speed of the electrode was stepped in increments up from zero to ~1.8 m/s (1,700 rpm, limiting motor speed), and then back down to zero, taking a measurement at each point. The electrode was polarized from the open-circuit potential, ±20 mV, scanning at 0.5 mV/s. These polarization resistance measurements were used to calculate a corrosion rate, in mil-

limeters per year, and the data were plotted against the peripheral (steel surface) velocity of the electrode. All experiments were repeated at least twice, and photographs and video recordings of the flow around the electrode were taken from different angles.

VALIDATION OF APPARATUS

Initially, a ferri-/ferro-cyanide solution was used to perform mass-transfer measurements to the rotating cylinder, to confirm the validity of the experimental setup. The potentiodynamic sweep technique was used to identify limiting currents, which were converted into mass-transfer rates and compared with the well-established mass-transfer correlation of Eisenberg, et al.¹⁵ The present results were within 10% of the proposed correlation, which was deemed satisfactory for the intended purpose.

Secondly, experiments were conducted using a CO₂ water solution. The effects of varying the pH of the solution and the rotational speed of the electrode were investigated and compared to the previously published values of Nešić, et al.¹⁶ The agreement was within the expected margin of experimental error and the equipment was then used to conduct the two-phase flow experiments as described below.

RESULTS AND DISCUSSION

Visual Observations

The appearance of the water/hexane interface at different speeds and water cuts is given in Figures 2 through 5. The left column of images shows the "front" side of the cylindrical electrode, where the steel surface emerges from the water phase, and the right column shows the "back," where the surface plunges back into the water. From the first row of images at any given water cut, showing a stationary electrode, it is clear that the steel surface is preferentially wetted by water as the water/hexane interface strongly bends upward in contact with the steel surface.⁽¹⁾

Once rotation was introduced, the interface was dragged upward at the front of the electrode and was slightly depressed at the back. This behavior common to flowing two-phase flow systems amounts to a change of the static wetting angles.⁶ The so-called dynamic wetting angle for water increased toward 180° at the front of the electrode and decreased somewhat at the back (the reverse being true for hexane).

At moderate speeds, water at the front of the electrode was dragged all the way around the electrode. This was true for all the water cuts used; however, it can be observed that the amount of water

dragged around the electrode became smaller with the decreasing water cut due to the effect of gravity. It also can be seen that frothing of the interface occurred at rotational speeds of 500 rpm to 1,000 rpm and higher. The frothing typically started at the front of the electrode (Figures 4[c] and 5[c]). Most of the short-lived bubbles appeared to be above the original level of the water/hexane interface, suggesting a hexane-in-water structure. Also, it can be noticed that at the back of the electrode, the interface was progressively more depressed (dynamic water wetting angle $\ll 90^\circ$) as the rotational speed increased. It appears that, in this velocity range, jets of hexane occasionally penetrated the water at the back of the electrode and emerged at the front forming the bubbles.

As the speed was increased further, the interface was progressively more depressed at the back of the electrode, until at a critical velocity the hexane phase "broke through" and completely separated the water phase from the electrode. This happened only at water cuts of 30% and lower. In Figures 2 through 5, one can observe how the critical velocity moved toward lower speeds as the water cut was reduced. It is assumed that the separation occurred when the momentum of the hydrocarbon phase was sufficiently high to completely displace the water at the steel surface held by adhesion, as illustrated on the schematic in Figure 6. It was initially suspected that the centrifugal forces played a major role in the observed transition; however, this explanation was discarded because the varied behavior observed at different water cuts could not be readily explained by using this argument.

Once the separation occurred, a thin layer of water could be seen attached to the steel surface, which disappeared with time and could not be observed at higher velocities. The hexane/water interface beneath the electrode was observed to bow downward because of the hydrocarbon phase gushing under the shaft.

Polarization Resistance Measurements

Polarization resistance measurements served a dual purpose. They enabled corrosion rate estimates and served as an additional indicator of the steel surface wetting.

A summary of the corrosion rate measurements as a function of the steel surface velocity (rotational speed) for a range of water cuts is shown in Figure 7. With the shaft stationary, the rate of corrosion is roughly proportional with the water cut (i.e., the submerged area of the electrode). However, the water cut was smaller than the actual water-wetted surface area fraction, since the interface tended to bow upward at the steel surface due to its hydrophilic nature.

As the electrode began rotating, the corrosion rate rapidly increased. This increase was steepest for

⁽¹⁾ A very different behavior can be observed on the PTFE-covered surface where the wetting angle was $\sim 90^\circ$ under stagnant conditions. PTFE showed poor affinity for either of the liquids when tested in air.

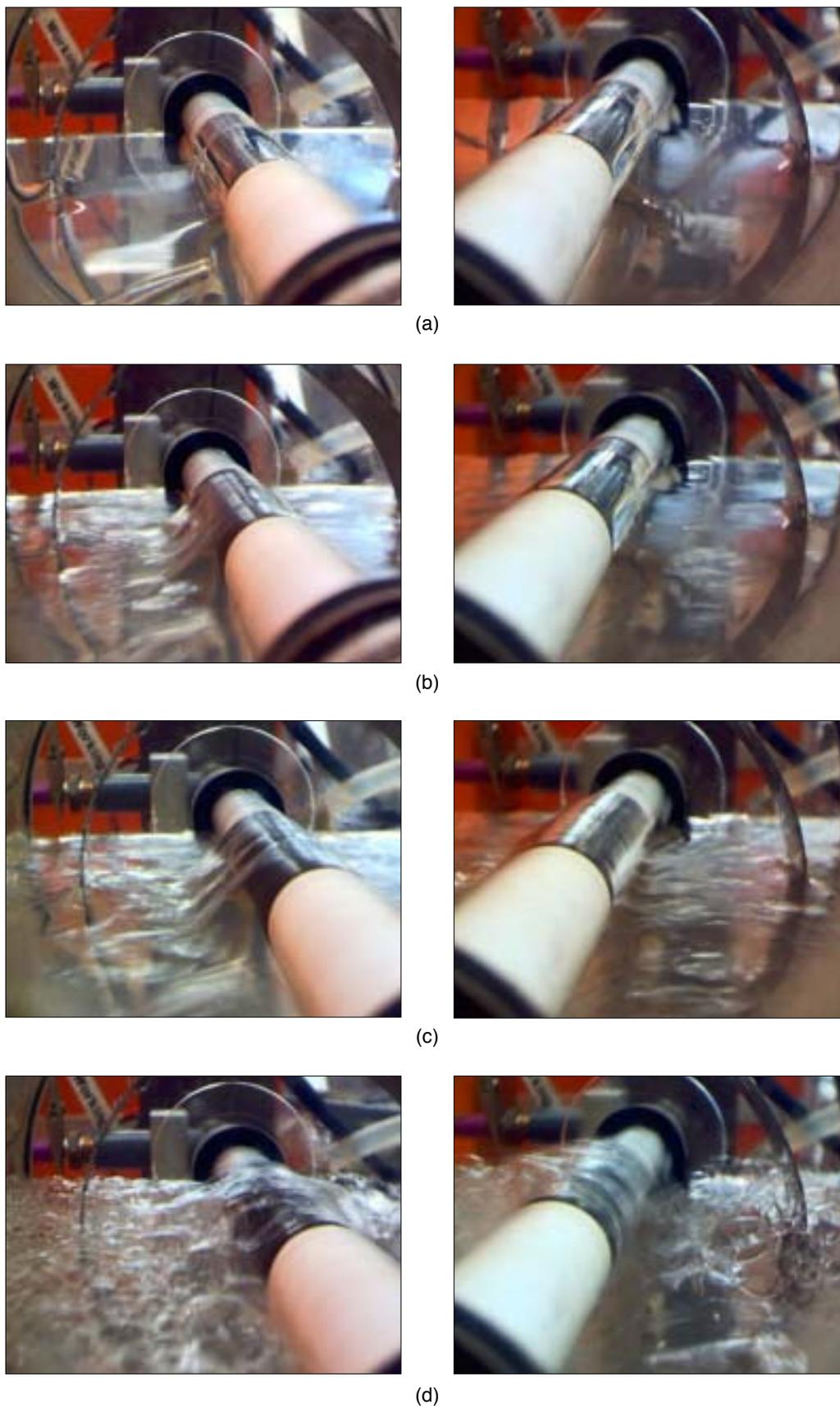


FIGURE 2. Images of the rotating cylinder and the water/hydrocarbon interface at 50% water cut and various speeds: (a) stationary, (b) 500 rpm, (c) 1,000 rpm, and (d) 1,500 rpm.



(a)



(b)



(c)



(d)

FIGURE 3. Images of the rotating cylinder and the water/hydrocarbon interface at 30% water cut and various speeds: (a) stationary electrode, (b) 500 rpm, (c) 1,000 rpm, and (d) 1,500 rpm.

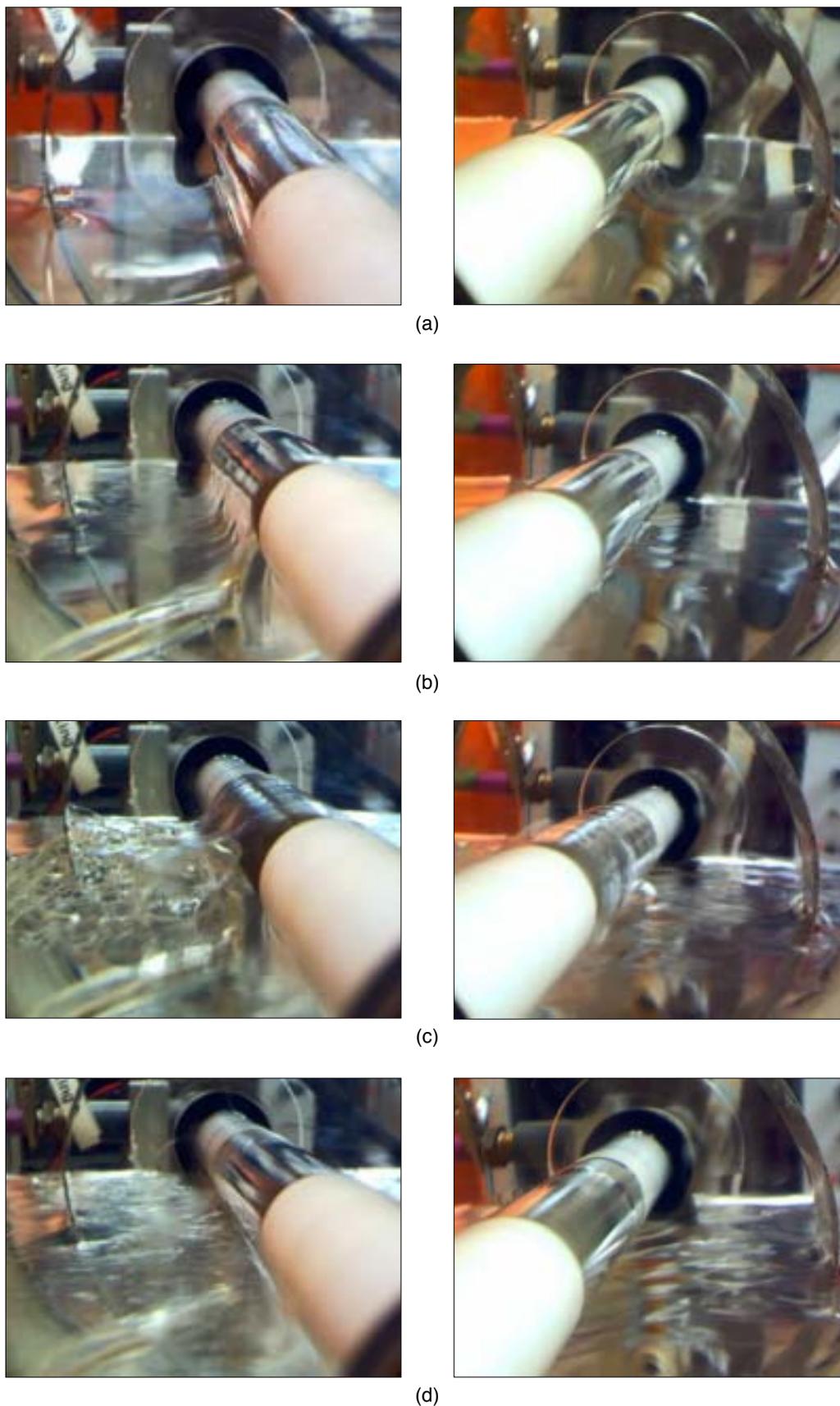


FIGURE 4. Images of the rotating cylinder and the water/hydrocarbon interface at 15% water cut and various speeds: (a) stationary electrode, (b) 500 rpm, (c) 1,000 rpm, and (d) 1,500 rpm.

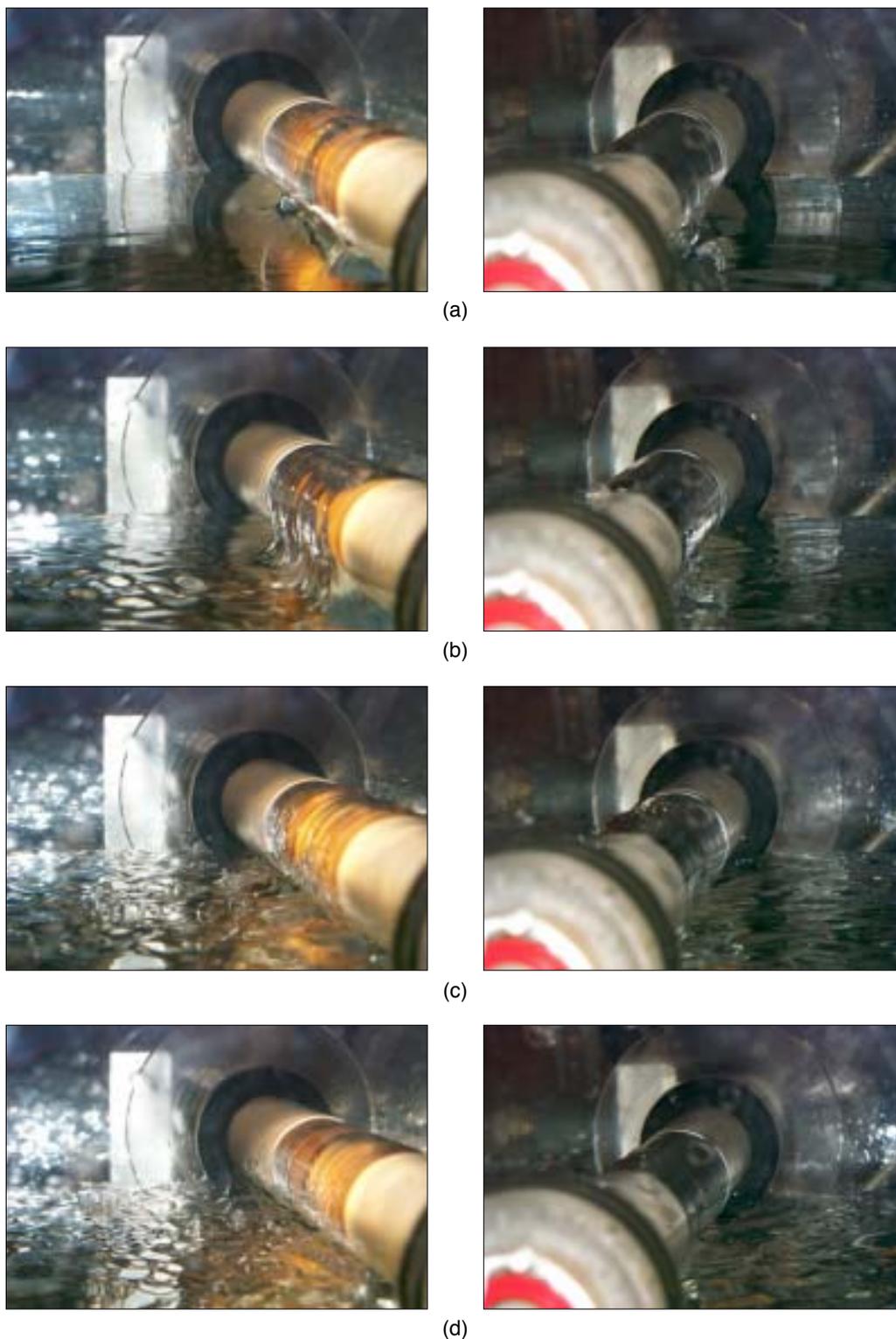


FIGURE 5. Images of the rotating cylinder and the water/hydrocarbon interface at 5% water cut and various speeds: (a) stationary electrode, (b) 500 rpm, (c) 1,000 rpm, and (d) 1,500 rpm.

the lowest water cuts. This can be explained by the water being dragged around the electrode (for example, Figure 5[b]), resulting in a sharp increase of the water-wetted area. This area increase was largest for the lowest water cuts.

At moderate rotation speeds (superficial velocity < 0.5 m/s), the corrosion rate kept increasing with increased velocity. This can be ascribed to the partial mass-transfer control of the CO_2 corrosion reaction under these conditions.¹⁶ Higher velocity led to more

turbulent flow and a better supply of the steel surface with the corrosive species. A support for this explanation can be found in the almost identical slopes of all the corrosion vs velocity curves seen in Figure 7 for the velocity range 0.1 m/s to 0.5 m/s, irrespective of the water cut. The difference between the corrosion rates at the same velocity for various water cuts can be ascribed to the thinner film of water dragged around the electrode at lower water cuts, which resulted in less turbulent flow in the water film and somewhat lower mass-transfer rates.

At even higher speeds (velocity >0.5 m/s) as the water/hexane interface began frothing (for example, Figures 4[c] and 5[c]), some of the hexane-in-water bubbles were entrained in the water film enveloping the electrode. This has effectively decreased the water-wetted area of the steel electrode leading to a slight reduction in the corrosion rate, as seen in Figure 7. Therefore, as the velocity was further increased, two opposing effects determined the overall corrosion rate: an increase in mass transfer due to higher turbulent mixing in the water film and the entrainment of the hexane bubbles into the water film, which decreased the water-wetted area. Progressively, the latter effect became dominant as more hexane jets gushed under the electrode. This led to a leveling of the corrosion rate and finally to its decrease with increasing velocity.

As the velocity was increased even further, above a critical value, the hexane displaced the water from the steel surface, enveloping the entire electrode (for example, Figures 3[d], 4[d], and 5[d]). This led to a loss of electrical contact between the working and counter electrodes, which was recorded as a zero corrosion rate in Figure 7. The critical velocity was reached only at water cuts of 30% and lower. The limitations of the electrical motor prevented us from identifying if there was a critical velocity at the 50% water cut; however, the downward trend in the corrosion rate is clear. The critical velocity decreased as the water layer adhering to the electrode being thinner at lower water cuts, making it easier for the hexane to displace it.

Hysteresis

The polarization resistance measurements reported above were repeatable as long as the velocity stayed below the critical value. This was true for all the water cuts tested, irrespective of whether the velocity was progressively increased (forward velocity scan) or decreased (backward velocity scan). However, once the critical speed was exceeded and the hexane displaced the water phase from the steel surface, a large hysteresis appeared during the reverse velocity scan. As shown in Figure 8, the reattachment of the water phase occurred at much lower rotational speeds than those at which it was separated.

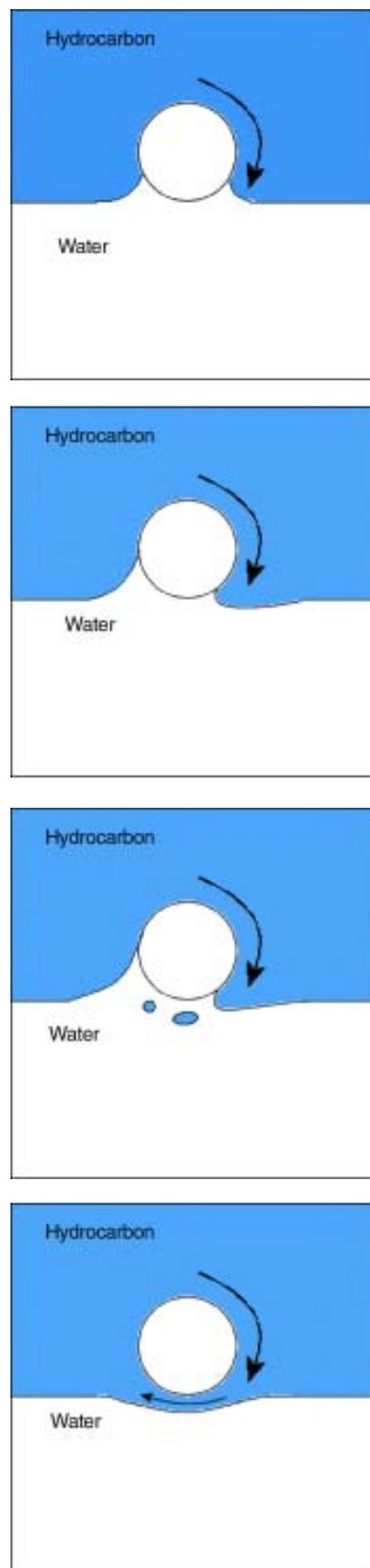


FIGURE 6. Schematic of the interface separation process as speed is increased.

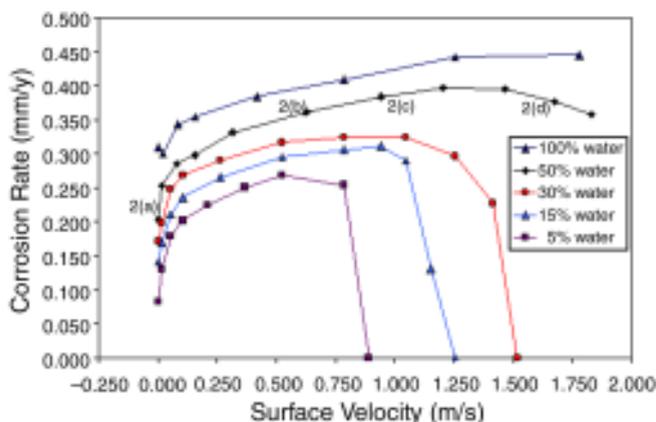


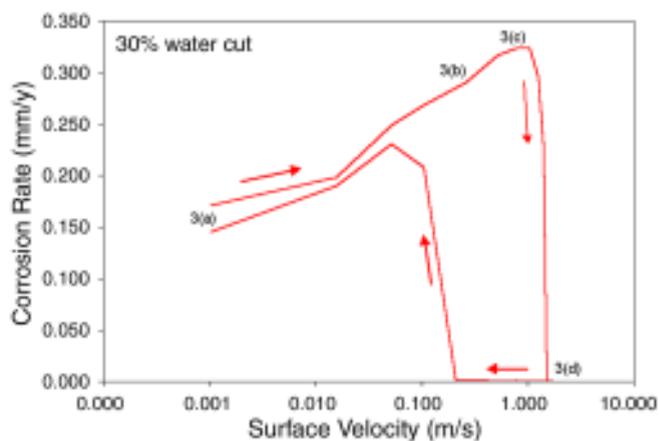
FIGURE 7. Corrosion rate trends with increasing velocity. Points 2(a) through 2(d) refer to the corresponding images in Figure 2.

In simple words, it appeared that it was easier for either phase to “hang on” to the steel surface than it was to displace the other phase from the surface. This is understandable as the detached phase does not have the “aid” of the adhesion forces in the same way as the one wetting the surface does. Logically, as the water cut was reduced, the hysteresis increased (i.e., it became more difficult for the water phase to displace hexane from the metal surface). At the lowest water cut tested (5%), the water phase reattached at the electrode surface only after the electrode rotation was stopped. This is not unusual; a similar behavior was reported by Teeters, et al.,⁶ (using a dynamic Wilhelmy plate technique) and was termed “hybrid wetting.”

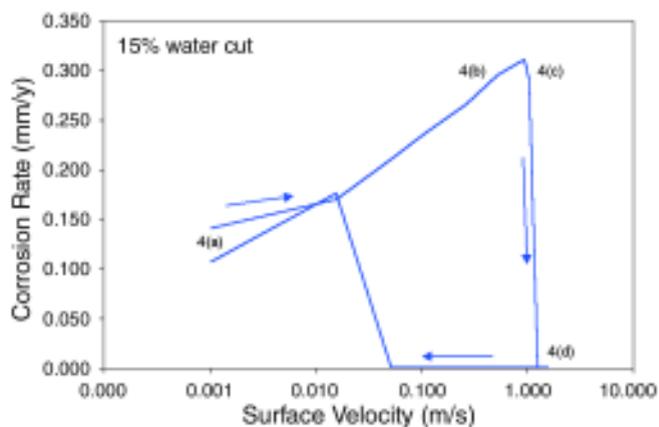
IMPLICATIONS OF THE FINDINGS

It is clear that the multiphase flow regimes and the surface wetting behavior described above cannot be transposed simply to a field situation due to numerous complicating factors such as different flow geometry and flow regimes, varying water/oil chemistry, high temperature, etc. However, this was not the intended purpose of the present study. The motivation was to devise and prove a relatively simple and cheap apparatus, which can be easily copied and developed further by other researchers in the field and which can enable rapid measurements of water wetting and corrosion rates under multiphase flow conditions. It is believed that such studies can be valuable to practicing engineers needing rapid identification of key parameters and main trends. Also, preliminary studies using the HRC can help researchers in the field of CO₂ corrosion in multiphase flow to optimize their experimental matrices before embarking on much more expensive multiphase flow loop studies.

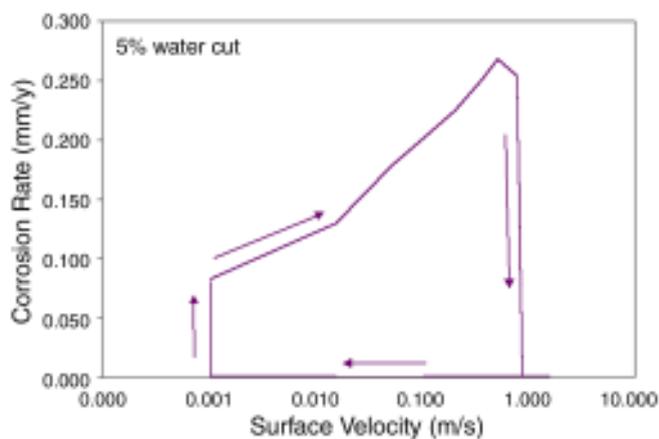
The HRC apparatus described above is relatively simple and cheap to build and operate. At the same time, it can produce more relevant information about



(a)



(b)



(c)

FIGURE 8. Corrosion rate trends with increasing and decreasing velocity at various water cuts. Points 3(a) through 3(d) and 4(a) through 4(d) refer to images in Figures 3 and 4, respectively.

water wetting effects on CO₂ corrosion when compared to previously used techniques such as sessile drops and stirred beakers. In many ways, the HRC is not meant to replace these simpler techniques but rather to complement them by including more realistically the effect of dynamic intermittent wetting of the steel surface.

With all these limitations in mind, it can be speculated that some of the results produced in this first series of experiments are practically valuable even if the tests were done using a clean, film-free steel surface, at low temperature and pressure, using a pure single-component hydrocarbon, with no additives. It is probably not a coincidence that in the present experiments, the oil wetting of the steel surface happened only at water cuts of 30% and lower (Figure 7), which is in broad agreement with the findings of Lotz, et al.³ The critical velocity that led to oil wetting of the steel was in the range from 0.75 m/s to 1.5 m/s, which is a similar velocity range as the one identified by Wicks and Fraser² for water entrainment in pipe flow. To the authors' knowledge, there are no accurate data from the field that would allow validation of these findings; however, the broad agreement with these two benchmark studies is very encouraging. Finally, the observed hysteresis (Figure 8) suggests that surface properties of the steel are important and that any future modeling of the dynamic wetting is not going to be simple. On the practical side, one can conclude that at very low water cuts, once the water becomes entrained and the steel surface becomes oil-wet, it is very likely that things will stay that way unless the flow is stopped.

CONCLUSIONS

- ❖ A HRC apparatus was used to investigate CO₂ corrosion of CS in a flowing water/hexane mixture at water cuts between 5% and 50%, $p_{\text{CO}_2} = 1$ bar, $T = 25^\circ\text{C}$, and pH 4.1.
- ❖ The metal surface was hydrophilic under stagnant conditions.
- ❖ Under flowing conditions, water was the predominant phase wetting the steel surface, particularly at low velocity and high water cut.
- ❖ At lower water cuts, a threshold velocity was identified when the surface became oil-wet and all corrosion stopped.

❖ It was confirmed that the dynamic wettability of the steel surface depends primarily on the hydrodynamics of the multiphase flow. However, surface adhesion of different phases lead to wetting hystereses observed in transient flow regimes.

ACKNOWLEDGMENTS

A number of colleagues and students contributed to the design, construction, and testing of this original experimental apparatus. The authors acknowledge S. Lillebo, G. Dick, B. Allsop, A. Kwok Wai Tham, and S. Coles.

REFERENCES

1. C. de Waard, U. Lotz, D.E. Milliams, *Corrosion* 47 (1991): p. 976.
2. M. Wicks, J.P. Fraser, *Mater. Perform.* 14, 5 (1975): p. 9.
3. U. Lotz, L. Van Bodegomard, C. Ouwehand, *Corrosion* 47, 8 (1991): p. 635.
4. W.P. Jepson, R. Menezes, "Effects of Oil Viscosity on Sweet Corrosion in Multiphase Oil/Water/Gas Horizontal Pipelines," *CORROSION/95*, paper no. 106 (Houston, TX: NACE International, 1995).
5. G. Schmitt, N. Stradmann, "Wettability of Steel Surfaces at CO₂ Corrosion Conditions, I. Effect of Surface Active Compounds in Aqueous and Hydrocarbon Media," *CORROSION/98*, paper no. 28 (Houston, TX: NACE, 1998).
6. D. Teeters, B. Smith, M.A. Andersen, D.C. Thomas, *J. Colloid Interface Sci.* 126, 2 (1998): p. 641.
7. T.D. Blake, "Wetting Kinetics—How Do Wetting Lines Move?," *AIChE Ann. Meeting*, paper no. 1a (New York, NY: AIChE, 1988).
8. T.D. Blake, K.J. Ruschak, "Wetting: Static and Dynamic Contact Lines," in *Liquid Film Coating*, ed. S. Kistler, P. Schwiezer (London, U.K.: Chapman & Hall, 1997).
9. R. Burley, R.P.S. Jolly, *Chem. Eng. Sci.* 39 (1984): p. 1,357.
10. A. Mestrovic-Markovic, D.J. Matic, *J. App. Electrochem.* 14 (1984): p. 675.
11. M.N. Esmail, M.T. Ghannam, *Can. J. Chem. Eng.* 68, (1990): p. 197.
12. R.T. Perry, "Fluid Mechanics of Entrainment through Liquid-Liquid and Liquid-Solid Junctions" (Ph.D. thesis, Univ. of Minnesota, 1967).
13. B. Craig, *Corrosion* 54, 8 (1998): p. 657.
14. A. Groysman, N. Erdman, *Corrosion* 56, 12 (2000): p. 1,266.
15. M. Eisenberg, C.W. Tobias, C.R. Wilke, *J. Electrochem. Soc.* 101 (1954): p. 306.
16. S. Nešić, J. Postlethwaite, S. Olsen, *Corrosion* 52, 4 (1996): p. 280.