

## THIRD QUARTERLY REPORT

Date of Report: *July 8, 2005*

Contract Number: *DTRS56-04-T-0002*>

Prepared for: *DOT, PRCI, SoCal Gas, Gaz de France, and Valero Energy*

Project Title: *Determining Integrity Reassessment Intervals through Corrosion Rate Modeling and Monitoring*

Prepared by: *Southwest Research Institute*

For quarterly period ending: *July 1, 2005*

**Table 1. Activities and Milestone Status Summary**

Activity #	Task #	Activity/Milestone	Expected Date	Status
11	1.4	Develop scaling parameters for external corrosion	5/31/2005	Simplified assessment methods were found for some conditions
12	2.2	Run internal corrosion calculations and compare to literature	6/30/2005	Initial calculations performed
13	3.2	Conduct a number of disbonded coating experiments	6/30/2005	Initial experiments conducted. Unanticipated problems were encountered.
14	4.2	Install MAS probe in pipeline facility and obtain field data	7/31/2005	Completed

### TECHNICAL STATUS

#### COMPUTER MODELING OF DISBONDED COATING CORROSION RATES/CHEMISTRY

##### Accomplishments

- (1) In 2D geometry, the effect of O<sub>2</sub> and CP on corrosion inside the disbonded coating was examined. Simplified guideline was developed.
- (2) In 2D geometry, the effect of flow on the crevice corrosion rate of pipeline due to O<sub>2</sub> transport was investigated.
- (3) Crevice corrosion due to O<sub>2</sub> in a seven component system containing NaCl and the complex ion of Fe(OH)<sup>+</sup> was investigated with and without CP.

- (4) Crevice corrosion due to CO<sub>2</sub> and O<sub>2</sub>, in a 12 component system including complexes, carbonate and bicarbonate species have been being under investigation.
- (5) Internal corrosion due to O<sub>2</sub> and CO<sub>2</sub> with consideration of ionic transport is being investigated.

### Problems

In performing the above tasks, it has been found that in the system containing CO<sub>2</sub>, numerical convergence is a problem. This problem is considered by colleagues to be a common challenge in the numerical computations.

### Background

Lack of penetration of CP (shielding) is not likely to lead to significant corrosion in the disbonded region in the absence of oxygen or CO<sub>2</sub> penetration. This is because cathodic reaction will not be sufficient to sustain significant corrosion under open-circuit conditions. Therefore, an important set of problem for estimating corrosion under shielded, disbonded coatings would be the consideration of oxygen or CO<sub>2</sub> penetration into the disbonded region.

Two types of common crevice geometries found in the field were addressed in the modeling: (i) wrinkles usually associated with disbonded high-density polyethylene (HDPE) coating that can be approximated by a rectangular shaped disbondment and (ii) disc shaped disbondment with fusion-bonded epoxy (FEB) coating. In the calculations reported here, a rectangular disbondment was modeled to simulate the crevice geometry used in the experiments.

### Results

Figure 1 shows the effect of flow on the crevice corrosion rate when there is CP applied at the holiday (-0.900 V vs. CSE). The crevice gap between the coating and steel is 4 mm and the length is 0.5 m, consistent with the experimental setup being done in collaboration with Gas de France. The solution resistivity used in the computation is 25 ohm-m and the O<sub>2</sub> pressure at the holiday is 0.2 atm. The crevice geometry is shown in Figure 2 where the velocity and O<sub>2</sub> pressure distribution in the geometry are also shown. Note that the y axis in Figure 2 has been scaled up and the holiday, not labeled, is located in the upper boundary with 1 cm in length from the left corner.

Figure 1 shows that both the crevice corrosion potential and current density curves have a maximum inside the crevice. In contrast, there is no such maximum when there is no flow. The potential and current density with flow are much higher, indicating that flow can increase the crevice corrosion rate significantly inside the crevice. With flow, O<sub>2</sub> is carried inside the crevice and it cannot be reduced by cathodic current which can have only very limited penetration into the crevice near the holiday. This computational result is qualitatively consistent with the experimental finding in a Gas de France report.

The distributions of velocity and dissolved O<sub>2</sub> pressure in the crevice, near the holiday area, are shown in Figure 2. The velocity used in the computation is low, less than 2 cm/s and hence, the flow is clearly shown laminar. It is quite clear that the flow forces O<sub>2</sub> to disperse into the crevice and distributed broadly inside. Hence, higher

corrosion rate is expected in comparison with the case of no flow where  $O_2$  can only diffuse into the crevice very near the holiday and it has a very low concentration inside the crevice.

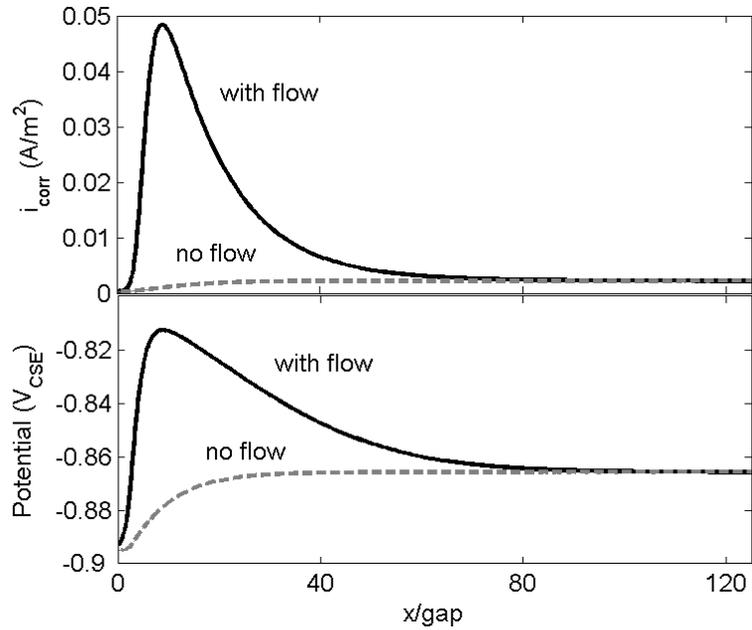


Figure 1: Crevice potentials and current densities computed at a holiday potential of  $-0.900$  V vs. CSE when there are flow or no flow.

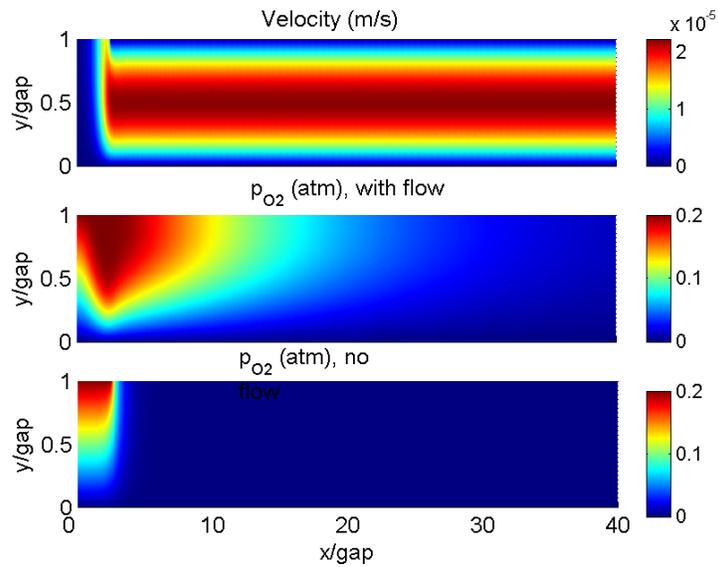


Figure 2: Distribution of velocity and dissolved  $O_2$  pressure where there are flow and no flow.

---(2) in the previous quarterly report, crevice corrosion in 2D was shown where the chemistry in the crevice was assumed uniform and Laplace's equation was used. This assumption is justified in Figure 3. The curve labeled with NP indicates results computed from Nernst-Plank transport equations. In both cases with either Laplace equation or Nernst-Plank equation, Tafel equation was used for the corrosion current density. Good agreement is shown.

Although the Tafel equation is mostly used in the literature to express corrosion current density, this equation may however become inaccurate under certain circumstances. Then, the more accurate Butler-Volmer equation should be used. As shown in Figure 4, there is a discrepancy in the results obtained from the Tafel expression in comparison to the Butler-Volmer equation. This discrepancy is attributed by the fact that the cathodic term in the Butler-Volmer equation could become large due to increase of ferrous ion concentration inside the crevice.

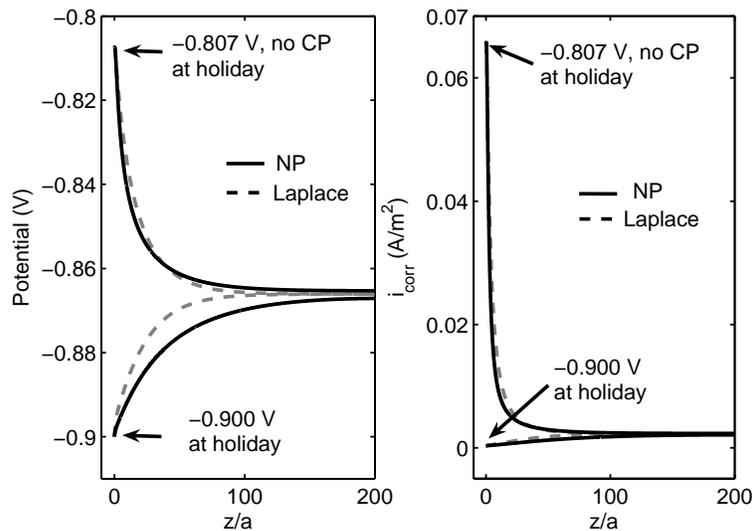


Figure 3: Justification of uniform chemistry assumption when Tafel equation is used to express the steel corrosion rate. Two cases: No CP and with CP at holiday potential of  $-0.900$  V vs. CSE were computed.

---(3) the combined effect of  $\text{CO}_2$  and  $\text{O}_2$  on the crevice corrosion of steel is investigated in 1D when there is co-precipitation of  $\text{FeCO}_3$  and  $\text{Fe}(\text{OH})_2$ . The dissolved  $\text{O}_2$  pressure at the holiday is set at 0.21 atm. The crevice corrosion rate and potential are shown in Figure 5, where the Butler-Volmer equation is used to compute the corrosion current density. The potentials at the end of the crevice are different at different holiday potentials because of the chemistry there is different. At the holiday potential of  $-0.830$  V, the corrosion rate is relatively large and hence may be considered as insufficient CP. In contrast, at the holiday potential of  $-0.850$  V the CP seems sufficient due to the low corrosion rate in the crevice and due to this rate at the holiday is smaller than in the rest of the crevice.

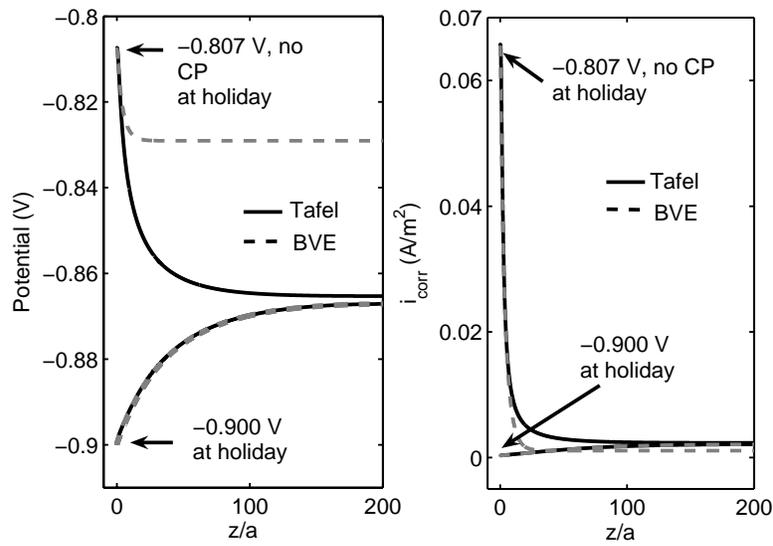


Figure 4: Discrepancy is shown when Tafel equation and Butler-Volmer equation are used respectively used to express the steel corrosion current density. Two cases: no CP and with CP, are compared.

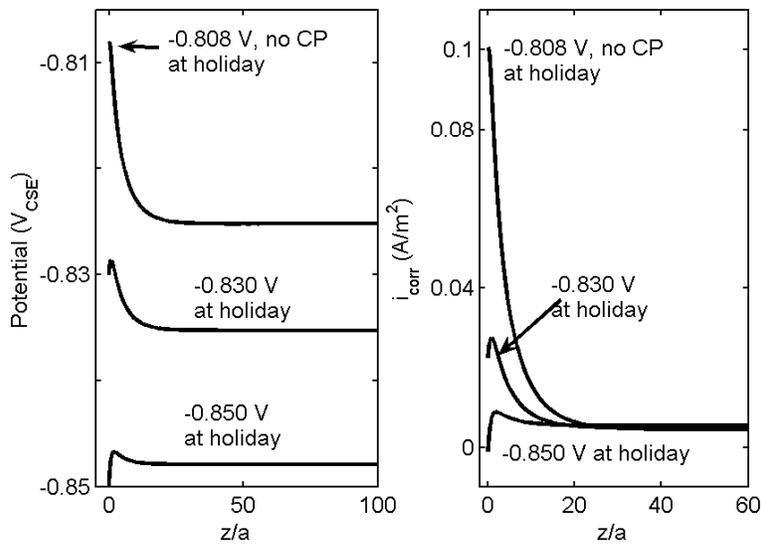


Figure 5: Crevice corrosion current densities and potentials with dissolved CO<sub>2</sub> in the system when FeCO<sub>3</sub> and Fe(OH)<sub>2</sub> co-precipitate and when there are CP and no CP.

### Future Work:

- (1) Summarize the above work and write down to record the findings;
- (2) Seek methods to simplify the models. These simplified models are hoped to be used conveniently by operators or they can be considered to be implemented into the NACE ICDA and ECDA standards;
- (3) Work needs to be done in completing the crevice corrosion with combined CO<sub>2</sub> and O<sub>2</sub>;
- (4) The numerical convergence problem needs to be resolved;
- (5) Introduce flow in the system with CO<sub>2</sub>;
- (6) Internal corrosion to include H<sub>2</sub>S in the system;
- (7) Simplification of the internal corrosion model.

### **EXTERNAL CORROSION VALIDATION EXPERIMENTS**

The experimental design was reported in the previous quarter. The design is meant to simulate slow flow of the solution through the disbanded region while maintaining aeration and other boundary conditions. Probes at various locations will measure the potential, pH, and corrosion rate distributions as functions of time. The cell was assembled and initial experiments were conducted with a low flow rate. However, many experimental difficulties have been encountered: (i) leakage of the crevice cell through gasketed joints, (ii) instability of potentials due to problems with reference electrode bubbles; (iii) problems with the potentiostat circuit cards; and (iv) breakage of glass electrodes used for measuring pH inside the crevice. Many of these problems have been addressed and we are awaiting new glass electrodes prior to proceeding with the experiments.

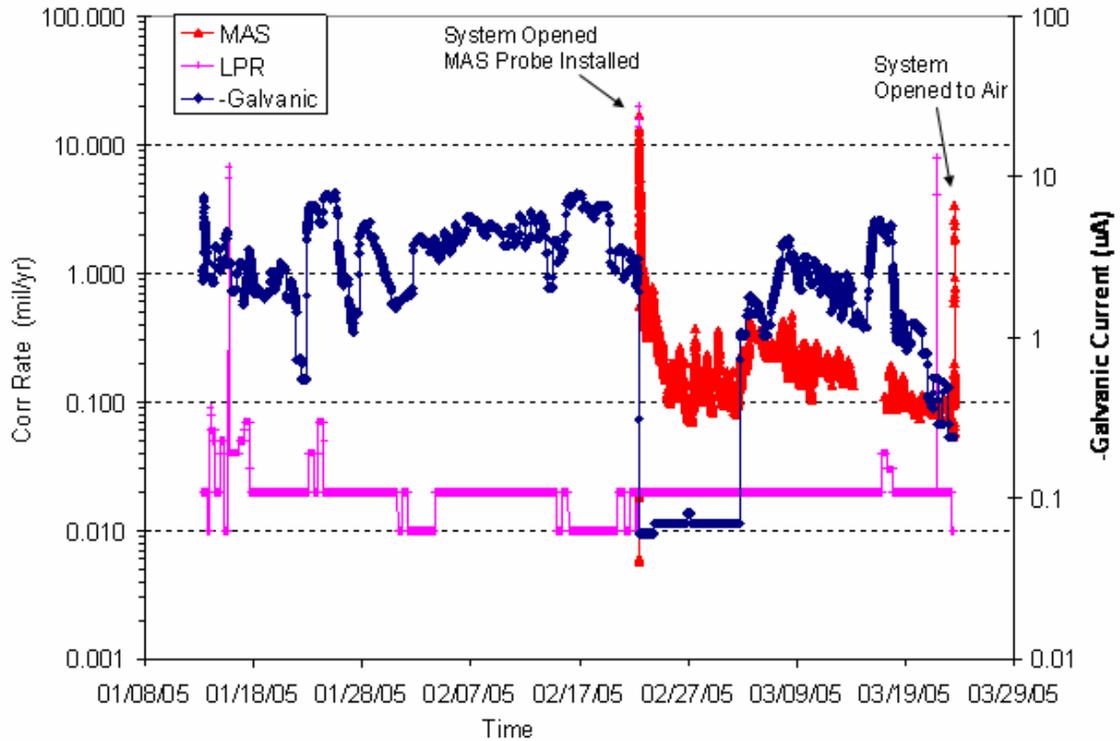
### **INTERNAL CORROSION VALIDATION EXPERIMENTS**

As reported before, Multielectrode Array Sensor probe was placed in the liquids pipeline side loop at two different locations of a pipeline company. First set of tests were performed in a plant (Figure 6), which is an intermediate point in the transportation of hydrocarbon liquids. The corrosion data from the MAS



**Figure 6. MAS probe installed in a liquids pipeline side loop**

probe and the galvanic probe that was already installed by the plant (that consisted of two dissimilar metals between which a current was measured) are shown in Figure 7.

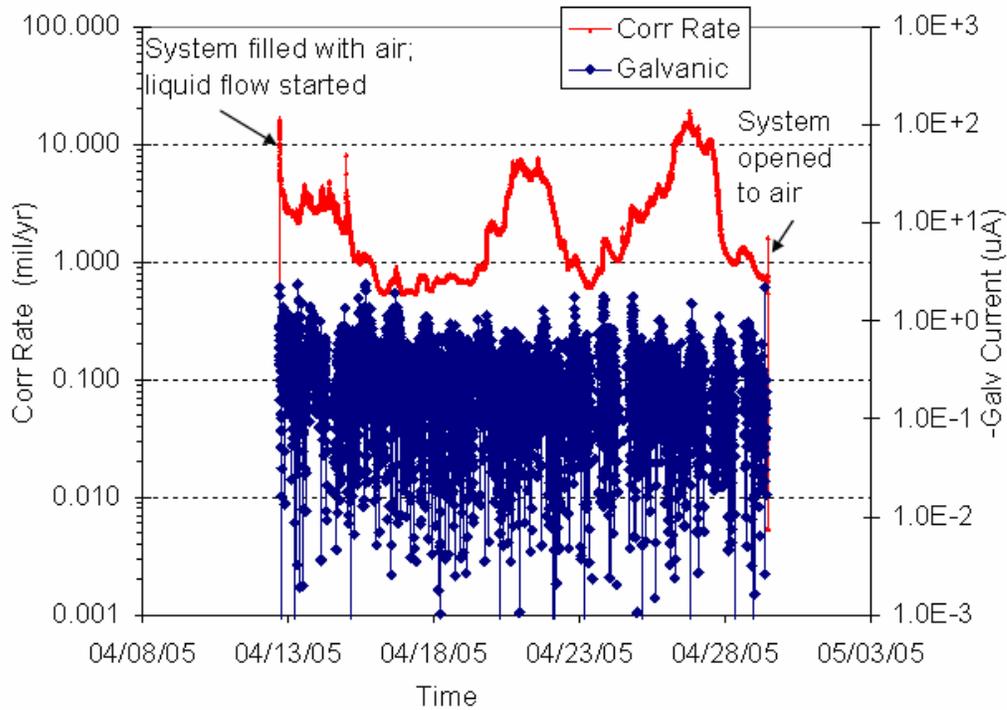


**Figure 7. The internal corrosion in the side loop of a liquids pipeline monitored by three different probes.**

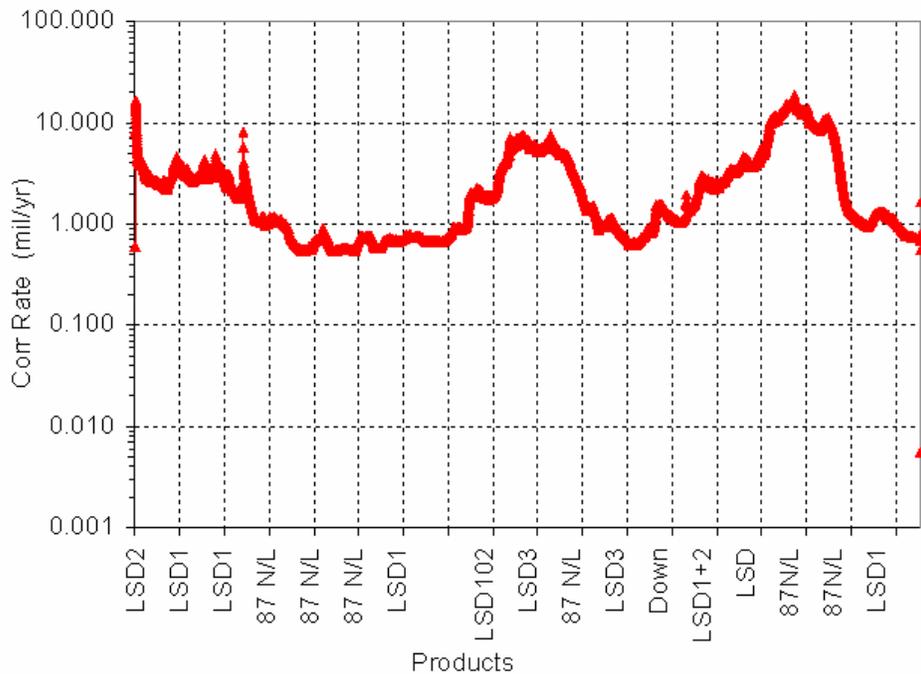
The LPR readings in Figure 7 indicated a low corrosion rate because this probe was not in the lower part of the pipe where water occurs. On the other hand, both MAS probe and the galvanic sensor responded similarly to changes in pipeline conditions. Note that the MAS probe indicates a corrosion rate that is somewhat lower than the actual corrosion rate because only a portion of the sensor area undergoes anodic dissolution. However, because the corrosion rate is calculated from the 3 sigma of the current distribution, the corrosion rates measured by MAS probe may not be highly non-conservative.

The probe was moved to another plant of the same company, which is a receiving terminal for the transmission system. The readings of both the Galvanic and MAS probes are shown in Figure 8. The variations in the corrosion rate of the MAS probe not only reflect ingress of air, but also variations in the products transported over this time period (Figure 9).

The corrosion rates can reach a value as high as 10 mm/y, but are more typically about 0.1 mm/y. A better understanding of the effect of input parameters on corrosion rates will be important in determining the corrosion rates in these liquid lines.



**Figure 8. Comparison of MAS probe versus galvanic probe in the liquids pipeline near a terminal area.**



**Figure 9. Variation of corrosion rates with products transported in the pipeline. No particular correlation is observed**

### **BUSINESS STATUS**

- The DOT portion of the funding has been expended slightly over 71 percent. The PRCI cash co-funding has been expended in the development and validation of the MAS probe.

### **SCHEDULE**

Several tasks are in progress and are on schedule. The external corrosion experimental program is behind schedule due to unforeseen experimental difficulties. We anticipate that a substantial portion of the experiments will be completed by the staff member from Gaz de France while he is here. Once he returns to France, we would complete any remaining experiments using SwRI staff.

Field data gathering is behind schedule and will be accelerated in the next reporting period.

### **PAYABLE MILESTONES**

Third quarterly report

### **ISSUES, PROBLEMS OR CHALLENGES**

These have been mentioned in the different tasks.

### **PLANNED ACTIVITIES IN THE NEXT 30 TO 60 DAYS**

- Continue modeling corrosion rates in disbonded coating using FEMLAB and MATLAB
- Obtain data on flow effects from the external corrosion cell
- Hold discussions with other co-funding organizations on field data needs
- Submit a paper on the model results after obtaining the needed permissions.

## **PUBLIC PAGE**

One of the factors important in determining the reassessment interval is the corrosion rate. Both external and internal corrosion rates are affected by a number of conditions. The objective of this project is to use mechanistic modeling to generate simplified guidelines for estimating external and internal corrosion rates. A need for such a model-based estimation is especially important for corrosion under shielded, disbonded coatings.

Significant progress has been made in modeling the corrosion rate under shielded, disbonded coatings for both static and low-flow conditions (low flow assumed for external corrosion is reasonable under most circumstances where pin-hole leaks in coatings can lead to slow flow of groundwater through the disbonded area). It is shown that with the diffusion of oxygen through the coating holiday, flow conditions can significantly increase the corrosion rate near the mouth of the disbondment. These calculations will be validated by laboratory experiments. The model calculations also explored the effect of carbon dioxide permeation through the coating on external corrosion rate. Based on these calculations, simplified estimation guidelines will be developed.

Internal corrosion in a liquids pipeline was monitored using a multielectrode array sensor. The sensor corrosion was quite sensitive to changing input conditions, such as air ingress. Corrosion rates ranging from 0.1 mm/y (4 mpy) to 1 mm/y (40 mpy) were measured. It should be noted that the high corrosion rates were transient phenomena that occurred when the system was open to install the probes, not long-term corrosion rates.