

## QUARTERLY REPORT

Date of Report: *December 21, 2004*

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: *December 31, 2004*

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

Activity #	Task #	Activity/Milestone	Expected Date	Status
1	1.1	Modify TECTRAN to include flow, gas permeation, and debug code	12/31/2004	Using another commercial code, FEMLAB
2	3.1	Plan validation experiments for external corrosion modeling	11/30/2004	Initial planning started
3	1.2	Compare predicted potential, pH, and rates to literature experiments	12/31/2004	Initial benchmark calculations performed
4	4.1	Test probes for internal corrosion monitoring	12/31/2004	Probe testing completed

## TECHNICAL STATUS

### Computer Modeling of Corrosion Rates/Chemistry

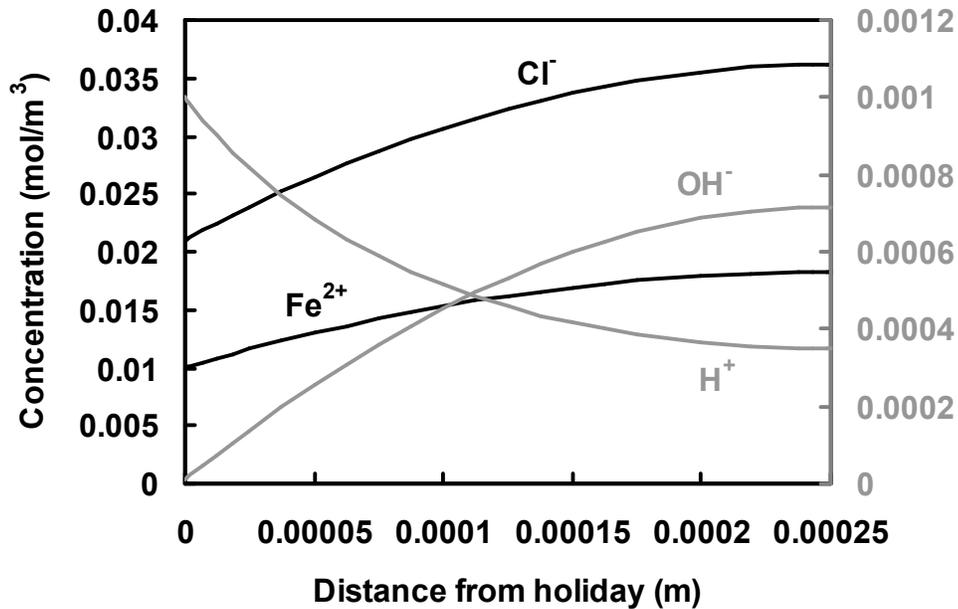
The project aims to use a computer model to predict the external as well as the internal corrosion of pipelines under extensive conditions. The corrosion system will involve disbonded permeable coatings, various levels of cathodic protection, transport and reaction associated with molecular (CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S) and ionic (H<sup>+</sup>, Cl<sup>-</sup>) species and flow. As stated in our original proposal, we had planned to modify a computer code previously developed at SwRI under a GRI Basic Research Program, called TECTRAN, to perform these calculations. However, during the past month, some effort was made to seek new methods that allow for achievement of the project goal more efficiently.

We have found that MATLAB, a high-performance language for technical computing, can be used to solve the disbonded corrosion problem for steady state including variable boundary conditions and flow, two factors that are required to be

integrated into the TECTRAN code in order to achieve the project goal. FEMLAB, a commercially available, multipurpose, software program based on MATLAB, is also being explored for use to solve the time-variant conditions in the disbanded region of the pipeline. The work to date has shown that this software would allow for the transient and steady state problems to be solved. We are confirming these initial findings prior to fully committing to its use in the project instead of TECTRAN.

Several benchmark problems were chosen and part of the validation has been completed in this month. We have developed analytical solution of the transient system of two-component ionic transport with one reaction at a constant rate (HCl solution, components of  $H^+$  and  $Cl^-$ , with hydrogen ion reduction under uniform cathodic polarization). For three-component ( $FeCl_2$  acidic solution, components of  $Fe^{2+}$ ,  $Cl^-$  and  $H^+$ ) and four-component ( $FeCl_2$  solution, components of  $Fe^{2+}$ ,  $Cl^-$ ,  $H^+$  and  $OH^-$ ) systems with electrochemical reactions following Tafel equations, steady state solutions were obtained from MATLAB.

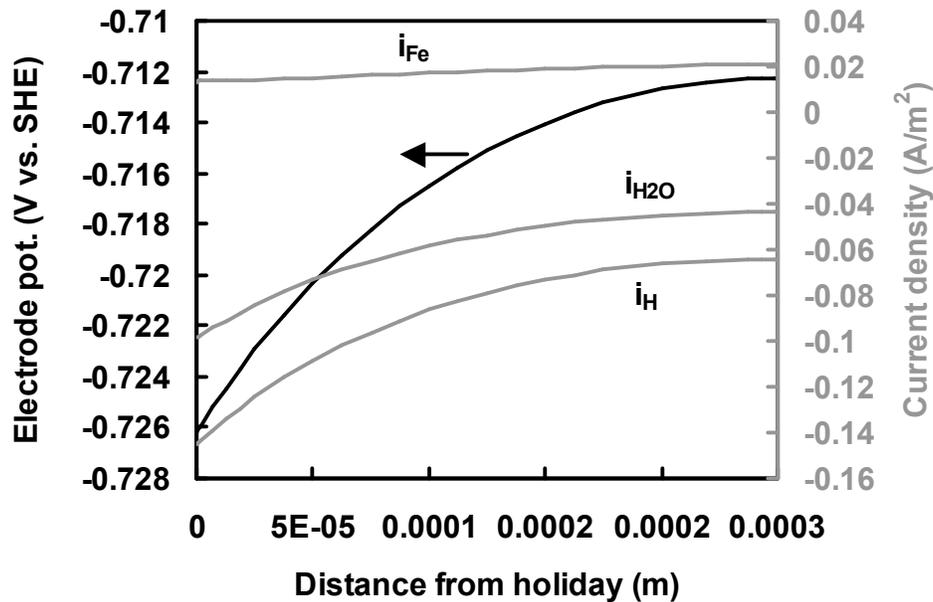
A solution obtained for the steady-state four-component system is shown in



**Figure 1. Concentration distribution in a four-component system at steady state calculated from MATLAB.**

Figure 1 for concentration distribution in a crevice and Figure 2 for electrode potential and current densities. Figure 1 shows that the  $Fe^{2+}$  concentration increases with distance into the crevice due to corrosion. In contrast, water reduction and hydrogen ion reduction decrease  $H^+$  concentration and conversely increase the  $OH^-$  concentration, and  $Cl^-$  balances the charge, consistent with expectation and findings by others.

Figure 2 shows that the electrode potential increases into the crevice and so the corrosion current density or rate. In the alkaline solution, water reduction current density is greater than hydrogen ion reduction and due to the short crevice, cathodic protection is

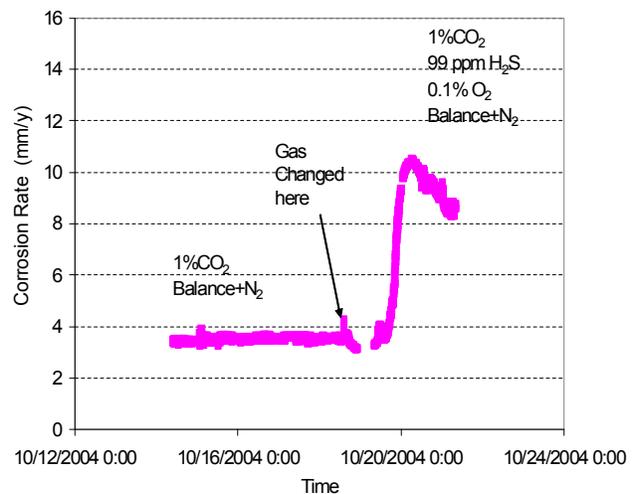


**Figure 2. Electrode potential and current density distribution in a four-component system at steady state calculated from MATLAB.**

still effective at the end of the crevice, which is demonstrated by the net current there being negative. Consistent with this, the predicted potential at the deepest end of the crevice is still  $-1.03\text{V}$  vs.  $\text{Cu}/\text{CuSO}_4$ , well below the protection potential.

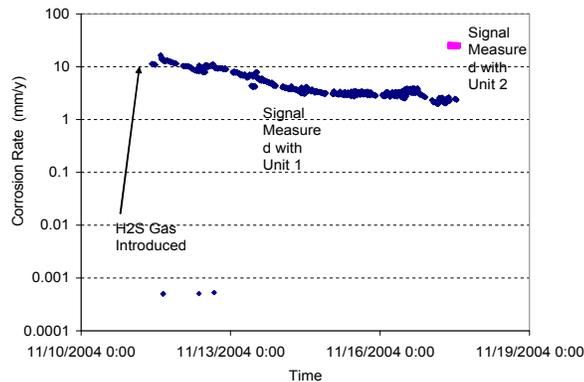
### **Testing Probes for Internal Corrosion monitoring**

The MAS probe was constructed for high-pressure application. This was then tested first in low-pressure systems with different corrosive constituents. The initial tests in an aqueous solution saturated at ambient pressure and temperature with different gases containing carbon dioxide, hydrogen sulfide, and methane continues. To address the concern that the MAS probe might not provide corrosion signals in  $\text{H}_2\text{S}$  containing environments because of the semiconductor properties of the iron and sulfide corrosion products, the probe was tested in a  $1\%\text{CO}_2 + 99\text{-ppm H}_2\text{S} + 0.1\%\text{ O}_2$  gas mixture. Figure 3 shows that the probe responded well in a solution saturated with the  $\text{H}_2\text{S}$ -



**Figure 3. Typical responses of a carbon steel probe in a solution saturated with two different gas mixtures.**

containing gas mixture. It was found that the electronic conductivity of the corrosion products formed in highly concentrated H<sub>2</sub>S gases (up to 100%) are substantially higher than the that formed in the 1%CO<sub>2</sub> +99-ppm H<sub>2</sub>S+ 0.1% O<sub>2</sub>. The signals from the MAS probes were significantly reduced because of the short-circuiting effect. Test has demonstrated that this effect can be avoided or minimized by an electronic unit that has input impedance lower than that of the conductive corrosion product (Figure 4).



**Figure 3. Carbon steel corrosion rates measured with two MAS units in a solution saturated with 100%H<sub>2</sub>S.**

**Note: The input impedance of Unit 2 is lower than that of unit 1**

A liquid solution has been inoculated with sulfate-reducing bacteria (SRB) and Vibrio Natriegen (slime former) microbes. Once the bacteria reach the log phase growth, the solution will be used to grow the bio-film on a multielectrode probe. A second multielectrode probe has been pre-corroded in sodium chloride solutions containing bicarbonate buffer agent. These two probes will be installed in an autoclave to measure the effect of relative humidity on the corrosion of carbon steel materials in simulated natural gas systems. The probes will also be used to detect the effective dew point under bio-film and corrosion products.

## BUSINESS STATUS

- A project kickoff meeting was held in Denver to present the approach and initial status to project manager, PRCI staff, and NIST staff. Coordination with NIST in their external corrosion program was discussed. We sent NIST staff a review paper on corrosion under disbanded coating.
- Participated in an industry group meeting on ICDA on December 14, 2004. Informal discussions were held with several pipeline company representatives on internal and external corrosion rates.
- Discussions are progressing with Gaz de France on laboratory experiments on disbanded coating corrosion.
- Arrangements have been made to visit a Valero Energy field location close to San Antonio to determine the installation of internal corrosion monitoring probe.

## SCHEDULE

Several tasks are in progress. We had originally planned to complete the modifications on TECTRAN code. However, we have decided to use a commercially

available software, FEMLAB, instead of TECTRAN because it will be more effective in the long run for the project and the industry.

### **PAYABLE MILESTONES**

First quarterly report

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

None

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

- Participate in the PRCI meeting/workshop on corrosion rate determination in January 2005.
- Continue validation process and modeling corrosion rates in disbonded coating using FEMLAB and MATLAB
- Complete the high-pressure test in CO<sub>2</sub>- and H<sub>2</sub>S-containing gases at different dew points.
- Complete the design and construction of external corrosion cell
- Hold discussions with other co-funding organizations on field data needs
- Visit Valero site for discussing placement of MAS probe in their system