

Galvanic Corrosion of Steel Coupled to Liquid Elemental Mercury in Pipelines

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Abstract

Galvanic interactions between steel and liquid mercury were examined in aqueous environments that simulate waters found in pipelines used in oil and natural gas transportation. Liquid elemental mercury is a poor cathode for hydrogen ion reduction and thus provides little galvanic influence to corrosion of steel in anaerobic aqueous systems containing either hydrogen sulphide or carbon dioxide. The measurements confirm industry experience that liquid mercury on steel in pipelines poses little risk to accelerate corrosion reactions and thus to compromise structural integrity, at least as far as galvanic corrosion is concerned. The measurements extend the conventional view of elemental mercury as a metal with low electrocatalytic efficiency for hydrogen ion reduction to environments containing mostly HS^- and HCO_3^- .

Keywords: mercury, galvanic corrosion, steel, pipelines.

Introduction

Mercury in several chemical forms is a naturally occurring constituent of oil and gas reservoirs [1]. When reservoirs containing mercury are produced, elemental mercury (Hg^0) and the other forms that may be present in the reservoir partition to separated phases (oil, gas and water) and travel throughout production and processing systems. In some parts of the world, mercury is present in gas reservoirs at much higher than average concentrations. For example, natural gas produced from reservoirs found in the Gulf of Thailand exhibits concentrations of elemental mercury that typically exceed $100 \mu\text{g}/\text{Sm}^3$ and some reservoirs are close to saturation (several hundred $\mu\text{g}/\text{Sm}^3$ depending on reservoir pressure and temperature). The world average for elemental mercury in gas is not known with statistical certainty but thought to be less than $10 \mu\text{g}/\text{Sm}^3$.

When produced gas is close to saturation with respect to Hg^0 , co-produced water and condensate also contain elemental mercury at close to saturation limits. In addition to the elemental species, produced water may contain dissolved ionic forms and suspended particulate mercury compounds. Produced condensate will contain, in addition to dissolved elemental mercury, those mercury species that have preferential solubility in the hydrocarbon phase. Liquid phase mercury may form by precipitation in liquids or condensation from gas when fluids close to saturation cool in transportation and processing. Compression of gas close to saturation also serves to condense elemental mercury to liquid phase. This situation is rare but exists occasionally nonetheless.

A gas pipeline was investigated that carried gas containing elemental mercury at very high concentrations. Cooling and compression produced liquid mercury deposits on the bottom of the pipe. The presence of liquid phase elemental mercury in the pipe was confirmed by pigging. Water condensation produced an aqueous environment containing some amount of chloride ions and other ionic species that derived from equilibrium with acid gases (H_2S and/or CO_2) in the gas stream. The question of interest in this situation is whether liquid elemental mercury that sits on the bottom of the pipe provides galvanic acceleration of the naturally occurring corrosion processes in the pipeline.

Experimental

Cylindrical steel coupons (3 cm x 0.4 cm diameter) were machined at mid-wall, parallel to the longitudinal axis of API 5LX -60 pipe (C – 0.065 wt. %; Mn – 1.410; P – 0.016; S – 0.002; Si – 0.255; V – 0.030). Measurements were made at ambient temperature (20 – 25 °C). Test environments are listed in Table 1. The aqueous solutions were purged with nitrogen for 2 hours prior to introduction of test gas (H_2S or CO_2 or N_2). The test gases were bubbled through the test solution for at least 2 hours prior to galvanic measurements.

Table 1 – Test Environments

| Test Solution | Purge Gas | Test Gas (1 atm) | pH |
|---------------|--------------|----------------------|-----------|
| 1 MNaCl | N_2 | CO_2 | 3.5 – 4.2 |
| 1 M NaCl | N_2 | H_2S | 3.8 – 4.1 |
| 1 MHCl | N_2 | N_2 | 0.9 – 1.5 |

Galvanic currents were measured in an electrochemical test cell (Figure 1). The current between steel and mercury was measured using a zero-resistance ammeter over a period of 24 hours. The surface area of the mercury exposed to the test solution was 15.9 cm² while that of steel was 3.6 cm², thus simulating a large cathode/small anode configuration.

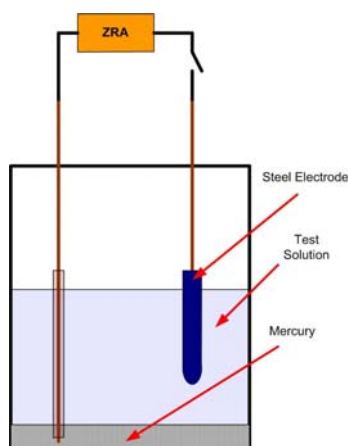


Figure 1 – Test Cell for Galvanic Measurements

Polarization curves were measured using standard electrochemical methods [2]. Test environments were constructed in the same manner as for galvanic measurements. Scans were in the cathodic to anodic direction at 1 mV/s.

Results

Galvanic Current Measurements

The galvanic current measurements for the steel – mercury couple are shown in Figures 2–4. Galvanic corrosion rates are summarized in Table 2. Polarization curves are shown in Figures 5 – 7.

Table 2 – Galvanic Corrosion Rates

| Test Solution | Purge Gas | Test Gas | Galvanic Current Density ($\mu\text{A}/\text{cm}^2$) | Rate (mm/y) |
|---------------|----------------|------------------|--|-------------|
| 1 MNaCl | N ₂ | CO ₂ | 1 | 0.0001 |
| 1 M NaCl | N ₂ | H ₂ S | 10 | 0.0010 |
| 1 MHCl | N ₂ | N ₂ | 5 | 0.0005 |

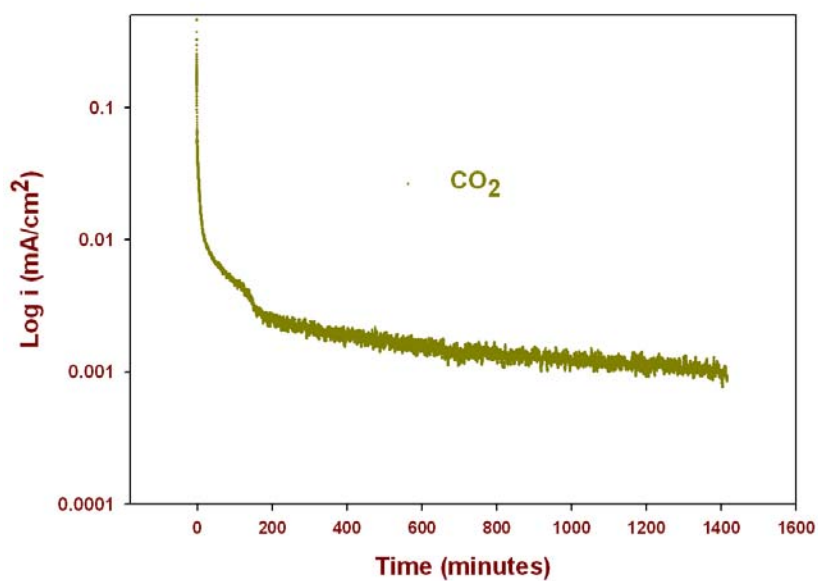


Figure 2 - Galvanic Current versus Time, 1 M NaCl – 1 atm CO₂

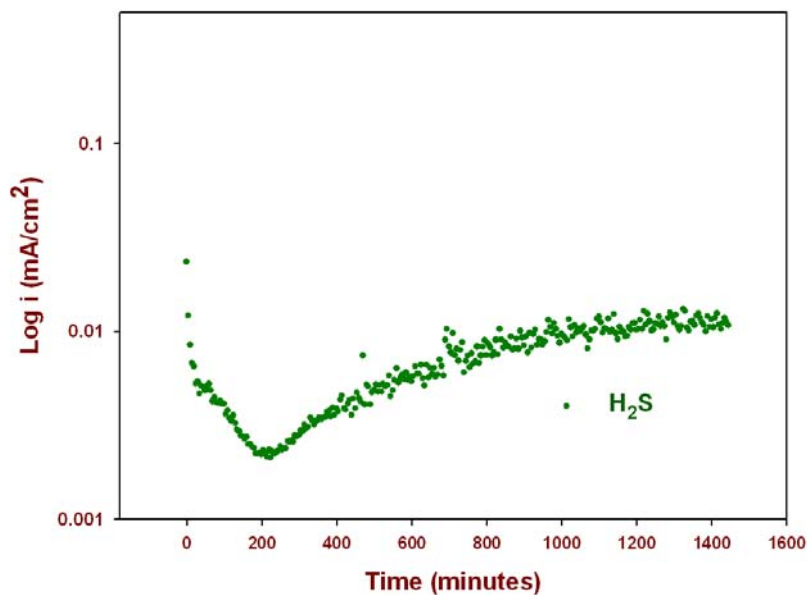


Figure 3 - Galvanic Current versus Time; 1 M NaCl, 1 atm H₂S

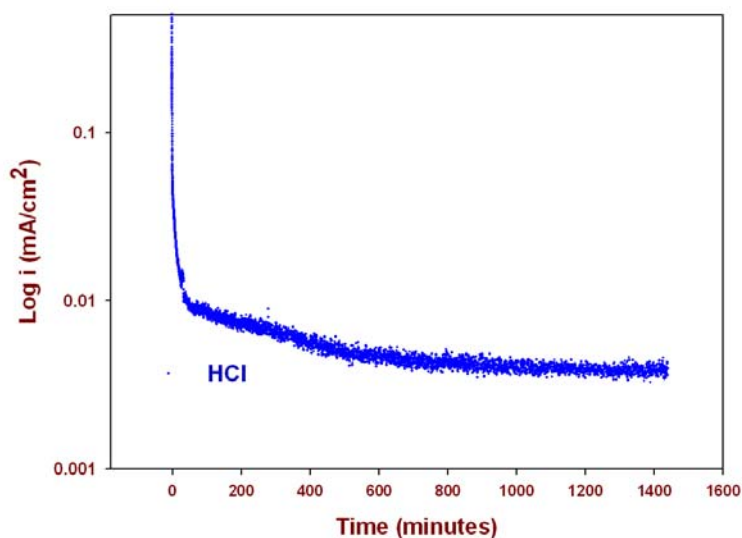


Figure 4 - Galvanic Current versus Time; 1M HCl, 1 atm N₂

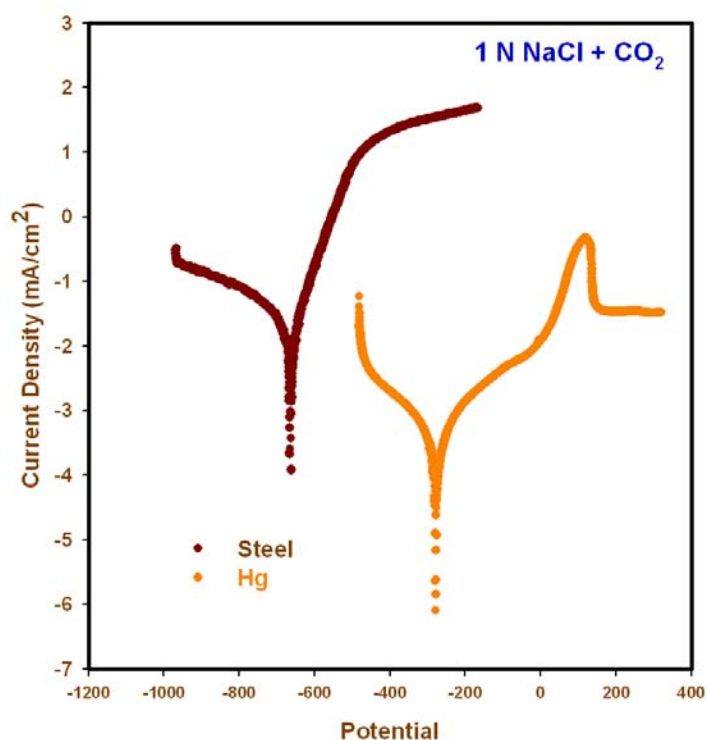


Figure 5 – Polarization Curves, 1 M NaCl, 1 atm CO₂

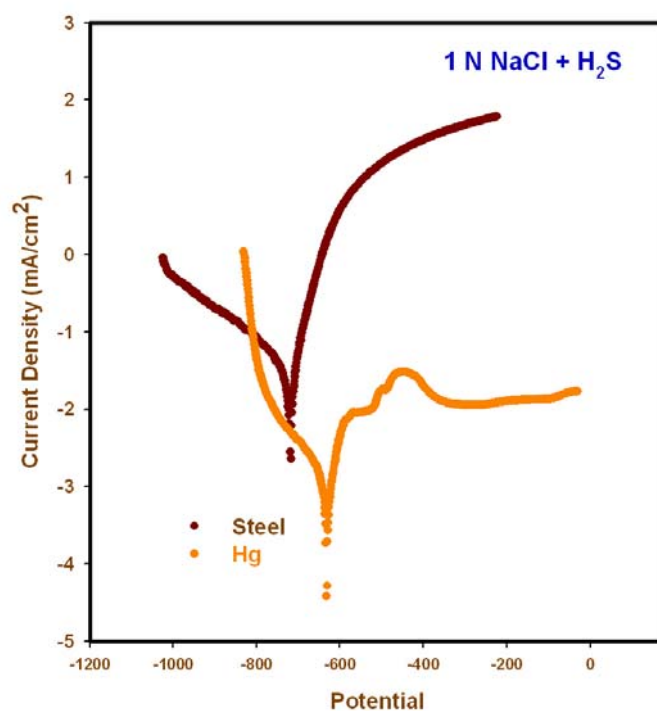


Figure 6 – Polarization Curves, 1 M NaCl, 1 atm H₂S

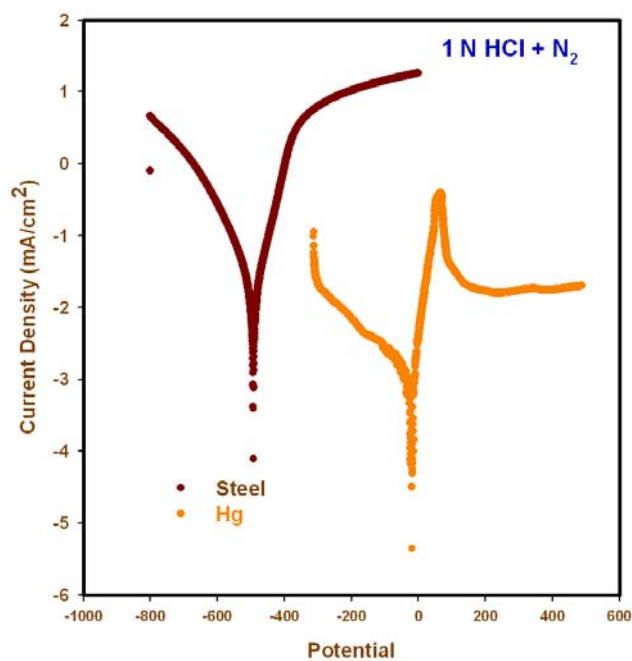


Figure 7 – Polarization Curves, 1 M HCl, 1 atm N₂

Hydrogen ion reduction rates (Table 3) were obtained from polarization curves by extrapolation of the linear cathodic Tafel region to the open circuit potential. An accuracy of ± 20 percent was estimated.

Table 3 – Hydrogen Ion Reduction Rate

| Test Solution | Purge Gas | Test Gas | Fe Current Density ($\mu\text{A}/\text{cm}^2$) | Hg Current Density ($\mu\text{A}/\text{cm}^2$) |
|---------------|----------------|------------------|--|--|
| 1 MNaCl | N ₂ | CO ₂ | 20 | 1 |
| 1 M NaCl | N ₂ | H ₂ S | 60 | 3 |
| 1 MHCl | N ₂ | N ₂ | 40 | 4 |

Discussion

In all cases investigated, galvanic currents were low. The current density supplied to steel by the mercury cathode, at an area ratio of approximately 4 to 1, was a few $\mu\text{A}/\text{cm}^2$. Galvanic corrosion rates (Table 2) suggest increases in the natural steel corrosion rate of less than approximately 10 percent would be produced. Given that most pipelines are treated with amine chemical corrosion inhibitors, which would lower both anodic and cathodic current densities, the impact of a Hg/steel galvanic couple on the anodic dissolution of the steel is expected to be virtually nil.

The reason for low galvanic power is that mercury is a very poor cathode for hydrogen ion reduction. This observation is in line with the classical position of mercury in a galvanic series. Mercury is listed at the bottom of the galvanic scale in sulphuric acid [3, 4], for example.

Hydrogen sulphide environments are slightly more complicated from the standpoint of galvanic corrosion because the corrosion products that form on steel in the presence of H₂S (FeS, Fe₂S₃) are conductors and provide galvanic influence to steel in addition to the mercury [5]. The rise in the Hg/steel galvanic current density seen for the H₂S environment is due to polarization arising from the formation of iron sulphide on the steel surface.

References

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