



## A Study Of Methanol Corrosion In Wet Sour Systems, With and Without Inhibition

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# A Study Of Methanol Corrosion In Wet Sour Systems, With And Without Inhibition.

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## **Abstract**

The corrosivity of methanol in a sour system is impacted by the concentration of methanol, the presence of inhibitors, and the dilution with brine. Methanol is known to cause corrosion within a system; however, the corrosivity is typically related to the loss of inhibitor films and not so much on the methanol itself. This study examines the corrosive role of mostly pure methanol. Understanding how methanol impacts corrosion rates can aid in the selection of products that can positively offset the effects of methanol and reliably inhibit the system.

## **Keywords**

Inhibited methanol, batch inhibitor, corrosion, electrochemistry, LPR

## **1.0 INTRODUCTION**

Techniques that are presently employed by the oil and gas industry for the prevention and/or dissociation of gas hydrates are: 1) remove the water to lower the dew point, 2) control the temperature of the system, 3) control the pressure of the system, 4) use methanol, 5) use hydrate inhibitors, or 6) under severe conditions, a combination of the above methods may be necessary.

To date, the preferred alternative for hydrate control has been to utilize large volumes of methanol.

## **2.0 HYDRATES AND CLATHRATES**

In solid crystalline hydrates, hydrogen bonding becomes important in addition to ion dipole attractions. Often the water molecules serve to fill in the interstices and bind together a structure which would otherwise be unstable because of the disproportionate size of the cation and anion.

In some cases hydrates form with neutral molecules (methane, ethane, etc.) The basic building block for this type of structure is typically a dodecahedron formed from 20 molecules of water. When these cage like structures pack together to form larger units, relatively large voids are formed within and it is in these spaces that the gas molecules reside. These gas hydrates in which the “guest” molecules are not bound chemically, but are retained by the structure of the host, are called clathrates.

## **3.0 HYDRATE CONTROL THROUGH USE OF METHANOL**

Gas hydrates form when produced hydrocarbon gas and water are subjected to extreme pressures and temperatures, often associated with production facilities. The point at which hydrates will form depends on the gas composition, fluid(s) production, the temperature and pressure of the system. Hydrates are a complex crystal similar to that of frozen water. The difference is that hydrates have a molecule of produced gas, usually methane, incorporated into the structure.

Traditionally, methanol has been used to control the formation of hydrates. Methanol works by lowering the temperature at which the hydrates form at a given pressure (thermodynamically). The critical temperature must be lowered to below that of operating temperature for methanol to be effective. To control severe hydrate problems, large quantities of methanol are often needed to reduce the hydrating temperature to an acceptable level.

#### ***4.0 DETRIMENTAL EFFECTS OF LARGE METHANOL CONSUMPTION***

The application of large volumes of methanol is an effective solution for hydrate control. However, there may be consequences that can impact the system integrity and perhaps the service life of the pipeline.

This paper is intended to share some of the corrosion evaluations studying methanol corrosion as performed in controlled environments in the laboratory.

#### ***5.0 TEST PROTOCOL***

**Test cells:** All of the evaluations were performed in high temperature, high pressure, stirrable autoclaves constructed of Hastelloy C256. The autoclave total volume is about 500 ml, of which 350 ml was liquid and the remainder was headspace. The autoclaves are fitted with three electrodes to facilitate electrochemical / LPR monitoring. The reference electrode was manufactured from Hastelloy C256 and the working / auxiliary electrodes were 1018 CS as supplied by Caproco.

**Methanol:** The methanol used in the experiments was a regular commercial grade containing a purity of 99.85%. The methanol received no special treatment. It was not stored in an oxygen free environment, the methanol was not purged to remove oxygen or other entrained gas(es) and it was not filtered. There were no compounds (i.e. salt etc) or products added that we would not normally blend into the methanol solutions. The intent was to evaluate the methanol as it would have been applied in the field. The

only part of typical field application that was not replicated was the use of a chemical pump.

**Acid Gas:** Pre-blended 50:50 H<sub>2</sub>S:CO<sub>2</sub> was used in some of the testing and other test protocols called for 99.6% H<sub>2</sub>S or 99.9% CO<sub>2</sub> all grades of which are commercially available.

### **Pressure Cycle**

A pressure cycle is defined as a safe connection of the gas cylinder to the autoclave, where the gas bottle / regulator valves are opened to allow the sealed autoclave to fill / equilibrate to the regulated pressure of the cylinder. Typically when aqueous fluids are utilized in the autoclave, the regulated pressure is achieved relatively quickly and the valves can be closed (for safety reasons) for the equilibrium period. The equilibrium period allows the gas in the head space to equilibrate into the test fluids. As the pressure in the headspace subsides, the pressure can be reapplied with another pressure cycle. After a relatively short period of time and several pressure cycles the headspace pressure remains constant and the fluids are charged with the select gas. This procedure is followed because of the toxic effects of H<sub>2</sub>S and it minimizes the volume of gas released in the event of a component failure.

Note: Hydrogen sulphide (H<sub>2</sub>S) is a highly toxic, flammable, colourless gas that has the smell of rotten eggs and even at very low concentrations, exposure can result in injury or death. This product must be handled by trained personnel and used in a suitable environment to protect human life.

## **6.0 CORROSION EVALUATIONS - OBSERVATIONS**

### **Test 1**

| <b>Test Parameters - Test 1</b> |   |
|---------------------------------|---|
| <b>Gas</b>                      | <b>50:50 H<sub>2</sub>S:CO<sub>2</sub></b>    |
| <b>Pressure</b>                 | <b>Two pressure levels - 50 &amp; 100 psi</b> |
| <b>Fluids</b>                   | <b>Methanol – uninhibited</b>                 |
| <b>Temperature</b>              | <b>35°C</b>                                   |
| <b>Test Duration</b>            | <b>~27 hours</b>                              |

The corrosive effects of pure methanol on carbon steel in a laboratory setting were uncertain and a literature search showed that there was minimal (none at the time) published material on the subject. The first test, (including only methanol, H<sub>2</sub>S:CO<sub>2</sub> acid gas and carbon steel), was intended to be a short duration, two pressure, typical system temperature experiment. Since most sour systems also contain CO<sub>2</sub>, the test was run with a 50:50 preblend mix of H<sub>2</sub>S:CO<sub>2</sub>. The autoclaves were set at 50 and 100 psi to reflect the typical partial pressures that were observed at that time. The test temperature was about 35°C. The autoclaves were prepared using normal assembly procedures and the methanol contained no inhibitor. The test cells were briefly prepurged with anaerobic CO<sub>2</sub> to purge the headspace of oxygen and then sealed and pressured / equilibrated with the premix 50:50 H<sub>2</sub>S:CO<sub>2</sub> acid gas.

The normal pressure cycling procedure of an autoclave requires a single or manifold type of mechanical connection to the selected gas bottle. Normally, when aqueous fluids (water or brine) are placed in the autoclave, only several cycles of pressure / equilibration were required to saturate the brine and the autoclave would approach the desired test pressure in a relatively short period of time.

Our observations showed the acid gas purge sequence for the methanol solution as being unmistakably different from a routine aqueous purge. The methanol test solution absorbed the H<sub>2</sub>S:CO<sub>2</sub> acid gas at an incredible rate and required extensive pressure cycling to finally achieve the target pressure in the autoclave. The increased volume of acid gas required to reach equilibrium (with methanol versus water) could not be quantified. However, anecdotal evidence indicated that the acid gas solubility in methanol was approaching an order of magnitude greater than water based fluids.

The methanol was commercially pure and was not expected to be overly conductive suggesting LPR measurements may be of limited value. Never-the-less, the electrochemical LPR corrosion rates were collected every 30 minutes for the test duration. Over the course of the test, the LPR data indicated very low corrosivity (not

unexpected - Figure 1). The cell set at 50 psi showed lower LPR corrosion rates than the 100 psi cell (0.3 mpy versus 0.45 mpy). The test was terminated at about 27 hours as the external indications suggested limited corrosion activity was transpiring within the test cell.

The gas de-pressurization cycle was the reverse of the pressuring cycle and a large volume of gas exited the autoclaves before they were safe to open. The blow down procedure required much more time than what was normally experienced when water based fluids were utilized. Regrettably, the means to actually measure the exiting volume of gas was lacking and it could only be qualitatively noted that it was significantly greater than when just water based/ brine test solutions were evaluated.

The methanol fluid remained colourless and contained suspended particulates. The methanol continued to effervesce for an extended time period; much greater than that observed with aqueous fluids. The electrodes were removed and results documented (Figure 2), the electrode solids were recovered and then the electrodes were cleaned / weighed. The test results showed the lower gas pressure cell (50 psi) generated a 27 mg weight loss (48 mpy) whereas the higher pressure cell (100 psi) showed a 20 mg weight loss (35 mpy – Figure 3). This was the reverse of what was observed on the LPR. All of the corrosion damage appeared uniform and no localized indications were observed.

The black solids recovered from the electrodes were analyzed by x-ray diffraction and they were identified as primarily mackinawite. As shown in Figure 2, the solid volume was substantial; they were very brittle and maintained the cylindrical shape even after detachment from the electrode. Normally iron sulfides are relatively adherent to steel and have never been observed to detach in a form that retains the shape of the corroding material.

## Test 2

| Test Parameters - Test 2 |   |
|--------------------------|---|
| Gas                      | 50:50 H <sub>2</sub> S:CO <sub>2</sub>                                |
| Pressure                 | 50 psi  |
| Fluids                   | Inhibited & uninhibited Methanol, 150K Cl <sup>-</sup> high TDS brine |
| Temperature              | 35°C  |
| Test Duration            | 24 hours  |

Test 1 had brought forth a number of points, which posed the question of how other environments might impact the corrosive nature of methanol. Test 2 included 1. pure methanol, 2. inhibited methanol, 3. 50:50 methanol:150K Cl brine and 4. 50:50 *inhibited* methanol and 150K Cl brine. The LPR data was similar to Test 1 where only low corrosion rates were observed (Figure 4). The exception was for the test cell containing 50:50 methanol (uninhibited):150K chloride brine, where typical elevated LPR corrosion activity was observed. Initially, the corrosion rate for this set was elevated (85 mpy) but it showed a rapid decline and settled to about 4 mpy from 12 hours to the end of the test. The other three cells showed LPR rates of 0.2 mpy over the course of the test.

As in Test 1, the LPR corrosion rates for the blank methanol were low, however, the weight loss was elevated. The pure methanol blanks showed 26 mg weight loss (54 mpy – consistent with Test 1 (Figure 5)). The weight loss was in the form of general / uniform corrosion damage

The inhibited methanol cell and the inhibited methanol:150K Cl brine cell both showed low weight loss (0.6 mg and 0.5 mg loss respectively). The 50:50 methanol:150K chloride brine (no inhibitor) test cells showed 6.1 mg weight loss (12.2 mpy) with corrosion damage in the form of pitting or localized corrosion. The electrodes from the two inhibited cells were presumed to have been uniform / general corrosion as there was only a minute weight loss recorded and surface damage at 50X magnification could not be readily identified. The inhibited sets showed very good corrosion protection and the 50:50 methanol:brine showed reduction in weight loss compared to the methanol only.

### Test 3

| <b>Test Parameters - Test 3</b> |  |
|---------------------------------|--|
| <b>Gas</b>                      | <b>50:50 H<sub>2</sub>S:CO<sub>2</sub></b>                                       |
| <b>Pressure</b>                 | <b>50 psi</b>  |
| <b>Fluids</b>                   | <b>Uninhibited Methanol, 20K Cl<sup>-</sup> brine, batch corrosion inhibitor</b> |
| <b>Temperature</b>              | <b>35°C</b>  |
| <b>Test Duration</b>            | <b>46 hours</b>  |

It was clear from Test 2 that the corrosivity of pure methanol was altered when brine was added to the mixture. Test 3 was intended to identify how the impact on corrosion would change if there was varying ratios of methanol and brine. Six methanol: brine ratio's were selected; 100:0, 75:25, 50:50, 25:75, 10:90, 0:100.

All of the carbon steel electrodes used in this set were pre-treated with a batch corrosion inhibitor.

The LPR data (Figure 6) showed low corrosion rates except for the 75:25 and 50:50 methanol: brine in spite of the batch inhibitor film. The 75:25 methanol:brine and 50:50 methanol:brine showed elevated LPR data and the weight loss showed good consistency (wt. loss 20 mg / 9 mg respectively). The remaining test cells showed low corrosion rates by LPR and weight loss is shown in Figure 7. The 25:75 uninhibited methanol:brine test showed a weight loss 1.9 / 2.9 mg and the 10:90 methanol:brine and 100% brine cells showed electrode sets with less than 1 mg weight loss. Clearly the methanol:brine mixture had an impact on the batch inhibitor filmed electrodes. The 100% methanol had no impact on the batch corrosion inhibitor, but when the brine was introduced and where it was methanol rich, the batch film did not provide acceptable corrosion protection. In fact most of the cells that contained appreciable water showed a challenging environment for the batch filmed electrodes. However, the batch film performed admirably when there was very little or no methanol present.

Note: The under performance of the batch inhibitor prompted additional laboratory testing and an eventual adjustment of the batch corrosion inhibitor formulation.

#### Test 4

| <b>Test Parameters - Test 4</b> |  |
|---------------------------------|--|
| <b>Gas</b>                      | <b>50:50 H<sub>2</sub>S:CO<sub>2</sub></b>                                     |
| <b>Pressure</b>                 | <b>50 psi</b>  |
| <b>Fluids</b>                   | <b>Inhibited Methanol, 20K Cl<sup>-</sup> brine, Batch corrosion inhibitor</b> |
| <b>Temperature</b>              | <b>35°C</b>  |
| <b>Test Duration</b>            | <b>119 hours</b>   |

Test 4 was intended to repeat Test 3 except this test included inhibited methanol. Six methanol:brine ratio's were selected; 100:0, 75:25, 50:50, 25:75, 10:90, 0:100. The experimental results showed that in every case there was a marked reduction of LPR corrosion activity (Figure 8) and most of the sets showed 1 mg loss per electrode or less (Figure 9). The weight loss within each test cell is mostly consistent and overall, none of the environments showed significant corrosion activity. The application of inhibited methanol had a profound impact on the corrosion activity within every cell.

#### Test 5

| <b>Test Parameters - Test 5</b> |  |
|---------------------------------|--|
| <b>Gas</b>                      | <b>50:50 H<sub>2</sub>S:CO<sub>2</sub></b>           |
| <b>Pressure</b>                 | <b>50 psi</b>  |
| <b>Fluids</b>                   | <b>Uninhibited Methanol – no corrosion inhibitor</b> |
| <b>Temperature</b>              | <b>20°C, 40°C, 60°C and 80°C</b>                     |
| <b>Test Duration</b>            | <b>119 hours</b>                                     |

The objective of this test was to identify how temperature might impact the test cell corrosivity, when the environment contained only 100% methanol and no corrosion inhibitor. Four autoclaves were prepared for the test and they were controlled to 20°C, 40°C, 60°C and 80°C. The LPR test data was depressed as previously observed (all at 1 mpy or less) and the delayed heat application was not apparent on the LPR data (Figure 10). The weight loss was found to increase with temperature from the 20°C, 40°C and 60°C electrode sets and showed consistency with the previous data collected in Test 1 and Test 2. The corrosion activity / weight loss reached a maximum at 60°C and then showed a decline at 80°C (Figure 11). The observed decline of the corrosion rate at 80°C may have been related to changes of the corrosion product crystallinity.

However, this was not explored at the time and the explanation remains undetermined. All of the cells were initially equilibrated at room temperature (for 18 hours) and the individual cell pressures escalated with the addition of heat. The carbon steel electrodes (post test) all showed significant corrosion damage, unlike damage normally observed in a regular aqueous brine / H<sub>2</sub>S:CO<sub>2</sub> system. There was significant weight loss due to localized / pitting corrosion damage.

### Test 6

| <b>Test Parameters - Test 6</b> |  |
|---------------------------------|--|
| <b>Gas</b>                      | <b>99.6% H<sub>2</sub>S and 99.9% CO<sub>2</sub></b> |
| <b>Pressure</b>                 | <b>50 psi</b>  |
| <b>Fluids</b>                   | <b>Uninhibited Methanol – no corrosion inhibitor</b> |
| <b>Temperature</b>              | <b>20°C, 40°C, 60°C and 80°C</b>                     |
| <b>Test Duration</b>            | <b>119 hours</b>                                     |

Test 5 had showed a good relationship of weight loss / corrosion damage with respect to temperature. The objective of Test 6 was to evaluate how pure acid gases would compare instead of the preblended gas mixes solely used up this point. The LPR data shows (Figure 12) that at RT and 40°C the corrosion is low for the H<sub>2</sub>S:methanol mix. We observed a dramatic spike in corrosivity at 60°C and an equally dramatic decline at 80°C. The gravimetric data (Figure 13) for the H<sub>2</sub>S only cells showed low weight loss at 20°C and 40°C, an order of magnitude increase at 60°C and an equally dramatic decline at 80°C.

The electrodes from the H<sub>2</sub>S only cells showed corrosion damage in the form of uniform / general corrosion. The CO<sub>2</sub> only experiments (weight loss) showed moderate corrosion at 20°C, a decline at 40°C, an increase at 60°C and a second decline at 80°C. The CO<sub>2</sub> only cells tended to generate more localized pitting indications. The separate application of H<sub>2</sub>S and CO<sub>2</sub> acid gas resulted in a deterioration of the data consistency generated to this point.

## Test 7

| <b>Test Parameters - Test 7</b> |   |
|---------------------------------|---|
| <b>Gas</b>                      | <b>99.6% H<sub>2</sub>S and 99.9% CO<sub>2</sub></b>        |
| <b>Pressure</b>                 | <b>50 psi</b>   |
| <b>Fluids</b>                   | <b>95% uninhibited Methanol – 5% tap water in each cell</b> |
| <b>Temperature</b>              | <b>20°C, 40°C, 60°C and 80°C</b>                            |
| <b>Test Duration</b>            | <b>66 hours</b>   |

This experiment was intended to repeat Test 6 except with the addition of 5% tap water introduced with the methanol. The LPR data for the entire set showed low corrosion rates as previously observed in Test 6 (Figure 14). The H<sub>2</sub>S only test cells showed an increasing / decreasing (repeated) pattern of weight loss as the cell temperature increased. The CO<sub>2</sub> only data showed significant weight loss at RT, however, the weight loss from 40°C, 60°C and 80°C were less and nearly equal. The weight loss data (Figure 15) for the H<sub>2</sub>S and the CO<sub>2</sub> environments were inconsistent with respect to the increase in temperature. Typically, greater test / system temperatures usually lead to greater corrosion rates.

## 7.0 METHANOL CORROSION CONCLUSIONS

1. The test environments containing pure methanol, H<sub>2</sub>S and CO<sub>2</sub> showed corrosion rates that were much greater than a comparable aqueous system absent of methanol.
2. The LPR corrosion rates for uninhibited methanol showed depressed (low) values that were inconsistent with the modest-moderate weight loss actually observed with the test coupons.
3. An H<sub>2</sub>S:CO<sub>2</sub> acid gas mixture was highly soluble in methanol; approaching an order of magnitude more soluble than in water. H<sub>2</sub>S and CO<sub>2</sub> were also independently observed to be more soluble in methanol than in water.
4. Inhibited methanol was very effective in controlling corrosion in corrosive methanol environments regardless of the water fraction or the presence of other corrosion inhibitors.
5. Some batch inhibitors that showed excellent good corrosion protection in sour aqueous systems did not necessarily perform well when methanol was present.

However, the use of inhibited methanol dramatically reduced the corrosion activity and corrosion rates were near zero.

6. Corrosion products generated in pure methanol could form removable thin films that imitated the physical contours of the cylindrical electrodes. These thin films were extremely fragile, were loosely adhering to the metal surface and were composed of typical iron sulphide corrosion products (i.e. mackinawite).
7. Methanol mixed in large volumes with high TDS produced water tended to form precipitated solids. This may prove problematic within a pipeline system, aggravating the corrosion activities (i.e. sub deposit corrosion).
8. Methanol combined with moderate to high TDS brine appeared to be a modestly corrosive fluid (greater than brine alone).
9. Corrosion damage resulting from the presence of methanol / H<sub>2</sub>S appeared to be uniform / general in nature. Pitting damage was only observed in CO<sub>2</sub> environments.
10. Methanol at 50 psi mixed acid gas (50:50 H<sub>2</sub>S:CO<sub>2</sub>) showed greater corrosion rates than the same gas mix at greater pressure (100 psi).
11. Experiments where methanol:water was employed tended to show scattered and inconsistent data compared with methanol only corrosion.

Figure 1

### Methanol Corrosion Test 1 LPR versus time

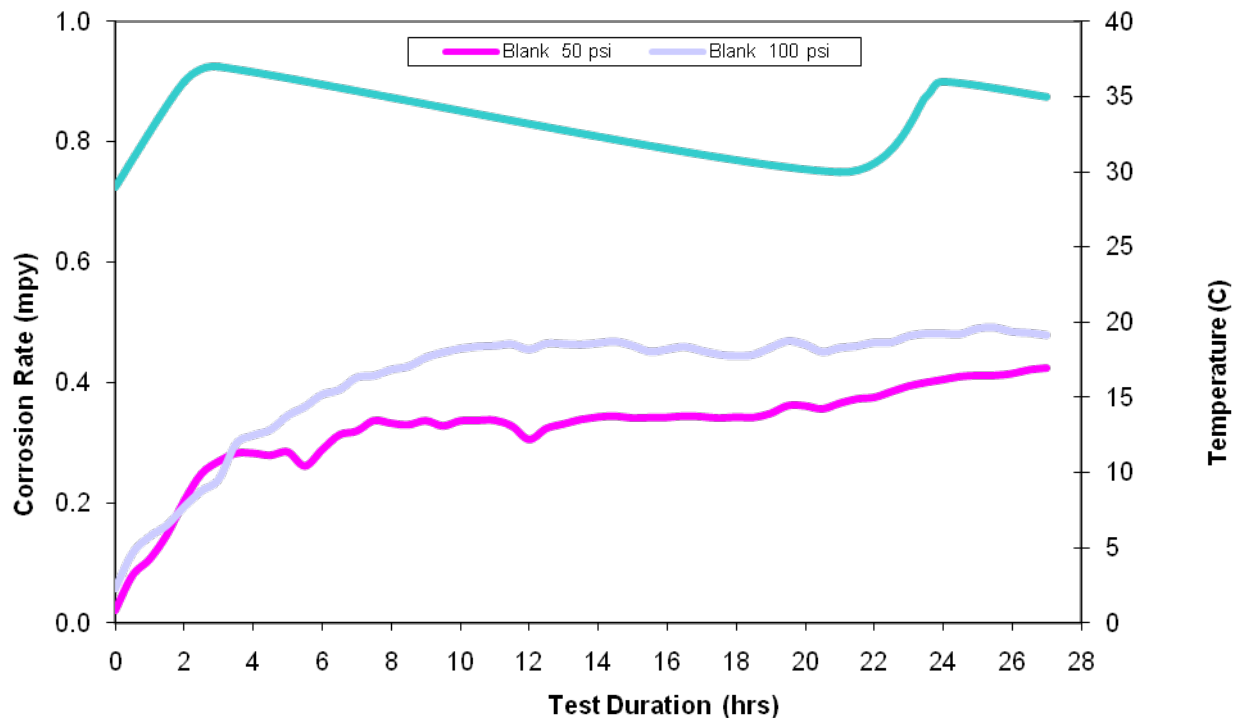


Figure 2

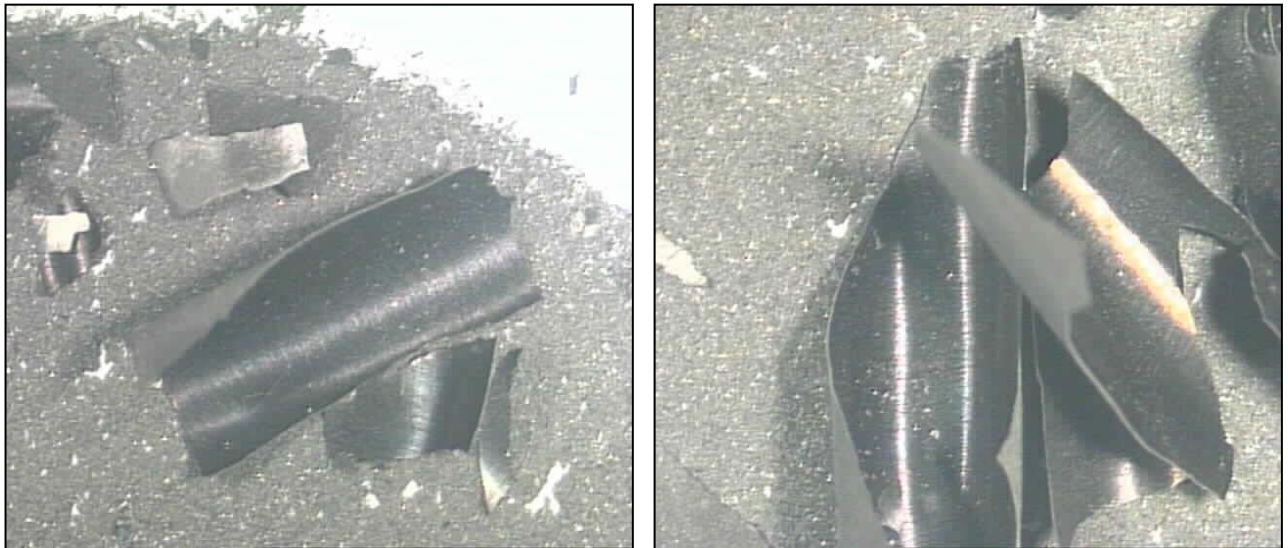


Figure 3

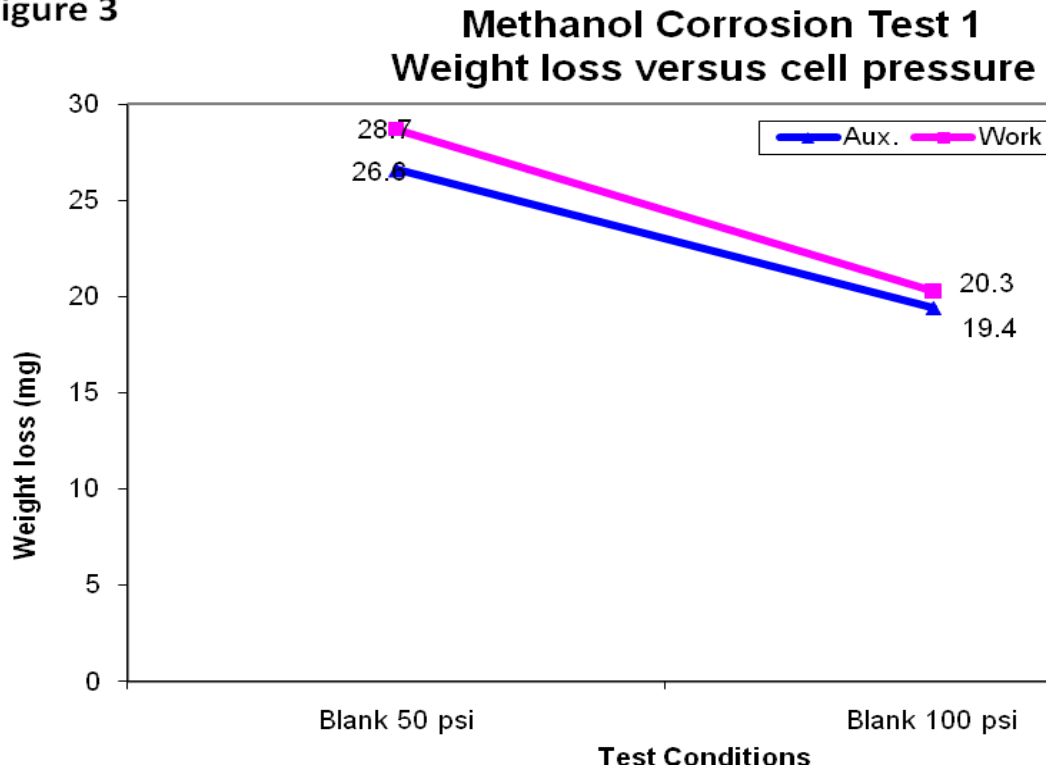


Figure 4

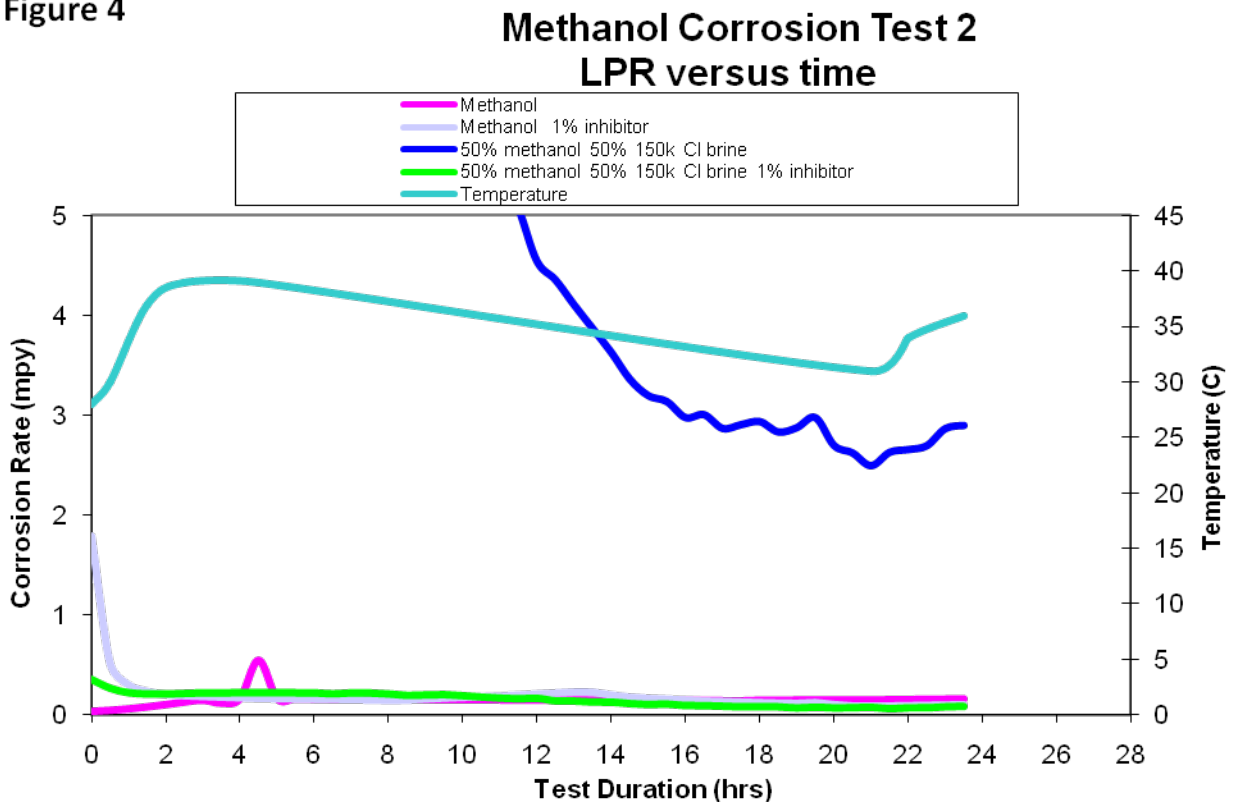


Figure 5

### Methanol Corrosion Test 2 Weight loss versus test conditions

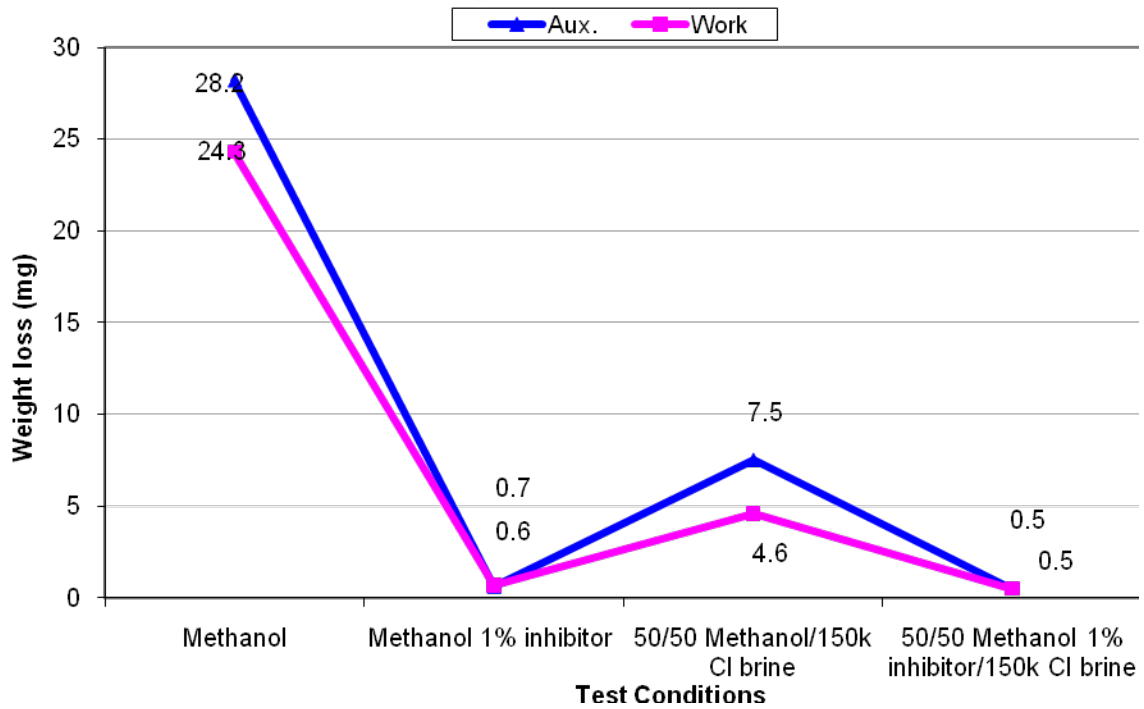
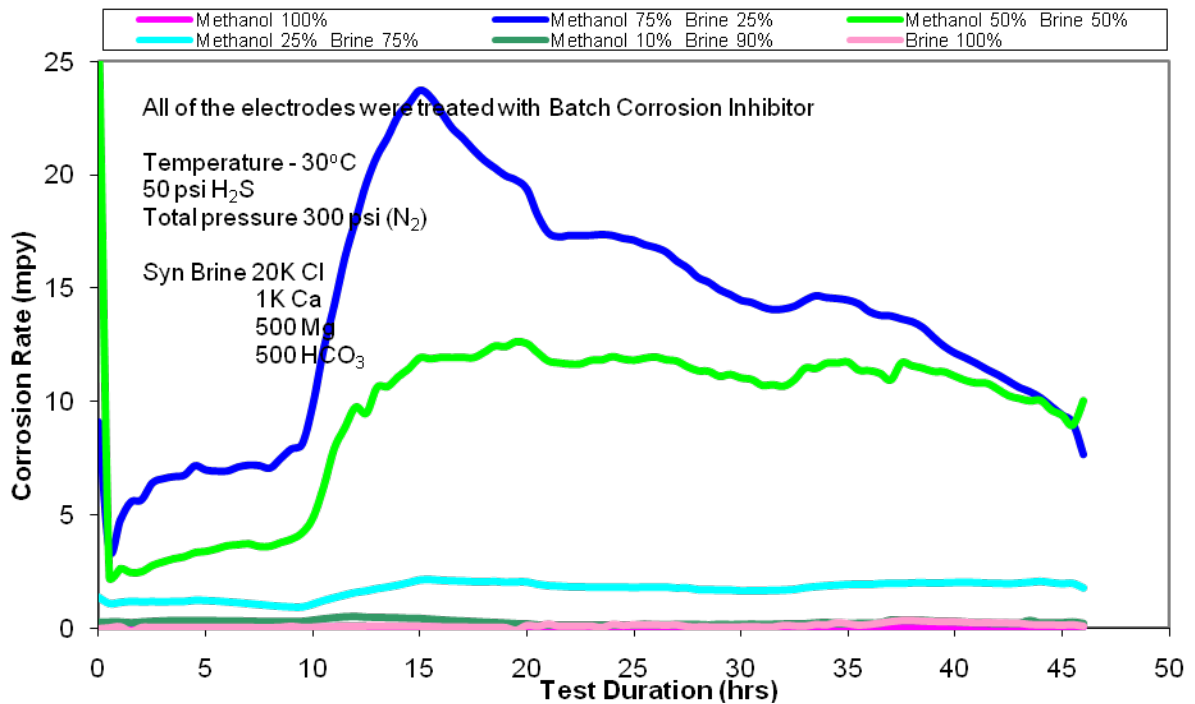
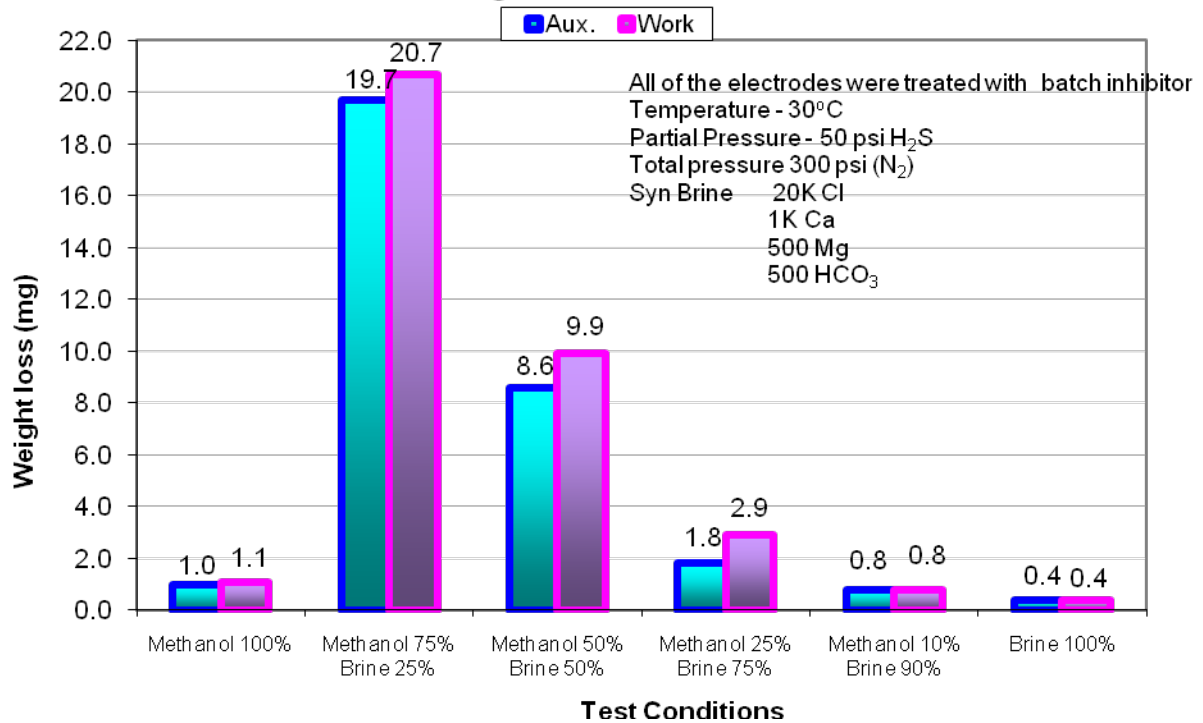


Figure 6

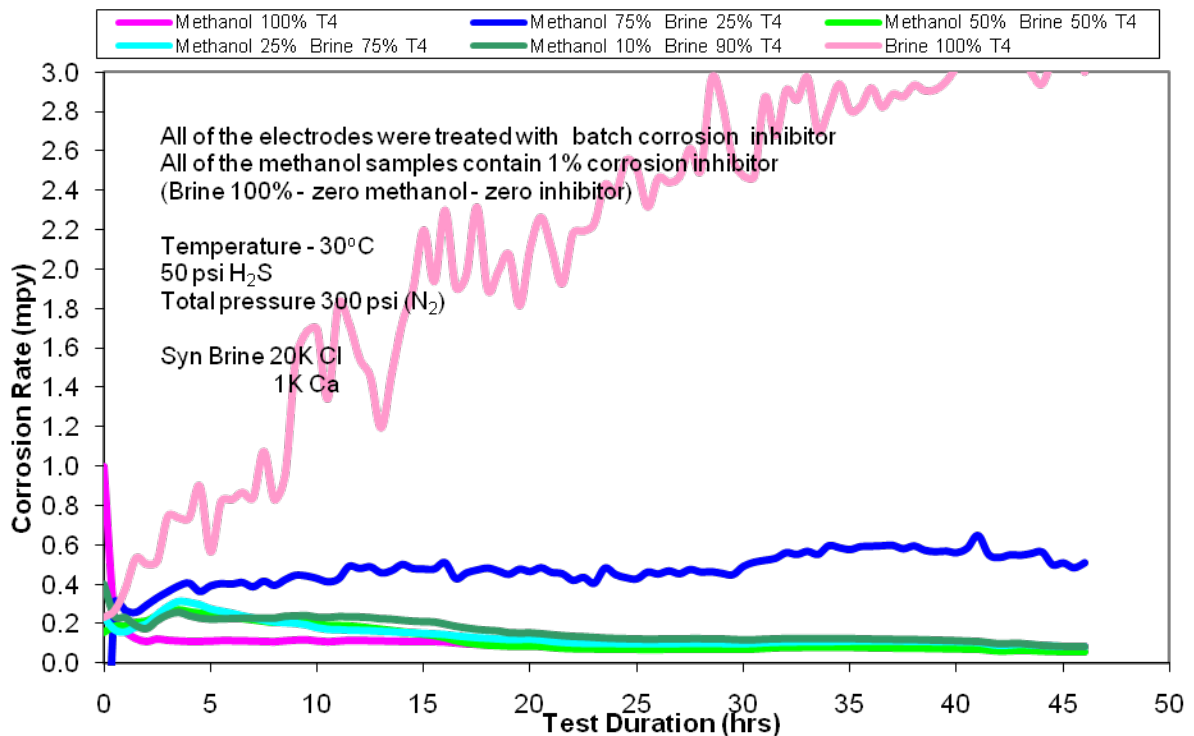
### Methanol Corrosion Research Test 3 Corrosion rate versus time



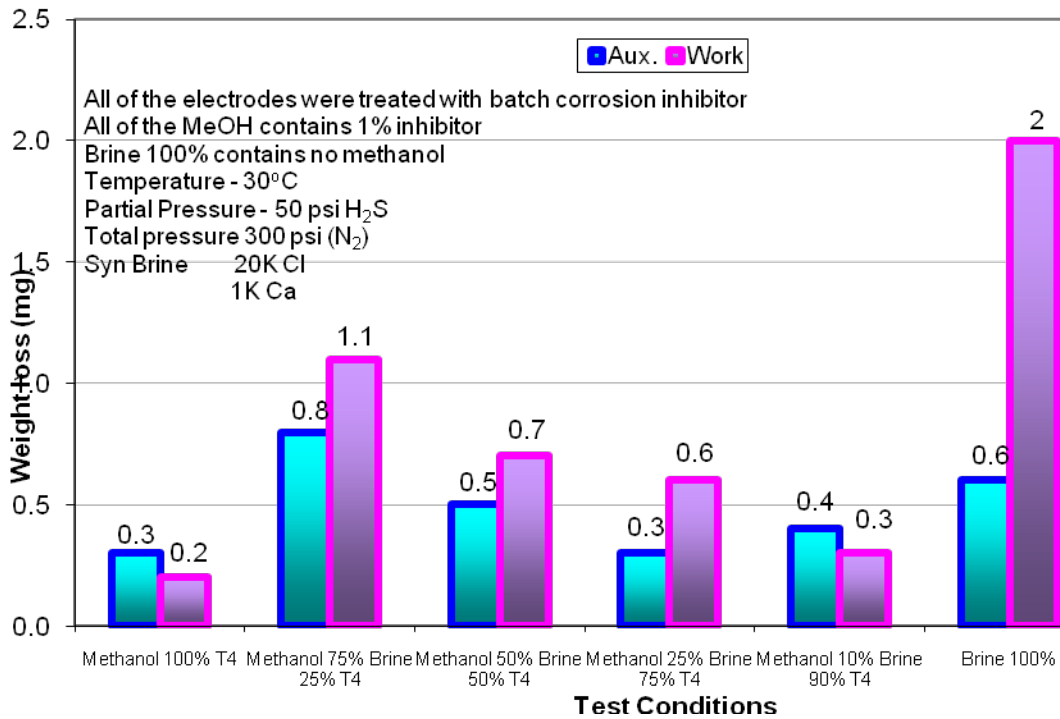
**Figure 7 Methanol Corrosion Research T3 Weight loss versus time**



**Figure 8 Methanol Corrosion Research Test 4 Corrosion rate versus time**



**Figure 9 Methanol Corrosion Research Test 4  
Weight loss versus test conditions**



**Figure 10 Methanol Corrosion Research Test 5  
LPR versus time**

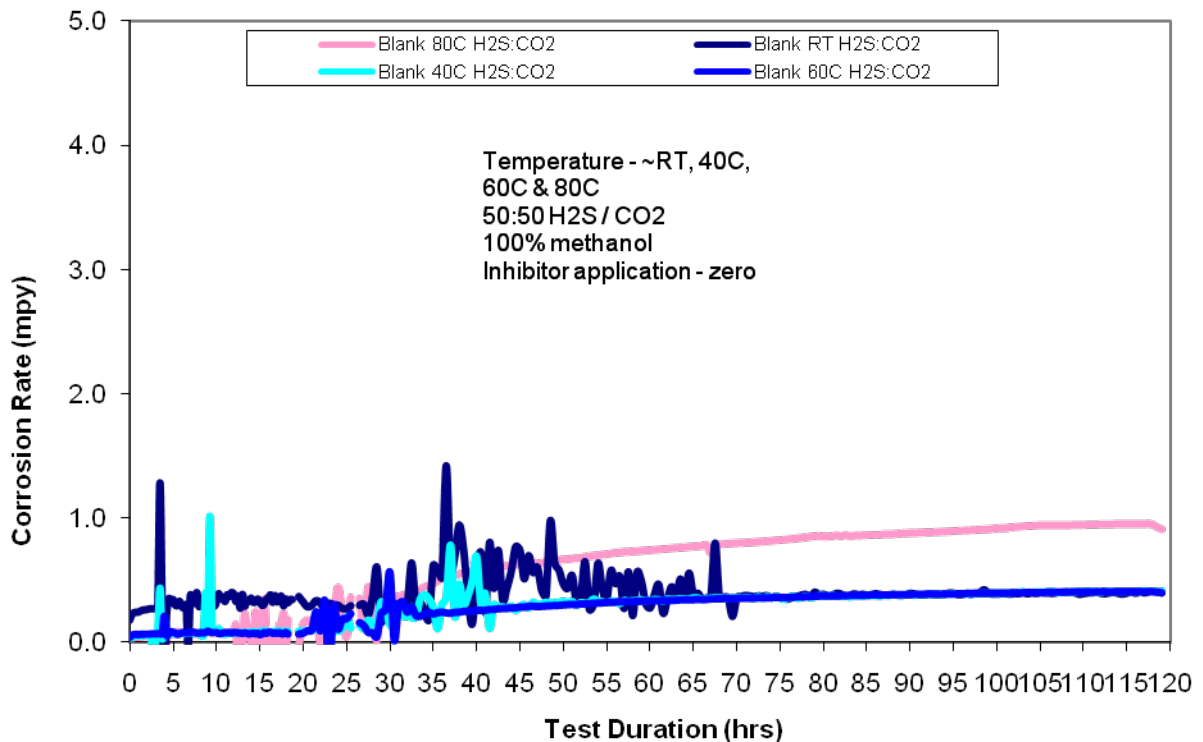


Figure 11

### Methanol Corrosion Research Test 5 Weight loss versus temperature

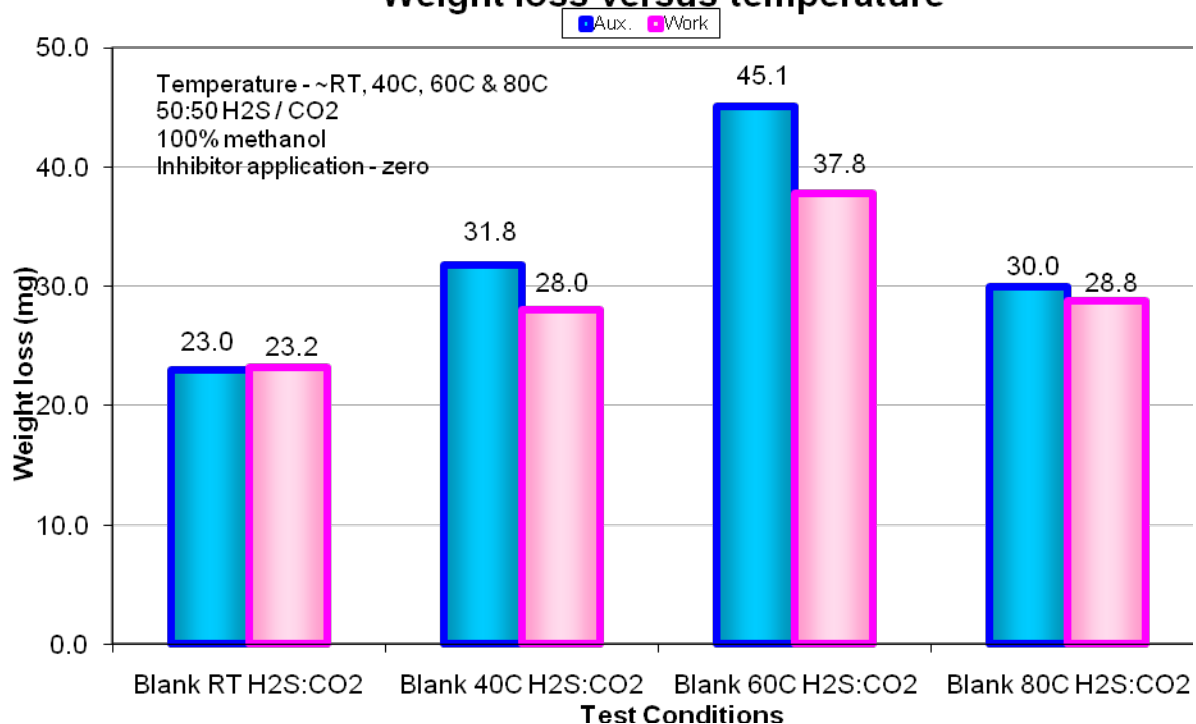


Figure 12

### Methanol Corrosion Research Test 6 LPR versus time

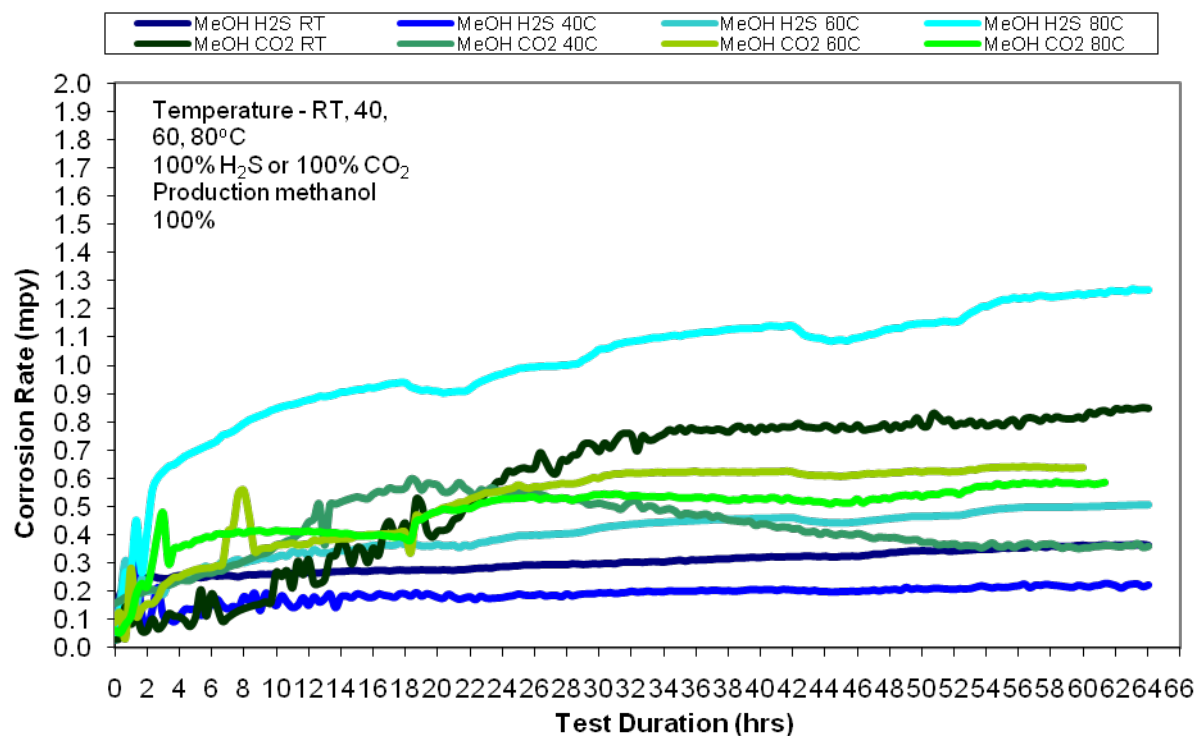


Figure 13

### Methanol Corrosion Research Test 6 Weight loss versus test conditions

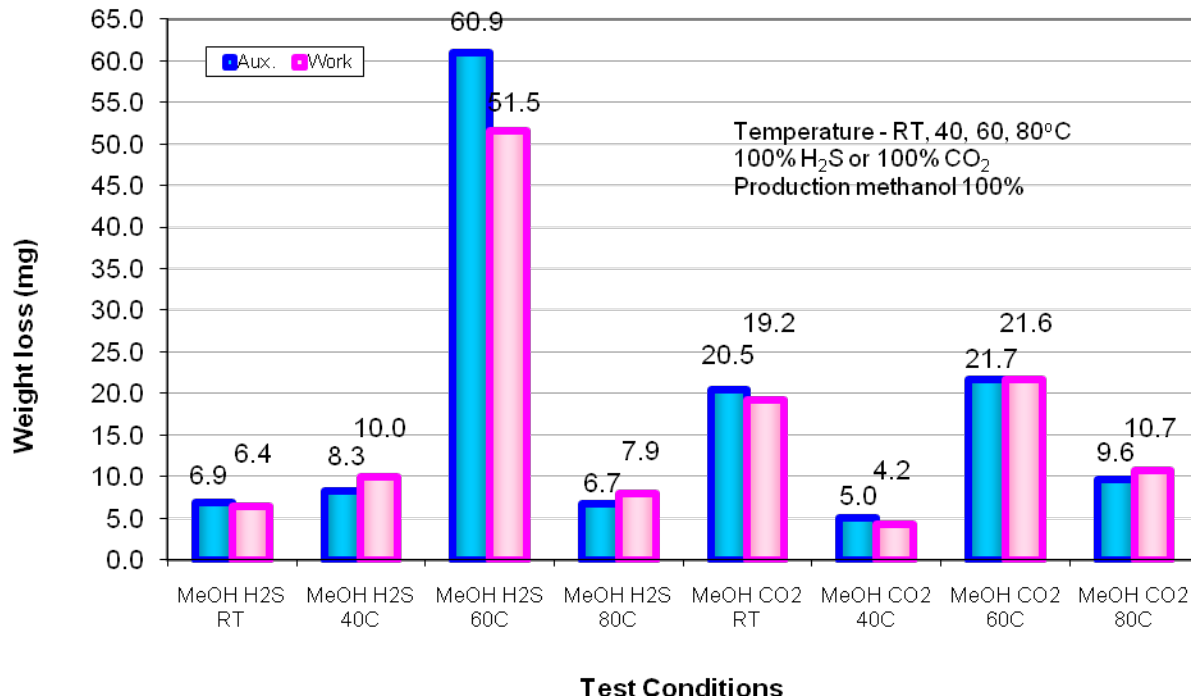
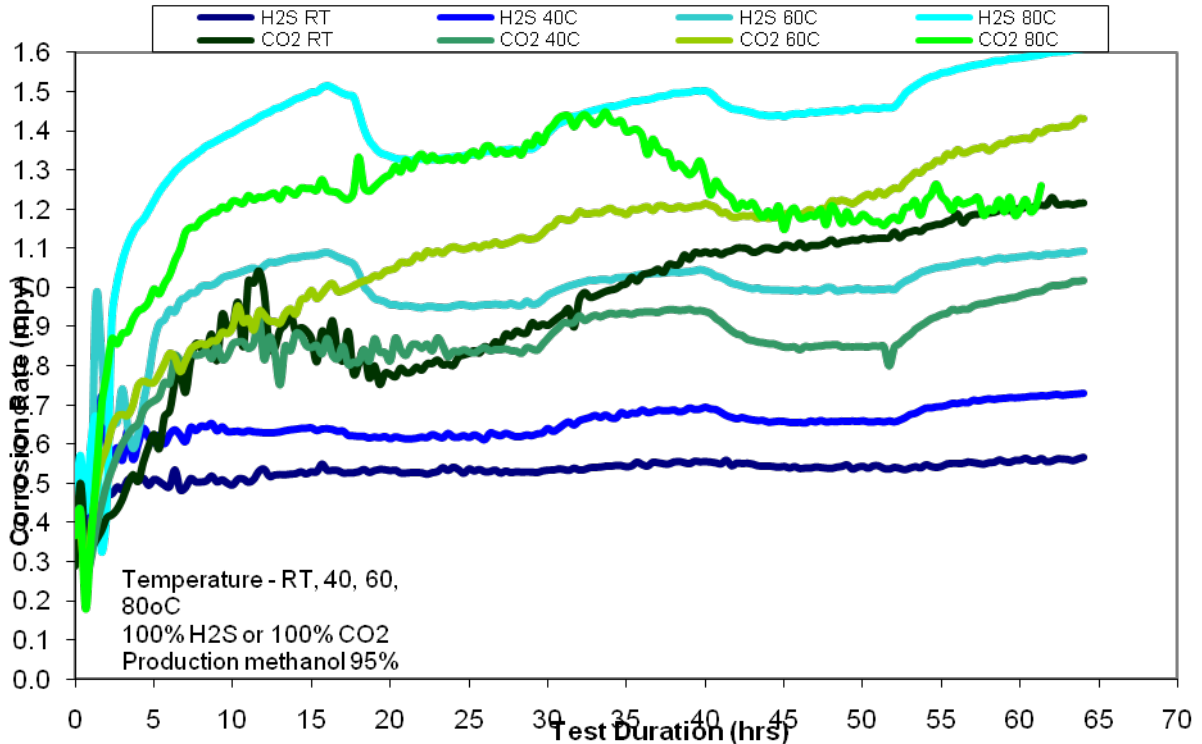


Figure 14

### Methanol Corrosion Research Test 7 LPR versus time



**Figure 15 Methanol Corrosion Research Test 7  
Weight loss versus test conditions**

