

Corrosion of Mild Steel in Concentrated Monoethylene Glycol (MEG)

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ABSTRACT

Material selection for Monoethylene glycol (MEG) regeneration units is a challenge due to the high temperature combined with high salt content. The oxygen level is low, and carbon steel is a cost-effective choice. The corrosion rate of carbon steel is too high in neutral or acidic conditions, but in alkaline solution, C-steel might be an alternative even without the use of film forming corrosion inhibitor.

The corrosion rate of carbon steel in ca. 97 wt% MEG at 120 °C, is quite low in alkaline solutions. If the MEG solution contains more than 2 mmol/kg alkalinity, the corrosion rate is in the range 0.1 mm/y to 0.3 mm/y when the CO₂ partial pressure is 300 Pa or less. The low corrosion rate is not due to passivity. In alkaline solutions with more than 97 wt% MEG, some test coupons showed a passive behaviour from start of experiments, but they became activated after cathodic polarisation and did not re-passivate in 4 weeks.

At 120 °C the cathodic reaction is activation controlled in solutions with more than 97 wt% MEG and alkalinity above 20 mmol/kg. The reaction rate is independent of shear stress and has a low alkalinity dependence. It is probably governed by the reduction of water.

Key words: Corrosion, anaerobic, glycol, low water concentration, alkalinity

INTRODUCTION

The thermodynamic hydrate inhibitor MEG is a robust choice for long distance gas-condensate tie-backs operating at low temperature. The possibility to regenerate and recycle the MEG enables cost effective operation with low discharges. The choice of regeneration process depends on the salt content of the produced water [1, 2]. Full reclamation implies flashing off MEG and water at low pressure (10-30 kPa) followed by distillation to the lean MEG specification. In this process, all salts and non-volatile chemicals remain in the reclaimers. The salts accumulate to saturation, crystallise and can

be removed by centrifuges, decanters, filters or similar. The boiling temperature is typically 110 to 150 °C depending on the MEG concentration in the feed and the pressure. At steady state the water to MEG ratio in the gas flashed off will be the same as in the rich MEG feed. The water concentration in the liquid remaining in the reclaimer will then be 0.5 to 5 wt%.

In most cases, the rich MEG feed to the reclaimer contains dissolved CO₂ and bicarbonate. CO₂ is boiled off and bicarbonate will be converted to carbonate and hydroxide. For a high CO₂ field (10-15 mol% CO₂ in the gas), the CO₂ in the rich MEG can be 300 mmol/kg. The CO₂ partial pressure in flash separator is then 100-200 Pa at 15 to 30 kPa total pressure.

As MEG reclaimers are operating below ambient pressure, leaks will result in air ingress. However, due to the large volume rate of steam and MEG vapour, the oxygen partial pressure will normally be low. Oxygen corrosion will only be an issue if the leak is in the utility systems where there is no gas phase. Oxygen will react with the MEG, and glycolic, acetic and formic acids can be reaction products. Organic acids in the produced fluids will also partition to the MEG.

All non-volatile species in the rich MEG feed will accumulate in the reclaimer liquid till they reach saturation and precipitate as NaCl, CaCO₃, CaSO₄, etc.. Acetate and other carboxylates are an exception, their salts are so soluble that they will not precipitate until the concentration is more than 10-20 wt%. Hence, if there are substantial amounts of organic acids in the produced water and they are converted to carboxylate, the liquid in the reclaimer must be bled off and after-treated. Calcium and Magnesium chlorides are also highly soluble at high temperature. So if the alkalinity of the produced water is sub-stoichiometric relative to divalent cations, carbonate can be added upstream or in the reclaimer in order to precipitate CaCO₃, Mg(OH)₂, SrCO₃ etc.. The liquid residing in MEG reclaimers will then be alkaline.

In many fields, the solution in the MEG reclaimer is alkaline and saturated with sodium chloride. The temperature is up to ca. 150 °C, and the solution is in equilibrium with a gas with maximum 300 Pa CO₂ partial pressure. Such conditions could potentially promote growth of protective carbonate and oxide films and thus enable selecting carbon steel as material of construction. The objective of the study described here was to determine the corrosion rate of carbon steel at such conditions. Specifically, if there is an operation window with respect to alkalinity and organic acid concentration where the general corrosion rate of carbon steel is less than 0.1 mm/y and where there is no or limited localised corrosion.

EXPERIMENTAL

The tests were run in a jet impingement loop (JIL) which allows for corrosion studies at the relevant temperature range (110 – 150 °C) and at high shear stress. A schematic drawing of the loop and details of the autoclave are shown in Figure 1. The main vessel is a Titanium Grade 2 autoclave designed for 3 MPa pressure at 150 °C. The pump which circulates the test solution through the jet nozzle, is made in Hastelloy C22, and can operate at 200 °C and 7.5 MPa. The piping and all other components in contact with brine are in Hastelloy C276. The flow velocity through the nozzle is measured by a Coriolis flow meter. Heating is provided by hot oil from an external heating system circulated through a heating coil inside the autoclave. There are electrical heating coils mounted on the outer surface of the autoclave to ensure homogeneous temperature. The set-up is not designed for boiling conditions and the experiments were run at a pressure that exceeded the boiling pressure at the test temperature.

The test specimen assembly is mounted on a Titanium holder underneath the lid. The jet specimen surface is facing downwards towards the vertically oriented jet nozzle entering from the bottom of the autoclave. A guide system ensures alignment of the nozzle and specimens. A cylinder specimen and an additional Titanium counter electrode are mounted on the side of the holder.

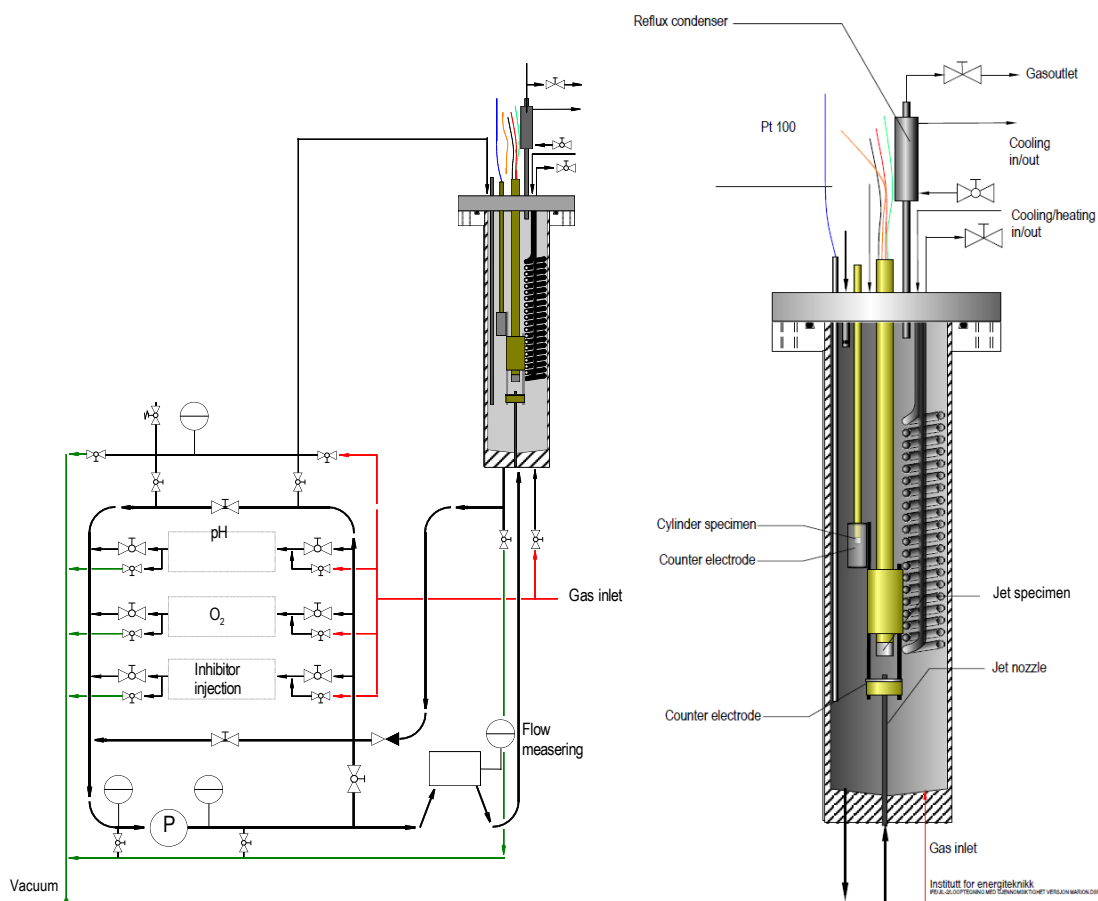


Figure 1: Schematic drawing of the jet impingement loop (left) and some details of the autoclave (right).

The jet nozzle has 2.5 mm internal diameter and is oriented perpendicularly to the centre specimen (jet specimen). The distance between the centre specimen and nozzle mouth is 12.5 mm. The wall shear stress is not constant along the radius of the specimen assembly but passes through a maximum. The maximum estimated shear stress along the surface is 700 Pa. Although there may be considerable shear stress on the surface of heat exchangers and tubing in a MEG reclaimer, it will not be nearly so high. In this study, the jet impingement was simply used to reveal if the corrosion rate is shear stress dependent.

The corrosion rates were monitored by the linear polarization resistance method (LPR) using a Gamry PCI4 potentiostat with a multiplexer. The measurements were performed in a three-electrode configuration with the steel specimens as the working electrodes. The counter electrodes were made of Titanium. The reference electrode was also carbon steel and the true corrosion potential could not be measured. The corrosion currents were calculated from polarization resistance (R_p) and converted to average penetration rates. The cylinder specimen (Figure 1) was used for mass loss determination and the corrosion rate measured by LPR was calibrated against this mass loss when possible. The solution resistance for IR drop compensation was determined by means of impedance spectroscopy (EIS). Potential sweeps were conducted by polarising the specimens first cathodically then anodically. At first these sweeps were performed towards the end of the experiment. However, it was observed that the cathodic sweeps activated the specimens and the corrosion rate increased about 10 times after polarisation. When this was recognised, cathodic polarisation became a parameter in the tests. The parameters for the electrochemical tests are summarised in Table 1.

Table 1
Parameters for electrochemical measurements

<i>Type of measurement</i>	<i>Parameter</i>	<i>Value</i>
LPR (Linear Polarisation Resistance)	Potential range	-5 to +5 mV
	Scan rate	0.1 mV/s
	Measurement frequency	30 minutes
Impedance spectroscopy	Frequency range	0.1 – 10000 Hz
	Points per decade	7
	AC voltage	10 mV rms
Cathodic sweep	Potential range	+5 to -300 mV
Anodic sweep	Potential range	-5 to +150 mV or 200 mV
Both sweeps	Scan rate	0.1 mV/s
	Sampling rate	1 per sec.

The test solutions were made up with technical grade MEG, distilled water and salts with purity 99% or better. The liquid volume in the JIL was 12.0 L. The water concentration in the MEG was 3 wt% on salt free basis, it decreased slightly during the tests and was ca. 2 wt% at the end for long time tests. The salt concentration and the alkalinity in the tests are given in Table 2. Sodium glycolate ($\text{NaC}_2\text{H}_4\text{CO}_3$) was included in some tests as it is a probable reaction product if MEG is oxidised. Otherwise Sodium acetate (NaCH_3CO_2) was used as a representative carboxylate.

Table 2
Salt concentration per kg MEG+H₂O

<i>Test no.</i>	<i>NaCl (g/kg)</i>	<i>NaC₂H₄O₃ (g/kg)</i>	<i>NaCH₃CO₂ (g/kg)</i>	<i>Na₂CO₃ (g/kg)</i>	<i>K₂CO₃ (g/kg)</i>	<i>KOH (g/kg)</i>	<i>Alkalinity¹ (m)</i>
1	26						0
2	26	10		1.06			0.002
3	26		164	1.06			0.02
4	20	10			6.9		0.1
5	20		123		6.9		0.1
6	20		123		6.9		0.1
7	10		123		6.9		0.1
8	10		8.2		6.9		0.1
9	10		8.2		6.9		0.1
10	10					56.11	1

¹ Not including glycolate and acetate

The test specimens were made of St52 construction steel corresponding to ASTM A537 Grade 1 and UNS K12437. It is normalised and heat treated and has a ferritic-pearlitic microstructure. The composition is given in Table 3. There were two coupons installed in each test; one cylinder specimen (10 mm diameter, 10 mm length) immersed in the liquid and one disc specimen (20 mm diameter) immersed in the liquid and exposed to jet impingement.