

Edith Cowan University
Research Online

ECU Publications Post 2013

2019

Effect of pretreatment process on scale formation in the re-boiler section of monoethylene glycol regeneration plant

Ammar Al Helal

Adam Soames

Stefan Iglauer

Edith Cowan University, s.iglauer@ecu.edu.au

Ahmed Barifcani

Rolf Gubner

Follow this and additional works at: <https://ro.ecu.edu.au/ecuworkspost2013>

 Part of the [Engineering Commons](#)

[10.1088/1757-899X/495/1/012106](https://doi.org/10.1088/1757-899X/495/1/012106)

Al Helal, A., Soames, A., Iglauer, S., Barifcani, A., & Gubner, R. (2019). Effect of pretreatment process on scale formation in the re-boiler section of monoethylene glycol regeneration plant. In *IOP Conference Series: Materials Science and Engineering*, 495(1), Article 012106. Available [here](#)

This Conference Proceeding is posted at Research Online.

<https://ro.ecu.edu.au/ecuworkspost2013/6359>

PAPER • OPEN ACCESS

Effect of Pretreatment Process on Scale Formation in the Re-Boiler Section of Monoethylene Glycol Regeneration Plant

To cite this article: Ammar Al Helal *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **495** 012106

View the [article online](#) for updates and enhancements.



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Effect of Pretreatment Process on Scale Formation in the Re-Boiler Section of Monoethylene Glycol Regeneration Plant

Ammar Al Helal^{1,2,*}, Adam Soames¹, Stefan Iglauer³, Ahmed Barifcani¹, Rolf Gubner¹

¹ Curtin University, Kent St, Bentley WA 6102, Perth, Australia

² Al-Khwarizmi College of Engineering, University of Baghdad, Jadriyah, Baghdad, Iraq

³ Edith Cowan University, Joondalup WA, Australia

*Corresponding author: 17610661@student.curtin.edu.au

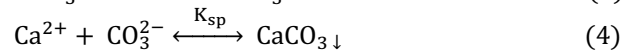
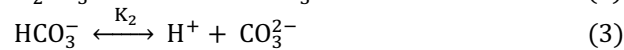
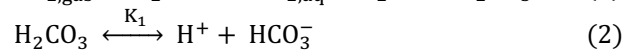
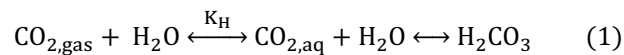
Abstract. Monoethylene glycol (MEG) regeneration plants often use pretreatment vessels to precipitate divalent cations, such as Fe^{2+} , Ca^{2+} , and Mg^{2+} , in order to avoid or reduce fouling in downstream reboilers and heat exchangers. This pretreatment process operates under alkaline conditions and moderate temperatures ($\sim 80^\circ\text{C}$) to accelerate the formation of low-solubility divalent salts. The objective of the present research was to determine whether the pretreatment process could be minimized, without negatively impacts on the MEG regeneration process from to the formation of scale on the heater bundle in the presence of low concentrations of divalent cations in the rich MEG stream. Scale formation was analyzed under MEG regeneration process conditions using a dynamic scale loop (DSL) test and verification experiments were performed in a MEG regeneration and reclamation pilot plant, both with and without pretreatment conditions. The scaling tendencies of several rich MEG-brine mixtures were evaluated at different pH pretreatment levels and dissolved CO_2 concentrations. An evaluation temperature of 180°C was chosen to match the skin temperature of the reboiler heater bundle during the MEG regeneration process. The experiments of pH 7.24 showed high amounts of precipitation scale within the reboiler due to high remaining concentrations of mineral ions. In addition, small concentrations of calcium and magnesium ions led to the precipitation of calcite, dolomite, and magnesium hydroxide on the reboiler bundle and within associated filtered outputs even when a pretreatment vessel was present. These results were confirmed by the differential pressure build-up and Scanning Electron Microscopy analyses for each experimental condition. Another interesting finding is that pH increased within the reboiler due to CO_2 gas boiling off at high operating temperatures, thus contributing to increased alkalinity levels, which in turn promoted scale formation. These results indicate that pretreatment should not be reduced, even with divalent ion concentrations as low as ~ 5 ppm TDS, due to the harsh conditions within the reboiler heater bundle.

1. Introduction

Natural gas transportation and production systems face significant operational concerns from the formation of scale, which can restrict or block flow and cause fouling issues [1, 2]. Chemical analyses and laboratory studies have shown that calcium carbonate, barium sulfate, and strontium sulfate are



the inorganic compounds most commonly found in oil and gas facilities [3, 4]; calcium carbonate is particularly abundant in deep saline wells [5-8]. Since calcium carbonate has low solubility, it forms large deposits within pipelines and industrial units [9-11]. Furthermore, its solubility is inversely proportional to temperature, which along with pH therefore has direct effects on the overall equilibrium of calcium carbonate precipitation [12, 13]. The previous publication reported general equilibrium reactions [14, 15], including CaCO_3 formation within the carbonate system [5]; they are summarized as reactions 1–4. Carbonate equilibrium models thus present a challenge for the transportation of natural gas and condensate from offshore facilities.



Where $\text{CO}_{2,\text{gas}}$ is CO_2 in the gas phase, and $\text{CO}_{2,\text{aq}}$ is the dissolved CO_2 in the aqueous phase. K_H , K_1 , K_2 , and K_{sp} are Henry's law, first and second dissociation constants, and the equilibrium constant [5], respectively.

In addition to this concern, long subsea transportation pipelines require minimal risks of hydrate formation. During the production of natural gas in deep water environments, there is a risk of gas hydrates forming in the pipelines [16, 17]. Gas hydrates are crystalline, ice-like solids made up of host molecules surrounded by water molecules [16]. Hydrate inhibitors are therefore used to ensure the flow of natural gas [16]. Monoethylene glycol (MEG) is among the most widely used gas hydrate inhibitors because it can be regenerated and/or reclaimed, thereby allowing it to be reused and minimizing operational costs [18, 19]. However, MEG and other gas hydrate inhibitors directly lower the saturation concentrations of inorganic salts, and therefore lead to an increased risk of scale formation [20-22]; it is therefore necessary to find an appropriate balance between the two. The saturation of calcium carbonate in the water/MEG system can be determined using the relationship between ion activity (calcium and carbonate) and the equilibrium constant, which can in turn indicate the influence of the MEG on the activity coefficient of ions (see Equation 5) [5].

$$SI_{\text{calcite}} = \log_{10} \left(\frac{[\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}^{2+}}^S \cdot \gamma_{\text{Ca}^{2+}}^N \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}^S \cdot \gamma_{\text{CO}_3^{2-}}^N}{K_{\text{sp}}} \right) \quad (5)$$

Where $\gamma_{\text{Ca}^{2+}}^N$ and $\gamma_{\text{CO}_3^{2-}}^N$ represent the effect of MEG on activity coefficients. $\gamma_{\text{Ca}^{2+}}^S$ and $\gamma_{\text{CO}_3^{2-}}^S$ represent the effect of salt on activity coefficients.

Several studies have also suggested that MEG concentrations affect the deposition of inorganic salts [20, 23]. For example, Flaten, Seiersten (24) observed that an increase in MEG concentration was accompanied by an increase of the calcium carbonate crystal formation induction time. They attributed this to the increase in viscosity (due to the increasing glycol concentration) inhibiting crystal formation. Two other studies found that, under gaseous treatment conditions, calcium carbonate crystals show a significant reduction in growth rates in experiments with more than 50 vol. % of MEG (rich MEG) [19, 25]. Other factors have been reported to have effects on the process of crystallization and growth rate of calcium carbonate crystals [15, 26, 27]. For example, changing the content of CO_2 gas in saline-glycolic solutions, especially during the regeneration process, can affect the deposition rate of mineral ions in the pretreatment and reboiler sections.

During the MEG regeneration process, excess water is boiled off to achieve the desired lean MEG concentration (> 75%). During this process, the bulk temperature in the reboiler may be as high as 130–150 °C [28, 29] and the reboiler heater element skin (wall) temperatures may be even higher, as the heating solution may be supplied to the unit at 177 °C [30]. If divalent cations are present within the rich MEG feed, these high temperatures may cause the precipitation of solid particles, resulting in either a fouling of the hot heat-exchanger surfaces or in solids suspended in the bulk liquid [30, 31]. This reduces heat transfer efficiency and may have adverse effects on the downstream system (e.g.,

blockage of lean MEG filters). However, the extent of this impact is not well understood at present. Moreover, the behavior of different concentrations of divalent ions within the MEG solution is not yet known. Some plants have taken a conservative approach by targeting a low residual cation concentration (e.g., < 1 ppm) in the feed that leads to the reboiler. However, this can require the injection of large quantities of a base (e.g., KOH or NaOH) into the MEG pretreatment system, which is associated with high operating costs as well as health, environmental, and safety risks related to handling and transportation of large volumes of highly concentrated and harmful chemicals.

Scale inhibitors are also commonly used to reduce crystallization during the production of oil and natural gas [8, 32, 33], but several studies have reported that MEG can reduce the performance of some scale inhibitors [34-36]. Laboratory tests are thus commonly performed to evaluate the degree of scale inhibition achieved by proposed scale inhibitors under conditions similar to those found in oil and natural gas fields. One of the most effective such laboratory tests uses the dynamic scale loop (DSL) method [33], which was adopted by the present study to investigate total dissolved solids at different concentrations and pH levels.

Ultimately, the purpose of this study was to determine the influence of the low concentrations of divalent ions in the reboiler's rich MEG feed solution. To this end, we evaluated the impact on reboiler performance of the different concentrations of divalent ions that remained after the MEG pretreatment process, in terms of fouling, scaling, or downstream effects, such as filter blocking or whether suspended solids were carried through. Considerable cost savings would be achieved if it can be demonstrated that a low divalent cation content does not have significant adverse effects on the downstream processes of the reboiler section. For plants without pretreatment facilities, this research can also provide a useful insight on the impact to the MEG regeneration process of the divalent cations that appear in the rich MEG feed (e.g., due to formation water breakthrough).

2. Experimental Methodology

2.1 Test Conditions

The absolute pressure of the CO₂ gas that reached the facility was set at 44 bar, while its partial pressure was 0.5, 1.0, 2.0, or 5.0 mol. To simulate the dissolved CO₂ concentration in the pretreatment vessel and its subsequent conversion to bicarbonate and carbonate (Fig. 1), the concentrations of the carbonate species at specific CO₂ concentrations, and their associated pHs, were calculated using carbonate–gas/brine/water equilibrium models [5, 14, 37, 38].

The carbonate species were introduced via their respective sodium salts. Calcium chloride dihydrate powder (Scharlau, reagent grade ACS, > 99 wt. %), magnesium chloride hexahydrate powder (Chem-Supply, reagent grade, > 99 wt. %), barium chloride powder (Chem-Supply, reagent grade, 99.7 wt. %), sodium hydrogen carbonate powder (Chem-Supply, reagent grade, 99.7 wt. %), and iron chloride powder (Chem-Supply, reagent grade, 99.9 wt. %) were used to prepare the brine solutions. MEG (Chem-Supply, reagent grade, > 99 wt. %), hydrochloric acid (Chem-Supply, reagent grade, 32 wt. %), and KOH (Chem-Supply, reagent grade, 99.9 wt. %) were used to prepare the MEG solutions. Ethanol (Chem-Supply, reagent grade, > 99 wt. %), ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) solution (Chem-Supply, reagent grade, 0.1 M), and citric acid powder (Rowe Scientific Pty Ltd, reagent grade, > 98 wt. %) were used for cleaning to remove residual precipitations.

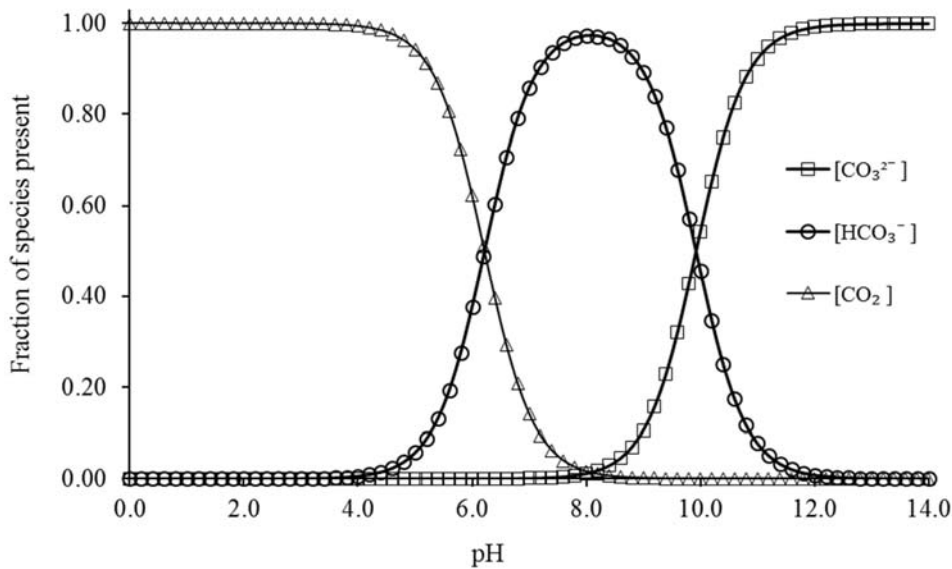


Fig. 1. Relationship between pH of Solution and Dissociation Status of Carbonic Acid in aqueous solution [39].

Two rich MEG (61.4 wt. % MEG in water) compositions were tested: case 1, which was high in calcium; and case 2, which was high in magnesium. In addition, we applied the following pretreatments: a) no pretreatment (pH < 5.0), b) pretreatment to >> 10 ppm TDS at pH 7.24, c) pretreatment to > 10 ppm TDS (pH > 8.85) and d) pretreatment to > 5 ppm TDS (pH > 9.40). All test cases are presented in Tables 1 and 2.

For each test involving a pretreatment step, we adjusted pH by adding varying quantities of KOH to achieve the initial desired pH. The removal of water from a rich MEG solution at a high temperature results in pH increases, since the remaining dissolved CO_2 also boils off during the process, thereby decreasing the concentration of dissolved carbonic acid (Fig. 2). In turn, this pH increase also increases the alkalinity of the aqueous glycolic system due to the accumulation of carbonate and bicarbonate ions [28, 40]. Since pH thus changes during the distillation process due to CO_2 removal, we adjusted the pH of the starting anion lean MEG solution to the value determined experimentally during lab-scale distillation (typically > 11.5) at each respective CO_2 concentration. For the experiments not involving a pretreatment, we used the pH of the initial rich MEG (typically 4.6) because any increase of pH during the regeneration process was found to be negligible.

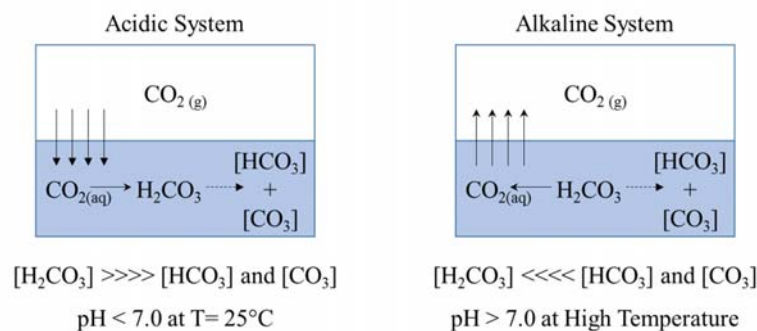


Fig. 2. pH change in carbonate systems at different temperatures [41].

All pH measurements were recalibrated by using the Sandengen, Kaasa (42) model due to the influence of MEG on the liquid junction potential, refer to Equation 6, where w_G is the weight fraction of MEG.

$$pH_{MEG} = pH_{measured} + 0.41 w_G - 0.393 w_G^2 + 0.606 w_G^3 \quad (6)$$

Using this method, we determined that the pH correction factor was 0.24 for 61.4 wt. % MEG solutions and 0.49 for 90 wt. % MEG solutions. The corrected pH values are presented in Table 1 and Table 2.

To evaluate the scaling tendency of each rich MEG solution (Table 1 and 2), we converted the divalent ion concentrations to their corresponding 90 wt. % lean MEG concentrations. This simulated the removal of excess water that occurs during the distillation process. We also checked the prepared concentration of lean MEG solution using the Al Helal, Soames (43) models, to ensure that the MEG concentration after water boil-off was within the suggested concentration range.

Table 1. The Remaining Divalent Ions Compositions in 61.4 wt. % rich MEG Solution for different Pretreatment (Case- 1)

Ions Species	No Pretreatment	With Pretreatment		
	pH <5.0	pH 7.24	pH > 8.85	
	High TDS		TDS~10	TDS~5
0.5 mole% CO ₂				
pH _{at Rich Tank}	5.0	7.24	9.57	9.90
Ca ²⁺ , ppm	58.73	42.97	0.72	0.52
Fe ²⁺ , ppm	14.65	0.16	0.0	0.0
Mg ²⁺ , ppm	14.71	14.70	7.55	3.33
Ba ²⁺ , ppm	14.71	14.70	1.84	1.10
T _k [*] , mmol/kg	0	1.634	3.298	3.518
TDS, ppm	102.81	72.55	10.12	4.96
1.0 mole% CO ₂				
pH _{at Rich Tank}	4.91	7.24	9.23	9.56
Ca ²⁺ , ppm	58.73	18.88	0.87	0.48
Fe ²⁺ , ppm	14.65	0.07	0.0	0.0
Mg ²⁺ , ppm	14.71	14.70	6.03	3.44
Ba ²⁺ , ppm	14.71	14.70	2.98	0.95
T _k , mmol/kg	0	3.367	8.134	8.401
TDS, ppm	102.81	48.36	9.88	4.87
2.0 mole% CO ₂				
pH _{at Rich Tank}	4.80	7.24	8.85	9.40
Ca ²⁺ , ppm	58.76	14.70	0.59	0.48
Fe ²⁺ , ppm	14.65	0.04	0.0	0.0
Mg ²⁺ , ppm	14.71	14.70	6.74	2.89
Ba ²⁺ , ppm	14.71	14.70	2.63	1.52
T _k , mmol/kg	0	6.216	17.453	18.287
TDS, ppm	102.81	40.62	9.96	4.89
5.0 mole% CO ₂				
pH _{at Rich Tank}	4.70	7.24	8.85	9.40
Ca ²⁺ , ppm	58.80	6.43	0.45	0.39
Fe ²⁺ , ppm	14.65	0.02	0.0	0.0
Mg ²⁺ , ppm	14.72	14.70	8.11	3.72
Ba ²⁺ , ppm	14.72	14.70	1.32	0.87
T _k , mmol/kg	0	11.862	44.521	46.488

Ions Species	No Pretreatment	With Pretreatment		
	pH <5.0	pH 7.24	pH > 8.85	
	High TDS		TDS~10	TDS~5
TDS, ppm	102.91	35.85	9.87	4.99

* T_k is Total alkalinity

Table 2. The Remaining Divalent Ions Compositions in 61.4 wt. % rich MEG Solution for different Pretreatment (Case- 2)

Ions Species	No Pretreatment	With Pretreatment		
	pH <5.0	pH 7.24	pH > 8.85	
	High TDS		TDS~10	TDS~5
0.5 mole% CO ₂				
pH _{at Rich Tank}	5.0	7.24	9.57	9.90
Ca ²⁺ , ppm	14.68	14.68	0.52	0.47
Fe ²⁺ , ppm	14.68	0.14	0.0	0.0
Mg ²⁺ , ppm	58.83	58.82	8.21	3.50
Ba ²⁺ , ppm	14.71	14.71	1.09	0.92
T_k , mmol/kg	0	1.832	4.255	4.538
TDS, ppm	102.81	88.34	9.82	4.89
1.0 mole% CO ₂				
pH _{at Rich Tank}	4.91	7.24	9.23	9.56
Ca ²⁺ , ppm	14.69	14.68	0.40	0.37
Fe ²⁺ , ppm	14.65	0.07	0.0	0.0
Mg ²⁺ , ppm	58.84	58.81	8.86	4.11
Ba ²⁺ , ppm	14.71	14.70	2.98	0.57
T_k , mmol/kg	0	3.594	8.88	9.338
TDS, ppm	102.88	88.27	9.90	5.05
2.0 mole% CO ₂				
pH _{at Rich Tank}	4.80	7.24	8.85	9.40
Ca ²⁺ , ppm	14.69	11.41	0.33	0.32
Fe ²⁺ , ppm	14.65	0.04	0.0	0.0
Mg ²⁺ , ppm	58.85	58.81	9.11	4.34
Ba ²⁺ , ppm	14.71	14.70	0.42	0.37
T_k , mmol/kg	0	6.372	18.083	18.921
TDS, ppm	102.91	84.97	9.87	5.04
5.0 mole% CO ₂				
pH _{at Rich Tank}	4.70	7.24	8.85	9.40
Ca ²⁺ , ppm	14.70	6.17	0.44	0.33
Fe ²⁺ , ppm	14.65	0.02	0.0	0.0
Mg ²⁺ , ppm	58.89	58.82	8.14	4.16
Ba ²⁺ , ppm	14.72	14.70	1.30	0.41
T_k , mmol/kg	0	12.289	45.524	47.280
TDS, ppm	102.98	79.72	9.89	4.89

Ions Species	No Pretreatment	With Pretreatment	
	pH <5.0	pH 7.24	pH > 8.85
	High TDS	TDS~10	TDS~5

* T_k is Total alkalinity

2.2 Dynamic Scale Loop

DSL is commonly used to test scale formation under controlled temperature, pressure, and flow rate conditions [44, 45]. Our experimental set-up is illustrated in Fig. 3. Separate solutions containing the required cations and anions were mixed and then subjected to a temperature of 180 °C (to replicate reboiler skin temperature) at atmospheric pressure. The formation of scale within the capillary tubing was monitored by measuring the differential pressure build-up across the capillary tube. A carbon steel disk (Fig. 3) was also installed after the capillary tubing chamber was heated to evaluate the formation of scale crystals on a carbon steel surface. Following each experiment, we analyzed the scale formation on the carbon steel disk using Scanning Electron Microscopy (SEM) to determine the morphology of the deposits.

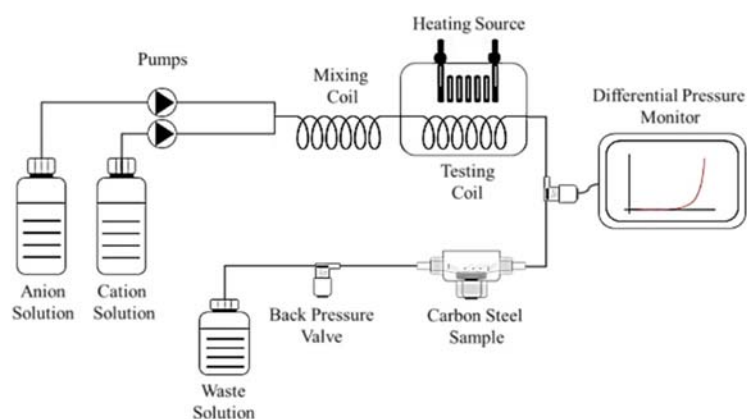


Fig. 3. DSL configuration and in-line carbon steel disk holder.

2.3 Pilot Plant Distillation

Next, we verified the experimental results generated from the DSL tests. An MEG regeneration pilot plant (Fig. 4) was used to investigate scale formation tendencies within the reboiler and heating bundle by applying two pretreatment conditions: at TDS \gg 10 ppm (pH 7.24), and at TDS \sim 10 (pH 8.85), both with 5.0 mol % CO_2 (Table 1). The reboiler was continually fed with the rich MEG solution (61.4 wt. %) to re-concentrate the solution in the reboiler to 90 wt. % (i.e., lean MEG). Prior to starting these tests, the rich MEG tank was sparged with 100% CO_2 gas to reach saturation. During the operation of the MEG pilot plant, the CO_2 gas that was boiled off in the distillation process was compensated for by sparging CO_2 gas into the feed blender to ensure that the rich MEG tank solution remained at constant saturation in each cycle. The reboiler was operated at 145 °C to achieve lean MEG (90 wt. %). A carbon steel sample was also installed in-line between the reboiler and lean MEG tank to assess the scaling tendency on carbon steel. A ten-micron filter was then installed to evaluate its ability to filtrate the lean MEG and remove suspended solids prior to being recycled to the lean MEG tank.

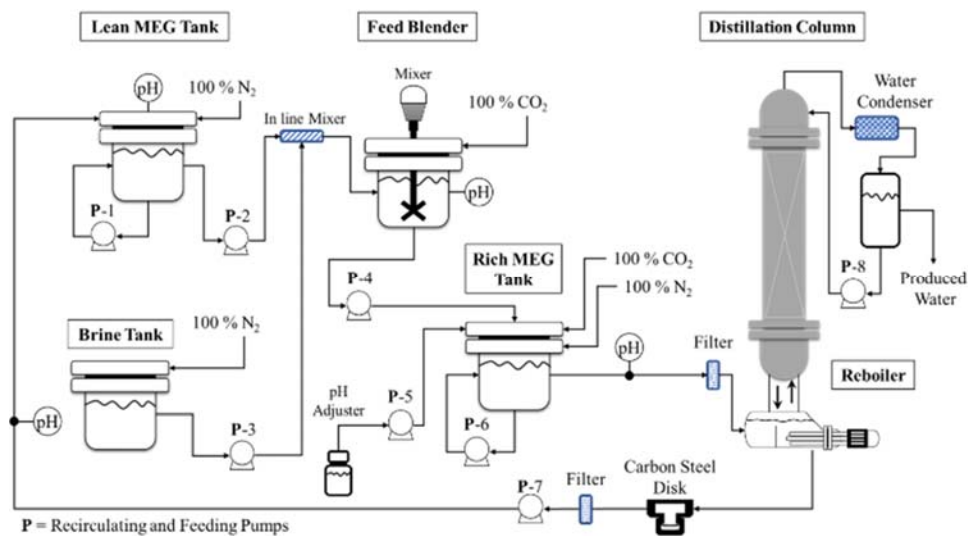


Fig. 4. MEG pilot plant configuration.

3. Results and Discussion

3.1 Alkalinity Measurements: Cases 1 and 2 before and After DSL Testing

The total alkalinity in aqueous glycolic solutions plays an important role in controlling the rate of scale precipitation in both pretreatment vessels and reboilers [37, 46]. As shown in Fig. 1, the number of carbonate and bicarbonate ions can be controlled by adjusting the pH value in the aqueous system. In addition, the total alkalinity can be increased by increasing the dissolved CO_2 mole% under alkaline conditions (Fig. 2). Carbonate ions often react with sparingly soluble ions (e.g., Fe^{2+} , Ca^{2+} , Mg^{2+}) when appropriate conditions prevail [23]. As shown in Table 1 and Table 2, in pretreatment trials with pH 7.24 at 0.5 mol % CO_2 , Ferrous carbonate (FeCO_3) tended to be consumed faster than other divalent ions. This was due to the Fe^{2+} ions' greater ability to precipitate at low carbonate concentrations than other divalent ions. These results are in line with Navabzadeh Esmaeely, Choi (47) findings, which reported that the formation of FeCO_3 was more rapid in solutions containing low concentrations of calcium ions (10 and 100 ppm) than in solutions containing high calcium ion concentrations (> 100 ppm).

When the pH of our experiment increased to > 8.85 at a constant CO_2 mol fraction, the precipitation of divalent compounds became greater. Similar responses were observed when the CO_2 mol fraction increased from 1.0 to 5.0 moles %.

3.2 Scale Analysis

Theoretically, the pH 7.24 pretreatment level was expected to produce the worst results due to its higher concentrations of remaining divalent ions in its feed stream in comparison to the pH > 8.85 pretreatment trials (Table 1 and Table 2): the remaining high concentrations of divalent ions in the reboiler could precipitate after the CO_2 gas was boiled off, due to the significant increase in the bicarbonate and carbonate ion concentrations [48]. In contrast, we expected the pH > 8.85 pretreatment to be less risky because of the high pre-precipitation of divalent ions in its pretreatment process, which could potentially contribute to lower depositions in the reboiler [49].

We performed experimental DSL trials using the rich MEG compositions (Table 1 and 2) to confirm these hypotheses; Table 3 and 4 summarize the results. These tables show the tendency of blockage and semi blockage inside the capillary tubing which has occurred only within a pH of 7.24 for cases 1 and 2. Furthermore, they show that the calcium ion concentrations played a crucial factor to precipitate more scale layers inside the capillary tubing when abundance amounts of carbonate ions are available, specifically at CO_2 mole fraction below 2.0%. High CO_2 mole fraction (5.0 mole %) does not show blockage or semi blockage within capillary tubing due to low Calcium ions concentration in the feed stream, but it can be seen that a thin scale layer has been precipitated over the carbon steel sample.





The tendencies of the solutions to form scale are indicated by a) complete blockage of the capillary tube and scale formation on the in-line sample (red), b) formation of scale on in-line sample (orange), c) partially blockage of the capillary tube and scale formation on the in-line sample (yellow), and d) no scale formation (green), respectively.

Table 3. Summary of Lab-Scale DSL Results at High TDS, ppm

CO ₂ mole %		No Pretreatment				With Pretreatment					
		pH 5.0				pH 7.24*					
		Ca ²⁺	Red	Orange	Yellow	Green	Ca ²⁺	Red	Orange	Yellow	Green
Case - 1	0.5	58.73				•	42.97		•		
	1.0	58.73				•	18.88	•			
	2.0	58.76				•	14.70	•			
	5.0	58.80				•	6.43			•	
Case - 2	0.5	14.68				•	14.68		•		
	1.0	14.69				•	14.68	•			
	2.0	14.69				•	11.41	•			
	5.0	14.70				•	6.17			•	

Table 4. Summary of Lab-Scale DSL Results at low TDS (10 to 5 ppm)

CO ₂ mole %		With Pretreatment									
		pH >8.85*									
		Ca ²⁺	Red	Orange	Yellow	Green	Ca ²⁺	Red	Orange	Yellow	Green
Case - 1	0.5	0.72				•	0.52				•
	1.0	0.87				•	0.48				•
	2.0	0.59				•	0.48				•
	5.0	0.45				•	0.39				•
Case - 2	0.5	0.52				•	9.66				•
	1.0	0.40				•	9.32				•
	2.0	0.33				•	9.15				•
	5.0	0.44				•	9.15				•

	Complete blockage of the capillary tube and scale formation on the in-line sample
	Partially blockage of the capillary tube due to low initial Ca ²⁺ concentrations
	Formation of scale on the in-line sample at very low Calcium ion concentrations
	No scale formation
*	The tests were re-adjusted to pH > 11.4 to match the re-boiler pH

3.2.1 DSL Method

With no pretreatment (pH < 5.0), no scale formation was observed. With the pH 7.24 pretreatment, scale formation was primarily observed for cases 1 and 2, with complete blockage of the capillary tube achieved at 2.0 mol CO₂ and 1.0 mol CO₂, and semi-blockage at 0.5 mol CO₂, as illustrated in Fig. 5, Fig. 6, 7 by a sharp increase in the pressure across the capillary tube. The feeding concentrations of the Ca²⁺ divalent ions were the highest of all the other evaluated cases at 2.0, 1.0, and 0.5 mole % CO₂. In contrast, lowered concentrations of divalent ions injected from the rich MEG tank reduced blockage (Table 3). As a result, the high remaining concentration of divalent ions ultimately facilitated the significant growth of calcium carbonate scale within the capillary tube, leading to increasing differential pressure build-up across the capillary coil.

We were also interested to observe that the differential pressure build-up fluctuated between 0.5 bar and 2.2 bar, leading to a semi-blocked capillary (Fig. 6 and 7). This was because the accumulated scale formation inside the capillary coil led to the acceleration of the blockage of the capillary coil, resulting in a pressure increase. The pressure build-up on the blocked area then caused a breakdown in the formed deposit layers, indicating that the amount of formed scale was insufficient to block the flow

through the capillary coil. However, over the long term, this issue could lead to the accumulation of several scale layers, thereby creating a full blockage.

In addition, with the 7.24 pH pretreatment, scale was formed on the in-line carbon steel samples, which were exposed to solutions containing 5.0 mol % CO₂. We expected greater scale formation with the pH > 8.85 pretreatment; however, for cases 1 and 2 at 5.0 mol % CO₂ content, we observed no differential pressure build-up (complete or partial blockage) due to the low concentrations of calcium ions that were fed to the DSL capillary coil (Tables 1 and 2). These low calcium ion concentrations were caused by the pretreatment process. Nonetheless, a thin layer of scale still formed on the surface of carbon steel disk, confirming the tendency for scale deposition on hot surfaces and pipelines, which can affect the long-term performance of hot surfaces.

Similar results were observed with the ~10 and ~5 ppm TDS pretreatment conditions. The formation of scale on the in-line carbon steel sample was observed in cases 1 and 2 for all CO₂ concentrations, but no tube blockage occurred (see Fig. 8 and Fig. 9). These results indicate that, at both pretreatment levels, the formation of scale on carbon steel surfaces at 180 °C (i.e., the reboiler bundle temperature) is likely. However, due to the low initial concentrations of calcium ions that were fed to the DSL system, the rate of solid formation within the capillary tube was insufficient to cause blockage under the continuous flow conditions present in the tube.

We also sought to investigate the amorphous dispersion of scale formation that caused the blockage and non-blockage behaviors. SEM analysis conducted on the carbon steel samples primarily indicated the formation of different calcium carbonate polymorphs, including calcite, vaterite, and aragonite. Where significant levels of magnesium were present, the formation of dolomite (a combination of calcium, magnesium, and carbonate) also occurred. The SEM images of the carbon steel in-line samples are presented in Fig. 9 and highlight the different types of scale; these were confirmed using Energy-Dispersive Spectroscopy (EDS). They indicate that CaCO₃ is aragonite amorphous at high temperatures and high MEG concentrations; this is in line with previously published conclusions [23, 50].

Another interesting result was the presence of a high concentration of Mg²⁺ ions (Table 2), which could affect the MEG pilot plant flow assurance, particularly in highly alkaline conditions. This was because of the fact that at pH values higher than 10, the Mg²⁺ ions tended to interact with the hydroxide ions in the reboiler, forming gel-like Magnesium hydroxide (Mg(OH)₂), which can accumulate on the surface of filters and prevent flow. These results are discussed in greater detail in section 3.2.2.4.

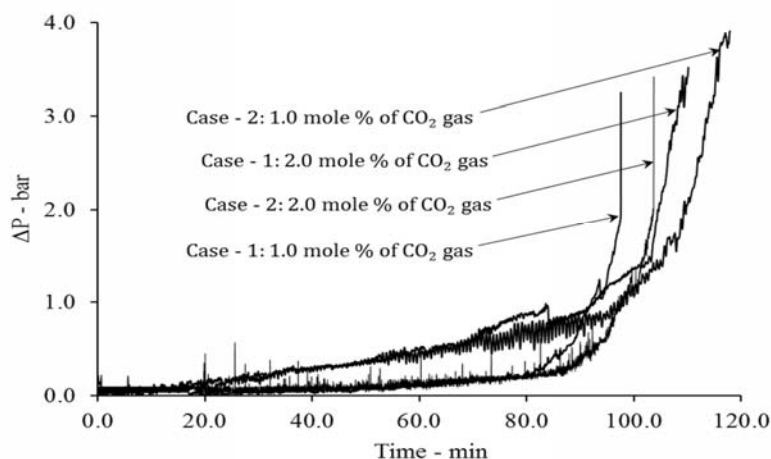


Fig. 5. Differential pressure drop over the capillary tube for case- 1 and case- 2 after pH adjustment to 7.24 (Complete blockage).

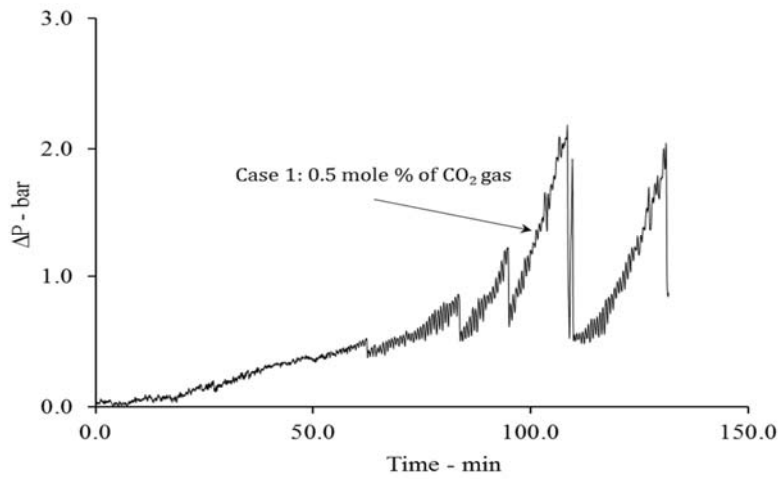


Fig. 6. Differential pressure drop over the capillary tube for case- 1 of CO₂ 0.5 mole % after pH adjustment to 7.24 (Semi-blockage).

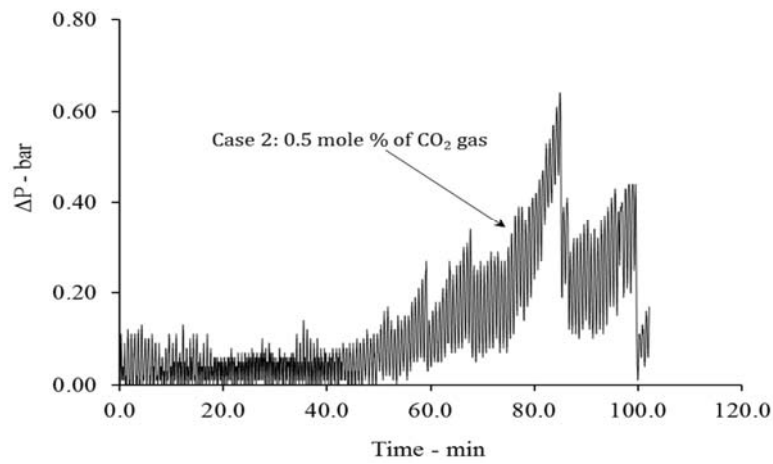


Fig. 7. Differential pressure drop over the capillary tube for case- 2 of CO₂ 0.5 mole % after pH adjustment at 7.24 (Semi-blockage)

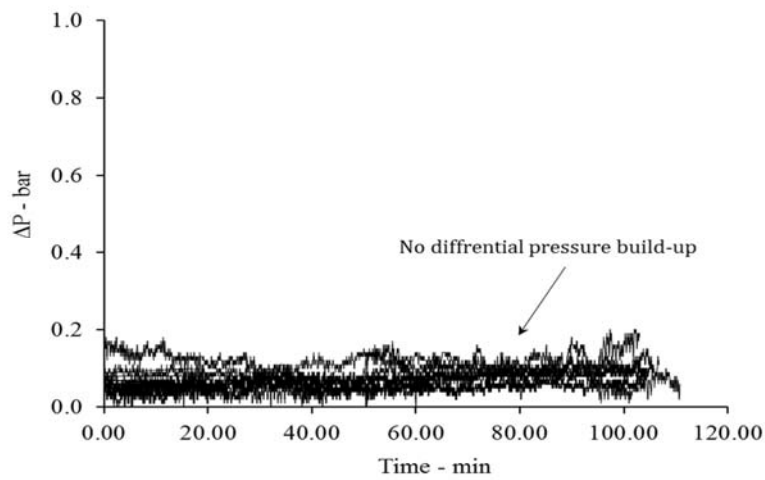


Fig. 8. Differential pressure drop over the capillary tube for case- 1 and case- 2 of some of the remaining red indicator trials after pH adjustment.

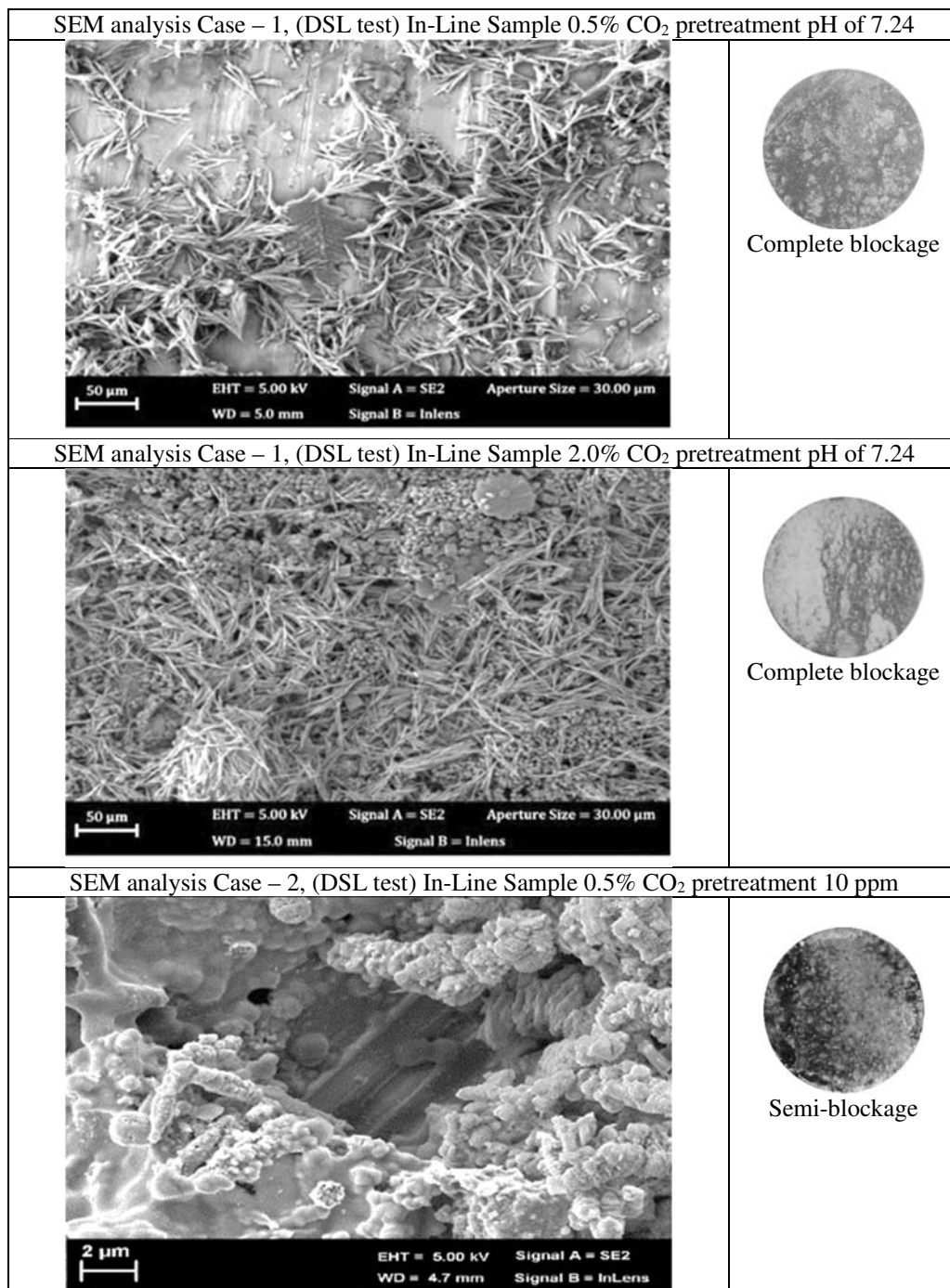


Fig. 9. Scale formation on carbon steel sample during select DSL trials

3.2.2 MEG Pilot Plant Distillation

To verify the scale formation within the reboiler, two additional case 1 tests (pH 7.24 pretreatment and TDS ~ 10 ppm pretreatment) were conducted in a MEG regeneration pilot plant to confirm the results generated by the DSL experiments.

3.2.2.1 Case 1: Pretreatment pH 7.24 at 5.0 mol CO₂

To maintain a pH of 7.24 within the rich MEG product, we continuously injected it with KOH to neutralize the incoming acidic CO₂-rich MEG mixture. The neutralized mixture was then pumped into

the reboiler of the distillation column to re-concentrate the rich MEG solution into lean MEG. Consistent with our lab distillation test results, we noted a significant increase in the pH readings in the reboiler section when the rich MEG solution was concentrated and reached 90 wt. % MEG (Fig. 10). We furthermore observed that the reboiler temperature caused the water content to be partially boiled off, including CO₂ gas, which affected the carbonate dissociation equilibria (reactions 1 and 2). The removal of CO₂ gas therefore concentrated the hydroxide and carbonate ions in the reboiler, promoting the formation of scale.

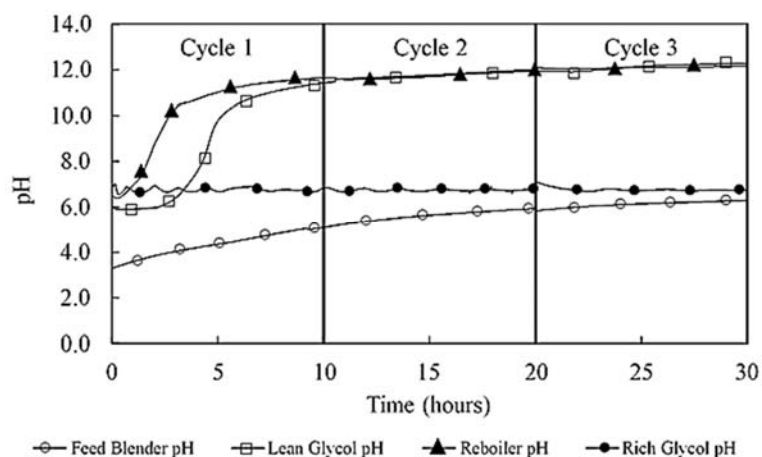


Fig. 10. Effect of CO₂ removal and hydroxide concentration on system pH.

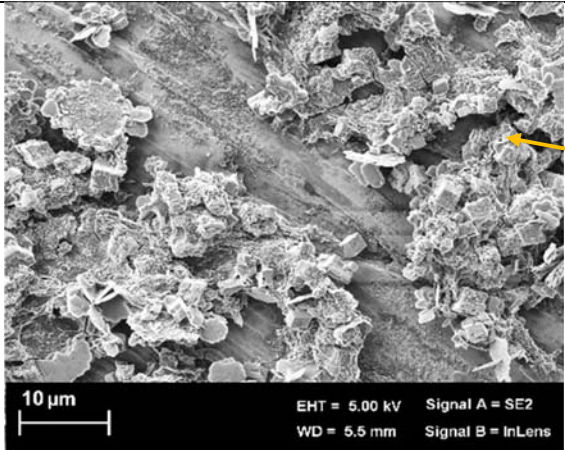
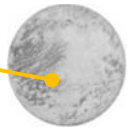
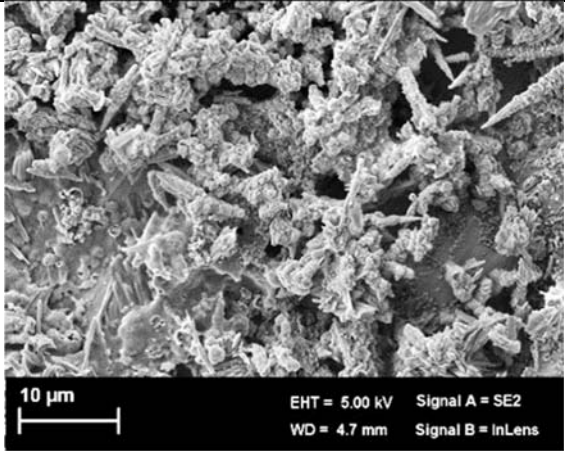
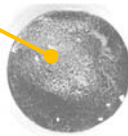
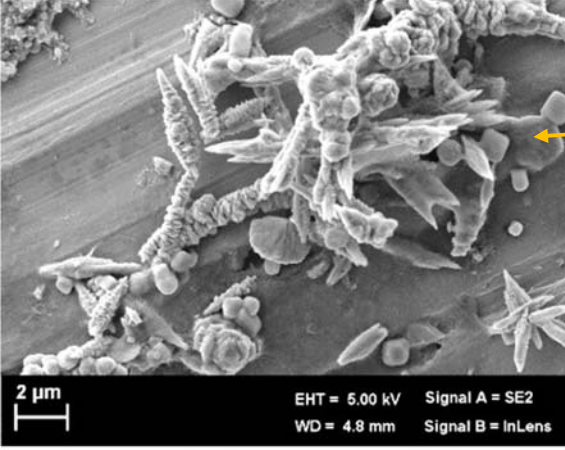
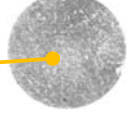
3.2.2.2 Formation of Scale within the Re-boiler System

After continually operating the MEG pilot plant for three inventory turnovers (cycles), significant scale formation in the reboiler was observed. As is shown in Fig. 11, scale accumulated along the inner wall of the reboiler. The in-line carbon steel disk also demonstrated strong scaling (Fig. 12). Fig. 12 also shows the similarity of the scale structures that formed in both the DSL and MEG pilot plant experiments. SEM analysis of the rough surface of the carbon steel disk indicated different CaCO₃ polymorph structures, including calcite, aragonite, and vaterite. The results of the pilot plant were thus again consistent with the DSL results. Furthermore, as can be observed from Fig. 12, the geometrical structure of the polymorph structures formed using both methods indicated to scaling issues.

The scale formation on the carbon steel disk highlights the high probability of scale formation along tubing lines and carbon steel reboiler bundles at high temperatures. However, a minimal amount of scale was observed along the reboiler's heating bundle. This can be attributed to the heating bundle's stainless steel material, which has a low surface roughness compared to typical industrial bundles manufactured from carbon steel. Overall, however, we concluded that a pH 7.24 pretreatment is not recommended due to its high probability of scale formation, which would require excessive reboiler cleanings to prevent the loss of heat transfer efficiency and tube blockage.



Fig. 11. Scale formation on Re-boiler wall.

5.0 mole % CO ₂ pH 7.24 Pretreatment In-Line Sample	
MEG Pilot Plant	Carbon Steel
	
5.0 mole% CO ₂ TDS 10ppm Pretreatment In-Line Sample	
MEG Pilot Plant	Carbon Steel
	
5.0 mole% CO ₂ pH 7.24 Pretreatment Sample	
DSL Test	Carbon Steel
	
5.0 mole% CO ₂ TDS 10 ppm Pretreatment Sample	
DSL Test	Carbon Steel

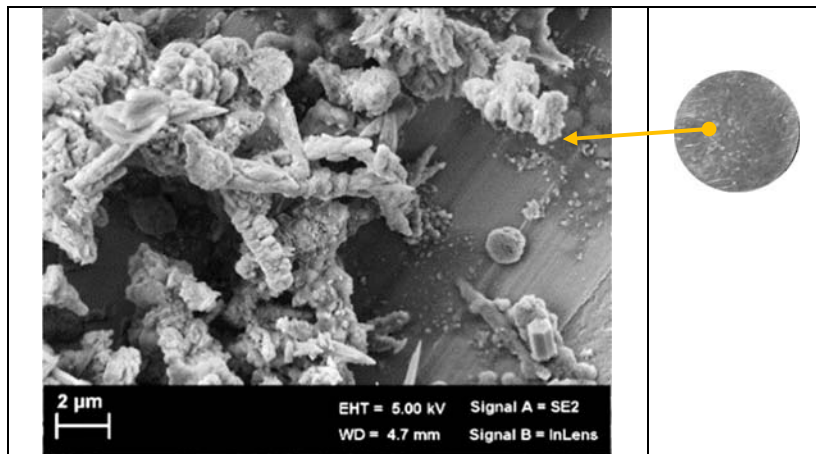


Fig. 12. Scale formation on carbon steel sample of selected MEG pilot plant trials of case - 1.

3.2.2.3 Case 1: Pretreatment TDS ~ 10 ppm at 5.0 mol CO₂

The entire regeneration system (including the reboiler walls and bundle, the in-line carbon steel sample, and the stainless steel level sensor submerged in the liquid) exhibited significant scale formation when using the ~ 10 ppm pretreatment divalent salt concentrations at 5.0 mol CO₂. A high pH (8.85) was maintained within the rich MEG tank to simulate the pretreatment and facilitate the conversion of bicarbonate to carbonate, which, once formed within the reboiler, ultimately promoted the formation of carbonate scale; this was also consistent with the DSL results. In addition, the rise in pH within the reboiler produced a lean MEG with a pH in excess of 11.5, thus increasing the potential for scale formation. SEM analysis indicated the formation of primarily calcium and magnesium carbonate scale, including calcite, vaterite, and dolomite; this was confirmed by EDS and X-ray diffraction tests for some samples. Fig. 13 and 14 illustrate the formation of scale within the reboiler and highlight the formation of a scale layer on the glass wall as well as a thick coat of white scale on the heating bundle. The scale formed on the walls of the reboiler was of an extremely fine nature, indicating primarily dolomite formation. In contrast, we judged that the scale formed on the heating bundle consisted primarily of calcium carbonate (white color and ease of removal using citric acid).

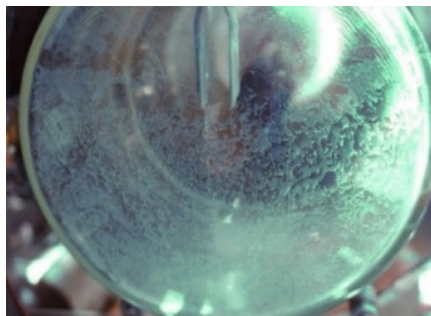


Fig. 13. Formation of scale upon re-boiler wall.

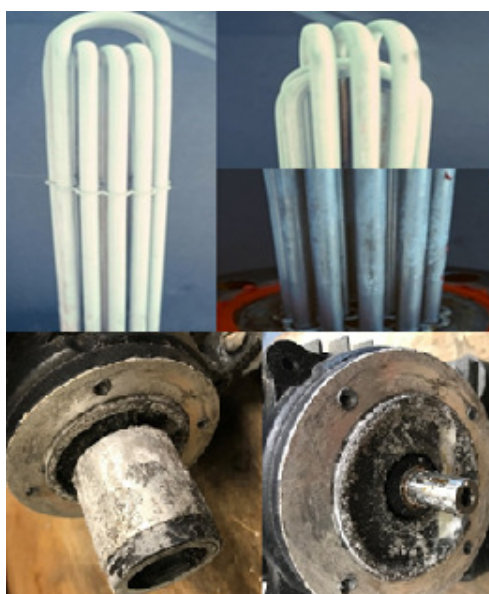


Fig. 14. Formation of scale on re-boiler bundle and pump head.

3.2.2.4 Microfilters Before and After the Reboiler Process

Our findings also highlight the ability of magnesium ions to precipitate under highly alkaline conditions. The solutions containing brine were passed through the DSL mixing coil using a 2 μm filter, which was used to protect the capillary tubing from impurities (Fig. 3). We found that a gel-like slurry started to accumulate on the surface of the micro-filter. A similar result was observed for a MEG pilot plant filter, as shown in Fig. 15. We analyzed the gel-like slurry using EDS and found it to be $\text{Mg}(\text{OH})_2$, likely formed by the high alkalinity within the reboiler [51, 52]. The slurry increased the viscosity of the MEG-brine solution since a 50 wt. % $\text{Mg}(\text{OH})_2$ slurry has an approximate viscosity of 400 cp [53]. Furthermore, increased viscosity influences scaling formation behavior on hot surfaces during shut-down and cool-down [17], and the diffusivity of CO_2 also drops with increasing viscosity [27]. The presence of $\text{Mg}(\text{OH})_2$ thus changes the physio-chemical properties of water-glycol solutions. However, several studies have reported that the solubility of $\text{Mg}(\text{OH})_2$ in water is very low and that it continues to decrease with increasing temperatures [51, 53]. These effects, particularly within a reboiler, would likely influence a MEG pilot plant operation.

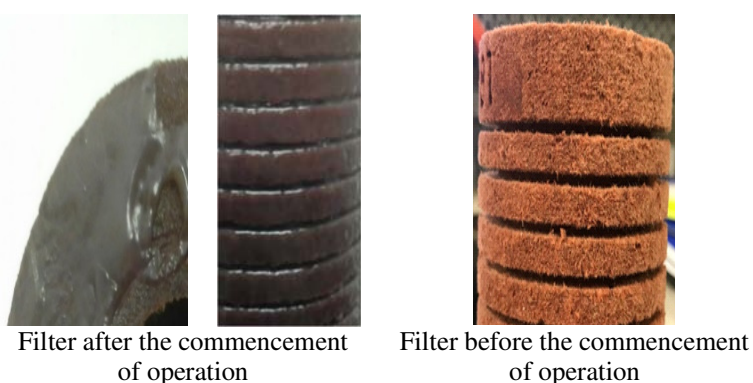


Fig. 15. $\text{Mg}(\text{OH})_2$ material formed on the micro-filter surface of the MEG pilot plant.

3.3 Proposed Scale Cleaning

3.3.1 pH 7.24 Pretreatment at High Divalent Ion Concentrations

Following the formation of scale within the reboiler, a 5.0 wt. % citric acid solution was used to remove residual scale from both the wall of the round flask and the carbon steel samples. The citric

acid solution easily removed the majority of the scale from the walls and bottom of the carbon steel samples (using a squeeze-bottle application). To ensure that all scale had been removed from the samples, the citric acid solution was then boiled and the carbon steel samples were re-washed using distilled water. However, some scale still remained, primarily on the top surface of the carbon steel samples. A variety of solvents were used to try and remove the remaining scale, including 10 wt. % citric acid, 1 wt. % HCl, ethanol, and acetate, but all were unsuccessful. Ultimately, to completely remove the scale from the carbon steel we had to physically remove it, much as we did with the scale from the lab-scale distillation testing. It thus became apparent that using the pH 7.24 pretreatment resulted in the formation of scale that is extremely difficult to remove; this treatment should therefore be avoided in the field to prevent the need for excessive cleaning and reductions in reboiler efficiency.

3.3.2 *pH > 8.85 Pretreatment at Low Divalent Concentrations*

The initial cleaning of the reboiler was conducted with a 5 wt. % citric acid solution. The carbon steel sample was immersed in 5 wt. % citric acid and allowed to soak for approximately six hours before being drained and subsequently cleaned with distilled water and ethanol. The initial cleaning with citric acid failed to remove all of the calcium carbonate scale from the carbon steel sample.

To remove the remaining scale, we applied a solution of 5 wt. % citric acid and 2 wt. % EDTA. EDTA and citric acid act as chelating agents, directly reacting with heavy metal ions to form complexes and thus allowing their removal [54, 55]. To facilitate the removal of calcium and magnesium with EDTA, the pH of the cleaning solution was increased to approximately 9–10 [54]. The high pH allowed the EDTA to readily dissolve in water and facilitated the reaction between the EDTA ions and the calcium and magnesium. The high pH also has the advantage of preventing the corrosion of carbon steel surfaces. We found that the EDTA was capable of removing a significant portion of the scale left on the carbon steel after approximately two hours of soaking time. However, some scale still remained on the top surface of the carbon steel. We recommend its complete removal using high-pressurized water.

The combination of EDTA followed by high-pressurized water cleaning procedure is recommended if heavy calcium and magnesium scaling occur within the reboiler along both the reboiler bundle and the walls. If the scale consists primarily of calcium carbonate, cleaning with 5.0 wt. % citric acid is sufficient.

4. Conclusions

Our results will allow MEG regeneration plant operators to evaluate reboiler units under harsh conditions to prevent the occurrence of worst-case scenarios during field operations. Our primary findings indicate that low concentrations of divalent ions have a high likelihood of forming scale inside conveyer tubing and reboiler bundles even when using a pretreatment process in a MEG regeneration plant. The pretreatment vessel thus cannot be minimized without harming the MEG regeneration process.

The following conclusions can be drawn from these results:

1. The primary scaling product identified for the rich MEG solution (cases 1 and 2) was calcium carbonate in the form of calcite, vaterite, and dolomite.
2. In both cases 1 and 2, complete blockage of the capillary coil occurred during the DSL tests at a pretreatment pH of 7.24 at 1.0 and 2.0 mol CO₂, while partial blockage occurred at 0.5 mol CO₂.
3. The formation of calcium carbonate scale primarily occurred inside the DSL capillary tube at divalent cation concentrations of 10 and 5 ppm at 5.0 mol CO₂, without any significant pressure build-up.
4. The DSL results were consistent with those from the MEG regeneration pilot plant.
5. The higher the concentration of CO₃²⁻ at the beginning of the experiment, the more likely the blocking of the capillary tubing.
6. Operating in highly alkaline conditions with a high concentration of magnesium ions led to the precipitation of magnesium hydroxide, which precipitated within the in-line filters and on hot surfaces.

5. Acknowledgements

The authors would like to acknowledge Curtin Corrosion Engineering Industry Centre (CCEIC) and the Department of Chemical Engineering at Curtin University for financial support. Furthermore, we would like to acknowledge the support of Chevron Australia Pty. Ltd. during the conduction of this study and Marisa Wongkaew for assistance with sample preparation.

6. References

- [1] Boak L S. Factors that impact scale inhibitor mechanisms: Heriot-Watt University; 2013.
- [2] Sandengen K. Prediction of mineral scale formation in wet gas condensate pipelines and in meg (mono ethylene glycol) regeneration plants: Norwegian University of Science and Technology; 2006.
- [3] Guan H 2011 Carbonate scaling prediction: The importance of valid data input *J Mater Sci Eng* **5** 220
- [4] Ferguson R J 2011 *Mineral scale prediction and control at extreme ids* International Water Conference ESWP Orlando, FL, USA p. 77
- [5] Lu H, Kan A T and Tomson M B 2010 Effects of monoethylene glycol on carbonate equilibrium and calcite solubility in gas/monoethylene glycol/nacl/water mixed systems *Spe Journal* **15** 714-25
- [6] Kan A, Fu G and Tomson M 2005 *Prediction of scale inhibitor squeeze and return in calcite-bearing formation* SPE International Symposium on Oilfield Chemistry Society of Petroleum Engineers
- [7] Fosbøl P L, Thomsen K and Stenby E H 2009 Modeling of the mixed solvent electrolyte system CO_2 - Na_2CO_3 - NaHCO_3 - monoethylene glycol- water *Ind Eng Chem Res* **48** 4565-78
- [8] Daniels J K, Littlehales I J, Lau L and Linares-Samaniego S 2014 *Laboratory methods for scale inhibitor selection for hp/ht fields* SPE International Oilfield Scale Conference and Exhibition Society of Petroleum Engineers
- [9] Babu D, Hosseinzadeh M, Ehsaninejad A, Babaei R, Kashkooli M and Akbary H 2015 Carbonates precipitation in meg loops—a comparative study of south pars and bass strait gas fields *J Nat Gas Sci Eng* **27** 955-66
- [10] Saifelnasr A, Bakheit M, Kamal K and Lila A 2013 Calcium carbonate scale formation, prediction and treatment (case study gumry oilfield-pdoc) *International Letters of Chemistry, Physics and Astronomy* **12** 47--58
- [11] Gal J-Y, Bollinger J-C, Tolosa H and Gache N 1996 Calcium carbonate solubility: A reappraisal of scale formation and inhibition *Talanta* **43** 1497-509
- [12] Muryanto S, Bayuseno A, Ma'mun H and Usamah M 2014 Calcium carbonate scale formation in pipes: Effect of flow rates, temperature, and malic acid as additives on the mass and morphology of the scale *Procedia Chemistry* **9** 69-76
- [13] Hu Y-B, Wolthers M t, Wolf-Gladrow D A and Nehrke G 2015 Effect of ph and phosphate on calcium carbonate polymorphs precipitated at near-freezing temperature *Cryst Growth Des* **15** 1596-601
- [14] Plummer L N and Busenberg E 1982 The solubilities of calcite, aragonite and vaterite in CO_2 - H_2O solutions between 0 and 90 c, and an evaluation of the aqueous model for the system CaCO_3 - CO_2 - H_2O *Geochim Cosmochim Acta* **46** 1011-40
- [15] Hyllestad K. Scaling of calcium carbonate on a heated surface in a flow through system with mono ethylene glycol: Norwegian University of Science and Technology; 2013.
- [16] AlHarooni K, Barifcani A, Pack D, Gubner R and Ghodkay V 2015 Inhibition effects of thermally degraded meg on hydrate formation for gas systems *J Pet Sci Eng* **135** 608-17
- [17] Brustad S, Løken K-P and Waalmann J G 2005 *Hydrate prevention using meg instead of meoh: Impact of experience from major norwegian developments on technology selection for injection and recovery of meg* Offshore Technology Conference Offshore Technology Conference
- [18] Yong A and Obanijesu E O 2015 Influence of natural gas production chemicals on scale production in meg regeneration systems *Chem Eng Sci* **130** 172-82
- [19] Tomson M B, Kan A T, Fu G and Al-Thubaiti M 2003 *Scale formation and prevention in the presence of hydrate inhibitors* International Symposium on Oilfield Chemistry Society of Petroleum Engineers
- [20] Kan A T, Fu G, Watson M A and Tomson M B 2002 *Effect of hydrate inhibitors on oilfield scale formation and inhibition* International Symposium on Oilfield Scale Society of Petroleum Engineers
- [21] Lu H, Kan A T and Tomson M B 2009 *Effects of monoethylene glycol on carbonate equilibrium and calcite solubility in gas/monoethylene glycol/water/salt mixed systems* SPE International Symposium on Oilfield Chemistry Society of Petroleum Engineers
- [22] Shipley H J, Kan A T, Fu G, Shen D and Tomson M B 2006 *Effect of hydrate inhibitors on calcite, sulfates and halite scale formation* SPE International Oilfield Scale Symposium Society of Petroleum Engineers
- [23] Flaten E M, Ma X, Seiersten M, Aanonsen C, Beck R and Andreassen J-P 2015 *Impact of monoethylene glycol and Fe^{2+} on crystal growth of CaCO_3* CORROSION 2015 NACE International
- [24] Flaten E M, Seiersten M and Andreassen J-P 2010 Induction time studies of calcium carbonate in ethylene glycol and water *Chem Eng Res Des* **88** 1659-68

- [25] Kan A T, Fu G and Tomson M B 2002 Effect of methanol on carbonate equilibrium and calcite solubility in a gas/methanol/water/salt mixed system *Langmuir* **18** 9713-25
- [26] Haque M E 2013 Ethylene glycol regeneration plan: A systematic approach to troubleshoot the common problems *Journal of Chemical Engineering* **27** 21-6
- [27] Ehsani H. Influence of monoethylene glycol (meg) on the corrosion inhibition of wet-gas flow lines 2013.
- [28] Zaboon S, Soames A, Ghodkay V, Gubner R and Barifcani A 2017 Recovery of mono-ethylene glycol by distillation and the impact of dissolved salts evaluated through simulation of field data *J Nat Gas Sci Eng* **44** 214-32
- [29] AlHarooni K, Pack D, Iglauer S, Gubner R, Ghodkay V and Barifcani A 2016 Analytical techniques for analyzing thermally degraded monoethylene glycol with methyl diethanolamine and film formation corrosion inhibitor *Energy Fuels* **30** 10937-49
- [30] Stewart E and Lanning R 1994 Reduce amine plant solvent losses; part 1 *Hydrocarbon Processing:(United States)* **73**
- [31] Nazzer C and Keogh J 2006 *Advances in glycol reclamation technology* Offshore Technology Conference Offshore Technology Conference
- [32] Xu B, Chen T, Chen P, Hagen T H, GUO Q and Yang X 2014 *Influence of calcium and bicarbonate ions on the kinetics of CaCO_3 formation at hthp in the absence and presence of scale inhibitors* SPE International Oilfield Scale Conference and Exhibition Society of Petroleum Engineers
- [33] Wang S and Wylde J 2009 *Scale inhibitor selection for deepwater high temperature applications* CORROSION 2009 NACE International
- [34] Jordan M M, Feasey N D and Johnston C 2005 *Inorganic scale control within meg/methanol treated produced fluids* SPE International Symposium on Oilfield Scale Society of Petroleum Engineers
- [35] Williams H, Herrmann T, Jordan M and McCallum C 2016 *The impact of thermodynamic hydrate inhibitors (meg and methanol) on scale dissolver performance* SPE International Oilfield Scale Conference and Exhibition Society of Petroleum Engineers
- [36] Hills E J, Hase A, Saeten J, Auflem I H, Turner K F, Brice S, et al. 2006 *Hydrate-inhibited scale inhibitor for use on sub-sea templates* SPE International Oilfield Scale Symposium Society of Petroleum Engineers
- [37] Kan A T, Lu H and Tomson M B 2010 Effects of monoethylene glycol on carbon dioxide partitioning in gas/methanol/water/salt mixed systems *Ind Eng Chem Res* **49** 5884-90
- [38] Pitzer K S and Simonson J M 1986 Thermodynamics of multicomponent, miscible, ionic systems: Theory and equations *The Journal of Physical Chemistry* **90** 3005-9
- [39] Gutz I G R. , curtipot – ph and acid–base titration curves, 2017 [Available from: http://www.iq.usp.br/gutz/Curtipot_.html].
- [40] Halvorsen A M K, Andersen T R, Halvorsen E N, Kojen G P, Skar J I, Biørnstad C, et al. 2007 *The relationship between internal corrosion control method, scale control and meg handling of a multiphase carbon steel pipeline carrying wet gas with CO_2 and cetic acid* NACE NACE International
- [41] Mehrbach C, Culberson C, Hawley J and Pytkowicz R 1973 Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure *Limnol Oceanogr* **18** 897-907
- [42] Sandengen K, Kaasa B and Østvold T 2007 Ph measurements in monoethylene glycol (meg)+ water solutions *Ind Eng Chem Res* **46** 4734-9
- [43] Al Helal A, Soames A, Gubner R, Iglauer S and Barifcani A 2018 Measurement of mono ethylene glycol volume fraction at varying ionic strengths and temperatures *J Nat Gas Sci Eng* **54** 320-7
- [44] Abidoeye L K and Das D B 2014 Scale dependent dynamic capillary pressure effect for two-phase flow in porous media *Advances in Water Resources* **74** 212-30
- [45] Al-Gharbi M S. Dynamic pore-scale modelling of two-phase flow: Imperial College; 2004.
- [46] Flaten E M, Seiersten M and Andreassen J-P 2010 Growth of the calcium carbonate polymorph vaterite in mixtures of water and ethylene glycol at conditions of gas processing *J Cryst Growth* **312** 953-60
- [47] Navabzadeh Esmaeely S, Choi Y-S, Young D and Nešić S 2013 Effect of calcium on the formation and protectiveness of iron carbonate layer in CO_2 corrosion *Corrosion* **69** 912-20
- [48] AlHarooni K, Gubner R, Iglauer S, Pack D and Barifcani A 2017 Influence of regenerated monoethylene glycol on natural gas hydrate formation *Energy Fuels* **31** 12914-31
- [49] Al-Rawajfeh A E, Ihm S, Varshney H and Mabrouk A N 2014 Scale formation model for high top brine temperature multi-stage flash (msf) desalination plants *Desalination* **350** 53-60
- [50] Flaten E M, Seiersten M and Andreassen J-P 2009 Polymorphism and morphology of calcium carbonate precipitated in mixed solvents of ethylene glycol and water *J Cryst Growth* **311** 3533-8
- [51] Amjad Z. The science and technology of industrial water treatment: CRC Press; 2010.
- [52] Al-Anezi K and Hilal N 2007 Scale formation in desalination plants: Effect of carbon dioxide solubility *Desalination* **204** 385-402
- [53] Green D W and Perry R H. Perry's chemical engineers' handbook. McGraw-Hill Professional; 1999.

- [54] Kim J and Vipulanandan C 2003 Effect of ph, sulfate and sodium on the edta titration of calcium *Cem Concr Res* **33** 621-7
- [55] Kawano M and Tokonami M 2014 Effect of organic acids on the precipitation rate and polymorphism of calcium carbonate minerals in solutions with Mg^{2+} ions *Clay Science* **18** 1-10