Technical challenges and solutions in a closed loop MEG regeneration system for gas field offshore, UK

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Abstract

Two UK gas/condensate fields are being developed as a single integrated subsea production system. Mono Ethylene Glycol (MEG) is used as a thermodynamic hydrate inhibitor. The main processes for recycling of MEG are regeneration and reclamation. Operational problems within closed MEG system are carbonate ($CaCO_3$) scaling deposits at MEG injection point, pipeline, and salt removal system as well as accumulation of corrosion products. This paper presents the results of prediction of precipitation of solids and corrosion in the closed MEG loop system and presents solutions for these challenges. The key points discussed in this paper are (i) The choice of acid to be used to neutralise excess alkalinity in the Lean MEG; (ii) The upper limit value of pH in order to keep a low corrosion rate and prevent scaling risk; (iii) The risk and consequences of HCl overdosage; (iv) The location of the injection point of this acid; (v) Calculation of the acid flowrate; (vi) The choice of the alkalinity source required to precipitate the divalent cations in the rich MEG pre-treatment; (vii) Calculation of the flowrate of this alkalinity source; and (viii) Monitoring of alkalinity and acid injection. The modeling methodology used as a basis for this study is a purely thermodynamic approach. The equilibrium calculations are done with the MultiScale software with the glycol add-in.
Keywords: scale, monoethylene glycol, alkalinity, corrosion, hydrochloric acid, sodium carbonate.

1   Introduction

Reservoir A and Reservoir B gas condensate fields are situated in the UKCS West of Shetland. They are being developed as a single integrated Subsea Production System.

Formation waters from the reservoirs are not available. The composition of aquifer water has been used to estimate the composition of the formation water from Reservoir A; Reservoir B formation water is assumed to be the same. The use of Mono Ethylene Glycol (MEG) for hydrate inhibition in gas production lines is well established and works effectively as long as the salt solubility is not exceeded. MEG is injected in high concentrations, higher than 85 wt%.

The objectives of the study were to:

- Evaluate the risk of mineral scaling from bottom hole to well head taking into account the provided formation water composition which has been used as the basis throughout the project design, as well as analogous formation waters from reservoirs close to reservoirs A and B.
- Evaluate the risk of mineral scaling inside the MEG units.
- Study the effect of Lean MEG specifications on the risk of scaling, especially carbonate scaling.
- Suggest Lean MEG specifications (salinity, bicarbonates, and calcium levels).

Depending on the reservoir, oilfield brines can be saturated with respect to calcite or gypsum, anhydrite and barite. MEG in water lowers the solubility of carbonates and sulphates [1–3]. The effect is most pronounced for sulphates (barite, gypsum and anhydrite) [3]. It is documented that MEG enhances barite scale problems at some conditions [4]. However, depending on temperature and the actual supersaturation, crystal nucleation and growth of barium sulphate can be delayed for long period of time [4]. The solubility of $CaSO_4$ decreases with MEG concentration [1]. Another thermodynamic effect is that anhydrite is observed at lower temperature in MEG solutions due to the lower water activity [4]. In contrast to $CaSO_4$, the effect of MEG on the solubility of $CaCO_3$ is small [1, 3]. When a $CaCO_3$ saturated brine is mixed with pure MEG, the dilution counteracts reduced solubility at most conditions [5, 6]. Furthermore, MEG decreases the nucleation growth rates of the calcium carbonate isomorphs. The effect is most pronounced at low temperature [2, 7].

2   Process overview

The MEG Regeneration system comprises three modules: pre-treatment module, regeneration module and desalination module. An overview of the MEG loop used in the simulation work is shown in Figure 1.
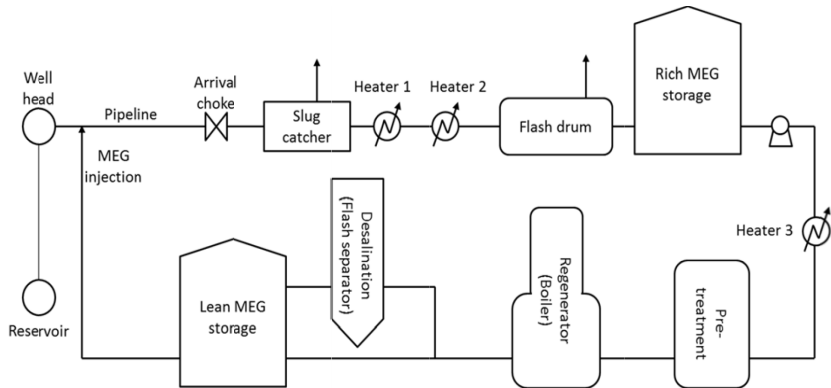
Figure 1:   Schematic overview of the MEG loop used in the simulation work.

3   Operating procedure

For the evaluation of the risk of scaling from bottom hole to well head for the two reservoirs, as well as for the sensitivity study using formation waters representative of other West of Shetland reservoirs, three software packages have been used; these are SCALE 2000 v.3.1, ScaleSoftPitzer and MultiScale. Software package MultiScale has been used to evaluate the scaling risk of scaling from bottom hole to well head, as well as inside the MEG loop. All three give purely thermodynamic predictions; they do not model nucleation and growth rates.

SCALE 2000 v.3.1 has been developed by BRGM, France. ScaleSoftPitzer has been developed by Rice University, United States. MultiScale has been developed by the Norwegian University of Science and Technology (NTNU). SCALE 2000 and ScaleSoftPitzer software work as a point simulation. The present version of MultiScale has been developed by NTNU in a project supported by Statoil and Norsk Hydro. Multiscale model is also a point simulation tool, but with a process module that makes it possible to use the output from the calculation at one point as input in the next point.

Saturation Ratio (SR) is used to quantify the thermodynamic driving force for precipitation and hence scaling risk. It is calculated from bottom hole to well head, and inside the MEG loop. As a general rule, the risk of scaling is predicted by the Saturation Ratio (SR) as the following criteria:

- If SR > 1, the water is oversaturated and salt might potentially precipitate.
- At SR = 1, the water is at equilibrium.
- If SR < 1, the water is under-saturated and scaling cannot occur.

Whether a salt actually precipitates at SR>1 depends on the nucleation and growth rate. However, the higher the Saturation Ratio, the faster the kinetics of precipitation. Generally, the SR required for precipitation onset decreases with

temperature. The simulation reported herein is based on the following assumptions and adjustments:

1. All reactions reach thermodynamic equilibrium.
2. Formation water tuning and adjustments:

   - The alkalinity is tuned to give $CaCO_3$ saturation at reservoir conditions with the calcium concentration given in the formation water analysis.

   - The organic acid concentration in the produced water is tuned to saturation with the tuned alkalinity.

   - The concentration of sulphate is tuned to give saturation of BaSO4 at reservoir conditions.

   - The concentration of chloride is adjusted to give electro neutrality.

3. Any precipitated salts (mainly divalent least soluble salts) from Rich MEG are left behind and not carried with the Rich MEG from rich MEG pre-treatment to the Lean MEG storage tank.
4. Precipitated solids (monovalent and divalent salts) are carried through from the pipeline to the pre-treatment.
5. The condensed water rate is set to water saturation of the gas at bottom hole conditions.
6. Slip stream to desalination is calculated as % of Lean MEG Mass Rate including salts (monovalent and divalent salts).
7. Na_2CO_3 injection in pre-treatment is tuned to precipitate all divalent cations to concentration less than 1 mg/kg solvent.
8. HCl injection in Lean MEG is tuned to neutralise alkalinity that forms HCO_3^- ("strong alkalinity") when balanced with the produced liquid phase (i.e. OH^-, CO_3^{2-} and HCO_3^-). That implies that organic acids are kept as carboxylates.

4   Scaling prediction from bottom hole to well head

Table 1 presents the analysis points from bottom hole to the Lean MEG storage. The composition of the formation water for Reservoir A has been estimated from the composition of formation water from Reservoir B; consequently, the concentrations of individual ions of Reservoir A water are very approximate (Table 2). The organic acids were counted as 60 mg/kg total acetic acid, i.e. HAc + Ac$^-$ = 60 mg/kg. Three formation waters from reservoirs close to Reservoir A and Reservoir B (Reservoirs C, D and E) have been tested (Table 2). The simulations performed with waters from reservoirs A, C, D and E show that there is no risk of calcium carbonate, barium sulphate and calcium sulphate scaling from bottom hole to well head (Table 3).

Table 1:   Analysis points from bottom hole to the Lean MEG storage.

	Reservoir A		Reservoir B	
	Pressure (bara)	Temperature (°C)	Pressure (bara)	Temperature (°C)
Reservoir	431 to 70	112	418 to 99	118
Bottom hole	412 to 63	112	400 to 92	118
Upstream well head	351 to 41	83 to 43	157 to 43	83 to 52
downstream well head	351 to 41	74 to 34	157 to 43	74 to 43
	Pressure (bara)		Temperature (°C)	
MEG injection	541 to 41		74 to 43	
Pipeline	125 to 42		-1 to 50	
Slugcatcher	29 to 10		-8 to 12	
Heater 1	25.1 to 6		16.9 to 1.6	
Heater 2	24 to 4		41 to 40	
Flash Drum	1.5		41	
Rich MEG storage	1		-7 to 40	
Heater 3	2.5		60	
MEG Pre-treatment – Filter press	2.5		60	
MEG Regeneration column	0 to 2.5		156	
Lean MEG storage	1		30	

Table 2:   Water compositions of formation waters of reservoirs A, C, D and E.

Ions	Reservoir A (mg/l)	Reservoir C (mg/l)	Reservoir D (mg/l)	Reservoir E (mg/l)
Sodium	9732	9000	10880	10890
Potassium	544	200	258	460
Calcium	4597	250	215	919
Magnesium	101	50	24	23
Barium	5	60	135	5
Strontium	33	25	53	35
Total iron	8	0	3	Not reported
Chloride	23550	14300	17340	9080
Sulphate	154	0	2	31
Bicarbonate	168.29	1050	1255	559
Total dissolved solids	40000	24935	30186	Not reported

Table 3:   Summary of results of calculation for the streams from the individual field for the Well heads (MEG injection point) and upstream.

	Reservoir		Bottom hole		U/S Well Head		Well head	
	Reservoir A	Reservoir B	Reservoir A	Reservoir B	Reservoir A	Reservoir B	Reservoir A	Reservoir B
Water	Reservoir A formation water							
SR $CaCO_3$	1.00	1.00	1.02	1.02	0.74	0.84	0.64	0.70
SR $BaSO_4$	1.02	1.00	1.03	1.01	1.25	1.39	1.34	1.54
SR $CaSO_4$	0.68	0.73	0.69	0.74	0.51	0.57	0.46	0.50
Water	Reservoir C formation water							
SR $CaCO_3$	1.00	1.00	1.02	1.02	0.66	0.90	0.56	0.73
SR $BaSO_4$	0.12	0.12	0.12	0.12	0.14	0.16	0.15	0.17
SR $CaSO_4$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	Reservoir D formation water							
SR $CaCO_3$	1.00	1.00	1.02	1.02	0.66	0.90	0.56	0.73
SR $BaSO_4$	0.12	0.80	1.12	0.80	0.14	1.07	0.15	1.19
SR $CaSO_4$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	Reservoir E formation water							
SR $CaCO_3$	1.00	1.00	1.25	1.02	0.66	0.86	0.56	0.68
SR $BaSO_4$	0.12	0.64	0.12	0.64	0.14	0.90	0.15	0.93
SR $CaSO_4$	0.00	0.07	0.00	0.07	0.00	0.05	0.00	0.05

5   Precipitation prediction from well head through the process system and the MEG regeneration unit

The results of the simulations downstream the wellhead through the process system and the MEG Regeneration Unit (MRU) is given in Table 4 and 5. Up to the rich MEG pre-treatment the software is set to carry solids from one point to another. This implies that the amount of solids given at each point is the total amount including the upstream solids. The calculated required Na_2CO_3 and HCl flowrates are presented in Table 5.

The results show risk of precipitation upstream of the MEG recovery unit, but only solid corrosion products are predicted. The SR for $FeCO_3$ exceeds 100 at the pipeline outlet. The total amount of corrosion products and the amount that will follow all the way to the MEG Regeneration Unit (MRU) are uncertain. The predictions are conservative in that the corrosion rate might be high taking the low CO_2 concentration into account and it is further anticipated that all corrosion products are produced to the Lean MEG and not left in the pipeline.

Table 4:   Simulations results upstream of the MEG unit.

	Pipeline	Slug Catcher	Heater 1	Heater 2	Flash Drum	Rich MEG storage	Heater 3
Pressure (bara)	124	29	25.1	24	1.5	1.1	2.5
Temperature (^{o}C)	-10	-8	1.6	40	41	-7	60
pH	6.38	6.74	6.75	6.57	7.30	8.05	7.14
Wt% MEG	58.27	58.30	58.30	58.30	58.49	58.49	58.48
CO_2 (mol/kg)	0.0045	0.0021	0.0019	0.0015	0.0001	0.0000	0.0001
Alkalinity (mmol/kg)	5.13	5.14	5.09	3.13	2.01	2.18	1.91
Density (kg/m^3)	1.09	1.09	1.09	1.09	1.09	1.09	1.09
Supersaturation ration (SR)							
$CaCO_3$	0.08	0.24	0.42	2.68	35.00	199.18	154.15
$FeCO_3$	0.17	0.51	1.04	11.58	152.57	436.5	764.67
$BaSO_4$	6.32	6.33	6.03	3.48	3.53	6.61	2.49
$CaSO_4$	0.02	0.03	0.03	0.03	0.03	0.01	0.02
Precipitation (kg/day)							
$CaCO_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$FeCO_3$	0.00	0.00	3.07	128.87	169.60	117.93	176.21
$BaSO_4$	0.02	0.02	0.02	0.02	0.01	0.02	0.01
$CaSO_4$	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 5:   Simulations results in the MEG unit

	Pre-treatment	MEG regeneration	Lean MEG storage
Pressure (bara)	2.5	1.7	1.1
Temperature (^{o}C)	60	156	30
pH	9.81	9.34	8.12
Wt% MEG	56.13	88.94	90.28
CO_2 (mol/kg)	0.000	0.000	0.000
Alkalinity (mmol/kg)	14.46	20.14	0.03
Density (kg/m^3)	1.06	1.14	1.10
Na_2CO_3 (mol/day)	45100		
Na_2CO_3 (m^3/day)	43.32		
HCl (mol/day)			16838
HCl (L/day)			1655
Supersaturation ration (SR)			
$CaCO_3$	3375.82	0.25	0.00
$FeCO_3$	71904.87	0.05	0.00
$BaSO_4$	1.69	1.33	2.08
$CaSO_4$	0.02	0.27	0.01
Precipitation (kg/day)			
$CaCO_3$	3459.21	0.00	0.00
$FeCO_3$	213.85	0.00	0.00
$BaSO_4$	0.02	0.00	0.00
$CaSO_4$	0.00	0.00	0.00

6 Neutralization of excess alkalinity in the Lean MEG

Alkalinity in the Lean MEG will increase the risk of calcium carbonate precipitation and possible scale formation in the pipe line at the injection point of Lean MEG due to the relative high concentration of calcium in the formation
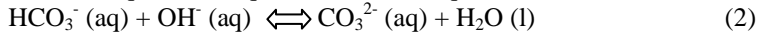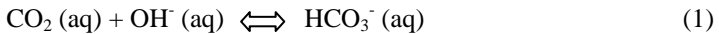
water. Alkalinity in the Lean MEG will increase the pH. The pressure difference across the production choke also enhances the scaling risk. For example, with alkalinity in Lean MEG amounting to 8.9 mmol/kg, the calculated SR (saturation ratio) is equal to 15.32 and precipitation of more than 137kg/d of $CaCO_3$ scale in the MEG injection point is predicted.

To avoid this, it is necessary to neutralize the Lean MEG with an acid in a vessel upstream of the Lean MEG storage tank; this will allow for venting out the CO_2 formed when carbonate/bicarbonate reacts with acid. The maximum concentration of dissolved CO_2 in Lean MEG will then be the saturation concentration in equilibrium with pure CO_2 at the pressure in the tank (atmospheric). The vessel could be purged with fuel gas to reduce CO_2 in the Lean MEG. The objective of the re-acidification should mostly be to reduce the alkalinity that reacts to bicarbonate at the MEG injection point to 1-2 mMol/l in order to mitigate scaling risks.

The type of acid to be used is HCl, the virtue of this acid is that it only adds chlorides; however it has to be carefully monitored and the pH controlled to a minimum of 6.5 in order to keep a low corrosion rate of the pipeline and MEG injection line. Theoretically, with a carbon steel injection line, the pH must be above 6 in order to keep the corrosion rate below 0.1 mm/y. In addition it is recommended to use a corrosion inhibitor (CI) to protect the pipelines and the MEG injection line. Continuous CI injection is required and the dosage must give a concentration in the rich MEG that is sufficient to protect pipeline. A monitoring of CI concentration in both Lean and Rich MEGs must be put in place.

7 Source of alkalinity to precipitate divalent cations in rich MEG pre-treatment

One might think that the source of alkalinity must be carbonate. However, in many cases there are considerable amounts of bicarbonate and dissolved CO_2 in the rich MEG that react to form carbonate when hydroxide is added. The reactions are:

$$CO_2 \, (aq) + OH^- \, (aq) \Longleftrightarrow HCO_3^- \, (aq) \tag{1}$$
$$HCO_3^- \, (aq) + OH^- \, (aq) \Longleftrightarrow CO_3^{2-} \, (aq) + H_2O \, (l) \tag{2}$$

As a consequence, hydroxide can be added when there are sufficient CO_2 and HCO_3^- in the rich MEG to give a carbonate concentration that can remove the divalent cations. In cases with high CO_2 content in the rich MEG, the chemical consumption (on mole basis) will be lower with hydroxide than with carbonate as hydroxide is the stronger base and hence converts more CO_2 to HCO_3^- with the same injection (in mole). The CO_2 and HCO_3^- concentration in the rich MEG is low when the CO_2 content in the gas is low, the alkalinity in the rich MEG is low and/or when gas flashing upstream has removed the CO_2. The CO_2 content in the Reservoir A and Reservoir B is low and this gives a low concentration of

CO_2 in the rich MEG. The mole ratio $Ca^{2+} + Fe^{2+}$ to $CO_2 + HCO_3^-$ is e.g. 0.9 to 2.8. Addition of hydroxide would then only remove 30-50% of these cations and carbonate injection is thus required in order to precipitate all of them. The dominant divalent cations in rich MEG are normally Ca^{2+} and Fe^{2+}. Calcium originates from the produced water and iron from corrosion. The objective of adding alkalinity in rich MEG pre-treatment is to precipitate these and possibly Sr^{2+} and in some cases Ba^{2+} as carbonates. Carbonates are preferred as hydroxides of these cations have a much higher solubility. Only Mg^{2+} precipitates as hydroxide. Na_2CO_3 is used as the alkalinity source.

8   Lean MEG specifications

Several aspects must be taken into account when specifying the Lean MEG composition:

- Content of monovalent salts; e.g. chlorides of sodium and potassium, which have small implications for scaling, but affect the Lean MEG viscosity.
- Content of potential scale forming ions; e.g. divalent cations (Ca^{2+}, Ba^{2+}, etc.) and SO_4^{2-}.
- The alkalinity that react with CO_2 and form bicarbonate and carbonate when equilibrated with the produced gas, must be kept at a minimum.
- Minimum pH with respect to corrosion of the injection line.
- Oxygen content.

The content of highly soluble salts is usually specified to be maximum 2 or 3 wt%. This is set well below the solubility limits for these salts (in the range 6–8 wt% depending on composition) in order to give acceptable viscosity of the Lean MEG and take into account lower solubility at low temperatures that might occur during unexpected pressure drops. The content of scale forming ions in the Lean MEG must be small when the formation water production rate increases. If the lean MEG injection line is carbon steel the pH must be above 6.5 in order to keep the corrosion rate below 0.1 mm/y. Oxygen in the injected lean MEG may also corrode the injection line, but the corrosion is slow due to the high MEG content and low temperature. Keeping the O_2 content to less than 300 ppb and the pH above 6 should limit the corrosion rate to much less than 0.1 mm/y. This will also limit the Fe pick up in the Lean MEG to a few ppm. Table 6 shows the lean MEG compositions used in the simulations.

9   The slip stream calculation

In order to keep the salt content of the Lean MEG below the target value, monovalent ions from the formation water and the sodium and chloride from the

Table 6:   Lean MEG compositions used in the simulations

Ion	mmol/kg	mg/kg
Na^+	298.37	6859.52
K^+	4.90	191.75
Mg^{2+}	0.00	0.70
Ca^{2+}	0.04	1.50
Ba^{2+}	0.00	0.00
Sr^{2+}	0.00	0.00
Fe^{2+}	0.00	0.00
Cl^-	301.59	10692.08
SO_4^{2-}	0.58	55.96
CH_3COOH / CH_3COO^-	0.60	36.03
Alkalinity	0.60	

Na_2CO_3 and HCl injections have to be removed from a slip stream. The slip stream has been calculated from

$$R_{LM} \sum_1^n C_{i,LM} = R_{RBM} \left(1 - \frac{SS}{100}\right) \sum_1^n C_{i,RBM} + C_A R_A \qquad (3)$$

where

C_i is molar ionic concentration (converted to total wt% for reporting);

R is rate (mass MEG + water);

SS is slip stream (% of reboiled MEG rate)

LM denotes Lean MEG;

RBM Reboiled MEG (Lean MEG upstream desalination);

A acid (HCl) added downstream desalination (acid added upstream desalination is one i in Ci, RBM).

In the present case, a slip stream rate of 38% gives 3wt% salt in the Lean MEG. The expected solids formation in the Desalination (Flash Separator), which is mainly NaCl and KCl including the ions from the added chemicals (Na_2CO_3, HCl) are equal to 560.8kg/h.

10 Monitoring alkalinity and acid injection

Careful monitoring is required for both the alkalinity injection in pre-treatment and especially the acid injection to the Lean MEG. Preferentially the alkalinity injection should be dosed according to the amount of divalent cations in the rich MEG. This is probably best measured by measuring the residual concentration of dissolved divalent cations in rich MEG sampled downstream the pre-treatment. The samples must be filtered in order to determine the true concentration of

dissolved ions. In order to determine the need for acid injection, the alkalinity should be determined in the same samples. The temperature in the pre-treatment is rather low (60°C). This is a challenge as both iron and calcium carbonate do not nucleate and grow instantaneously. Sufficient residence time is thus required in order to obtain solids that can be effectively removed. In this case, it is expected that iron carbonate precipitation starts upstream the pre-treatment. If iron carbonate does not precipitate to equilibrium, calcium carbonate precipitation may also initiate upstream. Neutralization of Lean MEG should preferentially be based on analyses of the alkalinity and its speciation. It is preferred to make the acid injection to Lean MEG upstream the Lean MEG storage tank. This should reduce the risk of over treating a large volume.

11 Corrosion

Some corrosion is expected in the pipelines, which will give increased Fe^{2+} and alkalinity in the aqueous phase along the transport pipelines. The corrosion rate was set to 0.1mm/year for both pipes (ID = 18 inch) and length of 143000 m each. It was assumed that 15% of the pipe area was water wetted. This approach is conservative as the low CO_2 content in the gas (0.02 mol% in Reservoir A and 0.2 mol% in Reservoir B) and low pressure give a moderate corrosivity and a low corrosion rate when a suitable inhibitor is applied. If the lean MEG injection line is carbon steel the pH must be above 6.5 in order to keep the corrosion rate below 0.1 mm/y. It has been confirmed that the use of a corrosion inhibitor carried out by the MEG is sufficient to protect the pipeline and MEG injection line; however this corrosion inhibitor has to be selected for this purpose, i.e. with consideration of the MEG – water mixture under the predicted operating conditions. Therefore a dedicated CI selection study has been carried out.

12 Conclusions

- In a complex medium of gas, condensates, condensed water, MEG, and formation water of uncertain composition, the prediction of scale risks is not very accurate.
- The simulations performed with Reservoirs A, C, D and E formation waters showed that there is no risk of scaling from bottom hole to well head for both Reservoir A and Reservoir B .
- The main solid that may precipitate in upstream of the MRU is $FeCO_3$. The amount will depend on the corrosion rate of the pipeline.
- The choice of acid to be used to neutralize the Lean MEG is HCl.
- The acid injection to Lean MEG should be performed upstream the Lean MEG storage tank.
- A maximum pH value equal to 7.5 is recommended in the Lean MEG to avoid scaling.
- A minimum pH value of 6.5 is recommended in the Lean MEG in order to keep a low corrosion rate (0.1 mm/y) in the pipelines and MEG injection line.

- Flow rates of acid HCl (32wt%) should be equal to 1655 L/day.
- Sodium carbonate, Na_2CO_3 (10wt%) is the recommended source of alkalinity to precipitate divalent cations in rich MEG.
- With the anticipated formation water composition and production the sodium carbonate (Na_2CO_3) injection rate is ca. 43 m^3/day.
- Careful monitoring is required for both the alkalinity injection in pre-treatment and especially the acid injection to the Lean MEG.

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