



## The influence of magnetic fields on calcium carbonate scale formation within monoethylene glycol solutions at regeneration conditions

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### ARTICLE INFO

#### Keywords:

Magnetic fields  
MEG  
Calcium carbonate  
Morphology  
Scale formation  
Dynamic scale loop

### ABSTRACT

One of the most discussed topics related to the effects of external magnetic fields (MF) on aqueous solutions is the influence on the scale formation of calcium carbonate ( $\text{CaCO}_3$ ). However, the extent of the effect of these forces on the scale formation in the non-aqueous solutions has not been investigated so far. So MFs will be applied to non-aqueous mixtures to find out the behavior of scale formation. This study presents the results of inorganic scale formation within MEG solutions containing  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions, which has been investigated using both static and dynamic scale loop (DSL) evaluation techniques. Furthermore, the influence of MFs on scale formation using the dynamic technique has also been studied. Results were generated using brine/MEG solutions exposed to an external MF produced by a 0.65 T Neodymium magnet for 2.5 s. The degree of scale formation was examined by measuring the pressure build-up across a capillary coil as scale was developed. Moreover, differences in  $\text{CaCO}_3$  morphologies were evaluated for the exposed and blank trials via the DSL technique and compared with the results obtained from the static scale evaluation method.

The results of this research have demonstrated that the short exposure (2.5 s) to a powerful MF can significantly reduce scale-formation in the rich MEG solutions within the capillary coil. This is due to the alteration of the proton spin inversion in the field of diamagnetic salts. Furthermore, a significant difference in  $\text{CaCO}_3$  morphology was observed for the scale formed during dynamic and static conditions. The generating results help to reduce the use of chemical scale inhibitors with MEG solution during the gas hydrate treatments, especially when the concentration of MEG in formation water is low and scale formation is more likely to occur.

### 1. Introduction

Calcium carbonate is a common mineral scale experienced in a wide range of industries including water treatment (Al Helal et al., 2018a; Amjad, 2010), paper mill industries (Dickinson et al., 2002), cooling water systems (Moriarty et al., 2001), natural gas transportation pipelines and MEG regeneration systems following the breakthrough of formation water (Babu et al., 2015; Yong and Obanijesu, 2015). The formation of  $\text{CaCO}_3$  occurs upon the surface of heat transfer equipment operating at high temperatures, such as heat exchangers and reboilers, leading to reduced heat transfer efficiency (Yang et al., 2001) and potential blockages or restrictions of flow along the inner surfaces of pipelines and tubing (Amjad, 2010; Chilingar et al., 2013). Several studies have been conducted to investigate the scale formation behavior of  $\text{CaCO}_3$  by examining various characteristics including crystalline phase, size distribution, and morphology (Muryanto et al., 2014; Flaten et al.,

2009; Gorna et al., 2008). The saturation index (SI) of calcium and carbonate ions have been the subject of extensive prior studies and represent a key factor in determining the tendency of  $\text{CaCO}_3$  to form (Al Helal et al., 2018a; Dai et al., 2016).

Muryanto et al. (Muryanto et al., 2014) reported that  $\text{CaCO}_3$  crystals are formed in three anhydrous polymorphs: calcite, aragonite, and vaterite. Calcite is known as the most stable form of  $\text{CaCO}_3$  crystal while aragonite and vaterite exhibit poor thermodynamic stability with the potential to convert to calcite after readjustment of certain conditions including fluid pH, temperature, supersaturation, and the presence of additives (Muryanto et al., 2014; Hu et al., 2015). For instance, Hu et al. (Hu et al., 2015) reported that at pH 9.0, the anhydrous polymorph (vaterite) is more likely to form compared to the hydrated polymorphs of  $\text{CaCO}_3$  such as monohydrate and hexahydrate (ikaite), which forms at high pH conditions of approximately 13.4 and greater within low temperature (Hu et al., 2015). However, in the presence of

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phosphate additives, the ikaite polymorph is more likely to precipitate at pH 9<sup>13</sup>.

In the last decade, the morphology of CaCO<sub>3</sub> has been extensively investigated following the application of MFs (Baker and Judd, 1996; Liu et al., 2012; Silva et al., 2015). Silva et al. (Silva et al., 2015) for instance, summarized the most significant results including the possibility of obtaining a morphology that has a lower tendency to attach to the walls of water-conveying pipes or the promotion of homogeneous precipitation of CaCO<sub>3</sub>. However, most of these studies have focused on aqueous solutions as part of attempts to modify scale formation in water systems. As such, little to no investigation has been conducted on the anti-scalent potential of MFs for use in MEG systems containing mineral ions, an application relevant to the hydrocarbon and natural gas industries.

MEG is used extensively in natural gas transportation pipelines as an inhibitor to prevent the formation of natural gas hydrates (Soames et al., 2018a,b,c; Zaboon et al., 2017; Halvorsen et al., 2007a). The use of MEG as a hydrate inhibitor is seeing increasing usage over other traditional hydrate inhibitors such as methanol due to its ability to be regenerated efficiently and reused reducing operational costs (Zaboon et al., 2017; AlHarooni et al., 2015). However, in such applications, several problems may arise following the breakthrough of formation water and subsequent introduction of mineral salts into the regeneration loop (Liu et al., 2012; Halvorsen et al., 2007a). The introduction of divalent cations including calcium, magnesium, and barium, pose a scaling risk within critical systems including subsea pipelines, and MEG injection points (Halvorsen et al., 2012) as well as within MEG regeneration systems operating at a higher temperature such as reboilers (Zaboon et al., 2017; Halvorsen et al., 2007b). Scaling within the MEG loop and associated systems can be controlled by careful control of system pH or by injection of suitable scaling inhibitors (Halvorsen et al., 2007b; Sandengen, 2006).

Flaten et al. (Flaten et al., 2009) claimed that the presence of MEG alongside water affects the supersaturation ratio due to changes in activity coefficients and the solubility of the dissolved salts. Therefore, the presence of MEG within brine solution may influence the morphology of CaCO<sub>3</sub> at the wellhead and within the pipeline under continuous flow conditions (Hyllestad, 2013; Flaten et al., 2010a). There is ample precedent to suggest that an increase in MEG weight fraction can decrease the growth rate of CaCO<sub>3</sub> and influence the polymorphism, transformation, and crystal size distribution (Flaten et al., 2015). Moreover, Flaten, et al. (Flaten et al., 2009) have reported that the morphology of the CaCO<sub>3</sub> changed at various MEG concentrations and temperatures from calcite to vaterite. The reason behind this behavior is that the activity-based supersaturation ratio represents the actual driving force of CaCO<sub>3</sub> precipitation within MEG solution (Tomson et al., 2003).

In aqueous glycol solutions, Rozhkova, et al. (Rozhkova et al., 2007a) proved that the results of the separation of MEG from the saline solutions by ionic exchange membranes improved significantly when electrolytes were present. They attributed this improvement to the apparent changes in the strength of hydrogen bonds between the OH groups of the MEG and the H groups of the water molecules. To describe this phenomenon more adequately, there is a clear reduction in the energy of hydrogen bonds between water and MEG, causing a rise in the MEG molecules mobile rates during the ionic separation process. Thus, the hydrogen bond between water-MEG has been ruptured by the presence of electrolytes that have created strong bonds with water molecules forming the first hydration shell (refer to Fig. 1). These bonds are often stronger than the hydrogen bonds formed between the water molecules and the OH group of MEG, where the large size of the MEG molecules usually causes hydrogen bonds to weaken and then rupture (Rozhkova et al., 2007a; Crupi et al., 1996). Therefore, any manipulation or modification of the hydration shell surrounding the electrolytes can distort the hydrogen bonds between both the water and the MEG molecules.

The majority of the published fundamental studies presented a

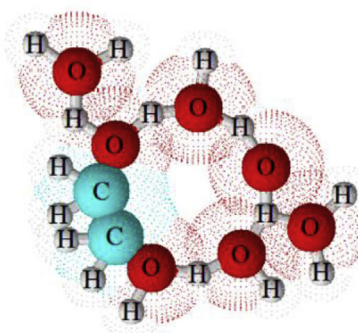


Fig. 1. (A) Hydrogen and covalent bonding of the MEG – water – Na<sup>+</sup> ion system as Rozhkova et al. (Rozhkova et al., 2007a) proposed. Images were generated using ACD/ChemSketch Freeware software (D/ChemSketch Freeware, 2015).

precise description of this shell in aqueous solutions, which they defined as a layer of water molecules arranged around the cations and anions linked to them by ion-dipole forces (Matvejev et al., 2012; Tansel et al., 2006). The thickness of the hydration shell often varies according to the size of the ions and the density of the electronic charge, giving it spatial and dynamic properties in the liquid phase (Matvejev et al., 2012). Several studies have indicated an inverse proportional relationship between the thickness of the hydration shell and the ionic mobility in aqueous solutions and a proportional relationship with the valence (Holysz et al., 2007). Previous literature has demonstrated the possibility of competition between the molecules of MEG and water molecules to form solvation shell in saline solution (Rozhkova et al., 2007a, 2007b). Therefore, the use of external forces such as the MFs may be able to induce some significant changes in the thickness of the hydration shell within the MEG solution.

This study evaluates the inhibitory performance of MFs on CaCO<sub>3</sub> growth at different MEG concentrations (50 and 80% vol.). Additionally, the EC and pressure variation were monitored and recorded continuously to evaluate the scale formation performance following MF exposure. All trials were conducted with the same initial mineral ions concentration and reboiler skin temperature of approximately 150 °C. The experiments were carried out using the DSL system with/without applying an MF source installed after mixing the calcium and bicarbonate ions. Jar tests were also conducted, but without magnetic treatment to provide a reference CaCO<sub>3</sub> scale morphology under static conditions.

## 2. Experimental methodology

### 2.1. Experimental equipment and chemicals

#### 2.1.1. Brine solutions

Two MEG solutions as shown in Table 1 were used in this study to evaluate the effects of MF treatment on scale formation at 50 and 80% by volume MEG fractions. Each experiment utilized equal concentrations of Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> ions (750 ppm) with the cationic and anionic species prepared separately within two individual containers to prevent premature reaction. The main reason behind the selection of these volume fractions is the prevalence of these percentages in MEG regeneration plants. The MEG concentration after induction at the wellhead is often 40–60% by volume (Bikkina et al., 2012; Ehsani, 2013; Latta et al., 2013), while post-regeneration is often exceeded 80% by volume of MEG (Ehsani, 2013; Latta et al., 2013) so that it can be recirculated and re-injected into the wellheads for reuse.

The cationic and anionic charges of all MEG-brine solutions were adjusted by the addition of NaCl as per Table 2. The two MEG volume fractions were utilized to simulate aqueous glycolic solutions at various

**Table 1**

Experiments for the exposed and blank tests of DSL technique and non-exposed Jar test technique at different conditions.

Trial No.	Vol. % of MEG	Temperature (°C)	Technique	Magnetic Fields
1	50	150	DSL	Yes
2	50	150	DSL	No
3	80	150	DSL	Yes
4	80	150	DSL	No
5	0	150	Jar	No
6	0	30	Jar	No
7	50	150	Jar	No
8	50	30	Jar	No
9	80	150	Jar	No
10	80	30	Jar	No

**Table 2**

Brine + MEG + Water concentrations for sets of 50% and 80% by volume of MEG.

Total Ions	Anion Solution, mg/L	Cation Solution, mg/L	Mixed Solution, mg/L
Na <sup>+</sup>	10600	10600	10600
Mg <sup>2+</sup>	0	100	50
Cl <sup>-</sup>	15475	19293	17384
Ca <sup>2+</sup>	0	1500	750
HCO <sub>3</sub> <sup>-</sup>	1500	0	750
pH	8.2	6.34	

MEG to water volume fractions at the same ionic strength to assess the effect of MFs treatment on the calcium and bicarb Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> ions within MEG solution. Jar cell trials were conducted within this study to compare the scale formation morphology of 0, 50 and 80% by volume of MEG solution with DSL technique but at 30 and 150 °C. Jar cell trials could not be controlled at 150 °C without using autoclave device due to the high evaporation rate, which changed the volume fraction of MEG. The mathematical model described by Al Helal et al. (Al Helal et al., 2018b) was used to measure the volume fraction of the glycolic solutions after adding mineral salts to ensure that the initial volume fraction of MEG before each test was correct.

### 2.1.2. Chemicals used

To produce the brine-MEG solutions, ultra-deionized water (18.2MΩ cm) was used for all experiments. The prepared solutions were sparged with N<sub>2</sub> gas to avoid contamination by CO<sub>2</sub> gas. The brine-MEG solutions consisted of, MgCl<sub>2</sub>.6H<sub>2</sub>O powder (> 99 wt %), CaCl<sub>2</sub>.2H<sub>2</sub>O powder (> 99 wt %), NaHCO<sub>3</sub> powder (99.7 wt %), NaCl powder (99.7 wt %), MEG solution (99.9 wt %) that provided by Chem-Supply (reagent grade). The pH of injected solutions (i.e. cation and anion solutions) were adjusted by using few drops of 0.1 N of NaOH to maintain the initial pH conditions.

### 2.2. Magnetic field device

An N45SH magnet was used in this study due to its high maximum energy product to affect scale formation operation. The diametrically magnetized orientation was selected due to its flexibility to utilize. Furthermore, it was placed before the mixing tubing coil before exposing the Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> solutions to the heating chamber as shown in Fig. 2. The cylindrical shape of the magnet orientation incorporates a small hole through the center generating rich MFs. Due to the small gap between the magnetic poles of the cylindrical shape, which reached about 0.1588 cm, the magnetic field strength will reach its maximum strength. This intensive strength will contribute to the modification of some thermodynamic characteristics of the mixture passing through it. The MF intensity of the cylindrical magnet was measured by using a Gauss-meter provided by the Wutronic instrument from Germany. The

N45SH magnet specifications and dimensions outlined in Table 3.

#### 2.2.1. Magnetic fields validation

Several hypotheses have been proposed to validate the effects of MFs on the thermodynamic properties of hydration shell. For instance, the expression of volumetric density of magnetic energy ( $\rho_E$ ) has been utilized to evaluate the direct potential of external MFs energy to break down the H-bonds of free water molecules (Kochmarsky, 1996). This expression represents the relationship between the magnetic susceptibility of water molecules ( $\chi$ ) and Magnetic strength (H) and Magnetic flux density (B) of the applied magnetic device. The relationship can be expressed as such:

$$\rho_E = \frac{\delta E_B}{\delta V} = \frac{\chi_{water} * H * B}{2} \quad (1)$$

where E<sub>B</sub> denotes the generated energy from the MFs that applied to the H-Bonds. By using the magnetic specification that is listed in Table 3, the generated energy (E<sub>B</sub>) from the MFs was estimated at approx 4.33\*10<sup>-6</sup> J/mol. The calculated value of E<sub>B</sub> was compared with the weakest H-bond energy of free water (5.43 kJ/mol (Kochmarsky, 1996)), which is found as such interval:

$$\frac{E_B}{E_{H-bonds}} = 4.43 * 10^{-5}$$

The comparison concluded that the effect of the external MF on the modification of the thickness of the hydration shell is not based on the generated magnetic energy effect. However, Another explanation has been proposed by Madsen (1995) which is related to the proton transfer from hydrogen carbonate to water molecules, due to proton spin inversion in the external MF. Moreover, MF effects were also described in terms of changes in the hydration of carbonate ions which might directly alter the polymorph phase equilibrium throughout the precipitation. As a result, the external magnetic field can cause weakening, distorting and alteration in the number of H-bond that generating between of water molecules and ions. Hence, affecting water molecules structure and its reaction potential with dissolved ions to form hydration shell.

#### 2.3. Scanning electron microscopy (SEM) analyses

Scanning electron microscope (SEM) analysis was used to identify the morphology of CaCO<sub>3</sub> of the exposed and the blank trials samples within different MEG concentration as described in Tables 1 and 2. The discharge solution of each test was collected and filtered using a 0.22 μm syringe filter. The filter papers were subsequently dried to remove any residual fluid. The filter papers were then coated with 5 nm platinum to allow analysis by SEM. SEM analysis of the dried samples was then generated using a Zeiss NEON, operating at 10 to 5 kV. Based on the energy dispersive spectroscopy (EDS), the scale formed was identified as polymorphs of CaCO<sub>3</sub>.

#### 2.4. Experimental setup of DSL techniques

The trials were performed to investigate the scaling tendency of MEG-Brine solutions containing HCO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup> ions in the presence of an MF using the dynamic technique, model MinDSL 1725-M from PSL Systemtechnik Germany (refer to Fig. 2). The DSL apparatus measures the differential pressure (ΔP) build-up across an inside capillary coil using a pressure detector placed at the inlet and outlet of the capillary coil with an accuracy of ± 0.009 bar. An increase in the ΔP across the capillary tube is indicative of the scale formation as the flow of solution is hindered. To investigate the influence of the MF on CaCO<sub>3</sub> formation, the ΔP across the capillary coil was monitored and measured until full blockage of the coil occurred as indicated by an increase in the ΔP recorded by the pressure detector. The time recorded for each experiment to attain full blockage of the capillary coil was used to assess

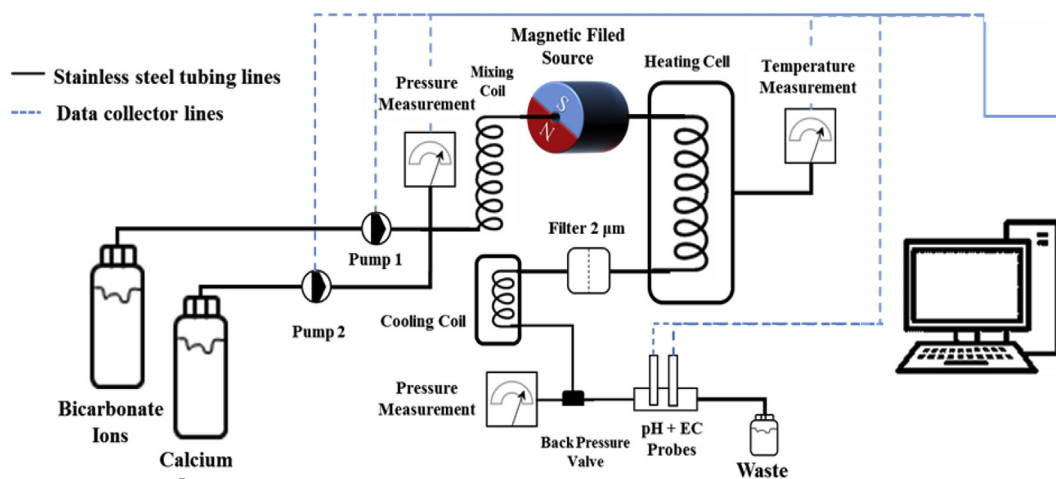


Fig. 2. Schematic of the DSL system.

**Table 3**  
Magnet specifications and dimensions.

Properties	Specification
Dimensions of Magnet	7.62 cm OD, 0.1588 cm ID, 10.16 cm Thickness
Materials and Grade	NdFeB and N45SH
Plating/Coating	Ni-Cu-Ni (Nickle)
Direction of Magnetization	Diametrically magnetized
Maximum operating temperature	150 °C, ± 5 °C
Generated Residual Flux Density $B_{rmax}$	13.499 T
The Maximum Energy Product $BH_{max}$	44.384 Megagauss Oersted (MGOe)
Magnetic susceptibility of water molecules ( $\chi$ )	$-12.63 \times 10^{-10}$ m (Dickinson et al., 2002)/ mol (Lide, 2004)
Magnetic strength (H)	$5.27 \times 10^5$ A/m
Magnetic flux density (B)	0.6500 T

the tendency of the MEG-brine solution to form  $\text{CaCO}_3$ .

The dynamic apparatus is illustrated in detail in Fig. 2 with specifications outlined in Table 3. The DSL pipelines and instruments were isolated to prevent changes in the operating temperature, brine solutions, and measurements of each trial. The cation and anion solutions were pumped separately into the dynamic apparatus through a Y shaped mixing stream by using two high-pressure pumps at room temperature. The entire flow rate for the cation and anion solutions was set at 300 ml/h. At room conditions, the scale formation rate should be very slow that it allows the study to evaluate the effects of MF on  $\text{CaCO}_3$  precipitation by following particle mechanism. The dynamic apparatus contains two individual stainless-steel coils; the first coil used to provide mixing of the MEG-brine solution. Following mixing within the primary coil, the MEG-brine solution is then passed through the center of a cylindrical magnet for a total time of 2.5 s with an MF flux density of approximately 0.650 T at the center as shown in Fig. 4 and Table 2. The second coil exposed the mixture to a heating room to accelerate the scale formation (refer to Table 3). The experimental conditions like temperature and flow rate were controlled and monitored by using the winDSL software. This study investigated the effects of particle mechanism and Lorentz force in  $\text{CaCO}_3$  deposit using DSL method.

The temperature of the heating room was set at 150 °C ( $\pm 1$  °C) during testing using a digital interface controller. A temperature of 150 °C was selected to simulate the skin temperature of the MEG regeneration column reboiler unit. A back-pressure regulator valve was placed on the outlet line of the testing capillary coil to set the  $\Delta P$  across the capillary coil. An EC and pH probes were installed to the discharge

**Table 4**  
DSL specifications.

Component	Specifications	Notes
Higher pressure pumps	0–300 ml/h, $\pm 0.6$ ml/h	Data-logger
Mixing Capillary Coil	10.0 cm Length, 3.171 mm OD and 1.01 mm ID	Stainless steel 316
Test Capillary Coil	100 cm Length, 1.411 mm OD and 0.76 mm ID	Stainless steel 316
Back Pressure Valve Range	0–172 bar, $\pm 0.01$ bar	Data-logger
Operating Pressure Range	1 bar–172 bar	Regulating
Operating Heating Chamber	+30 to +250 °C, $\pm 0.1$ °C	Regulating
pH-meter	1–14	Data-logger
Electrical Conductivity meter	0–1000 mS/cm, $\pm 0.1\%$	Data-logger
Micro Filter	2 $\mu\text{m}$	Stainless steel

tubing line to record the variation in pH and EC measurements after the MF exposure, as per Table 4 and Fig. 2.

## 2.5. Experimental setup of jar cell techniques

Closed jar testing was conducted to form different crystals of  $\text{CaCO}_3$  at different MEG concentrations and temperature levels. The jar tests were conducted using the same brine solution compositions used for the DSL trials to evaluate the difference in scale formation morphology compared to that produced using the dynamic process of the DSL system. The experimental temperatures were set at 30 °C, and 150 °C to form different  $\text{CaCO}_3$  structures and were exposed to the respective temperature for a period of 1 h. The operating temperature was maintained by using an autoclave system having an accuracy of  $\pm 2$  °C, refer to Fig. 3. Operation at 150 °C was performed under a pressure of 3.0 bar to prevent boiling of the MEG solution. The  $\text{CaCO}_3$  crystals formed were

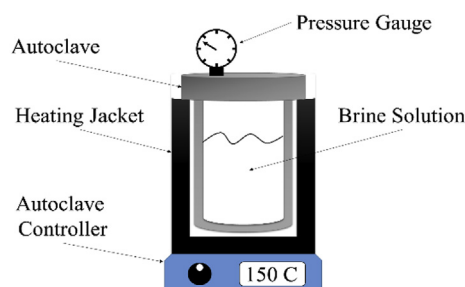


Fig. 3. Schematic diagram of jar cell techniques (autoclave).

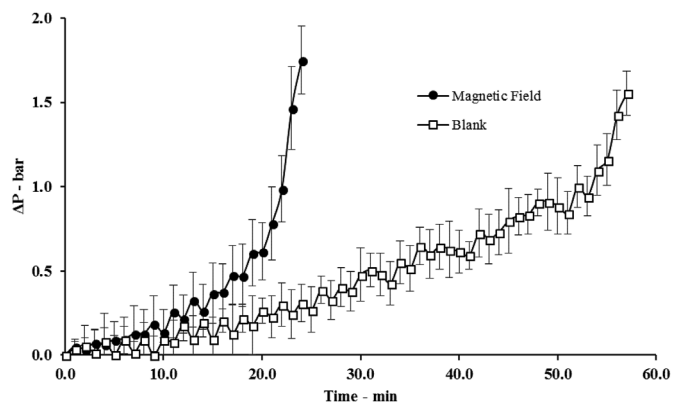


Fig. 4. Effect of MF exposure on the tendency of equal concentration of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  solution within 80 vol % MEG to form scale.

immediately filtered, dried and subsequently analyzed using SEM to distinguish the difference in the morphologies of the  $\text{CaCO}_3$ .

### 3. Results and discussions

#### 3.1. Influence of magnetic fields on scale formation at 80 vol % MEG solution

To evaluate the impact of MF exposure on the scale formation tendency of  $\text{CaCO}_3$  with MEG solution, 80 vol % MEG solutions containing an equivalent concentration of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions was exposed to MFs as discussed in Section 2.4. For comparison purposes, blank trials were conducted using the same 80 vol % MEG solutions with no exposure to the MF. The trials exposed to the MF and corresponding blank tests have been plotted in Fig. 4 with respect to the change in  $\Delta P$  across the capillary coil with time. Overall, 8 trials were performed for both the blank and exposed tests, with the average results plotted, error bars have been included demonstrating one standard deviation of the 8 tests away from the average result.

A consistent sharp rise in  $\Delta P$  across the capillary coil was observed for trials exposed to the MFs, whilst in comparison, a more gradual rise in  $\Delta P$  followed by a sharp increase which occurred during blank tests. The sharp increase in  $\Delta P$  is demonstrative of the capillary coil becoming fully blocked following the formation of scale. The duration time required for the blank tests to experience complete tube blockage was significantly longer than those trials exposed to the MF. As such, it is evident that exposure to the MF has promoted the formation of  $\text{CaCO}_3$  scale within the 80 vol % of MEG.

Furthermore, the EC of equal concentrations of bicarbonate-calcium solutions established a similar behavior exhibited during the studies by Al Helal et al. (Al Helal et al., 2018a) and Szczes et al. (Szczes et al., 2011) following exposure to an MF. As shown in Fig. 5, the application of the MF to equal bicarbonate-calcium concentration 80 vol % MEG solution has directly decreased the EC readings when compared with the corresponding blank samples results. The results of the magnetically exposed trials are consistent with the conclusions of Hasaani et al. (Hasaani et al., 2015) who reported a similar change in EC of  $\text{Ca}^{2+}$  -  $\text{HCO}_3^-$  solution following exposure to an MF. These changes were attributed to thermodynamic changes that altered the thickness of the hydration shell around those ions (Silva et al., 2015; Chibowski and Szcześ, 2018; Higashitani et al., 1993). Therefore, the generated result could suggest that the hydrated layer of the ions was influenced by exposure to the MF, and hence the electrophoretic activity of the electrolytes within 80 vol % MEG decreased.

Such a decrease in EC may occur due to the bonding of MEG molecules with aqueous solution leading to weakening the H-bonds of water-water molecules (Rozhkova et al., 2007a) (refer to Fig. 6). As a result, the weakening of hydrogen bonds tends to impact the hydration

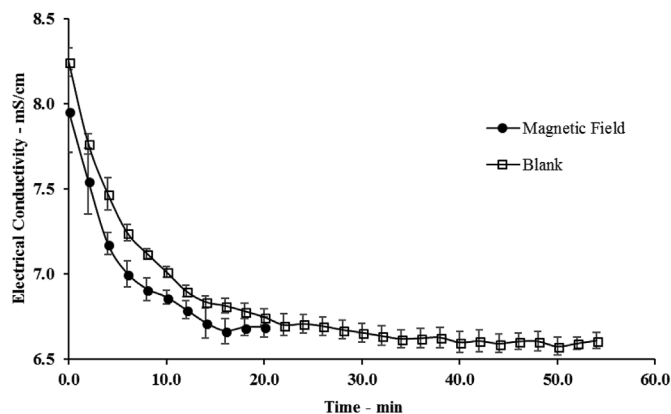


Fig. 5. Effect of MF exposure upon EC of equal concentration of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  solution within 80 vol % MEG.

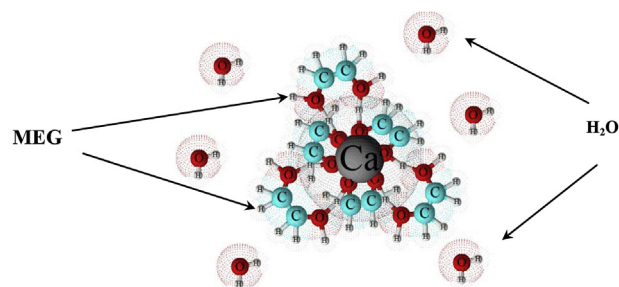


Fig. 6. Structure of the solvation shell with MEG molecules after exposure to MFs. The images were generated using ACD/ChemSketch Freeware software (D/ChemSketch Freeware, 2015).

shell thickness around dissolved ions (Chang and Weng, 2006; Zhou et al., 2000). Meanwhile, a number of publications stated that the MF effect led to an increase in EC of the aqueous solutions (Al Helal et al., 2018a; Szczes et al., 2011; Marcus, 2014). Furthermore, Silva, et al. (Silva et al., 2015) reported that less hydrated cations adhere more strongly to anions and vice versa after exposure to MFs within the aqueous solution. However, in the presence of MEG molecules, an opposite result was observed in terms of the EC reading following MF exposure.

The reduction in EC may have been caused by exchanging the water cluster typically around mineral ions with MEG molecules. Therefore, the hydration shell could be replaced with bulky MEG molecules that alter the thickness of the solvation shell around ions (less water content), refer to Fig. 6. As a result, the low hydration thickness and low solubility rate within 80 vol % MEG solution lead to a greater scale formation tendency after exposure to MFs. The proposed hypothesis was based on the conclusions of Rozhkova et al. (Rozhkova et al., 2007a) and Silva et al. (Silva et al., 2015) as mentioned in the introductory section. As a result, the bulky ions generated a weaker EC measurement within 80 vol % of MEG as shown in Fig. 5. Moreover, exposure of the ionic species to the MF may not be the only factor influencing the hydration shell thickness due to the potential of MEG molecules to swap with the water molecules to form thicker solvation shell layers around ions.

#### 3.2. Influence of magnetic fields on scale formation at 50 vol % MEG solution

Similarly to the performed 80 vol % MEG trials, the performance of MF treatment on equal concentration  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  50 vol % MEG solution has been conducted by monitoring  $\Delta P$  across the capillary coil. A contrary result was observed for  $\text{CaCO}_3$  formation in comparison to

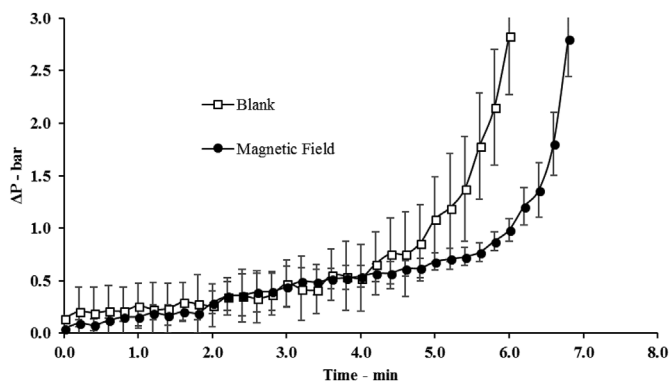


Fig. 7. Effect of MF exposure upon the tendency of equal concentration of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  solution within 50 vol % MEG to form scale.

the trails performed using 80 vol % MEG solutions as given in Fig. 7. Within the 50 vol % MEG solutions, the MF generated a positive effect after the fourth minute where the formation of the scale was inhibited in comparison to the blank trials leading to slower capillary tube blockage. The variation in scale formation behavior following MF exposure has highlighted an important difference in the performance of the MF treatment at varying MEG concentration. The adhesion of the deposits on the inner surface of the capillary coil was less frequent than the non-magnetized experiments. As such, it can be suggested that the inhibitory effect of MF treatment ultimately diminishes at higher MEG concentrations resulting in accelerated scale formation. The generated results are consistent with the findings of Higashitani and Oshitani (1998) who reported opposite effects of the MF when increasing of methanol concentration.

Rozhkova et al. (Rozhkova et al., 2007a) and Crupi et al. (Crupi et al., 1996) reported that the movement of MEG molecules within brine solution is higher than that in pure water. The increased movement of the MEG molecules was attributed to the rupture of a hydrogen bond typically formed between the water and MEG molecules. The presence of MEG solution leads to a significant reduction of the solubility index of ions resulting in a decrease of the saturation level and overall increasing scaling potential. However, when the rich MEG solution was exposed to the external MFs, the scale formation rate slowed, leading to a different scenario.

This scenario may have been caused by a decrease in solvation shell and an increase in the hydration shell thickness around the ionic species, therefore decreasing the potential for  $\text{CaCO}_3$  scale formation (Silva et al., 2015). Rozhkova et al. (Rozhkova et al., 2007a) further concluded that the addition of mineral ions to the MEG + water system may weaken but not rupture the hydrogen bond between the OH-group of MEG molecules and the H-group of the water molecules. Therefore, exposure to the MFs within the 50 vol % MEG trials are further contributing to the weakening of said OH-H bonds potentially leading to their rupture and reduction of the interaction of the MEG molecules and ionic species (refer to Fig. 8). The potential weakening OH-H bonds between water and MEG resulted in a significant increase in the measured EC readings following the MF exposure due to increase the ions solubility index.

Fig. 9 illustrates the differences in EC measurements of the exposed and blank trials within 50 vol % MEG containing equal concentrations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions. It is observed that exposure to the MF has initiated an increase in the measured EC when compared to the corresponding blank tests. In other words, it is apparent that applied external MFs exert an opposite effect on the number of water molecules and its inter, and intramolecular attraction compared to 80% by volume of MEG trials. Furthermore, the water-MEG molecules within the ions solvation shell followed a different arrangement pattern by keeping the water molecules inside the solvation shell leading to weakening the

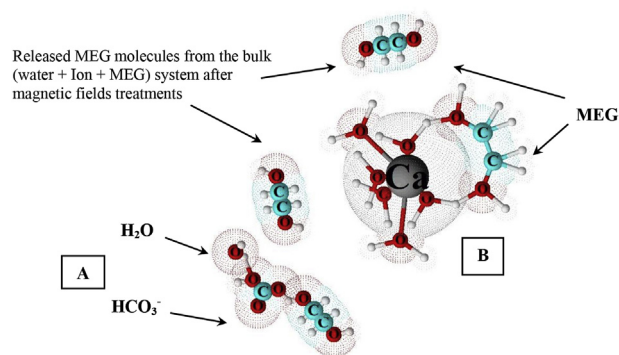


Fig. 8. (A) Structure of MEG – Bicarbonate ion - Water system at 50 vol % MEG after MFs treatment, and (B) Structure of MEG – Calcium ion - Water system at 50 vol % MEG after MFs treatment.

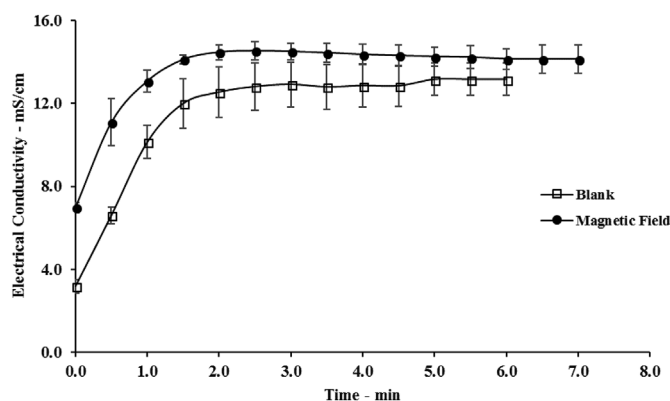


Fig. 9. Effect of MF exposure upon EC of equal concentration of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  solution within 50 vol % MEG.

effect of bulky MEG molecules (Chibowski and Szcześ, 2018; Higashitani and Oshitani, 1998).

In other words, these results indicate that the number of water molecules involved in the solvation shell was increased in a way that minimized the effect of MEG molecules. As a result, the external MF had a positive impact on rich MEG solution by attracting more water molecules into the solvation shell. The reason behind this behavior may be due to the smaller size of the water molecules compared to MEG molecules; this smaller size allows the water molecules to create more ion-dipole bonds with ions in the solution leading to a change in the hydration shell thickness and thus generating a different EC measurement. Since the EC measurement is dependent on the thermodynamic functions of hydration shell (Szcześ et al., 2011). As shown in Fig. 9, it can be observed that EC measurements after exposure to MFs confirm the decreasing in thickness of the solvation shell around the ionic species due to their inversely proportional relationship (Holysz et al., 2007) and thus the increase in the hydration shell (Silva et al., 2015). Furthermore, the effect of MFs within the 50 vol % MEG has shown an inhibitory effect on the scale formation due to increasing the number of water molecules within its hydration shell.

### 3.3. Morphology of the precipitates calcium carbonate after exposed to external magnetic field

After evaluating the influence of MFs exposure on the scale formation behavior within 50 vol % and 80 vol % MEG solutions by using the DSL technique, as discussed in section 3.1. The morphology of the formed  $\text{CaCO}_3$  has been investigated for both the exposed and blank trials. Furthermore, additional testing was performed by using the static jar technique to compare the produced  $\text{CaCO}_3$  morphology with the

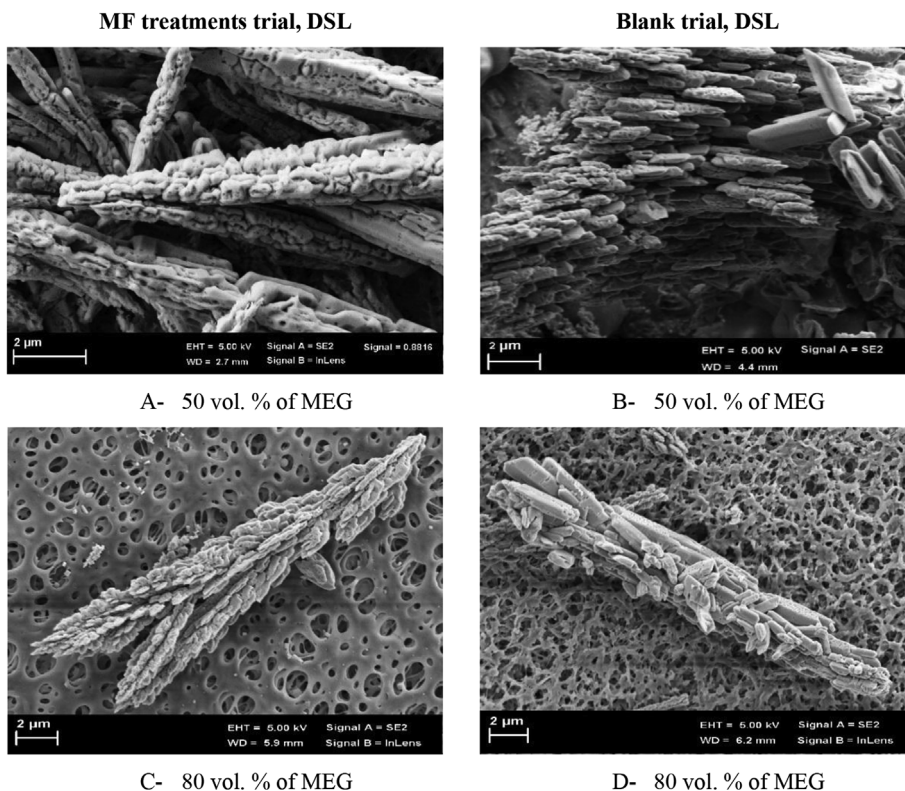


Fig. 10. SEM images of different MEG concentrations at 150 °C by using DSL technique.

results of DSL testing.

3.3.1. Crystal structure of the precipitates calcium carbonate at 50 and 80 vol % MEG within DSL technique

The SEM images of exposed and blank trials within 50 percent by volume MEG at 150 °C are illustrated in Fig. 10 A and B and Fig. 11 where needle-like aragonite morphology was formed at both conditions. The trials with MFs present generated a noticeably longer needle structure at low magnification that appeared to be more singular in nature whereas the blank trials formed shorter needle structures that agglomerated to form a cluster of scale particles. The formation of aragonite at the testing conditions is consistent with the findings of Flaten et al. (Flaten et al., 2009) who stated that at 80 °C and above, aragonite is the dominant morphology within all MEG concentrations.

Another interesting result has been observed as shown in Fig. 11-A,

where the precipitated CaCO<sub>3</sub> was slightly modified following MF treatment by forming dendritic cluster aragonite with a snowflake shape. Furthermore, the formation of the aragonite shape appeared to be nonstick and dry crystals. In contrast, the generated images for the blank tests highlight the formation of bulky aragonite spikes that are associated with other particles (refer to Fig. 11-B). Additionally, it can be observed in the image (B) that a thick fluid combined with the generated crystals to form a non-regular surface or liquid-like post-nucleation clusters, as was also observed by Coey (2012). Moreover, image (B) shows the impact of the MF treatment on the size of CaCO<sub>3</sub> crystals whereby larger bulky crystals were formed when no MF treatment was applied during DSL trials.

It is also important to consider the effect of varying MEG concentration when evaluating the performance of MFs treatment to influence scale formation behavior. The scale-formation products

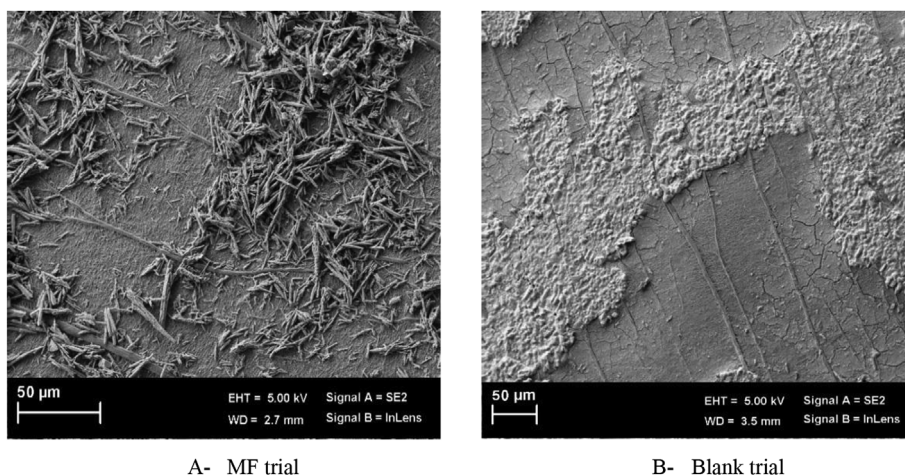


Fig. 11. Low magnification SEM images of 50% by volume of MEG concentrations at 150 °C by using DSL.

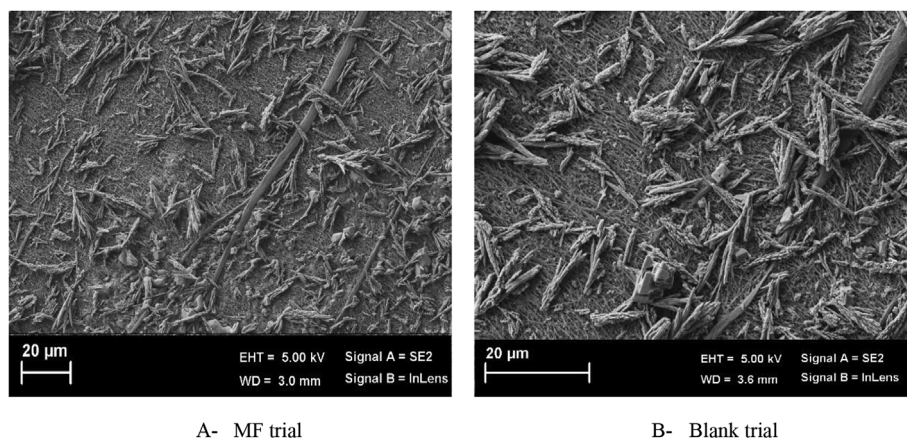


Fig. 12. High magnification SEM images of 80% by volume of MEG concentrations at 150 °C by using DSL.

generated within 80 vol % MEG solution utilizing the DSL testing technique (refer to Fig. 12) did not show any noticeable difference to that of corresponding 50 vol % DSL testing following magnetic exposure (Fig. 10 A and B). Furthermore, no impact on the scale morphology was observed after treatment with MFs in terms of shape, size, and structure within 80 vol % MEG as shown in Fig. 10 C and D and Fig. 12, a result contrary to the corresponding 50 vol % experiments where a small difference in the morphology was observed. This result suggests that the effect of the MF treatment in terms of the morphology formed is limited to solutions with equal or higher concentrations of water than MEG.

The reason behind this difference can be explained by the effect of the MF on the MEG-water molecules within the solvation shell of the dissolved ions. The effect of the applied MF alters the arrangement of the bulky MEG molecules within the hydration shell of the ion (refer to Fig. 8) whereby the ion's hydration shell thickness is more likely to be influenced by the number of water molecules (Rozhkova et al., 2007a, 2007b). The bonding energy between water molecules and the dissolved ions is greater than that between the ions and MEG molecules (Rozhkova et al., 2007a, 2007b). This greater bonding energy between the water molecules and ions may hence facilitate their interaction leading to the formation of the scaling depicted by Fig. 11 B. On the other hand, at higher MEG concentrations where the potential interaction of the ions and water molecules is limited, the drier singular dendritic clusters were formed regardless of if the MF was applied.

The scale formation layers generated with an irregular surface play an essential role in the accumulation of scale within fluid transportation pipelines. Therefore, using the MF treatment within 50 vol % of MEG and heat exchangers' skin temperature may provide a method to prevent the formation of thick fluid substances and, hence scale, by creating a dry dendritic cluster aragonite structure of which is less likely to accumulate upon the surface of thermal units and pipelines. As such, applying MF treatment to rich MEG solutions containing brine solutions could provide an economical and eco-friendly method to achieve scale formation control but not at 80% by volume of MEG.

### 3.3.2. Crystal structure of the precipitates calcium carbonate at 50 and 80 vol % MEG within jar cell technique

Prior comparison of the jar test and DSL techniques for scaling evaluation have demonstrated that different  $\text{CaCO}_3$  morphologies may be formed under the same conditions including temperature and composition (Amjad, 2010; Boak, 2013). Furthermore, different nucleation rates and growth kinetics can also be expected during comparison of each analysis method (Jung et al., 2000). It is well known that the nucleation rate and growth kinetics of  $\text{CaCO}_3$  depends on both the system temperature and the supersaturation of the solutions (Alamdari and Saffari, 2012). According to kinetic studies of  $\text{CaCO}_3$  formation, the nucleation process is more sensitive to the supersaturation level than

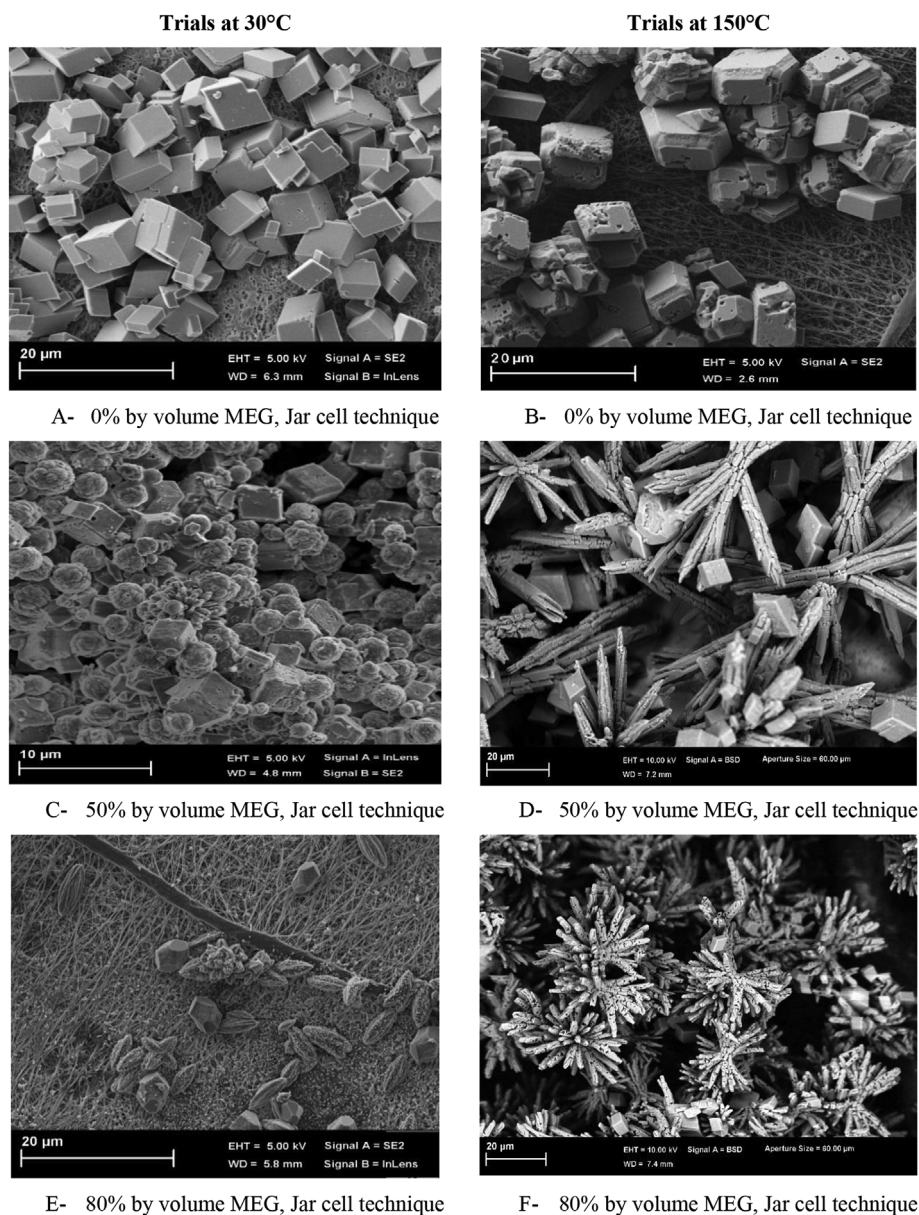
the growth process (Merkel and Geochemistry, 2005; Langmuir, 1997; Plummer and Busenberg, 1982). Therefore, the nucleation process may form smaller  $\text{CaCO}_3$  particles within high supersaturation conditions (Jung et al., 2000; Alamdari and Saffari, 2012).

In such applications within aqueous solutions, Montazaud (2011) have reported that the aragonite morphology is more likely to occur at a high temperature ( $> 90^\circ\text{C}$ ). On the other hand, Cowan and Weintritt (1976) concluded that aragonite could be observed at temperatures above  $30^\circ\text{C}$ . However, within MEG applications, Flaten, et al. (Flaten et al., 2009) stated that the morphology of  $\text{CaCO}_3$  may be influenced by increasing MEG content at  $50^\circ\text{C}$  with the conversion of aragonite to vaterite. The increase in MEG concentration may influence the supersaturation ratio of  $\text{CaCO}_3$  at high temperatures hence influencing the nucleation process.

To compare the differences in morphology formed when applying the jar and DSL test methodologies, jar test experiments were conducted at  $30^\circ\text{C}$  and  $150^\circ\text{C}$  ( $\pm 1^\circ\text{C}$ ) for varying MEG concentrations (0, 50 and 80 vol %) using the same brine composition outlined by Table 2. The  $\text{CaCO}_3$  scale at 0.0 percent by volume MEG within the jar test formed an abundance of idiomorphic calcite rhombohedra structure, which was the structure prevalent at room temperature (refer to Fig. 13-A). Additionally, Fig. 13-B shows SEM images of  $\text{CaCO}_3$  morphology formed from aqueous solution within the jar tests at  $150^\circ\text{C}$ . The increase in temperature facilitated the formation of primarily idiomorphic calcite rhombohedral structures with non-smoothed surfaces. As a result, jar tests conducted as a part of this study were in line with the prior literature findings at 30 and  $150^\circ\text{C}$  (Amjad, 2010; Flaten et al., 2010a).

On the other hand, at 50 and 80% by volume of MEG, the morphologies of  $\text{CaCO}_3$  produced during jar test experiments showed significantly different structures when compared to 0.0 vol % of MEG trials, as shown in Fig. 13C and E. The increase in MEG concentration had a significant impact on the type of crystal structure formed. It can be seen that vaterite crystals started to form at  $30^\circ\text{C}$  creating spherical shapes side by side with calcite within 50 vol% of MEG as shown in Fig. 13-C, while monoclinic and trigonal smooth surface shapes formed within 80 vol % of MEG as shown in Fig. 13-E. Upon raising the temperature to  $150^\circ\text{C}$ , a more complex assortment of crystals structures was found. Fig. 13-D and F illustrate the formation of branched needle-like aragonite crystals in combination with idiomorphic calcite rhombohedra particles as identified by Flaten et al. (Flaten et al., 2009). Moreover, Flaten, et al. (Flaten et al., 2009) reported that vaterite particles should transition to aragonite crystals when the temperature was raised to approximately  $80^\circ\text{C}$  within 60% wt. of MEG solution a result consistent with the findings of this study. Therefore, the generated results can be explained by the action of the MEG solution itself, which changes the kinetic control of morphology structure with regards





**Fig. 13.** SEM images of different MEG concentrations at 30 and 150 °C by using Jar cell.

to the jar test technique.

Overall, the jar test results are in line with the results of Flaten et al. (Flaten et al., 2009) with regards to the needle-like  $\text{CaCO}_3$  structure formed at approximately > 50 vol % of MEG. However, of the tests conducted, significant differences in morphology of the scale formation are evidently illustrating the joint impact of both MEG concentration and temperature on scale formation growth. Further impact on the type and size of  $\text{CaCO}_3$  scale formed is also apparently due to the dynamic nature of the DSL testing whereby the crystal structures are exposed to continuous liquid flow. In contrast to the static jar testing performed, non-branching needle-like aragonite crystals formed during DSL testing at 150 °C exhibited a different geometric structure with a lack of calcite particles present. Due to the dynamic nature, the DSL testing methodology more closely simulates actual pipeline conditions whereby continuous liquid flow occurs. As such, the DSL method presents a more realistic approach to investigate scale formation within industrial applications and likewise the effect and evaluation of scale inhibitors.

#### 3.4. Discussion of mechanism caused after exposure to magnetic fields

The influence of MFs on the strength of the intermolecular interactions in the aqueous system impacts on the hydration shell properties within the ionic solution (Holysz et al., 2007; Higashitani et al., 1993; Schwierz et al., 2013; Collins, 2004). Furthermore, the change in hydration shell thickness results in a change in EC due to an alteration in the number of  $\text{H}_2\text{O}$  molecules in the first ion shell and ion mobility rate in watery system (Al Helal et al., 2018a; Holysz et al., 2007; Szczes et al., 2011). This hypothesis has been proven in several investigations within aqueous solutions, where the change in EC with hydration shell thickness was discussed (Al Helal et al., 2018a; Holysz et al., 2007; Higashitani et al., 1995).

Regarding the viscosity of MEG solutions, several studies have concluded that an increase in solution viscosity leads to lowered scale growth and nucleation rates (Hyllestad, 2013; Flaten et al., 2010a, 2010b). This is due to the significantly slower diffusion of growing particles within high viscosity solutions (Flaten et al., 2010a, 2010b). Furthermore, according to the Nernst-Einstein equation, there is a relationship between fluid viscosity and its EC (Daintith, 2008).

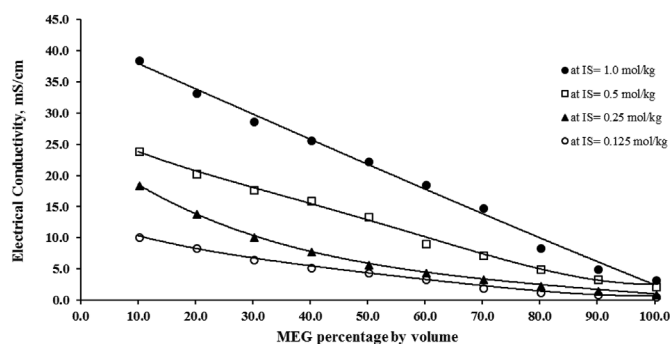


Fig. 14. EC of different MEG concentrations of varying ionic strength at 20 °C.

$$EC = \left( \frac{F^2}{RT} \right) \sum_i D_i z_i^2 (\gamma_i)^{a_i} c_i \quad (2)$$

where,  $F$  denotes Faraday's constant,  $T$  the temperature in Kelvin,  $R$  the gas constant and  $z_i$  and  $c_i$  the ionic species charge and molar concentration respectively.  $D_i$  denotes to the self-diffusion coefficient of ions, which can be calculated by the Stokes-Einstein equation.

$$D_i = \frac{k_B T}{6 \pi \mu r_i} \quad (3)$$

where  $k_B$  denotes Boltzmann's constant and  $r_i$  is the solvation radius of ions. A clear correlation is thus evident between EC and the viscosity of solution due to its influence on the diffusion of ionic species through the solution (see Fig. 14). As such, it can be expected that for higher MEG concentrations, a decrease in the measured EC would occur, consistent with Fig. 14 for a range of 10–100 vol % MEG concentration. However, further reduction in the EC occurred within the 80 vol % MEG solutions following exposure to the MF in comparison to the blank tests (refer to Fig. 5). The results can be further explained by the change in the radius of hydration and/or solvation shells around ions after exposure to the MFs as stated in the previous section.

According to equation 3, and 4, the solvation shell radius of ions is inversely proportional to the electrical conductivity, and self-diffusion coefficient. However, the activity coefficient of ions is proportional to the solvation shell ion radius. The best mathematical model to describe the relationship between the activity coefficient and solvation shell radius is the extended Debye-Hückel model (Hem, 1963), as shown in Equation (4).

$$\log(\gamma_i) = -A * z_i^2 \left( \frac{\sqrt{I}}{1 + a_i * B \sqrt{I}} \right) \quad (4)$$

where,  $I$ , is the ionic strength (mol/kg). The parameters  $A$  and  $B$  are constants and depend on the dielectric constant ( $\epsilon$ ) and temperature ( $T$ ) as such:

$$A = 1.82 * 10^6 (\epsilon * T)^{-\frac{3}{2}} \quad (5)$$

$$B = 50.3 (\epsilon * T)^{-\frac{1}{2}} \quad (6)$$

Therefore, the increase of the solvation shell radius (decreases the hydration shell) would result in the increase of ion pair formation would thus affect supersaturation with respect to calcium carbonate, as shown for the 80% MEG experiments. In contrast, the 50% MEG experiments showed a reduction in the scale formation rate due to a reduction of the solvation shell radius as indicated by the increased electrical conductivity, especially after exposure to the applied MF. Therefore, any change in the solvation shell radius influences the self-diffusion coefficient and the activity coefficient of ions and thus changes the scale formation rate. The influence of ions hydrated radius on the activity coefficient is illustrated in Fig. 15.

Finally, it is essential to mention the dielectric constant that could be manipulated by external MFs thus impacting upon the Extended

Debye-Hückel model (see Equation 4 through 6). To be more precise in this hypothesis, Shen (2011) reported that the dielectric constant of the electromagnetic field-treated water is 3.7% greater than the non-magnetized solutions, specifically under the extremely low electromagnetic field. While Pang and Shen (2013) stated that the dielectric constant of the magnetized solution decreases with increasing the frequency of the applied electromagnetic field and exposure time. These proposed results indicate that the dielectric parameter can be affected by controlling the intensity of the MFs and the exposure time. The Extended Debye-Hückel model can estimate the ionic activity coefficient ( $\gamma_i$ ) of ions by taking into consideration the radius of ions ( $a_i$ ) and the dielectric constant of the solution (Truesdell and Jones, 1974; Pitzer and Simonson, 1986; Marcus, 1988). However, the dielectric constant of water is higher than the dielectric constant of MEG, by approximately a factor of two (Sandengen, 2006). Therefore, the presence of external MFs could increase the dielectric constant of MEG-water solution, which in turn influences the ion activity and scaling potential. This phenomenon suggests the possible advantage of using MFs within scale formation treatments if it is used correctly.

#### 4. Conclusions

It was intended to use a high concentration of both calcium and carbonate ions in this study to make the deposition process inside the capillary faster so that we can observe the difference in magnetic field effects. Five conclusions were reached concerning the applications of MF treatment in inhibiting the scale formation of  $\text{CaCO}_3$  in aqueous solutions at different MEG concentrations. Firstly, the degree of scale formation, whether inhibited or promoted, is conditional on MEG content. Secondly, the exposure of the MEG + brine solutions to the applied MF had a significant impact on the EC measured. The results of the experiments conducted were consistent with previous studies of aqueous solutions where it was concluded that the solvation shell thickness of the  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions were subject to manipulation by MFs leading to variations in EC (Al Helal et al., 2018a; Holysz et al., 2007; Szczes et al., 2011). Thirdly, following trials at 50 vol % MEG concentration, bulky, and rough crystals were formed that may enhance a hypothesized clot-like build-up inside the transportation pipelines (Al Helal et al., 2018a). Similarly, jar tests highlighted the shift in crystallization processes that may occur at high MEG concentrations and high temperatures, although the jar test results cannot explain the morphology of real crystals in pipelines they can clarify the kinetic parameters that control crystals formed under different conditions.

Fourthly, previous studies suggested the external radius of ions to be the outer radius of hydration shells, not the actual ion radius in calculating the ionic activity coefficient (Langmuir, 1997; Truesdell and Jones, 1974; Marcus, 1988). This hypothesis has been reinforced after an improvement in the activity coefficient of ions occurring following exposure to MFs. Finally, due to the effective inhibition of scale formation produced by the external MF treatment within 50% by volume of MEG, it can be proposed that MF treatment could provide an environmentally friendly scale inhibition approach that could replace/reduce the use of traditional chemical inhibitors in industry. In this regard, we believe that research into the thermodynamic properties of an aqueous and non-aqueous solution in MFs is more promising.

#### Acknowledgment

The authors would like to acknowledge Curtin Corrosion Engineering Industry Centre (CCEIC) and the WA School of Mines: Minerals, Energy and Chemical Engineering at Curtin University for their support. Furthermore, I would like to thank Dr. Franca Jones for her important feedback which improved this work.

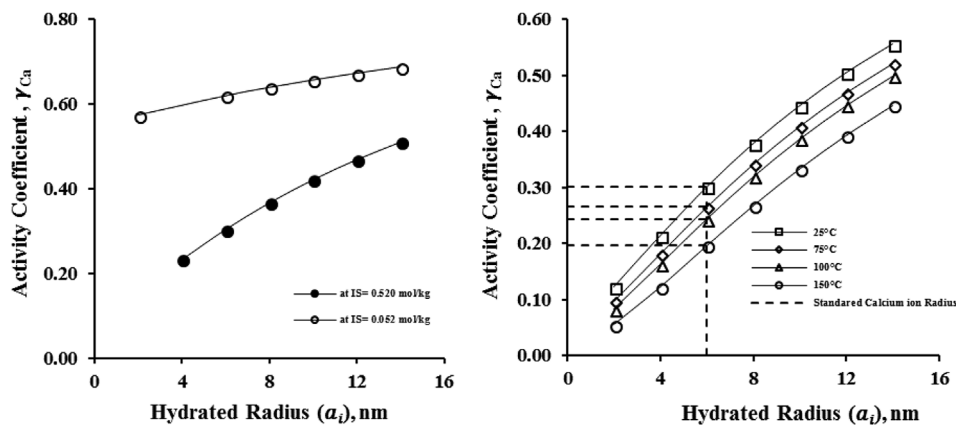


Fig. 15. Estimated activity coefficient of calcium ions as a function of ionic strength and temperature (using the extended Debye-Hückel model).

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petrol.2018.09.100>.

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