

Nucleation Kinetics of Calcium Carbonate in Gas Field Brine Containing Methanol.

Morteza Saffari, M.Sc. and Abdolmohammad Alamdari, Ph.D.*

Department of Chemical Engineering, School of Chemical and Petroleum Engineering,
Shiraz University, Shiraz, Post Code 7134851154, Iran

E-mail: alamdari@shirazu.ac.ir*

ABSTRACT

Precipitation in gas pipelines raises problems of scale formation, corrosion, and pressure drop. Calcium carbonate precipitation from synthetic gas-field brine under the influence of methanol was experimentally investigated in the present study. Experimental results showed that an increase in methanol concentration and in temperature will result in a decrease in induction time of calcium carbonate precipitation. A higher concentration of methanol resulted in more mass of precipitates from a fixed amount of solvent. The results of this research may be used in the petroleum industry to predict the scale formation of calcium carbonate in the field brine of gas production processes.

(Keywords: calcium carbonate, methanol, precipitation, nucleation, induction time, scale formation)

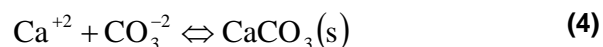
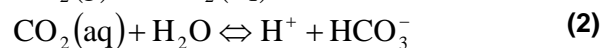
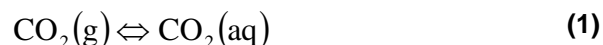
INTRODUCTION

Petroleum field-brines contain some traces of calcium ions due to intimate contact of brine with limestone layers of formation in reservoirs. Carbon dioxide in natural gas is absorbed in the brine containing calcium ions, and thus calcium carbonate will precipitate in the transportation pipes and equipment. Calcium carbonate scale jeopardizes flow assurance and increases the pressure drop in the transportation operations. Methanol which is usually injected to the pipe lines to prevent hydrate formation in free water will affect the solubility of calcium carbonate and change the thermodynamic conditions of the aqueous phase. Therefore, the intensity of precipitation and morphology of precipitates and their size would be influenced by methanol (Flaten and Andreassen 2007).

Precipitation of CaCO_3 from pure aqueous solution is well studied, but few studies have been reported about CaCO_3 precipitation from an aqueous solution containing considerable concentrations of alcohols. Kinetics of nucleation and growth of CaCO_3 crystals in the presence of alcohols have almost been left unstudied while the thermodynamics of their mother solutions have been considerably investigated (Flaten and Andreassen 2007; Statoil 2005; Kan *et al.* 2002).

Calcium carbonate crystals in the ascending order of stability are polymorphs of vaterite, aragonite, and calcite. These polymorphs have the same chemical formula but different crystal structures; therefore, their mechanical and physical properties of density, conductivity, refractive index, hardness, and thermodynamic properties of solubility, melting point and enthalpy may be different (Myerson and Ginde 1993). The three polymorphs of calcium carbonate may initially be generated in precipitation; however, due to a lower formation heat of calcite, the less stable polymorphs will gradually change to calcite, the more stable one (Andreassen 2005).

Gas field brine contains different compounds depending on the location and formation materials. A sample analysis of gas-field brine taken from Beryl-field located 200 miles north-east of Aberdeen in Scotland, is presented in Table 1 (Bonnett *et al.* 1991). Calcium carbonate is formed through the following reactions:



The solubility product of $K_{sp} = 5 \times 10^{-9}$ for calcite has been reported by Alkin and Lagerwerff (1965).

An increase in CO_2 partial pressure in gas phase will increase the carbon dioxide concentration in the solution, resulting in an increase in precipitation. An increase in temperature will also increase the precipitation due to a lower solubility product, K_{sp} , at higher temperatures. Alcohols such as ethylene glycol and methanol will also affect the calcium carbonate precipitation (Flaten and Andreassen 2007; Kan *et al.* 2002).

In the present study the effect of methanol on induction time of calcium carbonate precipitation and crystal morphology will be investigated experimentally.

EXPERIMENTAL

In order to isolate the effect of methanol on calcium carbonate precipitation and to prevent the influence of other species like K^+ , Mg^{2+} , Ba^{2+} , SO_4^{2-} reported in Table 1, synthetic solutions containing Ca^{2+} and CO_3^{2-} were applied in the precipitation experiments. Calcium carbonate was produced by the reaction between a 0.4 molar (mole/kg H_2O) solution of calcium chloride (CaCl_2)

and a 0.4 molar solution of sodium bicarbonate (NaHCO_3). Both solutions were maintained at 25°C and were CO_2 saturated by bubbling for 10 minutes using a sparger at the end of injecting tube.

The solution of sodium bicarbonate was added to the crystallizer containing the solution of calcium chloride while the temperature was controlled at 25°C , and CO_2 bubbling in the crystallizer at a constant flow rate was continued. The average value of dissolved CO_2 in the solution was 500 ppm (0.011 molality). The diameter of bubbles rising in the solution was around 3 mm. The stirrer speed was adjusted at 200 rpm. The experiments were performed for concentrations of methanol from zero to 60 wt%.

Figure 1 shows the experimental setup used in the present study. The setup included a two-liter-crystallizer, a water bath and a carbon dioxide capsule. The crystallizer was equipped with a heat transfer jacket mounted around the draft tube in the crystallizer. The water bath was equipped with a heating element, a pump for circulating the heating water from the bath to the jacket in the crystallizer, a cooling coil, a thermometer, and a controller on the heating element.

Table 1: A Sample Analysis of Gas-Field Brine taken from Beryl-Field located 200 miles North-East of Aberdeen in Scotland.

Ion	Na^+	K^+	Ca^{2+}	Mg^{2+}	Ba^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Concentration (mg l^{-1})	25000	600	1300	210	150	4200	10	650

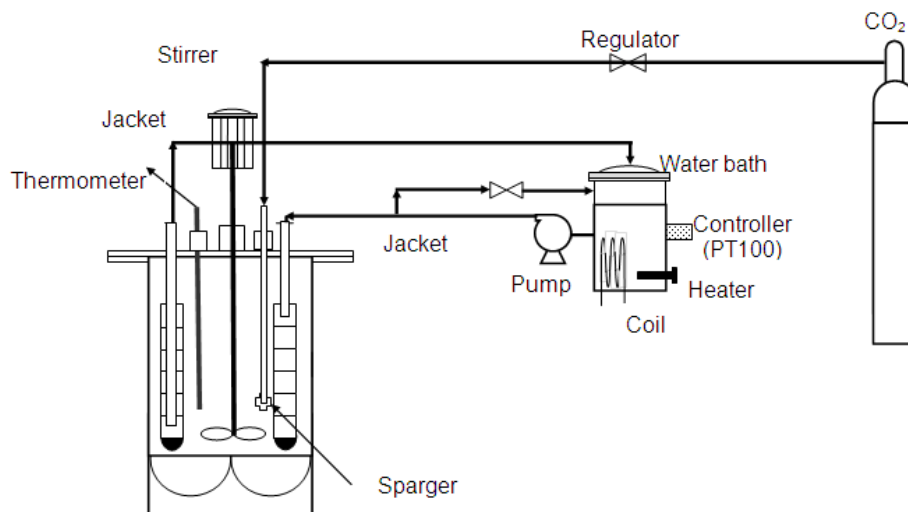


Figure 1: Experimental Setup used in the CaCO_3 Precipitation from Gas-Field Brine.

The crystallizer was also equipped with a thermometer, a 4-blade impeller, and a gas sparger. The internal and external diameters of the draft tube and the internal diameter of the crystallizer were 55, 85, and 112 mm, respectively. In order to avoid developing a dead space with no flow at the bottom of the crystallizer, a Teflon block was machined and mounted at the bottom as shown in Figure 1.

A ring of Teflon was also installed at the bottom end of the draft tube to adjust the circulation pattern and to make the streamlines inside the crystallizer smooth. Sufficient mixing may be introduced to the solution with a minimum speed of agitator in the draft tube configuration. Sufficient mixing uniform concentrations in the solution and prevents settling of crystals and non-uniformity of supersaturation.

Induction time of precipitation has been measured by different workers through methods of measuring the solution turbidity, conductivity, or refractive index (Sohnel and Mullin 2001). The method of conductivity was used in the present study to measure the induction time for nucleation of calcium carbonate precipitation.

The conductometer used was CTR80, Zag Chemie Company, Iran. Each experiment at specified condition was repeated three times. Therefore, the induction times and precipitation yields reported in this study are the average of three values. In order to cut costs of XRD analysis, the three samples were mixed and analyzed for crystal shape, crystal structure, and density.

Chemical Analysis

A total organic carbon analyzer (TOC-500, Japan) was used to measure CO₂ content in the solution. Two 10-ml-samples from the crystallizing solution at the beginning were filtered using filter paper of 2.5 μm and used for measuring the dissolved CO₂ and pH. The suspension, at the end of experiment was filtered under the vacuum condition using filter paper of 2.5 μm. The filter cake was kept in an oven at 100 °C for about 12 hours until the precipitates were well dried before analysis treatments.

Particle Characterization

The morphology of CaCO₃ precipitates was determined using methods of powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD instrument was D8 Advance, Bruker Co., Germany, and the microscope was S360 Cambridge, Oxford. To prepare the precipitates for specific gravity measurement, the sample was kept in the oven adjusted at 110 °C for 24 hours to remove any water absorbed on the precipitates.

The sample was poured in a clean, dry picnometer equipped with a thermometer. Then the picnometer was filled with distilled water, put aside for 12 hours, then was weighed. The specific gravity of particles was calculated using Equation 5:

$$G_s(T_b) = \frac{M_o}{M_o + M_a - M_b} \quad (5)$$

where $G_s(T_b)$ is the specific gravity of precipitate at temperature T_b , M_o is the weight of dry sample,

M_a is the weight of picnometer full of only water,

M_b is the weight of picnometer full of water, and

precipitate at T_b , and T_b is the room temperature at time of weighing (ASTM D 844-887).

RESULTS AND DISCUSSION

Methanol Influence on Mass of Precipitates

The mass of precipitated calcium carbonate particles per kg of water at different concentrations of methanol, 25 °C, and stirrer speed of 200 rpm is shown in Figure 2. As the methanol concentration in the brine increases from zero to 60 wt%, the precipitation will increase from 5.33 to 5.92 g- crystal/kg-water indicating an increase in yield of 11%. An increase in methanol concentration will increase the supersaturation in the brine due to removal of free water from availability to the solute species. This will increase the precipitation yield of calcium carbonate.

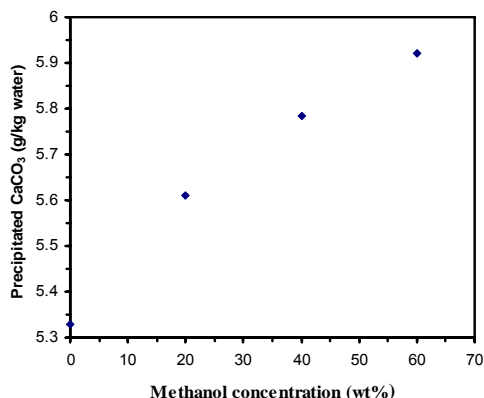


Figure 2: Mass of CaCO₃ Particles Precipitated from Brine Containing Different Concentrations of Methanol at 25 °C, 1 atm, and Stirrer Speed of 200 rpm.

Table 2 shows the supersaturation values at different concentrations of methanol. Supersaturation for calcium carbonate precipitating from a solution containing methanol, salt and CO₂ was defined through Equations 6-9 (Kan *et al.* 2002):

$$S = \log \left\{ \frac{[\text{Ca}^{+2}] \cdot [\text{HCO}_3^-] \cdot \gamma_{\text{Ca}^{+2}}^S \cdot \gamma_{\text{Ca}^{+2}}^N \cdot \gamma_{\text{HCO}_3^-}^S \cdot \gamma_{\text{HCO}_3^-}^N}{[\text{CO}_{2,\text{aq}}] \cdot \gamma_{\text{CO}_{2,\text{aq}}}^S \cdot \gamma_{\text{CO}_{2,\text{aq}}}^N \cdot K_1 \cdot K_{\text{sp}}} \right\} \quad (6)$$

$$K_1 = \frac{10^{-(pH_{\text{meterreading}} + \Delta pH_j - \delta)} \cdot [\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}^S \cdot \gamma_{\text{HCO}_3^-}^N}{[\text{CO}_{2,\text{aq}}] \cdot \gamma_{\text{CO}_{2,\text{aq}}}^S \cdot \gamma_{\text{CO}_{2,\text{aq}}}^N} \quad (7)$$

$$K_2 = \frac{10^{-(pH_{\text{meterreading}} + \Delta pH_j - \delta)} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}^S \cdot \gamma_{\text{CO}_3^{2-}}^N}{[\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}^S \cdot \gamma_{\text{HCO}_3^-}^N} \quad (8)$$

$$K_{\text{sp}} = [\text{Ca}^{+2}] \cdot \gamma_{\text{Ca}^{+2}}^S \cdot \gamma_{\text{Ca}^{+2}}^N \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}^S \cdot \gamma_{\text{CO}_3^{2-}}^N \quad (9)$$

where S is the supersaturation, [] is the molality of solute, γ is the activity coefficient, γ^N and γ^S are the activity coefficient due to alcohol and salt

effects, K_1 , K_2 , and K_{sp} are the equilibrium constants in gas-mixture of CO₂-methanol-H₂O-salt defined through Eqs. 7-9. $S < 1$ denotes for dissolution of solid CaCO₃ in the solution and $S > 1$ denotes for precipitation of solid CaCO₃ out of solution (Nason 2006).

Table 2: The Variation of pH and Supersaturation during the course of Experiment at 1 atm, 25 °C , and Stirrer Speed of 200 rpm.

Methanol concentration (wt%)	pH	S
0.0	6.05	4.64
20.0	6.26	5.12
40.0	6.52	5.81
60.0	6.78	7.28

It seems from SEM photomicrographs shown in Figures 3, 4, 5 and 10 that size of precipitated particles increases as the concentration of methanol in the brine increases. As the methanol concentration increases, the viscosity of brine increases (Flaten and Andreassen 2007); therefore, a lower rate of diffusion due to an increase in viscosity will result in a lower rate of nucleation, and consequently a larger size of precipitates, as observed by comparing Figures 3, 4, and 5. However, a deduction in particle size variation through photograph observations is scarcely precise. These figures show the calcium carbonate particles precipitated from brines containing 0, 20, and 40 wt% methanol, respectively.

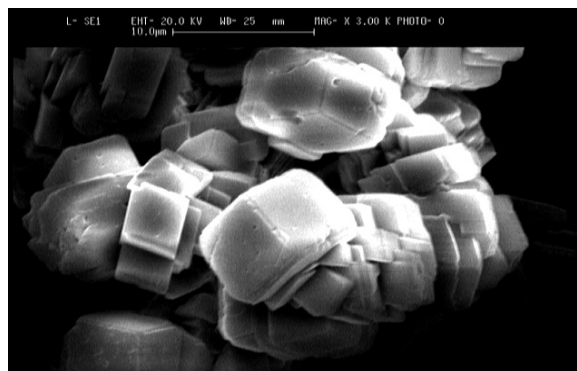


Figure 3: CaCO₃ Particles Precipitated from Pure Water at 25 °C, 1 atm, and Stirrer Speed of 200 rpm.

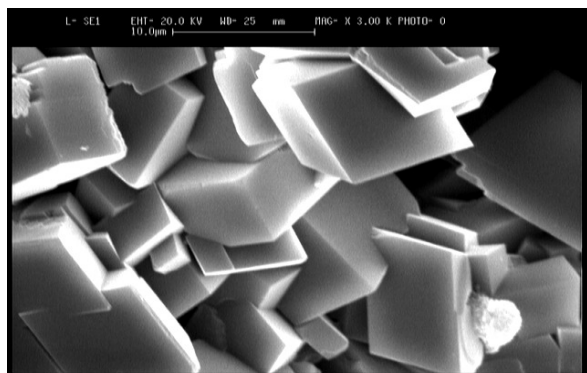


Figure 4: CaCO₃ Particles Precipitated from Aqueous Solution containing 20 wt% Methanol at 25 °C, 1 atm, and Stirrer Speed of 200 rpm.

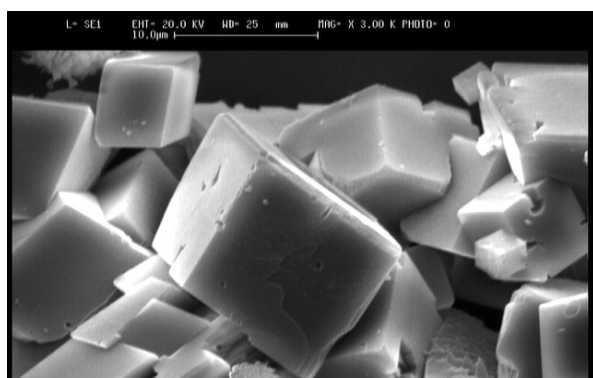


Figure 5: CaCO₃ Particles Precipitated from Aqueous Solution containing 40 wt% Methanol at 25 °C, 1 atm, and Stirrer Speed of 200 rpm.

Methanol Influence on Morphology of Precipitates

The results of XRD for CaCO₃ particles precipitated from brines containing 0, 20, 40, and 60 wt% methanol are shown in Figures 6, 7, 8, and 9, respectively. Peaks obtained at 25.0°, 29.5°, and 45.9° C on axis 2θ are assigned to vaterite, calcite, and aragonite, respectively (Dickinson and McGrath 2001).

No peak with significant height at 45.9° was observed indicating negligible amount of aragonite precipitated from brine at conditions experienced in the present study. This is perhaps due to a low reaction temperature of 25 °C. Aragonite is usually pseudo-stable and is generated at higher temperatures (Agarwal 2002). While the height of peak at 29.5° assigned to calcite was major, the height of peak assigned to vaterite was minor perhaps due to the conversion of unstable types of CaCO₃ to more

stable type of calcite. Figure 9 demonstrates a peak of significant height at 25° assigned to vaterite, possibly due to higher supersaturation generated at 60 wt% methanol concentration. Vaterite is usually formed at unstable conditions (Flaten and Andreassen 2007), resulted at higher supersaturations. Due to low solution temperature in the present study (25 °C), there was low possibility of aragonite formation as mentioned earlier. However, at high concentrations of methanol the possibility of vaterite formation was high (Flaten and Andreassen 2007).

The SEM photomicrograph at Figure 10 at the bottom middle part illustrates an oval egg-shaped crystal precipitated from brine containing 60 wt% methanol seemingly to be vaterite. Table 3 presents the mole fractions of polymorphs at different concentrations of methanol.

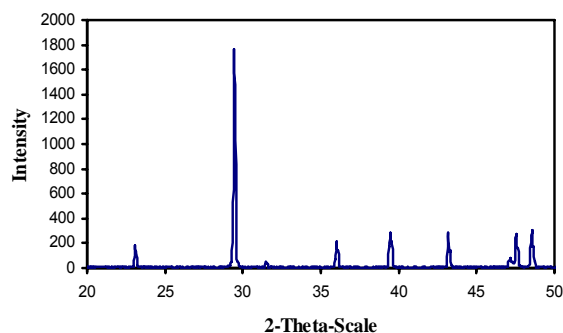


Figure 6: XRD Micrograph for CaCO₃ Particles Precipitated from Aqueous Solution in the Absence of Methanol at the Experimental Conditions of 25 °C, 1 atm and Stirrer Speed of 200 rpm.

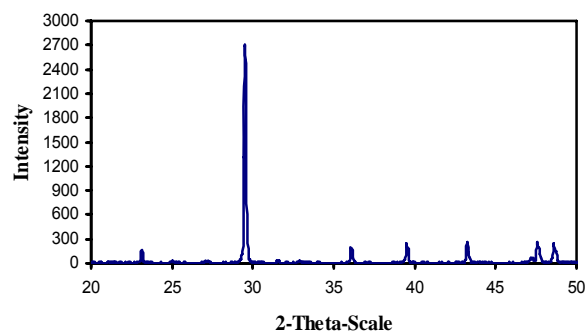


Figure 7: XRD Micrograph for CaCO₃ Precipitated Particles from Aqueous Solution Containing 20 wt% Methanol at the Experimental Conditions of 25 °C, 1 atm and Stirrer Speed of 200 rpm.

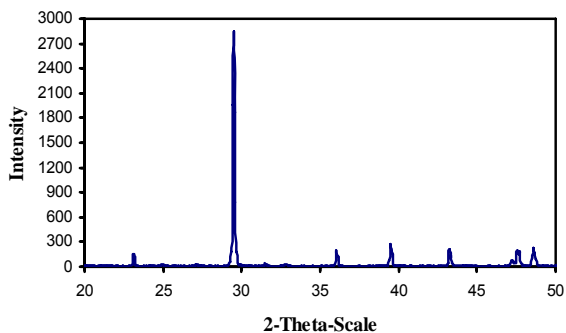


Figure 8: XRD Micrograph for CaCO₃ Particles Precipitated from Aqueous Solution Containing 40 wt% Methanol at the Experimental Conditions of 25 °C, 1 atm and Stirrer Speed of 200 rpm.

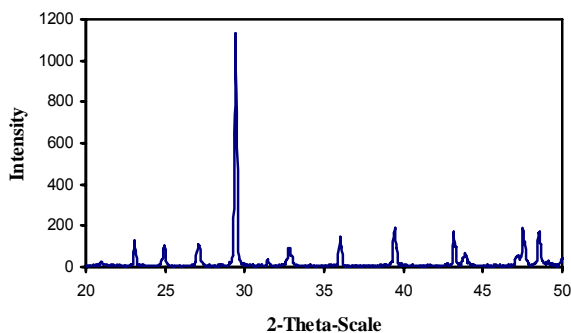


Figure 9: XRD Micrograph for CaCO₃ Particles Precipitated from Aqueous Solution Containing 60 wt% Methanol at the Experimental Conditions of 25 °C, 1 atm and Stirrer Speed of 200 rpm.

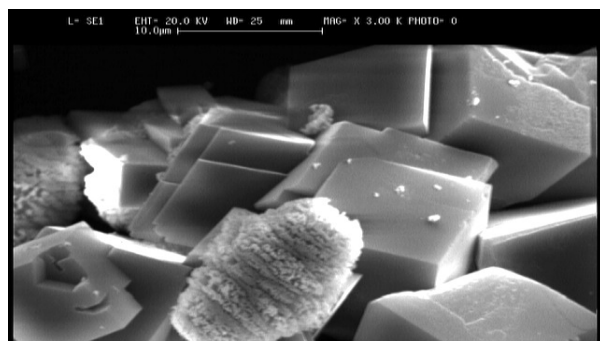


Figure 10: CaCO₃ Particles Precipitated from Aqueous Solution Containing 60 wt% Methanol at Experimental Conditions of 25 °C, 1 atm, and Stirrer Speed of 200 rpm.

Methanol Effects on Induction Time

Induction time was defined as the time between generation of supersaturation and appearance of nuclei detected through concentration change. At

the onset of nucleation, a drop in the concentrations of crystallizing ions and molecules occurs due to their incorporation into the solid phase, thus the conductivity which is proportional to concentration will undergo a decline (Sohnel and Mullin, 2001). This point of drop in conductivity was detected as the induction time. However, the measured induction time is the sum of nucleation time for appearance of critical size nuclei and growth time of nuclei from critical size to the size possessing enough mass at solid phase to decline the solute concentration in the solution at a detectable extent through conductometry.

In the present study, the reaction was continued for about 60 minutes after the induction time until the nuclei were visible by the naked eye. Figure 11 shows the changes in conductivity during the course of nucleation experiment in the absence of methanol at 40 °C.

Experimental results showed that the induction time was essentially under the influence of methanol concentration. As Figure 12 shows, the induction time decreased as the methanol concentration at 25 °C increased from zero to 40 wt%. This effect was assumed to be due to an increase in supersaturation through an increase in methanol concentration. However, at concentrations of methanol higher than 40 wt% a longer induction time was observed. The experimental results of present study showed that the induction time for precipitation increased from 39 minutes for a brine solution containing 40 wt% methanol to 53 minutes for a solution containing 60 wt% methanol.

Comparing Figures 12 and 13 showed that at higher temperature of 40 °C, however, the induction time was much less than that at 25 °C and was almost independent to methanol concentrations. As Eq. 10 indicates, at higher supersaturations and temperatures a lower value of induction time is expected; however, temperature will be more influential than supersaturation due to its order and logarithmic function of effectiveness (Mullin 2004):

$$t_{\text{ind.}} = A \exp \left[\frac{16\pi\gamma^3 V_m}{3(kT)^3 (\ln S)^2} \right] \quad (10)$$

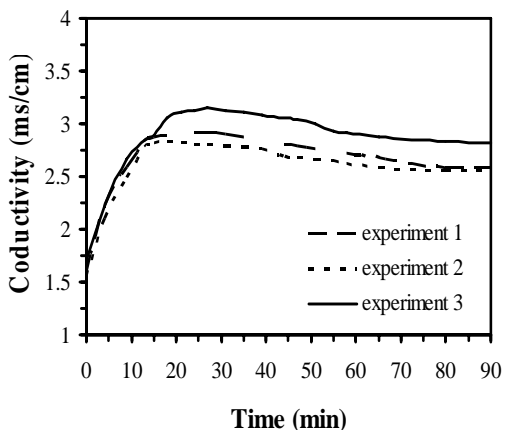


Figure 11: Variations of Conductivity during the course of Precipitation in the Absence of Methanol at 40 °C.

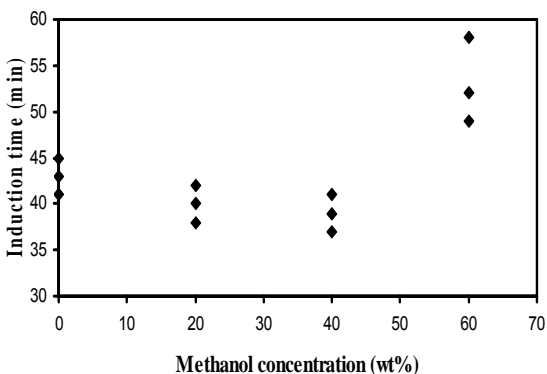


Figure 12: The Effect of Methanol Concentrations on the Induction Time at the Experimental Conditions of 1atm, Stirrer Speed of 200 rpm, and Temperature of 25 °C.

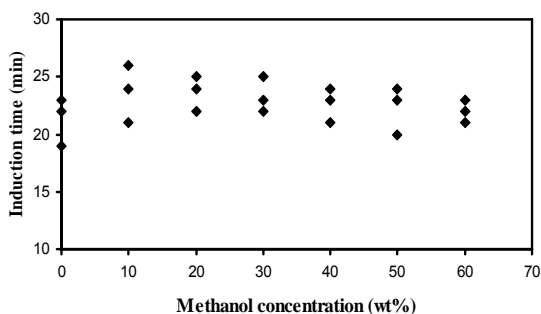


Figure 13: The Effect of Methanol Concentrations on the Induction Time at the Experimental Conditions of 1atm, Stirrer Speed of 200 rpm, and Temperature of 40 °C.

CONCLUSIONS

The precipitation of calcium carbonate from synthetic gas field-brine containing different concentrations of methanol was investigated. Experimental results showed that an increase in methanol concentration up to 40 wt% and in temperature will result in a decrease in induction time. Morphology of calcium carbonate crystals was also affected by methanol concentration. As the methanol concentration increases, the habit will shift from calcite to vaterite, and the mass deposition and particle size will also increase.

The results of this research may be used to predict the induction time and mass deposition of calcium carbonate from gas-field brine in the petroleum industry.

SYMBOLS

A	impact factor, ($l^{-1} s^{-1}$)
a_i	activity of component i in supersaturated solution, ($\text{mole}(\text{kg H}_2\text{O})^{-1}$)
$a_{i,eq}$	activity of component i in saturated solution, ($\text{mole}(\text{kg H}_2\text{O})^{-1}$)
$G_s(T_b)$	specific gravity at temperature T_b , (-)
J	primary nucleation rate, ($l^{-1} s^{-1}$)
M	mass of dried sample in oven, (g)
M_a	mass of picnometer full of water at T_a , (g)
M_b	mass of picnometer full of water and precipitates at T_b , (g)
S	relative supersaturation, (-)
T	absolute temperature, (K)
t_{ind}	induction time, (s)
T_b	The temperature of picnometer contents, (K)
V_m	average molar volume, ($\text{cm}^3 (\text{g mol})^{-1}$)

[]	molality, (mole (kg H ₂ O) ⁻¹)
<i>i</i>	counter of components in Eq. 6
<i>N</i>	denotes for alcohol in activity coefficient
<i>S</i>	denotes for salt in activity coefficient
Greek Letters	
γ	surface tension, (N m ⁻¹)
γ^N	activity coefficient under the influence of methanol, (-)
γ^S	activity coefficient under the influence of salt, (-)
$\Delta\mu$	chemical potential difference, (J mol ⁻¹)
μ_L	chemical potential in liquid phase, (J mol ⁻¹)
μ_S	chemical potential in solid phase, (J mol ⁻¹)
<i>v</i>	molar volume, (cm ³ (g mol) ⁻¹)

REFERENCES

1. Agarwal, P. 2002. "Calcium Carbonate Crystallization in the Presence of Polymeric Additives". Michigan State University, Ph.D. Thesis.
2. Alkin, G.W. and Lagerwerff, J.V. 1965. "Calcium Carbonate Equilibria in Aqueous Solutions Open to Air". *Geochimica et Cosmochimica Acta*, 29:343-352.
3. Andreassen, J.P. 2005. "Formation Mechanism and Morphology in Precipitation of Vaterite Nano Aggregation or Crystal Growth". *Journal of Crystal Growth*. 274:256-264.
4. Bonnett, N. 1991. "Application of a Novel Squeeze Scale Inhibitor in the Beryl Field". SPE 23107.

5. Dickinson, S.R. and McGrath, K.M. 2001. "Quantitative Determination of Binary and Tertiary Calcium Carbonate Mixtures using Power X-ray Diffraction". *The ANALYST*. 126:1118 -1121.
6. Flaten, E.M. and Andreassen, P. 2007. "Polymorphism and Nucleation Kinetics in Precipitation of Calcium Carbonate in Water and Ethylene Glycol". 14th International Workshop on Industrial Crystallization. BIWIC 2007, University of Cape Town: Cape Town, South Africa, 58-64.
7. Kan, A.T., Gongmin.T.K., and Tomson, M.B. 2002. "Effect of Methanol on Carbonate Equilibrium and Calcite Solubility in a Gas/Methanol/Water/Salt Mixed System". *Langmuir*. 18:9713-9725.
8. Mullin, J.W. 2004. *Crystallization*. Butterworth-Heinemann: Boston, MA. 280:185-198.
9. Myerson, A.S. and Ginde, R. 1993. *Handbook of Industrial Crystallization*. Myerson, A.S. (editor). Butterworth-Heinemann: Boston, MA. 126,216.
10. Nason, J.A. 2006. "Experimental Measurement and Mathematical Modeling of Simultaneous Precipitation and Flocculation". Michigan State University, Ph.D. Thesis.
11. Sohnel, O. and Mullin, J. 2001. "Precipitation of Calcium Carbonate". *Journal of Crystal Growth*. 60:239-250.
12. Statoil, B.K., Sandengen, K., and Ostvold, T. 2005. "Thermodynamic Predictions of Scale Potential, pH, and Gas Solubility in Glycol-Containing Systems". SPE 95075.
13. Van der Eerden, J. P. 1993. *Handbook of Crystal Growth, Vol 1 a*. Chapter 6. North-Holland, Amsterdam.

SUGGESTED CITATION

Saffari, M. and A. Alamdari. 2011. "Nucleation kinetics of Calcium Carbonate in Gas Field Brine Containing Methanol". *Pacific Journal of Science and Technology*. 12(2):348-355.

 [Pacific Journal of Science and Technology](http://www.akamaiuniversity.us/PJST.htm)