Experimental investigation and kinetic modeling of nanocrystal growth for scale reduction in mono-ethylene glycol regeneration unit

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Abstract

Scale formation is the major problem in mono-ethylene glycol regeneration units of gas refineries. In this study, the effect of adding different concentrations of silica nanoparticles on the growth rate of salt crystals in a rich mono-ethylene glycol solution is investigated, and the corresponding mathematical model is introduced. To obtain the crystallization kinetics, the particle size distribution was measured in continuous intervals of time and temperature using a dynamic light scattering. Measurements were taken at four temperature levels, in 20-min intervals, and 1, 3, 5, and 9 wt% of silica nanoparticles. Results showed that silica nanoparticles reduced the activation energy needed for nucleation and crystallization by more than 50%. However, increasing the concentration of nanoparticles did not result in a further reduction in the activation energy. Rather, it contributed to the formation of larger primary nuclei that form a larger crystal structure. An increase in temperature from 25 to 50 °C led to an increase of 8.8% in the initial crystal growth. On the other side, increasing the concentration of nanoparticles from 1 to 10 wt% at a constant temperature increased the crystallization growth rate by 3.4%. The proposed mathematical model predicts the kinetics of crystal growth with an acceptable accuracy with the mean relative error of 6.19% for the whole range of concentration and temperature.

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Graphic abstract

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List of symbols

A	The surface area of crystal	ΔC^g	Molar supersaturation for crystal growth (ppm)
b	Order of crystal length	dm/dt	Mass of solid deposition in time (kg s^{-1})
C	The molar concentration of solute in the solution for crystal growth (ppm)	E_g	Growth activation energy (kJ)
C_A	The molar concentration of solute in liquid bulk (ppm)	G	Overall growth rate
C_n	The concentration of nanoparticles in solution (ppm)	HEPA	High-efficiency particulate air
C_s	The molar concentration of solute in a saturated solution (ppm)	i	Summation index, Eq. (14)
ΔC	Molar supersaturation	j	Summation index, Eq. (14)
		k	Summation index, Eq. (14)
		k	Rate constant in Eqs. (5) and (7)
		k^0	Rate constant in Eq. (13)
		k_g	Crystal growth rate coefficient, Eq. (8)

k_g^0	Constant in the Arrhenius equation, Eq. (9)
L	The characteristic size of crystal
ΔL	Length increment
MARE%	Mean average relative error %
n	Order of crystal growth process
N	Total number of laboratory data
OF	Objective function
R	Universal gas constant, $8.315 \text{ (J mol}^{-1} \text{ K}^{-1})$
Re	Reynolds number
R_G	Mass deposition rate per unit of crystal surface ($\text{kg s}^{-1} \text{ m}^{-2}$)
RMSD	Root mean square deviation
t	Time
T	Temperature (K)
ϑ	Mean linear velocity (m s^{-1})
Δt	Time intervals
Greek symbols	
α	Volume shape factor
β	Surface shape factor
ρ_c	Crystal density (kg m^{-3})

1 Introduction

During the transfer of wet gas from offshore gas condensate wells to onshore gas refineries, gas hydrates may form especially during the cold seasons due to high pressure, low temperature, and the presence of natural gas and water [1]. To avoid the formation of hydrate, an inhibitor like mono-ethylene glycol (MEG) is injected into the outlet streams of the wells. MEG can be mixed with water in any proportion and form the aqueous phase (rich MEG) and enter gas refinery. Due to the significant economic value of MEG and to avoid environmental pollution problems, it cannot be disposed of; rather, it should be separated from the gas stream and reused. Injection of various chemicals, corrosion product of pipelines, and wells formation water make this aqueous phase rich in salt-forming ions. During regeneration of MEG, water that has a lower boiling point is removed by boiling, while the ions remain in MEG solution. After a while, the concentration of these ions in the MEG loop reaches the supersaturation level. In this condition, a rise in temperature, drop in pressure, or increase in pH result in precipitation and deposition of salts as scale on the surface of the equipment [2]. In that, precipitation mostly occurs on surfaces that have a higher operating temperature, including heat exchangers, re-boilers, and MEG regeneration columns. The solubility of all sodium and potassium salts, calcium chloride, nitrite and nitrate salts, magnesium acetate, chlorides, nitrates, and sulfate salts increases with increasing temperature. In contrast, the solubility of salts such as iron, calcium and magnesium

carbonate, and calcium hydroxide is reverse and reduces as temperature increases (inverse solubility). Also, the solubility of calcium acetate, bicarbonate, and sulfate does not change much with temperature [2, 3]. The equilibrium solubility of calcium carbonate and calcite has a strong temperature dependence. Also, its solubility is a function of the partial pressure of CO_2 and the pH of the solution at a constant temperature [2]. At low pH or high CO_2 partial pressure, much of the carbonate ions are converted to bicarbonate ions, which results in higher solubility of Ca^{2+} [4]. The solubility of calcium carbonate in the water at 25°C and ambient CO_2 partial pressure is about 13 ppm [5]. However, the mineral salts are generally less soluble in co-solvent like MEG solution [6, 7] which causes decreases in the solubility of these salts in MEG solution.

From economic and environmental points of view, there is a dire need for minimization or elimination of scale formation. For more than a century, scale formation processes are investigated to find a suitable method [8]. Some scale prediction models were developed to control and manage the formation of scale [2, 9–11]. Crystal growth of CaCO_3 in mixed MEG water solvent was studied by Flaten et al. [12], and its impact on the performance of re-boilers was tested by Kananah et al. [13]. Moreover, the impact of using different kinds of inhibitors like hydrate, scale, and corrosion inhibitors on scaling under oilfield condition was discussed, as an inappropriate selection of these chemicals can lead to severe fouling, foaming, and emulsion issue in the facilities of MEG line [6, 14–18].

There are several methods for controlling and preventing scale formation. These methods are divided into two general classes of physical (mechanical) and chemical techniques. Physical techniques are pretreatment methods that prevent supersaturation of solution and include dilution, filtration, reverse osmosis, and precipitation by coagulation and flocculation. These methods are not cost effective because of the high amount of chemical consumption and heavy equipment repairs and maintenance. For instance, when a divalent ion pretreatment process is used, pH above eight is required. To establish this pH, sodium hydroxide is used which consequently leads to the accumulation of sodium ions within the MEG regeneration loop. As a result, removal of this additional sodium requires a greater slip-stream rate at reclamation section and causes an increase in operational costs [19, 20]. Common chemical techniques include chemical pretreatment, ion-exchange softening, and application of scale inhibitors. These methods are not much successful. Apart from expensive continuous chemical usage, most chemicals are harmful to the environment [21]. Furthermore, dissociation of scale and corrosion inhibitors causes an increase in salt loading of the system which may contribute to scaling as well as corrosion, and finally causes emulsion

and foaming in onshore process facilities [22]. Also, they are not able to overcome the scale formation efficiently and cause other problems. For example, chelate inhibitors often require a stoichiometric ratio, which contributes to a lot of waste. Also, such inhibitors are sensitive to equilibrium changes. This can be a reason why a particular inhibitor loses its effectiveness after a while, and scale forms even more aggressively [15, 20, 23]. Particularly, the ion-exchange softening unit used to remove cations and anions from MEG solution may not operate efficiently due to leakage and many other maintenance issues in its hydrochloric acid equipment. Besides these challenges, we should consider another problem arising from the use of corrosion inhibitors in conjunction with MEG to protect pipelines. Two main types of corrosion inhibition techniques are using pH stabilization agents or corrosion inhibitors. The use of a pH stabilization motivates salts precipitation and scaling by elevating pH of fluids and corrosion inhibitors may be incompatible with MEG reclaiming unit resins or cause a malfunction in other equipment due to the formation of sticky sludge or scales, emulsion, and foaming issues or maybe degraded at high temperature during regeneration of MEG [17]. Therefore, the application of different production chemicals throughout a MEG loop can cause more scaling problems, while the current methods have not been successful yet. In 2015, Al Nasser et al. studied the effect of silica nanoparticles on the formation of calcium carbonate precipitation in water using in situ turbidity. The aqueous solutions were prepared with different concentrations of calcium carbonate, and silica nanoparticles with different sizes and functional groups were added to the solution. They studied the potential of nanoparticles for controlling nucleation and crystallization rates and the effect of different functional groups on the induction time of calcium carbonate precipitation. Results of their research showed a decrease in induction time in the presence of nanoparticles [24]. The objective of this study is to investigate the effect of adding silica nanoparticles on the reduction of scale formation on the MEG regeneration unit equipment. A sample of rich MEG solution containing different kinds of salts was prepared from a gas refinery in South Pars gas field located in the northern bank of Persian Gulf. Next, the effects of temperature and concentration of silica nanoparticles on crystallization kinetics of salts in rich MEG solution were studied using dynamic light scattering (DLS) technique. As many studies focus on the kinetics of salt crystal growth, the kinetics of growth in the presence of nanoparticles is not studied yet. Also, the kinetic models are mostly limited to water solvent and particular salts such as calcium carbonate, whereas in the MEG regeneration loop, water plays a less role and the dissolved salts are not limited to calcium carbonate. Therefore, using the experimental

data, a mathematical model for calculating the final size of salts in solution as a function of temperature and silica nanoparticle concentration was derived. The presence of nanoparticles in MEG solution assists the formation of salts crystal at a lower temperature, and grow them to the desired size to be ready to be removed before entering to the hot surfaces. Using this model, it is possible to find the best temperature and concentration of silica nanoparticles for achieving the required size of final particles in rich MEG solution. With the aim of impurities removal from the rich MEG, the silica nanoparticles can add to this stream while it flows through the line. Because adding these nanoparticles to the rich MEG solution increases the crystal growth rate of impurities, one can remove them by cartridge filters or if necessary by a cyclone.

2 Materials and methods

2.1 Experimental methods

2.1.1 Chemicals

Sample of rich MEG was taken from the inlet stream of MEG regeneration unit. This solution contains MEG, methyl di-ethanol amine (MDEA), water and a wide range of organic and inorganic salts with pH of 7.7, the total hardness of 1144 mg/L, and density of 1.1 g/cm³ at 25 °C. Also, silica nanoparticle, silicon dioxide (purity > 98%, 20–30 nm in diameter, 180–600 m²/g special surface area, and 2.4 g/m³ density), was purchased from Iranian Nanomaterials Pioneers Company.

2.1.2 Sample preparation

To maintain the stability of MEG solution including the concentration of anions and cations, pH and the composition of solvent in all experiments, the same initial conditions were considered for all samples. Therefore, the prepared rich MEG sample was divided into six portions.

Fig. 1 The setup used to perform the test

The first part was used to characterize the components, and the rest was considered for the growth rate study of salts crystals.

2.1.3 Characterization of rich MEG solution

The concentration of MEG and MDEA in the solution was measured using gas chromatography analysis equipment, model Varian CP 3800 GC-gas chromatograph. The amount of water was measured using Karl Fischer titrator, model Metrohm 960 KF Thermoprep. Ion chromatography (Metrohm 820 IC) and atomic absorption (PerkinElmer Analyst 200) were used to measure the concentration of anions and cations in the solution, respectively.

2.1.4 Growth rate study of salts crystal

One part of the sample was used as a control solution (without silica nanoparticles), and the next four parts were kept for adding 1 wt%, 3 wt%, 5 wt%, and 9 wt% of silica nanoparticles. Each sample was tested at four different temperatures, process time, and concentrations of silica nanoparticles using DLS technique, model CILAS Nano DS. In other words, the test was done for each concentration of silica nanoparticles in a closed system. In order to provide a safe environment during working with nanomaterials, personal protective equipment including safety glasses, laboratory coats, and gloves was used. Also, the place of setup and sample preparation were under the laboratory hood, and all the tests were performed in a room with local exhaust ventilation equipped with HEPA filters. To make the MEG solution uniform, the bare MEG solution was stirred for 15 min by a magnetic stirrer. The speed of 300 rpm for stirrer was selected to be near the velocity of stream in real condition. Then, silica nanoparticle was added to the solution, and the sample was placed in a Bandelin RK-100H ultrasonic bath (320 watts and 35 Hz) for 15 min to homogenize the nanoparticles in MEG solution. The homogeneous MEG solution containing silica nanoparticle was placed in a water bath, as shown in Fig. 1 to study the effect of temperature on the kinetics of crystal growth in the presence or absence of nanoparticles. Each experiment was performed at four levels of temperature (25 °C, 50 °C, 70 °C, and 81 °C).

When the solution temperature reached the set point, samples were taken at 0, 20, 40, and 60 min. The size of particles in the MEG solution was determined using DLS technique. All DLS measurements were repeated three times, and the relative standard deviations were less than 3% for all particle size measurements. Also, to examine the effect of nanoparticles concentration, temperature, and process time on the kinetics of crystal growth, experimental tests carried out on the control solution as well.

2.2 Mathematical modeling

To obtain the effect of nanoparticles on the crystal growth rate, it is necessary to know the mechanism and factors affecting the crystallization process. Crystallization is a two-step process containing nucleation and crystal growth, which both require a change in Gibbs free energy. Both stages are dependent on supersaturation, but the amount of energy and supersaturation necessary for the nucleation stage is much greater [25]. Crystals grow by several mechanisms in which the speed of nucleation and growth is of great importance. Growth of crystals is usually expressed by models of surface energy, diffusion–reaction, adsorption layer, and kinematic theories. Crystallization is a complex process that depends on several factors like temperature, supersaturation, particle characteristics (size, shape, and behavior), and the turbulence of the system. There is no simple or general model proposed for predicting crystal growth rate. Generally, the growth rate of a crystal, R_G , can be expressed as a mass deposition rate per unit crystal surface area is related to the mean linear velocity, ϑ , or the overall linear growth rate, G . The relationship between these parameters is given by Eq. (1) [26]:

$$R_G = \frac{1}{A} \frac{dm}{dt} = \frac{3\alpha}{\beta} \rho_C \cdot G = \frac{6\alpha}{\beta} \rho_C \cdot \vartheta \quad (1)$$

where m , A , and ρ_C , are density, mass, and surface area of the crystals, respectively. Also, α and β are volume and surface shape factors of crystals, respectively. The overall linear growth rate, G , was proposed by the change of the characteristic length of the crystal, dL , in time [26]:

$$G = \frac{dL}{dt} \quad (2)$$

The problem with these theories is that they cannot predict the growth rate coefficients and require experimental corrections based on operating conditions such as temperature and concentration. Temperature affects the relative velocity of diffusion and particle settling on the surface. Besides, crystal parameters like size, shape, and type can change with temperature. Impurities also affect the growth rate of crystals with two opposite effects. Impurities usually lead to a reduction in the growth rate, but sometimes enhance it. They cause a decline in growth rate by blocking the areas where the crystal grows or increase the rate by reducing the interfacial tension [25]. The velocity of the solution also has a great influence on the growth rate since the diffusion boundary layer around the crystal and flux affect the solid–liquid mass transfer. This appears as the Reynolds number in the crystal growth equations [26].

The thermodynamic driving force for precipitation is the difference between the chemical potential of a substance in a stable and unstable region. The stable region refers to the region in which the ions dissolve in the solution, and the unstable region is referred to as a region where the precipitation occurs spontaneously. Moreover, a metastable region can be described where the driving force is not large enough to form a solid surface except in the presence of a surface to act as nuclear sites which lead to a reduction in required free energy for crystallization. The supersaturation is defined as the difference in concentration of the supersaturated solution and the solution in equilibrium with the crystal [3]:

$$\Delta C = C - C_s. \quad (3)$$

Supersaturation is caused by factors that affect the solubility of ions in solution. These factors include temperature, pressure, and pH of the solution [20]. Moreover, the addition of the third substance can also decrease the solubility of dissolved salts and cause supersaturation [3]. In 1929, McCabe studied the particle size distribution of crystals in a continuous crystallization system and under the following assumptions introduced the ΔL law, Eq. (4) [3]:

1. All crystals have the same shape and size and grow equally.
2. Supersaturation field in solution is uniform.
3. The temperature of the system and the relative velocity between crystals and liquid phase are constant.
4. Nucleation does not occur.

Considering these points, the final length of all crystals in the solution, L , over the same time interval, t , is similar and is obtained by Eq. (4) [3]:

$$\Delta L = G \cdot \Delta t. \quad (4)$$

Equation (4) is ideal and cannot be used at all circumstances, as the temperature and supersaturation gradient exists in the solution and the same growth rate of particles is rarely observed. As the growth rate of a particle depends on the velocity of liquid around it, particles grow at different speeds. This means that the growth rate of crystals is a function of particle size, $G = G(L)$, [3, 26, 27]. Bransom et al. considered the real case of simultaneous nucleation and subsequent growth of crystals and assumed first-order growth rate shown in Eq. (5) [27]:

$$\frac{dL}{dt} = k \Delta C. \quad (5)$$

Butler (1950) showed that the process is more complicated than that expressed by Eq. (5) and proposed Eq. (6) [27]:

$$\frac{dm}{dt} \propto (C_A - C_S)^n \quad \text{where } n > 1. \quad (6)$$

Equation (6) implies that the growth rate is not first order. Bransom considered a more general form of growth rate in which the particle size was an effective factor on the turbulence and thickness of the layer around the crystal and inserted the Reynolds number in the crystal growth equation [27]:

$$\frac{dL}{dt} = k \text{Re}^b \Delta C^g. \quad (7)$$

Replacing the length of the particle, L , as equivalent to Reynolds number, Eq. (7) changes to the following form:

$$\frac{dL}{dt} = k_g \cdot L^b \cdot \Delta C^g. \quad (8)$$

During the growth of a crystal, solute molecules/ions reach the growing faces of a crystal by diffusion, convection, or a combination of both mechanisms. At the surface, these molecules/ions become organized into the space lattice through an adsorbed layer, which described as the surface integration or the surface reaction process. Since temperature affects the relative rates of diffusion and surface integration steps, it affects the growth of the crystal. The relationship between the kinetics of growth and temperature is expressed by the Arrhenius equation:

$$k_g = k_g^0 e^{\left(-\frac{\Delta E_g}{RT}\right)} \quad (9)$$

where ΔE_g is activation energy and adjusted using experimental data. Replacing the quantity of k_g from Eq. (9) in Eq. (8) results in Eq. (10):

$$\frac{\Delta L}{\Delta t} = k_g^0 e^{\left(-\frac{\Delta E_g}{RT}\right)} L^b \cdot \Delta C^g \quad (10)$$

where exponent b is an adjustable parameter and can be obtained using a line search trial and error process. If the concentration of salts in solution, C , is much greater than the saturation limit, C_s , Eq. (10) simplifies to Eq. (11):

$$\Delta C^g = (C - C_s)^g \approx C^g. \quad (11)$$

Combining Eq. (11) in Eq. (10) results in Eq. (12):

$$\frac{\Delta L}{\Delta t} = k_g^0 e^{\left(-\frac{\Delta E_g}{RT}\right)} L^b C^g. \quad (12)$$

If the concentration of different salts in the solution is very high, it can be assumed that C^g does not change very much with time. In other words, the consumption of ions used for crystallization is negligible compared to their initial concentration. Based on this assumption, we can consider the value of C^g constant during the growth process

Fig. 2 The flowchart used to optimize the parameters of Eq. (13)

Table 1 Solvent specification of rich MEG solution

Name of component	Method of measurement	Weight percent
MEG	Gas chromatography	32.5
MDEA	Gas chromatography	7.3
Water	Karl Fisher	60
Total		99.8

and integrate Eq. (12) with constant k_g^0 . As a result, Eq. (12) simplifies to Eq. (13):

$$\frac{\Delta L}{\Delta t} = k^0 e^{\left(-\frac{\Delta E_g}{RT}\right)} L^b. \quad (13)$$

In this equation, k^0 is a function of the initial solution type and composition. Also, activation energy changes, ΔE_g , can be a function of the concentration of stimulating substance that forms solid crystals in the solution. The adjustable parameters of the model, k^0 and ΔE_g , can be optimized using laboratory data of crystal growth as a function of initial concentrations of silica nanoparticles, process time, and temperature. For this purpose, the mean relative error for predicting the crystal growth rate of salts was defined as the objective function:

$$OF = AAD\% = \frac{1}{N} \sum_{i=1}^5 \sum_{j=1}^4 \sum_{k=1}^4 \left| \frac{\left(\frac{\Delta L}{\Delta t}\right)_{i,j,k}^{exp} - \left(\frac{\Delta L}{\Delta t}\right)_{i,j,k}^{mod}}{\left(\frac{\Delta L}{\Delta t}\right)_{i,j,k}^{exp}} \right| \times 100 \quad (14)$$

where i , j , and k are the initial concentration of silica nanoparticle, process time, and temperature, respectively. In addition, N is the total number of laboratory data. Moreover, the “exp.” and “mod.” superscripts represent laboratory and modeling values, respectively. The model parameters can be optimized using a nonlinear optimization algorithm of the generalized reduced gradient (GRG) method through the flowchart shown in Fig. 2. Then, the kinetic model of nanocrystal growth is suggested by comparing the results for the solution containing silica nanoparticles and the control solution (without silica nanoparticles) and nonlinear regression.

3 Results and discussion

3.1 Composition of rich MEG solution

Table 1 demonstrates the gas chromatography and Karl Fischer results of MEG solution. In addition, the analysis of ions in the original solution is also given in Table 2. Based

Table 2 The concentration of anions and cations in rich MEG solution

Number	Cation/anion	Measurement method	Value	Unit
1	Na	Atomic absorption	0.78	Weight percent
2	K	Atomic absorption	0.07	Weight percent
3	Ca	Atomic absorption	0.02	Weight percent
4	Mg	Atomic absorption	83	ppm
5	Cr	Atomic absorption	< 1	ppm
6	Ni	Atomic absorption	< 1	ppm
7	Fe	Atomic absorption	< 1	ppm
8	Mn	Atomic absorption	< 1	ppm
9	Formate	Ion chromatography	123	ppm
10	Acetate	Ion chromatography	7110	ppm
11	Propionate	Ion chromatography	66	ppm
12	Butyrate	Ion chromatography	142	ppm
13	Glycolate	Ion chromatography	< 1	ppm
14	Succinate	Ion chromatography	136	ppm
15	Oxalate	Ion chromatography	< 1	ppm
16	Chloride	Ion chromatography	17,152	ppm
17	Nitrate	Ion chromatography	78	ppm
18	Nitrite	Ion chromatography	< 1	ppm
19	Sulfite	Ion chromatography	44	ppm
20	Sulfate	Ion chromatography	151	ppm
21	Thiosulfate	Ion chromatography	156	ppm
22	Thiocyanate	Ion chromatography	24	ppm
23	Phosphate	Ion chromatography	< 1	ppm

on these results, sodium, potassium, calcium, chloride, and acetate ions have the highest proportion in the initial MEG solution. As a result, among all the salts present in the MEG solution, the salts that mostly contribute to the

Fig. 3 Effect of silica nanoparticles with different concentrations on the size of crystals in MEG solution versus time and temperature

Fig. 4 Effect of temperature on crystal growth of salts in MEG solution with different concentrations of silica nanoparticles

formation of deposits on process equipment and hot surfaces include calcium and magnesium carbonate.

As observed in Table 2, calcium carbonate forms the major part of the insoluble salts in the MEG solution. Since the concentration of calcium ions in the rich MEG solution is greater than the solubility of calcium carbonate in the water and as it was discussed before, the mineral salts are generally less soluble in co-solvent like MEG solution. Therefore, the concentration of calcium ions, C^g , in this solution is much higher than the supersaturation limit, C_s . In addition, the high concentrations of C^g in the solution make it possible to assume that C^g remains constant during experiments.

3.2 DLS results of crystal growth

Effect of silica nanoparticles with different concentrations on the size of crystals in MEG solution versus time is shown in Fig. 3. Moreover, for comparison, the size of the particles in the control solution was measured and is shown in this figure.

According to Fig. 3, the crystal size increases over time, but this increase is not significant for the control solution. It is also observed that by increasing concentrations of silica nanoparticles, the size of crystals increases. Meanwhile, it can be seen that the size of the crystal is in the micron range. Effect of temperature change on crystal growth is shown in Fig. 4. Based on the results, temperature rise led

Fig. 5 Effect of concentration of silica nanoparticles on the growth of crystals in MEG solution at different temperatures

Table 3 Levels of temperature, time, and concentration of nanoparticles

Variable	Index	Level				
		1	2	3	4	5
Nanoparticle concentration (%)	<i>i</i>	0	1	3	5	9
Sampling time (min)	<i>j</i>	0	20	40	60	–
Solution temperature (°C)	<i>k</i>	25	50	70	81	–

Table 4 Optimized parameters of Eq. (12)

Nanoparticle concentration (%)	Adjustable parameters	
	k^0 (s ⁻¹)	$\Delta E_g/R$ (K)
0	0.0213	797.6
1		359.6
3		359.6
5		359.6
9		359.6

to an increase in the size of crystals for all samples. Results also show that the presence of nanoparticles greatly enhanced the growth rate of crystals.

Figure 5 shows the effect of concentration of silica nanoparticles on the particle size distribution. It is clear that increasing concentration of nanoparticles increases the size of crystals. It is also observed that increasing the crystal size at temperatures of 70 °C and 81 °C is far more than 25 °C and 50 °C.

In general, there was a significant difference between the growth of crystals in a MEG solution without silica nanoparticles and a MEG solution containing silica nanoparticles. Besides, according to Figs. 3, 4, and 5, the higher

the concentration of silica nanoparticles, the higher the size of the initial crystal core will be obtained.

3.3 Growth models of crystallization

Based on the variable levels in Table 3, the optimization of the adjustable parameters of the developed model was performed. The optimized values are shown in Table 4.

The value of parameter *b* was considered equal to one with a trial and error approach to find the lowest value of the objective function. Results show that the addition of silica nanoparticles to the MEG solution causes the nuclear activation energy to be reduced to about half. This decrease in activation energy can be a reason for the acceleration of the crystal growth in the presence of silica nanoparticles. Moreover, comparing the activation energy of crystallization was found to be independent of nanoparticle concentration.

Using the optimized values of adjustable parameters, the growth models of crystallization deposition in a MEG solution without and with silica nanoparticles can be expressed by Eqs. (15) and (16), respectively:

$$\frac{\Delta L}{\Delta t} = 0.0213e^{\left(-\frac{797.6}{T}\right)}L \quad (15)$$

Fig. 6 Comparison of empirical data and proposed model

Table 5 Errors of Eqs. (15) and (16)

Nanoparticle concentration (%)	Errors	
	MARE%	RMSD
0	7.64	0.09
1	6.05	0.08
3	9.93	0.11
5	3.40	0.04
9	3.90	0.04

Results of the developed model and experimental data are shown in Fig. 6.

Moreover, the RMSD and MARE% of these equations in predicting the length of crystals were calculated for each concentration of nanoparticles using Eqs. (17) and (18):

$$\text{RMSD} = \sqrt{\frac{\sum_{r=1}^N \left(\frac{L_r^{\text{exp}} - L_r^{\text{mod}}}{L_r^{\text{exp}}} \right)^2}{N}} \quad (17)$$

$$\frac{\Delta L}{\Delta t} = 0.0213 \left(-\frac{359.6}{T} \right) L.$$

$$\text{MARE\%} = \frac{1}{N} \sum_{r=1}^N \left| \frac{L_r^{\text{exp}} - L_r^{\text{mod}}}{L_r^{\text{exp}}} \right| * 100. \quad (18)$$

Fig. 7 Effect of nanoparticle concentration on the initial particle size in the MEG solution

These results of errors are reported in Table 5.

It is obvious that there is a very good agreement between experimental results and developed model of crystal growth. The experimental data for the initial size of crystals in the presence of various concentrations of silica nanoparticles are shown in Fig. 7. As mentioned, the initial size of the crystal is a function of the concentration of the silica nanoparticles.

Fitting an exponential relationship to these data, we can obtain the relationship between the initial size of crystals and the concentration of silica nanoparticles, as follows:

$$L|_{t=0} = 1608e^{(0.0037C_n)}. \quad (19)$$

In Eq. (19), the coefficient 1608 and C_n are the initial particle size in MEG solution without nanoparticles and the nanoparticle concentration in solution in ppm, respectively. By replacing Eq. (19) into Eq. (16), Eq. (20) will be obtained:

$$\left. \frac{\Delta L}{\Delta t} \right|_{t=0} = 34.26e^{\left(-\frac{359.6}{T} + 0.0037C_n\right)}. \quad (20)$$

Sensitivity analysis shows that at constant concentration of silica nanoparticle, increasing the temperature from 25 to 50 °C leads to an increase of 9.8% in the initial growth of crystal, while at constant temperature, increasing concentration of nanoparticles from 1 to 10% causes an increase of 3.4% in the initial growth of crystal. Therefore, it can be concluded that the effect of temperature rise on the initial crystal growth rate is greater than the effect of the initial concentration of nanoparticle. Therefore, by means of this model, it is possible to determine the optimum operating temperature and silica nanoparticle concentration to achieve a micron size of particles in MEG solution so that it can be readily separated from MEG loop by existing filters and prevent scale formation on process equipment.

4 Conclusion

Composition analysis of rich MEG solution showed that calcium and magnesium carbonate salts had the highest contribution in scale formation on the hot surfaces and process equipment. Also, results of DLS analysis showed that silica nanoparticle accelerates the crystallization rate of different salts. In the temperature range of 25 to 75 °C, the rate of crystal growth per unit length increased about 3.5 to 4.3 times. Modeling crystal growth showed that the addition of silica nanoparticles causes a reduction of nucleation energy by more than 50% and accelerates the growth of salts crystals. As a result, the salts deposit from MEG solution at a concentration lower than the supersaturation. Furthermore, results showed that the concentration

of silica nanoparticles did not have a significant impact on the reduction of nucleation activation energy. Laboratory results showed that increasing concentration of silica nanoparticles leads to the formation of larger nuclei at the early stages of crystal growth, and as a result, larger crystals formed over time. If the concentration of silica nanoparticles increases from 1 to 10 ppm, the size of the initial crystal of salts will increase by 54 nm. Results also demonstrated that temperature has a direct effect on the crystal growth of salts. Raising temperature from 25 to 75 °C increased the growth rate of crystal per unit length by about 19%. Considering the economic policy and combined application of the simultaneous increase in temperature and concentration of silica nanoparticles, it is feasible to find the optimal crystallization condition for separation by pretreatment filters in the MEG regeneration units.

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Compliance with ethical standards

Conflict of interest The authors declared that they have no competing interest.

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