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Study the Effect of Silica Gel Powder on Clathrate Hydrate Formation Behavior for HFC-134a Gas.

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Abstract

One of the important aims of gas hydrate technology is to enhance the formation of hydrate or reduction the induction time for clathrate formation. The effect of the different promoter silica gel powder on R-134a gas hydrate formation has been investigated in the isochoric system experiment. It is noted that the purse media have a significant effect in increasing the speed of nucleation as well as improving the growth of hydrate. In the experiment, the effect of silica gel powder was studied to determine their effect on the composition and cooling capacity of 134 hydrates. From kinetic models were obtained many objective functions such as the amount of gas consumed (Δn), the growth rate (r (t)), and conversion of the water to hydrate. The gas consumed (Δn) of binary system increased with increase initial pressure of hydrate formation, also the hydrate growth rate (r (t)) and increase conversion of water to hydrate increase when this the first time that the effect of silica gel pweder on these functions with average active size (900) nm, BET surface area (0.65) m^2/g, pore volume 210.85 cm^3/g and average pore size (900) nm that studied for use in industrial applications and water treatment. The improvement of hydrate growth is marked by the addition of silica gel powder, which in turn increase the solubility of hydrate gas and reduce the contact angle. In addition, silica gel powder positively the contact with the gas through the increase of the interaction surface between gas and water and this increases the rate of formation of hydrate.

Key words: Clathrate; Gas hydrate; Silica gel powder; Refrigerant; Thermodynamics model.

1. Introduction

A clathrate is a complex molecule formed by the contact between gas and water at a high pressure and a low temperatures that cavities within hydrate formation are formed by the hydrogen bonds which occupied by the gas molecules that are the guest molecules [1]. The labile clusters will form by dissolve molecules of gas in water with a number of water molecules surrounding each guest molecule. The clusters will, in turn, associate with each other to form the so-called basic hydrates, gas molecules was occupied basic cavities and all linked cavities left empty as shown in figure (1) [2]. For many years, Clathrate hydrates are well-known structures that were considered as harmful by the oil and gas industry because of their annoying tendency to plug pipelines. The investigations have been undertaken on the positive application of gas hydrates to date, there is a need to perform more studies to clarify various processes using clathrate hydrate formation phenomena, and to conclusively prove its sustainability [3].

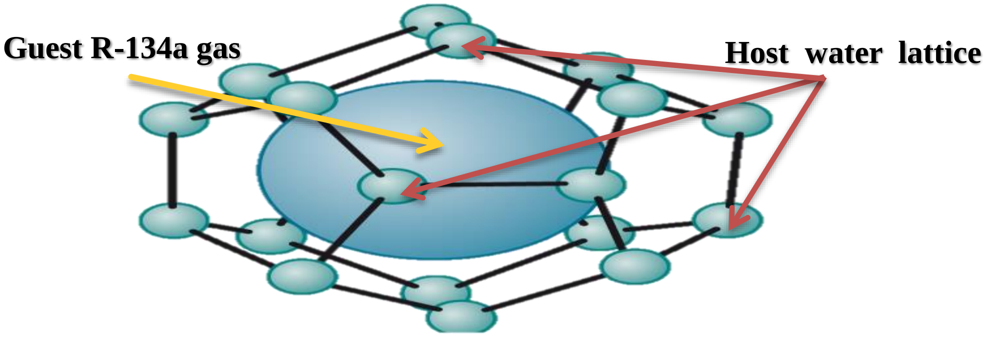

Figure (1). Simple of clathrate hydrate structure [1].

Enhancing the formation of hydrate and the tendency to reduce the induction time needed to form hydrates is one of the main objectives of gas hydrate technology. Induction time is **o**ne of the important parameters used to characterize hydrate Nucleation, This time elapsed to form water and gas groups and their growth towards a stable nucleus with critical size known as the nucleation stage .The induction time can be expressed by the relationship between the pressure-time of the system in which the gas hydrates are formed as shown in figure (2). The initial pressure drop from P_0 to P_{sol} caused by dissolution of gas in the liquid aqueous phase. At a steady-state condition, the pressure stabilizes until formation at which a sudden pressure drop is gas hydrate starts formation. The process of gas consumption continues to lead to low pressure until it reaches a stage where the hydrate is not formed **[4]**. The induction time is calculated as:

$$\text{Induction time} = t_{induction} - t_{sol} \qquad (1)$$

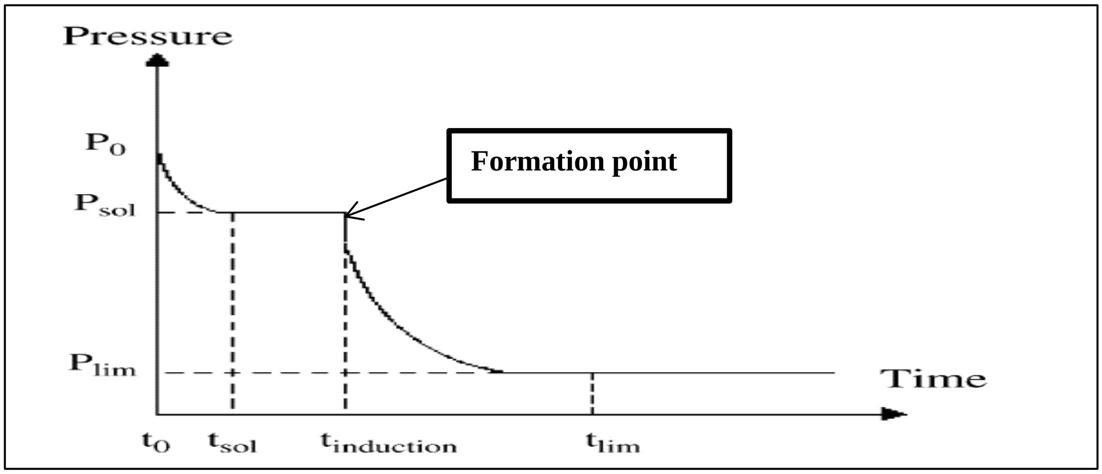

Figure 2. Typical pressure-time-temperature plot obtained during a hydrate formation at constant volume [4].

Scientists have revealed the advancement impact of a few added substances on the formation of gas hydrate and hydrate gas content. One of the techniques for enhancing the hydrate formation increases the interface accessible for the reaction of hydrate [5]. This can be done effectively by different methods such as mixing water and gas, spraying the water with gas, or by immersing a porous medium in water [6]. Lots of researchers are trying to use additives to promote hydrate generation. Surfactant is in common use, for examples, SDS, TBAB and TBAF, LABS, CTAB, ENP, Tween, Span20 etc. Porous medium can also accelerate the hydrate formation, such as glass powder, silica gel, molecular sieve that promote hydrate formation through the enhancement of mass transfer [7].

Handa showed that the dissociation pressures of both methane (CH4) and propane (C3H8) hydrates in small pores were higher than those in bulk phases [8]. Uchida confirmed that the pore effect on the hydrate equilibrium conditions depends on the pore diameter, and it is predicted by the activity of water [9]. Seo showed the decrease of pore diameter made hydrate formation more shifted toward lower temperature with high pressure [10]. Henry proposed a thermodynamic model of gas hydrates that includes the pore size [11]. Kang showed the average pore diameter is greater than 100 nanometers lead to increased hydrate formation because of increased diffusion in the larger pores [12]. Al-Mukhtar studied kinetics dissociation for the binary system (water-R-134a) system and for ternary salts (NaCl, KBr, and NaF) system at different concentrations (0.09, 0.17, 0.26)mol/Kg in the isochoric cell. They used Claperyon equation to estimate dissociation heat for the systems with Peng-Robinson – PRSV equation applied for gas compressibility factor Z. They concluded that dissociation heat increased when salt concentration increased. The NaCl salt with high concentration gave the highest value among the other salt in the study [13].

In this study, growth rate, induction time, gas consumed, apparent rat constant, storage capacities and conversion of water to hydrate of the hydrates formed in presence of Porous medium (Silica gel powder). The aim has been to find the effect of the difference concentration of silica gel powder, which achieves best values.

2. Thermodynamics model

2.1 Gas consumed

The moles of the hydrate former consumed throughout formation of hydrate are obtained by applying the real gas law as follows:

$$\Delta n_H = n_{g,0} - n_{g,t} = \left(\frac{PV}{ZRT} \right)_0 - \left(\frac{PV}{ZRT} \right)_t \qquad (2)$$

The "0" Subscripts refer to the initial conditions where "t" refers to conditions at time, t, of the system, P pressure and T temperature at the phase equilibrium state, R was the universal constant, and Z was the gas compressibility determined by the Pitzer's correlation [14] :

$$Z=1+B^0\frac{Pr}{Tr}+\omega\ B^1\frac{Pr}{Tr} \tag{3}$$

Where $$B^0=0.083-\frac{0.442}{T_r^{1.6}} \tag{4}$$

And $$B^1=0.139-\frac{0.442}{T_r^{4.2}} \tag{5}$$

The hydrate number (number of water molecules) is identified by the partial filling the large and small cavities. The simple hydrate number is calculated VRWt is the reacted water's volume [1]:

$$M=\frac{136}{(8\theta_S+16\theta_L)} \tag{6}$$

Where θS and θL are is the fraction of linked large and small cavities occupied by guest molecules respectively, as follows [1]:

$$\theta_i=\frac{(C_i\times f_i)}{1+(C_i\times f_i)} \tag{7}$$

Ci is the Langmuir constant for large cavities and small cavities for R134a hydrate. Where fi is the fugacity of (R134a) gas which calculates by the apply equation of state (Peng–Robinson) [15]. The Langmuir constant of R-134a Ci is formulated as follows [16]:

$$Ci=\frac{Ai}{T}\exp(\frac{Bi}{T}) \tag{8}$$

Where Ai and Bi are constants with values 0.00575 and 4908 for large cavities respectively and Cs equal to zero for (R134a) gas [17].

The gas hydrate volume is not like the aqueous solution volume, To estimate volume of R134a gas hydrat inside a cell the next equation used:

$$V_t=V_{cell}-Vs_0+V_{RWt}-V_{Ht} \tag{9}$$

where Vcell is the cell volume with value equal 1500 cm3; Vs0 is the initial aqueous solution volume with value equal 200 cm3; VHt is the produced hydrate's volume and VRWt is the reacted water's volume which calculated by using the following equation:

$$V_{RWt}=M\times\Delta n_H\times V_w^L \tag{10}$$

Where v_W^L displays the molar volume of water that may calculated by the next relation [18]:

$$v_W^L=18.015\times[1-1.0001\times10^{-2}+1.3339\times10^{-4}(1.8(T-273.15)+5.50654\times10^{-7}(1.8(T-273.15)+32)^2]\times10^{-3} \tag{11}$$

The hydrate molar volume, VHt, can be estimated by next equation:

$$V_{Ht}=M\times\Delta n_H\times V_w^{MT} \tag{12}$$

The gas hydrate molar volume can be assumed equal to the empty hydrate lattice molar volume. Klauda and Sandler presented the $v_W^{MT}$is the volume occupied by empty hydrate lattice (in K and m3/kmol) as a function of temperature and pressure by following equation [18]:

$$v_W^{MT}=(17.13+2.249\times10^{-5}\times T+2.013\times10^{-6}\times T^2\times\frac{10^{-30}N_A}{136}-8.006\times10^{-9}\times P+5.448\times10^{-12}\times P^2 \tag{13}$$

T and P are the temperature and pressure given in K and MPa units, respectively.

2.2 The growth rate of hydrate formation

The growth rate of hydrate formation be presented using the below equation [19]:

$$r(t) = -\frac{dn_{R134a}}{dt}\Big|_{ti} = \frac{\Delta n_{R134a}}{\Delta t}\Big|_{ti} = \frac{(n_{R134a,i-1}-n_{R134a,i+1})}{(t_{i+1}-t_{i-1})*n_{Wo}} \qquad (14)$$

$n_{R134a,i-1}$ And $n_{R134a,i+1}$ present moles of R134a gas which is hydrate former at t_{i-1} and t_{i+1}respectively. nw0 is the initial number of moles of water.

2.3 Water to hydrate conversion:

The water convert to hydrate for each mole of water feed can be estimated by relation below [20]:

$$\text{The Water conversion} = \frac{M\times \Delta n}{n_{wo}}\times 100\% \qquad (17)$$

2.4 The storage capacity (SC)

The storage capacity is a volume of gas stored in per volume of hydrate which calculate by following equation [19]:

$$SC = \frac{V_{STP}}{V_H} = \frac{\Delta n \times (\frac{R\times T_{STP}}{P_{STP}})}{V_H} \qquad (18)$$

Where subscript STP stands for the standard conditions and VH is the gas hydrate volume at the end of the reaction, which is calculated by Eq. (11). Figure (4) shows the algorithm of previous calculations.

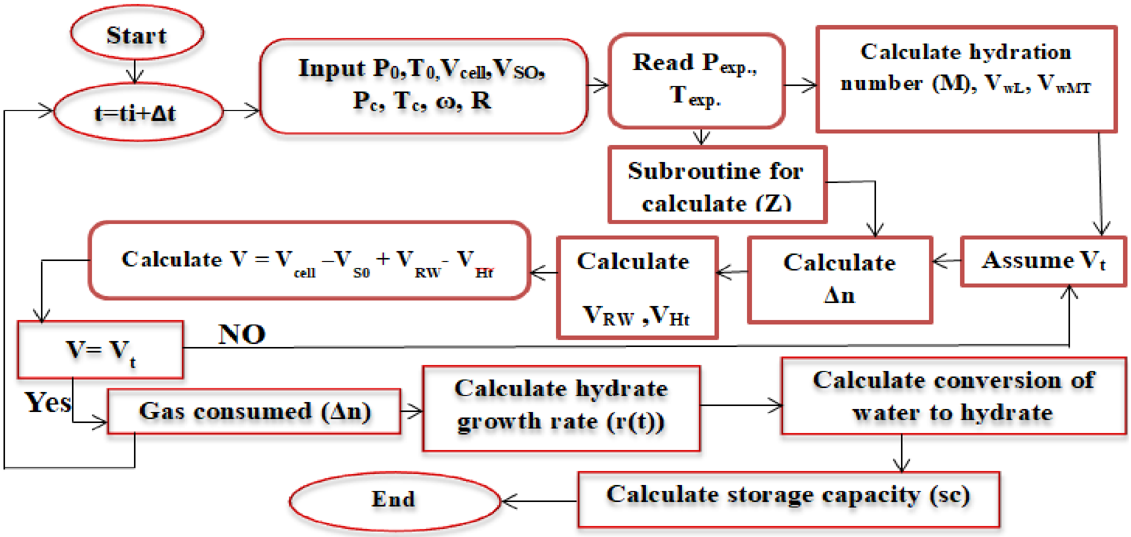

Figure (4): The suggested algorithm to calculate the gas consumed and the apparent rate hydrate formation of R134a.

3. Experimental Work

Figure(3) shows the experimental schematic diagram which used in this study. The most important part in system is the glass cell with a total volume of 1500 cm3 consist of internal diameter of 14 cm and height of 14.5 cm, the cell was equipped with a magnetic stirrer.

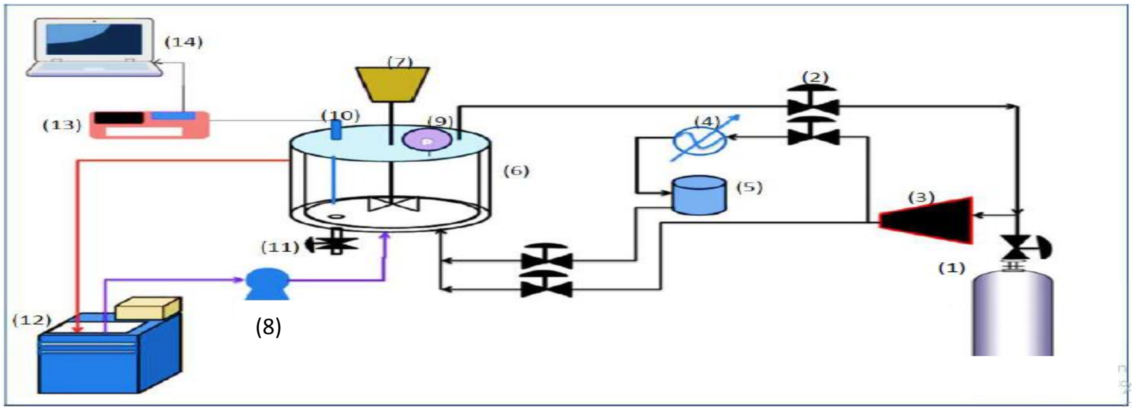

Figure.3(1) gas cylinder; (2) needle valve; (3) gas compressor; (4)condenser; (5) accumulator of gas; (6) Experimental cell; (7) magnetic stirrer; ; (8) water pump; (9) digital pressure gauges; (10) temperature sensor; (11) valve drain; (12) chiller; (13) interface system; (14) computer.

A thermocouple type k with a division scale of 0.1 K and a digital pressure gauge with a division scale of 0.005 bar were to measure the temperature and pressure. The cell connected to the system through pipes and controlled by a valve for gas injection, water input, and drain valve. The cell surrounded by transparency plastic vessel as heat jacket to maintain the temperature inside the cell, cooling water supplied from bath type Julabo F10-VC was which contains a cooling medium made of ethylene glycol / water. The temperature of the medium is adjusted by controllable circulator. Refrigerant gas (R-134a) with a high purity equal to 99% was utilized to form a hydrate with distilled water. In experiments , porous medium used was silica gel powder with average active size (900) nm, BET surface area (0.65) m^2/g, pore volume 210.85 cm^3/g and average pore size (900) nm.

The constant volume (isochoric) system search strategy was utilized to investigate hydrate formation in this study **[13]**. At to start, distilled water was used to wash the cell and after that washed with acetone to flush the cell. Washed water and acetone lingering were depleted. The cell was emptied to vacuum pressure for a time of 30 min to guarantee that there were no traces of contamination. The air is evacuated from the reactor using the compressor after the feeding of 200 ml of the water solution mixture inside the cell. A specific measure of R-134a was acquainted with the cell with achieving the coveted pressure of 0.45 MPa (4.5 bar) at a temperature of 313.15 K (10 C^0). The mixer was rotates at 200 rpm after the gas pressurized to the cell is completed. The pressure of cell reducing consistently because of hydrate formation until the point when achieving the study state condition.

4. Results and discussion

In the isochoric system, the pressure drop and the variation of gas consumed in the system of pure water ,HFC-134a and in the system of pure water ,HFC-134a and deferent concentration for silica gel are the result of dissolution (region A) , the nucleation (region B) and formation process (region C). However, when the hydrate formation growth stops, the pressure is stabilized because of the HFC-134a is supersaturated and phase equilibrium has been reached as shown in fig. (5a,b,c,d, and e) and described by Kang ang Negma [12][17].

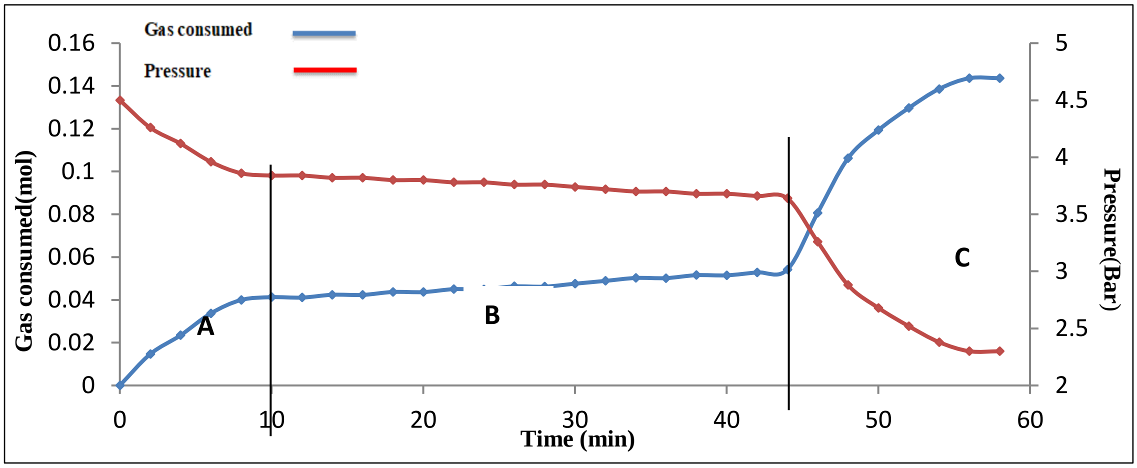

Figure 5a. Pressure-Time-Gas consumed behavior obtained with pure water and (without silica gel)

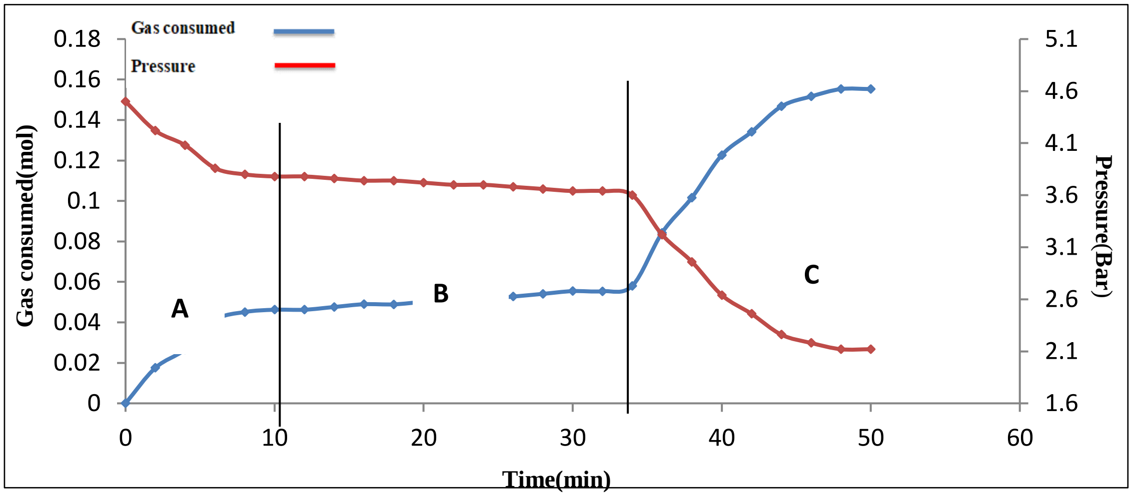

Figure 5b. Pressure-Time-Gas consumed behavior obtained with 25-ppm concentrations of silica gel.

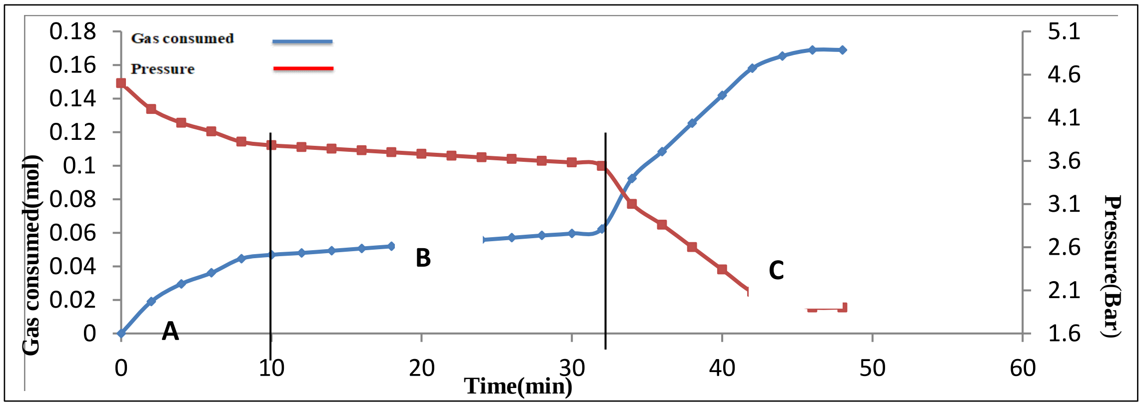

Figure 5c. Pressure-Time-Gas consumed behavior obtained with 50-ppm concentrations of silica gel

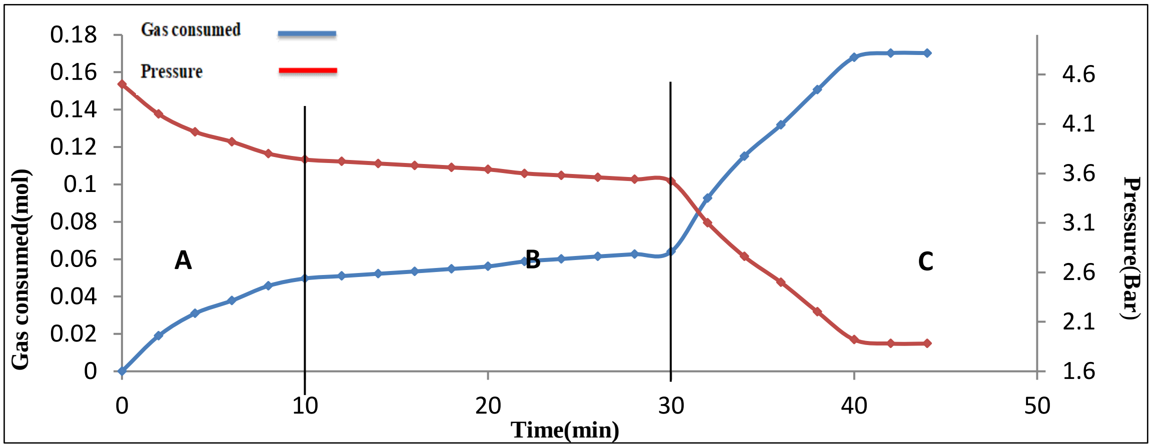

Figure 5d. Pressure-Time-Gas consumed behavior obtained with 75-ppm concentrations of silica gel

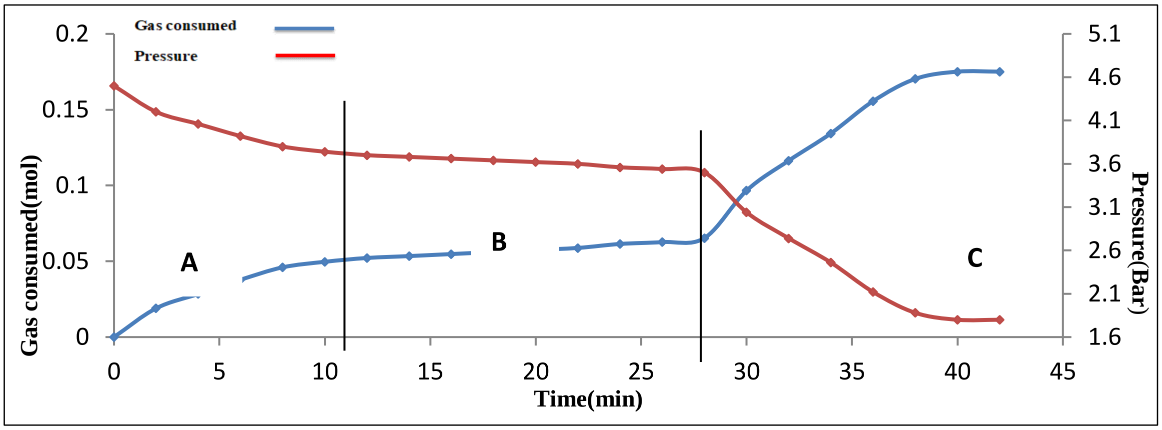

Figure 5e. Pressure-Time-Gas consumed behavior obtained with 100-ppm concentrations of silica gel

From fig. (5a,b,c,d, and e), it can be seen that when formation region is reached, the gas hydrate forms in pure water is about 48 min, in the water solution with 25 ppm of silica gel in about 40 min, in the concentration of 50 ppm about 38 min, in the concentration of 75 ppm about 36 min and in the concentration of 100 ppm about 32 min.Hence, the formation process of HFC-134a hydrate is shorted with ingreasing mass fraction of silica gel in the water solution. The gas consumed amount increases when the silica gel powder concentration increase. As Fig.(6) shows, maximum gas consumed amount was achieved at a surfactant concentration of 100 ppm and the the steady state of hydrate is realized in about 42 minutes

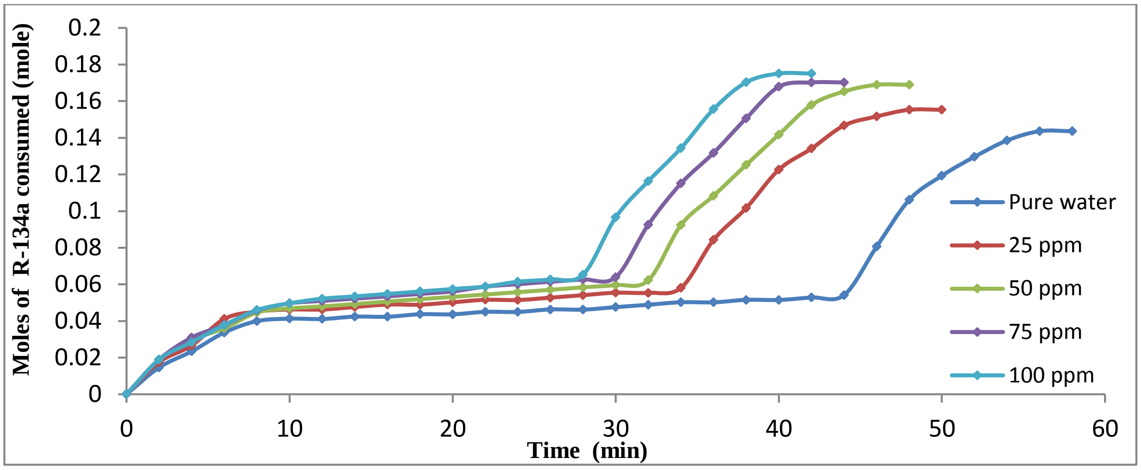

Figure.6. Refrigerant gas (R-134a) consumed without and with different concentrations of silica gel.

From fig. (7), induction time at 50 and 25 ppm is 26 and 30 min respectively that behavior is supported by Sabil [7]. At 75 ppm, the hydrate attains a steady state in about 44 minutes and the induction time is 24 min which is longer than that of 100 ppm. Due to the low solubility of gas in water, hydrates appear on the waterfront in the pure water system. Hydrates also cover the water interface which prevents further water conversion to hydrates, even when stirred due to the low water density compared to water that shows in Fig(8).

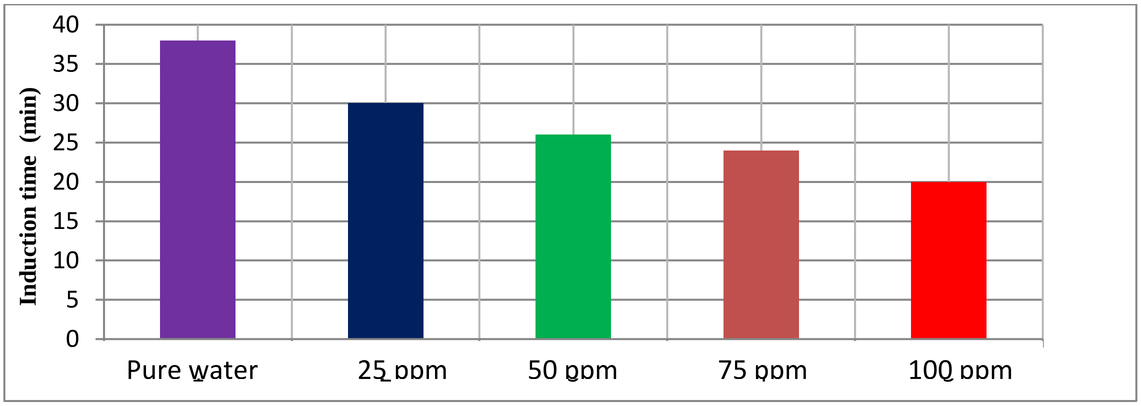

Figure.7. Compare the induction time of pure water agents' different concentration of surfactant silica gel.

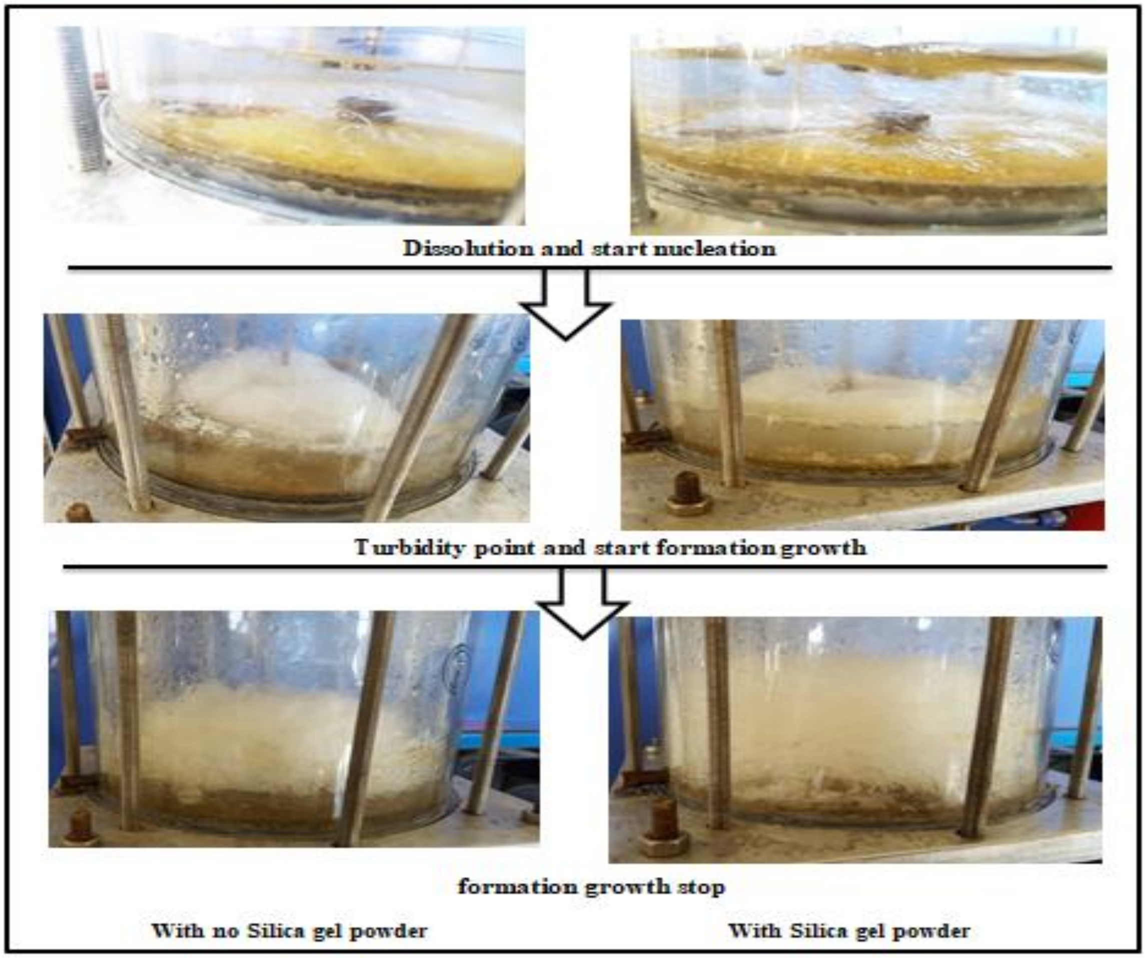

Figure. 8. gas hydrates presenting out in the cell with different concentration of silica gel when A)25ppm, B)50ppm, C)75ppm and D)1000ppm .

As fig. (9) Shows, surfactant promoter increase the storage capacity of gas hydrate. 0.0863 Mole is the maximum gas amount in hydrate and 60 V/V is the maximum storage capacity of hydrate at standard condition that supported by Hashime [19].

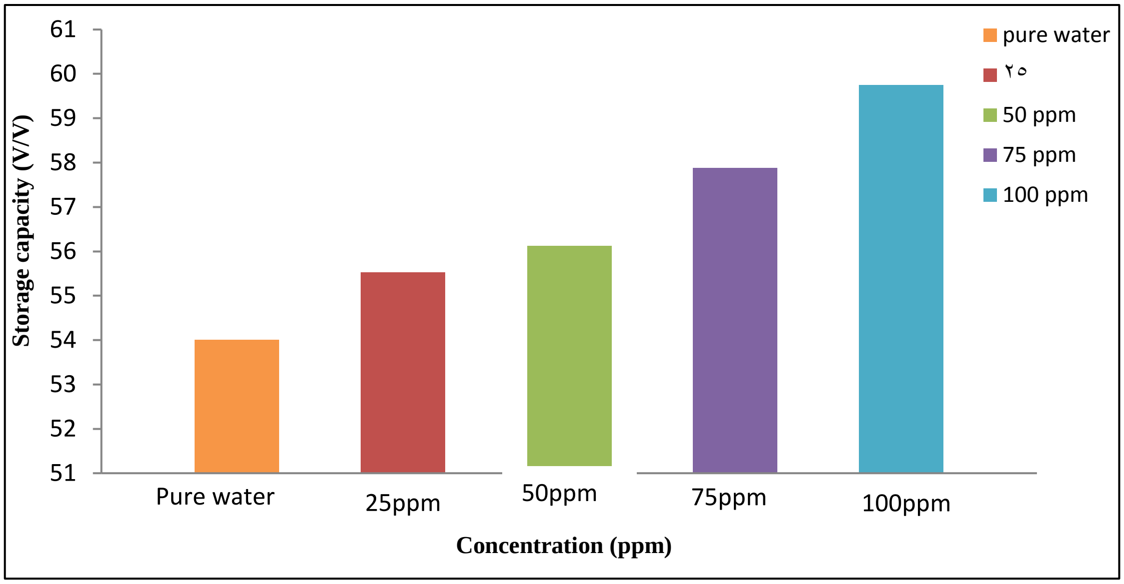

Figure.9. Compare the storage capacity of pure water agents' different concentration of surfactant silica gel.

The moles of water transform to hydrate during the hydrate growth process were calculated for the binary system and ternary system. Figure (10) showed the water conversion increased due to increase the driving force with time.

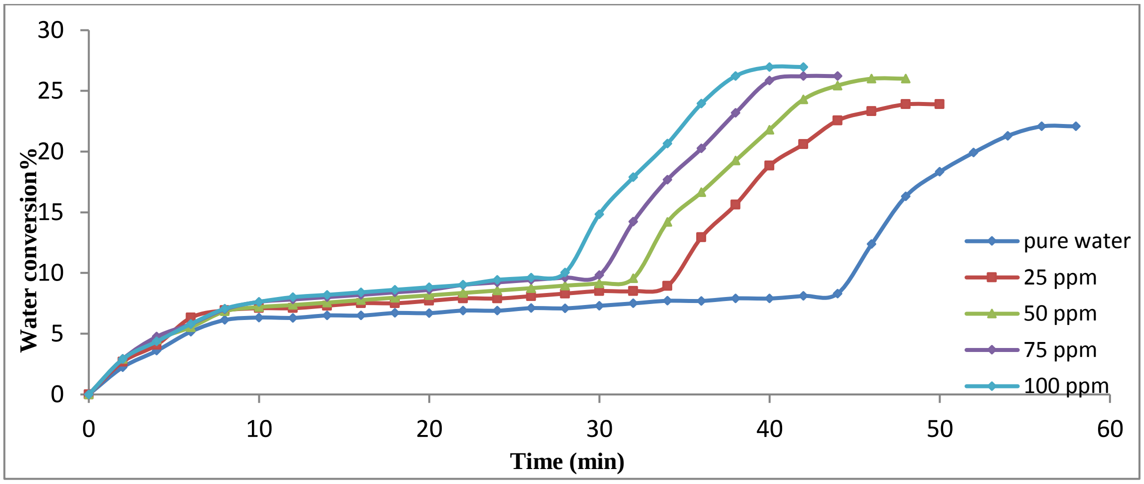

Figure (10): The water to hydrate conversion as faction with time at different concentrations of silica gel

Hydrate growth represented in the figure (11) for different concentration of silica gel. The growth rate in the presence silica gel for ternary system increase gradually until reaching the maximum value at 18 minutes in 50-ppm silica gel. The rates of growth reduce when time increases, because of the drooping in the driving force with time. As a result of the use of the silica gel, the solubility of the gas increases in the water, causing an increase in the particles of the micro hydrates and thus generates a higher surface area by reducing the contact angle and thus a higher mass transfer rate that supported by Henry [11].

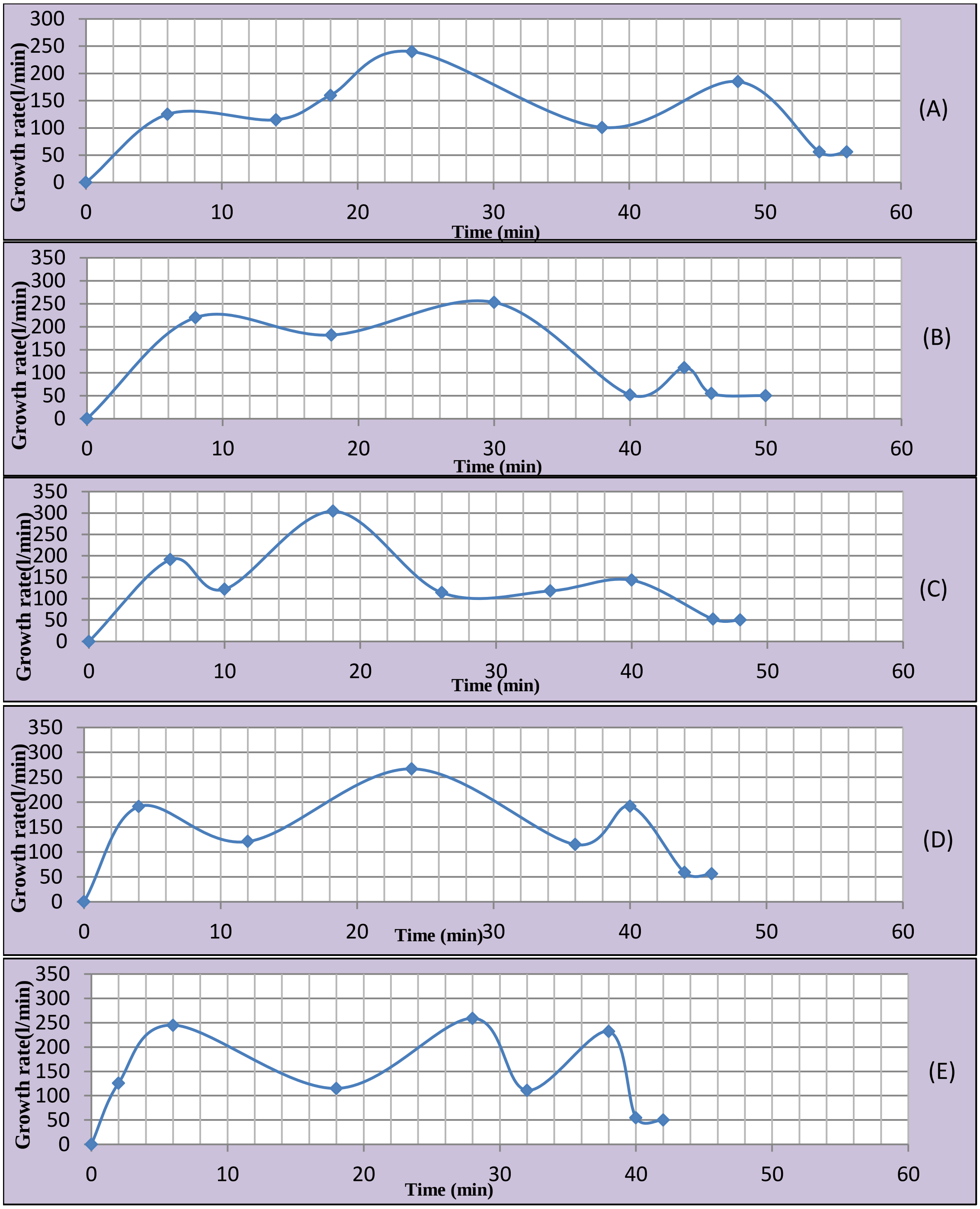

Figure (11): The R134a hydrate growth rate against time at different concentration of Silica gel powder:(A)pure water, B)25 ppm, C)50ppm ,D)75 ppm , E)100 ppm).

The effect of the different concentration of Silica gel powder on the formation of R-134a gas hydrates was observed in terms of improved hydrate nucleation and hydrate growth rate. The presence of silica gel improves the gas solubility and its spread in the water effectively, as well as to reduce the contact angle and improve contact with the gas-water, which in turn positively affects the rate of formation of hydrates. After using different concentrations of the silica gel and with different concentrations 25, 50, 75 and 100 ppm, the following conclusions were reached:

(1) In general, Silica gel powder with its different concentrations (25, 50, 75 and 100 ppm) promotes the formation of R-134a gas hydrates effectively.

(2) The maximum effect of Silica gel powder on the induction time of R-134a gas hydrates can be achieved at a concentration of 25 ppm.

(3)Maximum promotion effect of Silica gel powder on R-134a hydrate growth rate was achieved at the concentration of 50 ppm.

(4)Maximum theoretical value of storage capacity is 60 V/V at the standard condition that is achieved at a concentration of 100 ppm of Silica gel powder.

Gas separation process in hydrate form increases due to increased hydrate nucleation and increased hydrate growth. Desalination, storage, and transport have benefited greatly from improved hydrate formation kinetics.

CONFLICT OF INTERESTS.

- There are no conflicts of interest.

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دراسة تأثير مسحوق جل السيليكا على سلوك تشكيل الكلاثريت هيدرات الخاص بغاز HFC-134a.

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الخلاصة

الكلاثريت هيدرات عبارة عن جزيئات معقدة تتكون من الاتصال بين الماء والغاز عند الضغط العالي ودرجات الحرارة المنخفضة. أحد الأهداف الهامة لتكنولوجيا هيدرات الغاز هو تعزيز تكوين الهيدرات أو تقليل وقت التنوي لتشكيل الكلاثريت .تم دراسة تأثير مسحوق هلام السيليكا كمحفز على تركيبة هيدرات الغاز R-134a في تجربة نظام ايزوكوريك (حجم ثابت). من الملاحظ أن للوسط المسامي تأثير كبير في زيادة سرعة التنوي وكذلك تحسين نمو الهيدرات. في التجربة ، تمت دراسة تأثير مسحوق هلام السيليكا لتحديد تأثيرها على تكوين وتبريد 134 هيدرات و تم الحصول على العديد من الوظائف الموضوعية من النماذج الحركية مثل كمية الغاز المستهلكة (Δn) ومعدل النمو (r (t)) وثابت المعدل الظاهري (Kapp) وتحويل الماء إلى هيدرات. ازدادت كمية الغاز المستهلكة (Δn) في النظام الثنائي مع زيادة الضغط الأولي لتكوين الهيدرات ، وأيضا معدل نمو الهيدرات (r (t)) وزيادة تحويل الماء لزيادة الهيدرات عندما تكون هذه هي المرة الأولى التي يؤثر فيها مسحوق هلام السيليكا .على هذه الوظائف بمتوسط حجم نشط (900) نانومتر ، مساحة سطح (0.65) م^2 / جم ، حجم المسام 210.85 سم 3 / جم ومتوسط حجم المسام (900) نانومتر الذي درس للاستخدام في التطبيقات الصناعية ومعالجة المياه. بإضافة مسحوق هلام السيليكا يتحسين نمو الهيدرات و ذلك لانه يزيد من ذوبان غاز الهيدرات ويقلل من زاوية التلامس. بالإضافة إلى ذلك ، مسحوق هلام السيليكا يؤثر بشكل إيجابي على الاتصال الماء مع الغاز من خلال زيادة سطح التفاعل بين الغاز والماء وهذا يزيد من معدل تكوين الهيدرات.

الكلمات الدالة: كلاثريت، هيدرات الغاز، مسحوق هلام السيليكا، التبريد، نموذج الديناميكا الحراري.