EFFECTIVENESS OF PVP AND CMA AS HYDRATE INHIBITOR

By

MOHAMAD FIKREE BIN OTHMAN
11986

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons) (Petroleum Engineering)

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CERTIFICATION OF APPROVAL

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UNIVERSITI TEKNOLOGI PETRONAS
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September 2012

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TRONOH, PERAK
SEPTEMBER 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(MOHAMAD FIKREE BIN OTHMAN)

ABSTRACT

Flow assurance mean to ensure the successful and economical flow of hydrocarbon stream from reservoir to the point of sale. In other term, it is actually multiphase transport, which covers the transmission of oil, gas and water in the same pipeline from the reservoir to processing plant. Somehow, gas hydrate may occur in the flow line due to variation of pressure and temperature. Nowadays, thermodynamic hydrate inhibitor (THI) had been used widely in order to prevent this gas hydrate problems. Methanol is one of the well known chemical inhibitor that had been used for many years due to its effectiveness and proven tract-record. Nevertheless, using methanol is very expensive and not cost-effective. This is because methanol needs to be added at high concentration which is 10-60 wt% in aqueous phase. So, in order to overcome this problem, researched activity has concentrated on the development of low dosage hydrate inhibitor (LDHI) which in this case is kinetic hydrate inhibitor (KHI). KHI is very cost effective and environmentally acceptable compared to THI. The objective of this study is to study the effectiveness of Polyvinylpyrrolidone (PVP) and Calcium Magnesium Acetate (CMA) as KHI. Besides that, another objective is to study the effective concentration of PVP and CMA as KHI.

The project title: “Effectiveness of PVP and CMA as hydrate inhibitor” is to determine the ability and the effectiveness of Kinetic Hydrate Inhibitor (KHI) in delaying crystal growth of hydrate formation. This project starts by doing some research on journals in order to get reliable references regarding the topics. Then, this project will involve a lot of lab work and experiment in order to test the effectiveness of PVP and CMA as hydrate inhibitors. Equipment used in this project is the High Pressure Differential Scanning Calorimetry (DSC) & Calorimetry - HP Micro DSC. Originally designed under a IFP (Institut Français du Petrole) license to study the gas hydrates formation and dissociation, the high pressure version of the µDSC7 evo offers unique capabilities on the market: on a wide temperature range, from the subambient temperature of -45°C up to 120°C, it is possible to carry out high sensitive DSC measurements under high and very high pressure, up to 1000 bars (14 600 psi). Experiments under gas supercritical conditions, such as CO2, are also available.

This project involves two type of chemical which is the Polyvinylpyrrolidone (PVP) and Calcium Magnesium Acetate (CMA). Polyvinylpyrrolidone (PVP) was chosen as the testing chemical because of its characteristic where it is very soluble in water, not hydrolyze to insoluble compounds, and adsorb well on a polar surface of hydrate micro crystals forming and external surface preventing the association of hydrate crystal. In other hand, even though there are no researched had been done in order to prove CMA as the hydrate inhibitor, it is believe that its ability to capture the Carbon Dioxide (CO_2) will somehow help in delaying the crystal growth of the hydrate.

The result of this research shows that PVP and CMA thus have potential to be effective KHI. Discussion conclude that concept of kinetic inhibitor as low-dosage inhibitor was proven because less concentration of sample (0.1 wt% & 1.0 wt %) tested prove to be still effective in delaying hydrate induction time. Somehow for PVP, the higher the concentration of the solution used, the more effective it will be in delaying the formation of hydrate. Vice versa, for CMA, it is more effective in lower concentration (0.1 wt %) compare to higher concentration (1.0 wt %). In addition, additive such Polyethyleneoxide (PEO) thus increase the effectiveness of PVP by increasing the hydrate induction time.

Through this research, it is believe to unlock this potential of CMA and hope that one day this product will be able to compete with other commercial hydrate inhibitor. Furthermore, this research will be stepping stone for future CMA research in order to prove the ability of CMA to be new alternative of Kinetic Hydrate Inhibitor (KHI) compared to Polyvinylpyrrolidone (PVP).

ACKNOWLEDGEMENTS

The author would like to express the utmost gratitude to project supervisor, Pn. Mazuin Jasamai, for the guidance and support provided along with the progression of this project. A gratefully acknowledge financial support from Universiti Teknologi PETRONAS. The author also wishes to express his appreciation to the lab technologists Mr. Redzuan and Mr. Shahrul from Reservoir laboratory for the assistance rendered during the course of this project. Appreciation also given to Mr.Hazri from mechanical laboratory for assistance in using the micro-DSC equipment. A grateful appreciate is addressed to all who had contributed to the accomplishment of this project, for the constant encouragement and timely help throughout.

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CHAPTER 1: INTRODUCTION

1.1 Project Background

Gas hydrate is solid crystalline compounds, which have a structure when guest molecules are entrapped in a cage like framework of the host molecules without forming a chemical bond. It is a result of the hydrogen bond that water can form hydrates. The hydrogen bond causes the water molecules to align in regular orientations. Then presence of certain compounds causes the aligned molecules to stabilize, and a solid mixture precipitates. The water molecules are referred to as the host molecules, and the other compound, which stabilize the crystal are called the guest molecules. The hydrate crystal have complex, three dimensional structures in which the water molecules form a cage and the guest molecules are entrapped in the cage [1]. At moderate high pressure and low temperature conditions, stable gas hydrate can form. The formation of stable gas hydrates may occur and block gas pipelines (Ostergaard et al., 2005) which will lead to safety hazards and huge economic loss.

Hydrate-related issues become a growing concern for the industry when oil and gas developments moving to deeper subsea environments. Hydrate blockage, beyond the safety risk they represent, result in time-consuming and costly mitigation and remediation operation. The preventions of hydrate formation and aggregation to maintain flow assurance cost the oil and gas industry over US200 M annually (K.Moussa,S.Aditya,H.Ronny.,2008; Sloan, 1998).

There are various method and techniques that had been developed in order to mitigate the hydrate formation such as:

- Prevent free water in gas stream by dehydrating the gas or elevating the temperature to vaporize more water.
- Increase the gas temperature above the needed for hydrate formation at operating pressure

- Decrease the pressure below that is needed for hydrate formation at operating temperature
- Introduce inhibitor [*Thermodynamic Hydrate Inhibitor (THI), Kinetic Hydrate Inhibitor (KHI) and Anti-Agglomerant Hydrate Inhibitor (AA*)]
- Redesign piping system

In this section, the discussion is mainly focuses on hydrate inhibitors that are currently available in the oil and gas industry such as THI, KHI and AA . Below are short descriptions regarding these three type of inhibitors (Kelland *et al.* 1995a & 1995b) :

Thermodynamic Hydrate Inhibitors (THIs) – These chemicals work by altering the chemical potential of the aqueous phase such that the equilibrium dissociation curve is displace to lower temperatures and higher pressures. They are added at relatively high concentration (10-60 wt% in the aqueous phase) and examples include methanol and monoethylene glycol (MEG). In addition, the naturally occurring inorganic salts which exist in both sea water and formation water also act as thermodynamic inhibitors.

Kinetic Hydrate Inhibitors (KHIs) – This type of chemicals does not alter the thermodynamics of hydrate formation but instead modifies the kinetics of hydrate formation. They decrease the rate at which hydrate form, preventing plugs for a period longer than free water residence time in a gas line. They bond with hydrate surface, delaying crystal growth for a period of time that is longer than the residence time of free water in the system. Their effect is time dependent and ultimately hydrates will form and block the pipeline but only if the transit time through the pipeline is sufficiently long. KHIs are added at low concentration (typically less than 1 wt% in the aqueous phase) and example include poly[N- vinyl pyrrolidone] or poly [vinylmethylacetamide/ vinylcaprolactam]

Anti-Agglomerants (AAs) – These are surface active chemical (surfactants) which do not attempt to prevent hydrate crystals from forming but rather prevent them from agglomerating to form hydrate plug. Thus they do not display the same pressure-temperature limitations as KHIs. The anti-agglomerant works by emulsifying hydrates in the hydrocarbon liquid. Hydrates are carried as non – agglomerated slurry, without viscosity increase up to 50% water cut. Somehow, AAs only work in system with a continuous hydrocarbon liquid phase and the effectiveness is dependent on the type of oil/condensate, the salinity of the formation water and water cut. AAs are added in low doses (typically less than 1% in the aqueous phase) and examples include alkyl aromatic sulphonates or alkylphenylethoxylates. AAs can also display a kinetic inhibition effect and are sometimes include in the class if KHIs.

Studied also had been done to new chemical which is Calcium Magnesium Acetate (CMA) which show KHIs characteristic in order to inhibit hydrate inhibition. There are still no proven track record that shows the effectiveness of CMA as hydrate inhibitors. Further discussion regarding this chemical will be discussed in literature review part later.

1.2 Problem Statement

The formation of gas hydrate may occur and block gas pipelines, which can lead to safety hazards and huge economic loss. Thus, to prevent the hydrate formation, we use inhibitors to inhibit the hydrate formation. A variety of inhibitors are utilized by the petroleum industry to prevent hydrate plug formation; however, these inhibitors are not designed for high water content production.

There are three types of inhibitors that are use nowdays: thermodynamic, kinetic and anti-agglomerant. These chemicals work by altering the chemical potential of the aqueous phase such that equilibrium dissociation curve is displaced to lower temperatures and higher pressures.

Methanol as the thermodynamic hydrate inhibitor is much cheaper than ethylene glycol and triethylene glycol per unit volume and the use of glycols is usually justified on the basis of regeneration. Methanol has a lower viscosity and hence requires less pump horsepower for injection. Thermodynamic inhibitor, methanol, is volatile and some of it is lost into the gas phase, as opposed to the aqueous phase where it should be inhibiting hydrates. Corrosion problems may also result from methanol use because there may be dissolved oxygen in the methanol leading to corrosion in the pipe, and the presence of methanol can reduce the efficiency of some corrosion inhibitors. Overall, the major challenge with using thermodynamic inhibitors is the large attendant costs when they are required in high concentrations.

Laboratory and field tests since 1991 have shown the feasibility of replacing the classical inhibitors (methanol and ethylene glycol) with kinetic inhibitors. Although the kinetic inhibitors have limitations, they have been shown to be effective in preventing the formation of hydrate plugs in field situations. In many cases, there is an economic advantage to using the kinetic inhibitors. An analysis of the conditions in the production facilities must be done to ascertain the applicability of a kinetic inhibitor. The data and tests that are required to determine the applicability of a kinetic inhibitor are discussed. The application of kinetic inhibitors to flow lines in producing fields is presented.

This project aim to study the effectiveness of the Kinetic Hydrate Inhibitor (PVP and CMA) in order to be adapted into the oil and gas industry as it is proven that kinetic inhibitor can be applied economically to field-production system. So, saving in the range up to 50% of the chemical cost and reduced downtime can be realized in many cases.

1.3 Objectives

Objective of this project are:

- To study the effectiveness of Polyvinylpyrrolidone (PVP) and Calcium Magnesium Acetate (CMA) as Kinetic Hydrate Inhibitor (KHI).
- To study effective concentration of Polyvinylpyrrolidone (PVP) and Calcium Magnesium Acetate (CMA) as Kinetic Hydrate Inhibitor (KHI).

1.4 Scope of Study

The scope of the project is to perform experiment study which involves two chemicals which are Polyvinylpyrrolidone (PVP) and Calcium Magnesium Acetate (CMA) by using HP Micro DSC equipment. This experiment involves calculation associated with the different concentration of chemical used. The tested gases in this experiment are nitrogen and carbon dioxide. The result from this experiment will analyze so that it will reflect the effectiveness if the chemical being used. Comparison is being made between the two chemical used in orders to know which one is better as KHI.

1.5 The Relevancy of the Project

Hydrates formation always become a major concern in transportation of the crude oil using offshore pipelines. Among all alternative, hydrate inhibitor is the most economical and also effective to handle the problems. In the market, thermodynamics inhibitor already dominates the industry for a long time, but not for kinetic inhibitor. And among all these alternative, environmental issue is the concern. Using PVP and CMA as a kinetic hydrates inhibitor are still new for the industry and less paper are published regards with these topics.

1.5 Feasibility of the Project

This project is fully experimental based. In the time given, the project could be done. This project can be done within seven months given that everything goes fine. The objective can be achieved if the procedures are closely followed.

The study is feasible to be conducted after considering the following:

I. Sufficient budget allocation
II. PVP and CMA are readily available in the market
III. Carbon Dioxide gas are readily available in the laboratory
IV. Numerous related researches and article available for reference
V. A well-planned milestone has been set.

CHAPTER 2: LITERATURE REVIEW

2.1 Nature of Hydrate

Hydrates are crystalline compound formed in mixture of water and non- or low polar molecule (eg: methane, ethane, propane, carbon dioxide nitrogen and etc.) when subjected to appropriate pressure and temperature. This hydrogen bond creates a cage structure (known as cavities) and these cavities must be filled with guest molecule. In this case, it seems like the water is solidifying at temperature higher that the freezing point of water. The size and structure depends on the guest molecule. Currently, 3 structures of hydrates had been identified (structure I, II and H). The density of hydrates component is smaller than ice. ***Figure 1*** presents schematics of the three different structures (Sloan 1998).

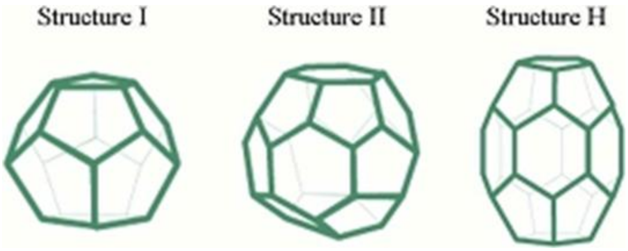


Figure 1 - Schematics of Structure I, II and H Gas Hydrates

Structure I hydrate contain 46 water molecules per 8 gas molecules giving a hydrate number of 5.75. The water molecules form two small dodecahedral voids and six large tetradecahedral voids. The sizes of the voids are relatively small meaning that the guest molecules are restricted in size to essential methane and ethane. Structure II hydrate contain 136 water molecules per 24 gas molecules giving a hydrate number of 5.67. The water molecules form 16 small dodecahedral voids and 8 large hexakaidecahedral voids. The larger voids are able to accommodate molecules including propane, isobutene, cyclopentane, benzene and others (Makagon, 1997 & Sloan, 1998).

Structure H hydrate were discovered recently (Ripmeester *et al.*1987) and contain 34 water molecules for every 6 gas molecules giving a hydrate number of 5.67. The structure has three cavity sizes with the largest cavity able to accommodate larger molecule than both sI and sII.

For stable hydrate crystals to form in oil and gas production systems, four essential elements must be present: a supply of hydrate forming guest molecules, access to a supply of water conditions of low temperature and high pressure [2]. In multiphase oil and gas production pipelines containing hydrocarbon gas and liquid phases together with a free water phase, hydrate form preferentially at the water-hydrocarbon interface having the highest availability of hydrate forming molecules. Thus, in gas-condensate-water, hydrate tends to form at the abundant gas-water interfaces, whereas in low GOR, gas-oil-water systems they tend to form at the oil-water interfaces.

Although in the case of gas-oil-water systems, the distribution of the oil and water phases (i.e. water-in-oil or oil-in-water dispersions) also plays a key role in determining which interfaces govern the formation of hydrates as does the gas-oil-ratio (GOR) which determines the extent of gas-water interfaces [3].

As shown in ***Figure 2***, the white region covers pressures and temperatures at which hydrates are set thermodynamically unstable and therefore 'hydrate free' as indicated. The region labeled 'hydrate risk' is where stable hydrate can exists, although in practice they may not form due to a failure to nucleate and or slow formation kinetics. In the 'hydrate zone' the degree of supercooling is sufficient such that hydrate form spontaneously [3].

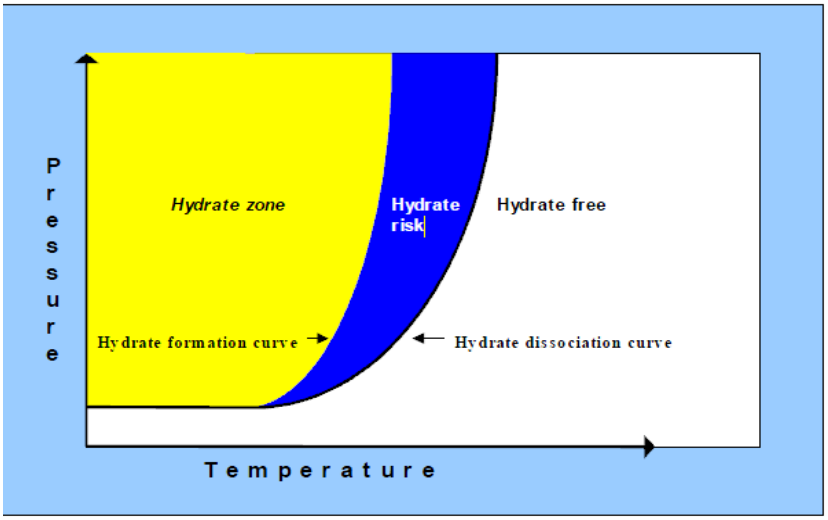


Figure 2 - Typical Hydrate Formation Diagram

In ***Figure 3***, typical experiment results (Edmonds et al. 1998) are shown that illustrate the metastable region which defines the extent of the hydrate risk zone. The experiment commences from point A, the fluids are cooled progressively to point B where the hydrate dissociation locus is traversed. The system then enters the metastable region where hydrates are thermodynamically stable but may or may not form depending on the kinetic considerations. The fluid are then cooled slowly to point c where hydrate are formed spontaneously and rapidly causing the system pressure to reduce (due to the abstraction of gas into the crystal structure) to point D. The system temperature is then increased slowly at almost isobaric conditions, until hydrate dissociation begins at point E. The system then follows an upwards trajectory as the temperature is increased (due to liberation of gas) until point B is reached once more when the hydrate dissociation curve is crossed at the 'thermodynamic point'.

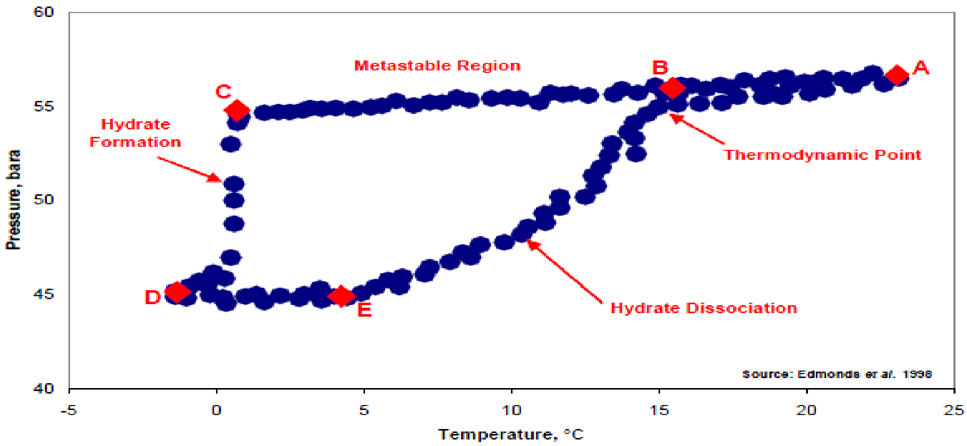
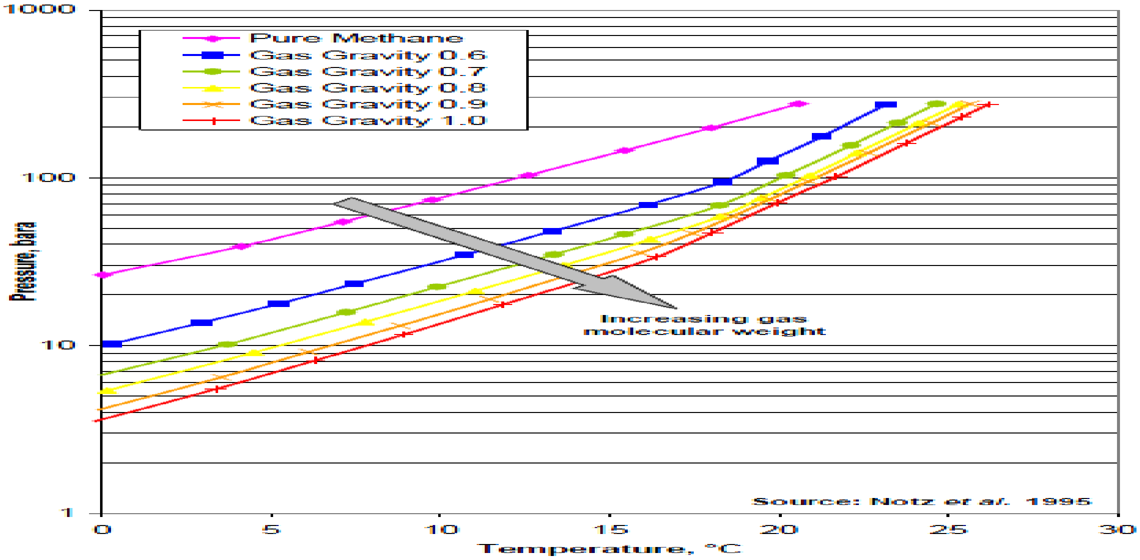


Figure 3 - Typical Experimental Hydrate Formation/ Dissociation Results

Reported by Katz (1945), the formation of hydrate is also dependent on the composition of the gas forming hydrate. ***Figure 4*** shows result that the hydrate dissociation curved is displaced towards lower pressures and higher temperatures as the gas gravity or molecular weight increases (Katz 1945). The effect on hydrate formation of adding an oil phase to a gas had been investigated where the addition of oil produced a beneficial reduction in the hydrate formation temperature (Becke *et al* 1992).This was explained as due to absorption of ethane and propane into the oil and a consequential reduction in the molecular weight of the gas; this occur with Katz's findings.



Source: Notz *et al.* 1995

Figure 4 - Effect of Gas Gravity on Hydrate Formation

Figure 5 show that the inclusion of the higher molecular weight sII formers shifts the stability curve towards lower pressures and higher temperature. The impact is only circa 1-2^{o}C for the case examined, but could be greater for different composition. This prediction report were done by Edmonds *et al* (1998) by using hydrate dissociation model (available in the physical properties prediction software *MULTIFLASH*) which demonstrate the effect of including higher molecular weight sII formers on the position of the sII hydrate stability boundary. In other words, this illustrates the effect of increasing gas molecular weight.

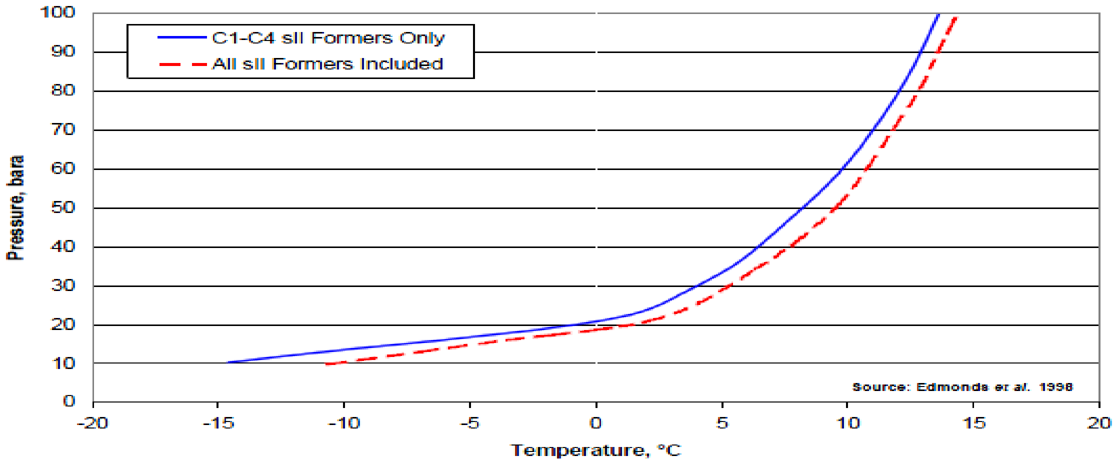


Figure 5 - Effect of sII Formers on sII Stability Boundary

2.2 Carbon Dioxide Clathrate

Carbon dioxide hydrate is a Type I gas clathrate (Sloan 1998). Clathrate is a snow like substance that can exist below 283K (10°C) at a range of pressures of carbon dioxide.

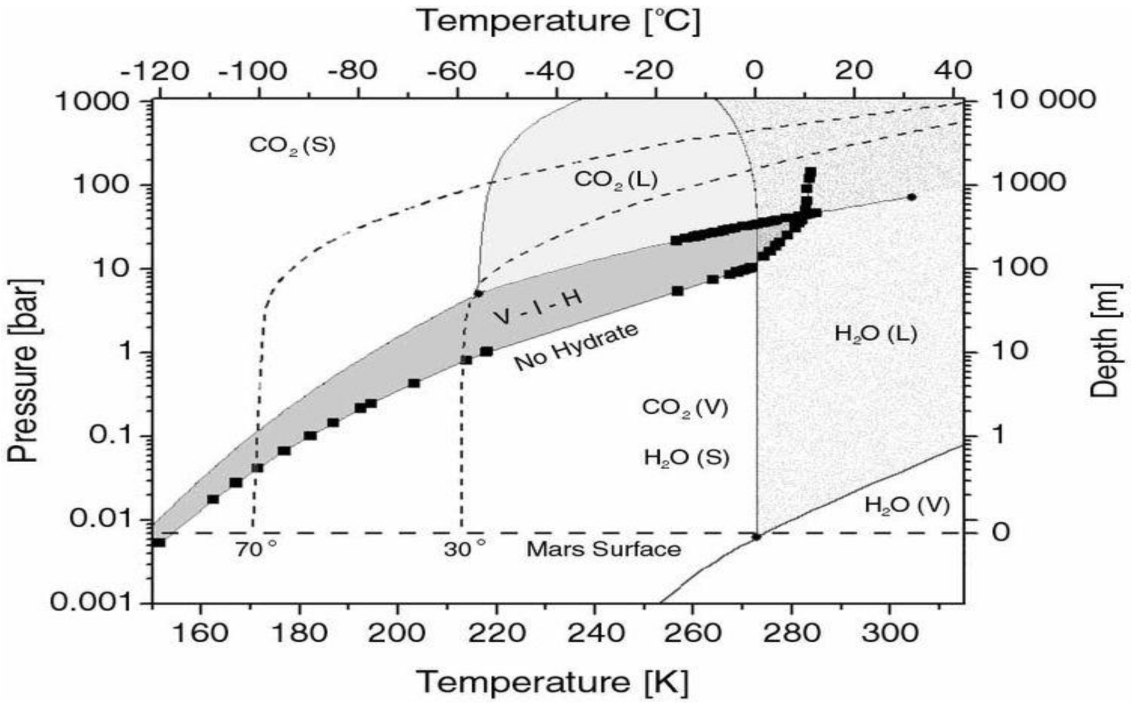


Figure 6 - CO2 Hydrate Phase Diagram

The hydrate structures are stable at different pressure-temperature conditions depending on the guest molecule. Here is given one Mars-related phase diagram of CO_2 hydrate, combined with those of pure CO_2 and water (Genov 2005). CO_2 hydrate has two quadruple points: (I-Lw-H-V) (T = 273.1 K; p = 12.56 bar or 1.256 MPa) and (Lw-H-V-LHC) (T = 283.0 K; p = 44.99 bar or 4.499 MPa) (Sloan, 1998). CO_2 itself has a triple point at T = 216.58 K and p = 5.185 bar (518.5 kPa) and a critical point at T = 304.2 K and p = 73.858 bar (7.3858 MPa). The dark gray region (V-I-H) represents the conditions at which CO_2 hydrate is stable together with gaseous CO_2 and water ice (below 273.15 K). On the horizontal axes the temperature is given in kelvins and degrees Celsius (bottom and top respectively). On the vertical ones are given the pressure (left) and the estimated depth in the Martian regolith (right). The horizontal dashed line at zero depth represents the average Martian surface conditions. The two bent dashed lines show two theoretical Martian geotherms after Stewart & Nimmo (2002) at 30° and 70° latitude.

2.3 Polyvinylpyrrolidone (PVP)

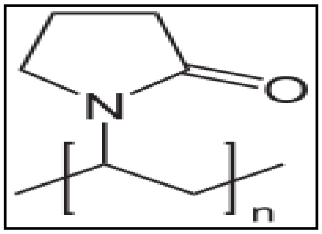


Figure 7 - Chemical Structure of PVP

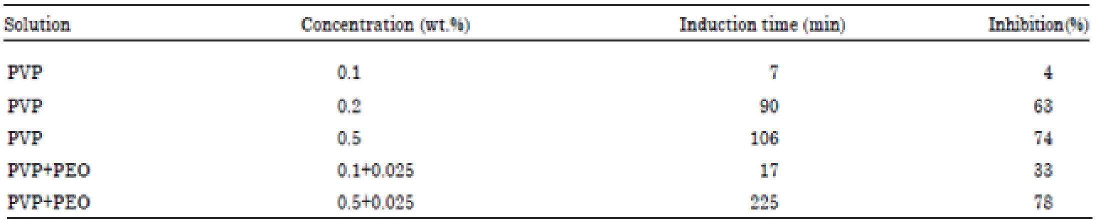
PVP, of which is also known as polyvinode, is a water-soluble polymer made from the monomer N-vinylpyrrolidone with molecular formula of $(C_6H_9NO)_n$.It is a unique polymer that offers a good initial tack, chemical and biological inertness and is very low in toxicity. The polymer powder is white to light yellow in colour and has a density of $1.2 g/cm^3$ at standard condition and widely used in pharmaceutical industry as binder and adhesive.

In 1995, an experiment was done and it was found out that inclusion of salts into aqueous PVP solution leads to decreasing of the theta temperature and intrinsic viscosity but this experiment was however conducted using inorganic salt thus said effect might be differ from test using tap water.

An experiment had been done by Mostafa Keshavarz Moraveji (2012) in order to study the effect of inhibitor (PVP) concentration on Methane hydrate formation process (on the percentage of inhibition and induction time). Hydrate nucleation also called the induction period is process where small hydrate crystals nuclei grow and disperse until they reach a critical size or radius for continuous growth (Bishnoi and Natarajan, 1996). The impact of Polyethylene Oxide (PEO) on the performance of kinetic inhibitor (PVP) was also demonstrated.

In polymeric inhibitors, an increasing in the inhibitor concentration increases induction time. As shown in ***Table 1*** induction time is around 106 min for 0.5 wt. % PVP solution.

Table 1 - Experiment conditions and consumed rate after 30 min of hydrate growth in the presence of inhibitors



Solution	Concentration (wt.%)	Induction time (min)	Inhibition(%)
PVP	0.1	7	4
PVP	0.2	90	63
PVP	0.5	106	74
PVP+PEO	0.1+0.025	17	33
PVP+PEO	0.5+0.025	225	78

Inclusion of polyethylene oxide (PEO) into a kinetic inhibitor solution was found to enhance the performance of the inhibitor. Polyethylene oxide is a commercially available high molecular weight polymer that is not a kinetic inhibitor by itself (Lee and Englezos, 2005). The enhanced inhibition effect of using this polymer on increasing time of methane hydrate formation for 0.1 and 0.5 wt.% solutions of PVP inhibitor can be seen in ***Table 1***.

Induction time for 0.1 wt.% PVP solution is 7 min and for 0.5 wt.% PVP solution 106 min. Increasing 0.025 wt.% of PEO increases these times to 17 and 225 min correspondingly that indicates the increase of efficiency of PVP kinetic inhibitors in the present of PEO polymer.

Figure 8 shows the methane mole consumed after 30 min of hydrate growth in different concentrations of PVP polymer inhibitor. By increasing PVP polymer concentration, mole consumed by methane hydrate has descending process and as a result the percent of inhibition increases. So that in a solution involving 0.5 wt.% PVP polymer we would have the maximum percent of hydrate inhibition which is 74%.

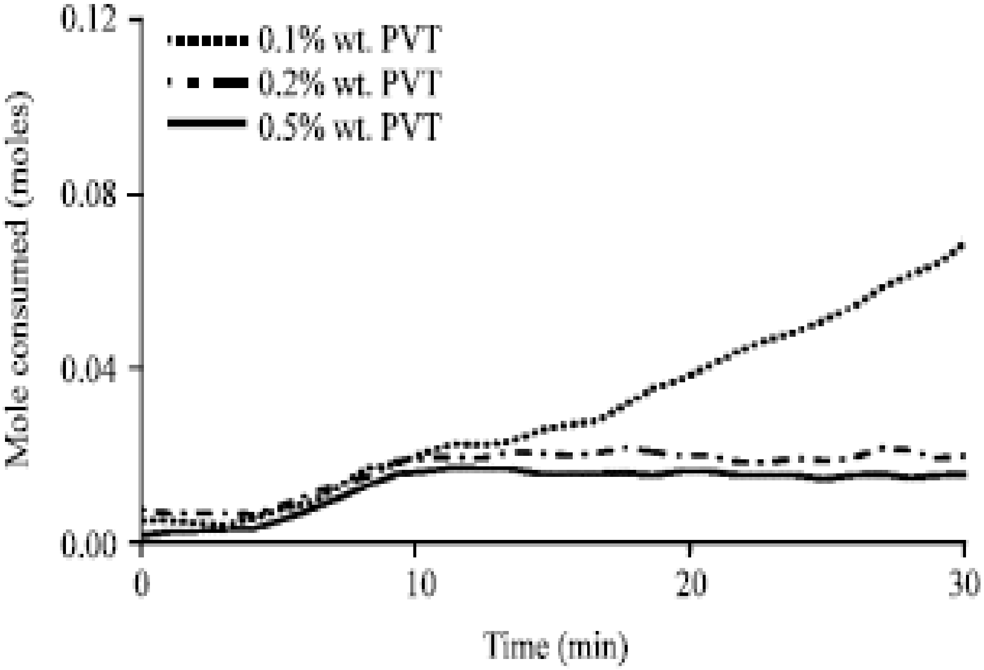


Figure 8 - Methane mole consumed after 30 min of hydrate formation with polymeric inhibitor at an initial temperature of 276.6K and pressure of 60 bar

In ***Figure 9***, methane hydrate inhibition percentage which increases with PVP polymer concentration is seen in the form of bar chart.

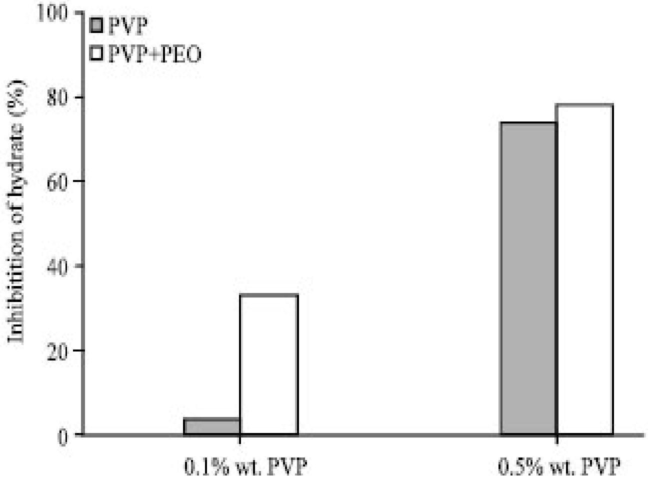


Figure 9 - Hydrate inhabitation percentage after 30 min of hydrate formation with different concentration of polymeric inhibitor and PEO at an initial temperature of 276.6 K and pressure of 60 bar

In ***Figure 10***, PEO effect on hydrate formation time can be seen, based on this figure, time of methane hydrate formation in the present of PVP inhibitor equals 188 min and with increasing PEO polymer this has increased to 335 min.

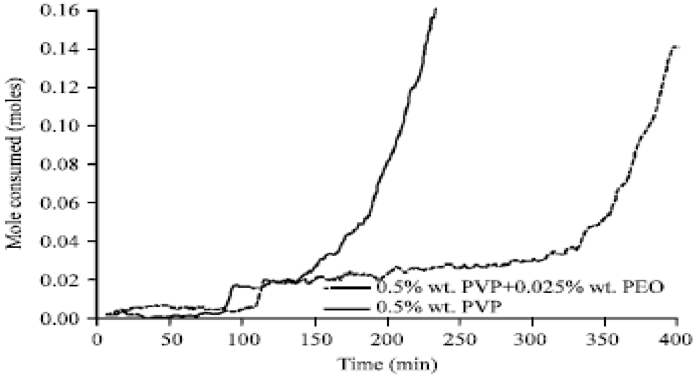


Figure 10 - Methane mole consumed after 30 min of hydrate formation with polymeric inhibitor and PEO at an initial temperature of 276.6 K and pressure of 60 bar

So PEO causes the increase of efficiency of kinetic and polymer inhibitors.

2.4 Calcium Magnesium Acetate (CMA)

CMA is a simple combination of dolomitic lime and acetic acid (a principalcomponent of vinegar) and is produced at Cryotech's manufacturing facility in Fort Madison, Iowa.There has long been a concern for damage to the environment andto structures like bridges and parking garages caused by the use ofchloride deicers. In the 1970's, the Federal Highway Administration(FHWA) identified calcium magnesium acetate as the only low-corrosionchemical alternative to road salt that also protected the environment.Years of research and field applications have proven CMA is no more corrosive than tap water and does not harm vegetation orreceiving waters.

CMA offer this advantages:

- Low Corrosion - About as corrosive as tap water
- Safe for Concrete - No more damage than from water
- Excellent Inhibitor - Reduces chloride corrosion
- Safe for the Environment - Low toxicity and biodegradable
- Residual Effect - Requires fewer applications
- Multi-Purpose - Use straight, with salt, with sand, or as a liquid

Recent study had been done by Saquib *et al* (2010) where synthetic sorbents of calcium magnesium acetate (CMA) with differing molar ratios of Ca/Mg were tested in a fluidized bed to determine their capacity to absorb CO_2 over several cycles of carbonation, via $CaO_{(s)} + CO_{2\ (g)} \rightarrow CaCO_{3(s)}$, and the reverse calcination. Their performances were compared, at 750°C, on the basis of moles of CO_2 absorbed per mole of CaO present in the sorbent, to those of a U.K. limestone and a dolomite when carbonated in a gas containing 15 mol % CO_2 and N_2 balance and calcined in pure N_2. Three of the CMA sorbents were also carbonated in gases containing 30 and 50 mol % CO_2 (N_2 balance). All experiments were at atmospheric pressure. It was found that, with a mole fraction of CO_2 of 15 mol % during carbonation, the dolomite and CMA 7:3 (7 mol of Ca to 3 mol of Mg) exhibited the highest uptake of CO_2 over the 10 cycles of the experiment. It was also found that these sorbents had the highest pore volume using the method of Barrett, Joyner, and Halenda (BJH), which measures the volume in pores <200 nm in diameter, confirming the theory that the fast stage of the carbonation reaction occurs predominantly in pores of this size range. Thus, the materials with the largest BJH volume were also those with the largest capacity to take up CO_2. The effect of increasing the concentration of CO_2 for carbonation was found to increase the uptake of CO_2 for each of the synthetic sorbents tested.

Figure 11 and ***Figure 12*** show the uptake percentage of CO_2 over 10 cycles experiment.

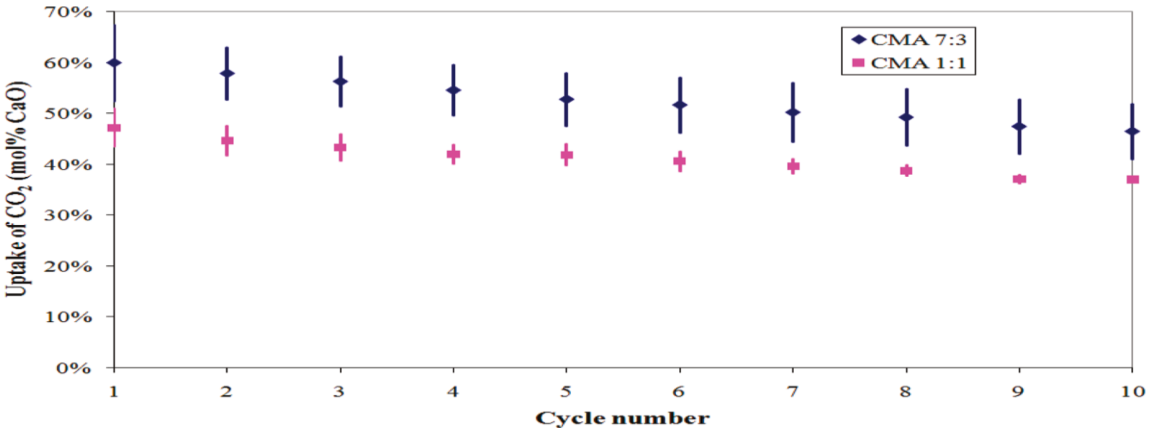


Figure 11 - Mean molar carrying capacity for CO2 per mole of CaO for CMA 7:3 and 1:1, carbonated in ~15 mol % CO2. T = 750°C

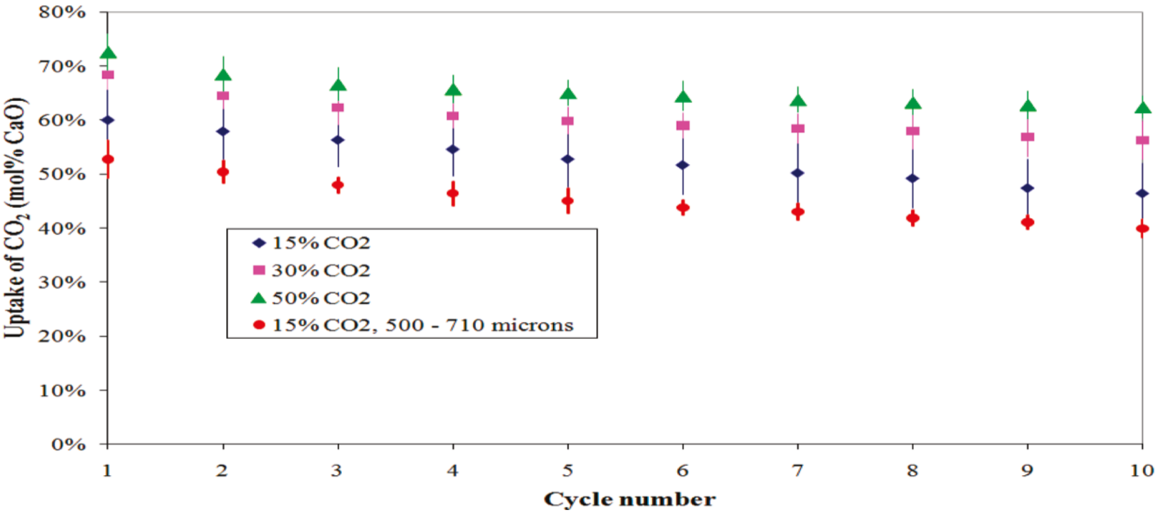
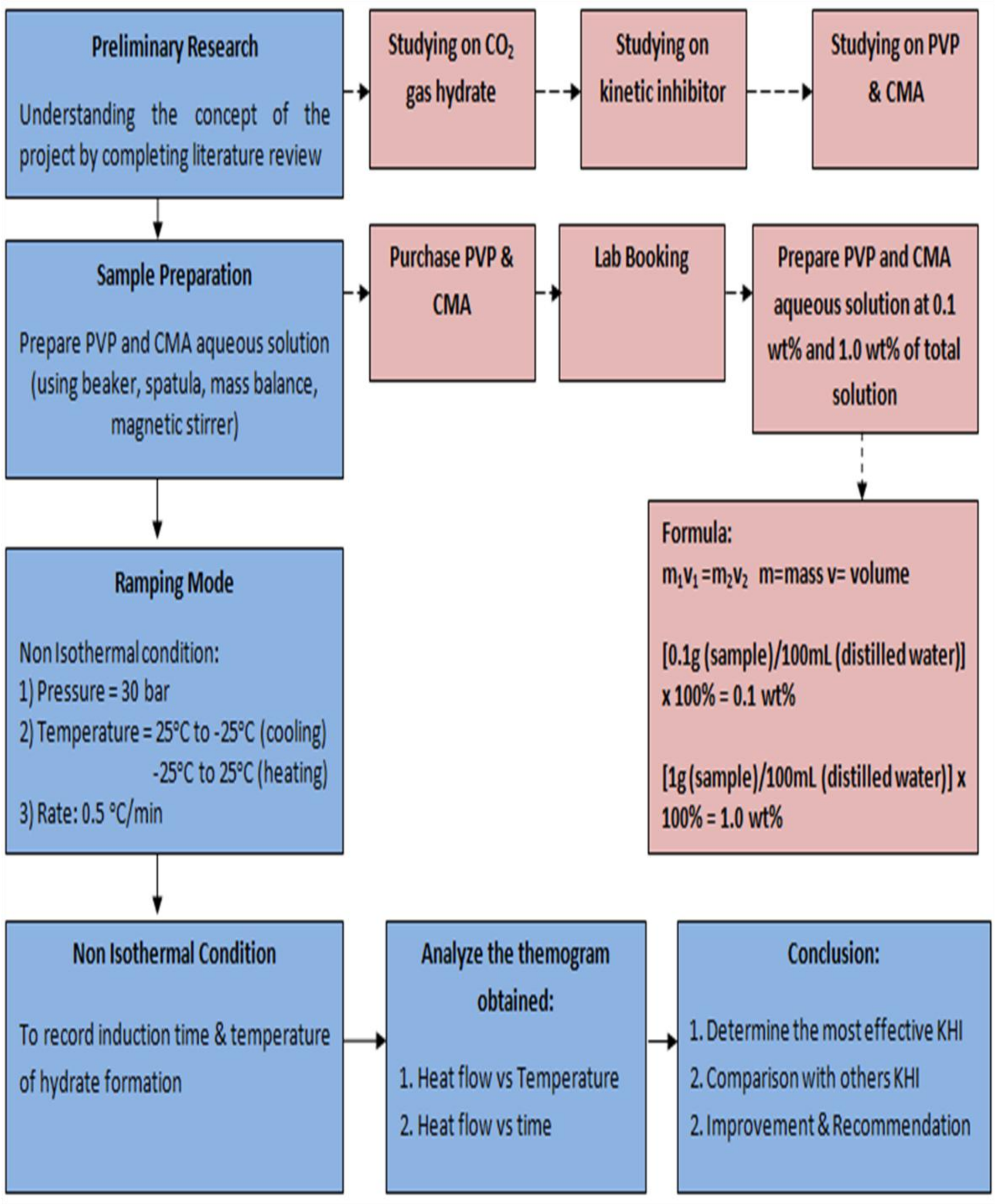


Figure 12 - Mean molar carrying capacity of CO2 per mole of CaO for CMA 7:3, carbonated in 15, 30, and 50 mol % CO2. T = 750°C

From the figures above, it clearly shows the ability of the Calcium Magnesium Acetate (CMA) to capture CO_2 gas. This characteristic will somehow contribute in interrupting one of the elements that lead to hydrate formation.

CHAPTER 3: METHODOLOGY

3.1 Research Methodology



3.2 Project Activities

Title Selection

Select of the most appropriate final year project title

Preliminary Research

Understand fundamental theories and concept, performing literature review and tools identification

Hardware/ Experimental Setup

Selection and design of experiment apparatus, material and procedures

Experiment Work

Conduct experiment and collect results

Analysis of Result

Analyze the findings, relate with theoretical facts and correlate with other researcher finding (if any)

Discussion of Analysis

Discuss the findings from the result obtained and make a conclusion out of the study, determine if objective has been meet

Report Writing

Compilation of all research findings, literature reviews, experimental works and outcomes into a final report

3.3 Experimental Procedure

Table 2: Experiment Temperature Program

No.	**Start Temp (^OC)**	**End temp (^OC)**	**Heating/Cooling rate (^OC/min)**	**Duration (min)**	**Gas use**	**Remarks**
1	**25**	**25**	**-**	**10**	**CO_2**	**stabilization**
2	**25**	**-25**	**0.5**	**60**	**CO_2**	**cooling**
3	**-25**	**-25**	**-**	**10**	**CO_2**	**stabilization**
4	**-25**	**25**	**0.5**	**60**	**CO_2**	**heating**
5	**25**	**25**	**-**	**10**	**CO_2**	**stabilization**

3.4 Key Milestones

3.4.1 Key Milestones for FYP 1

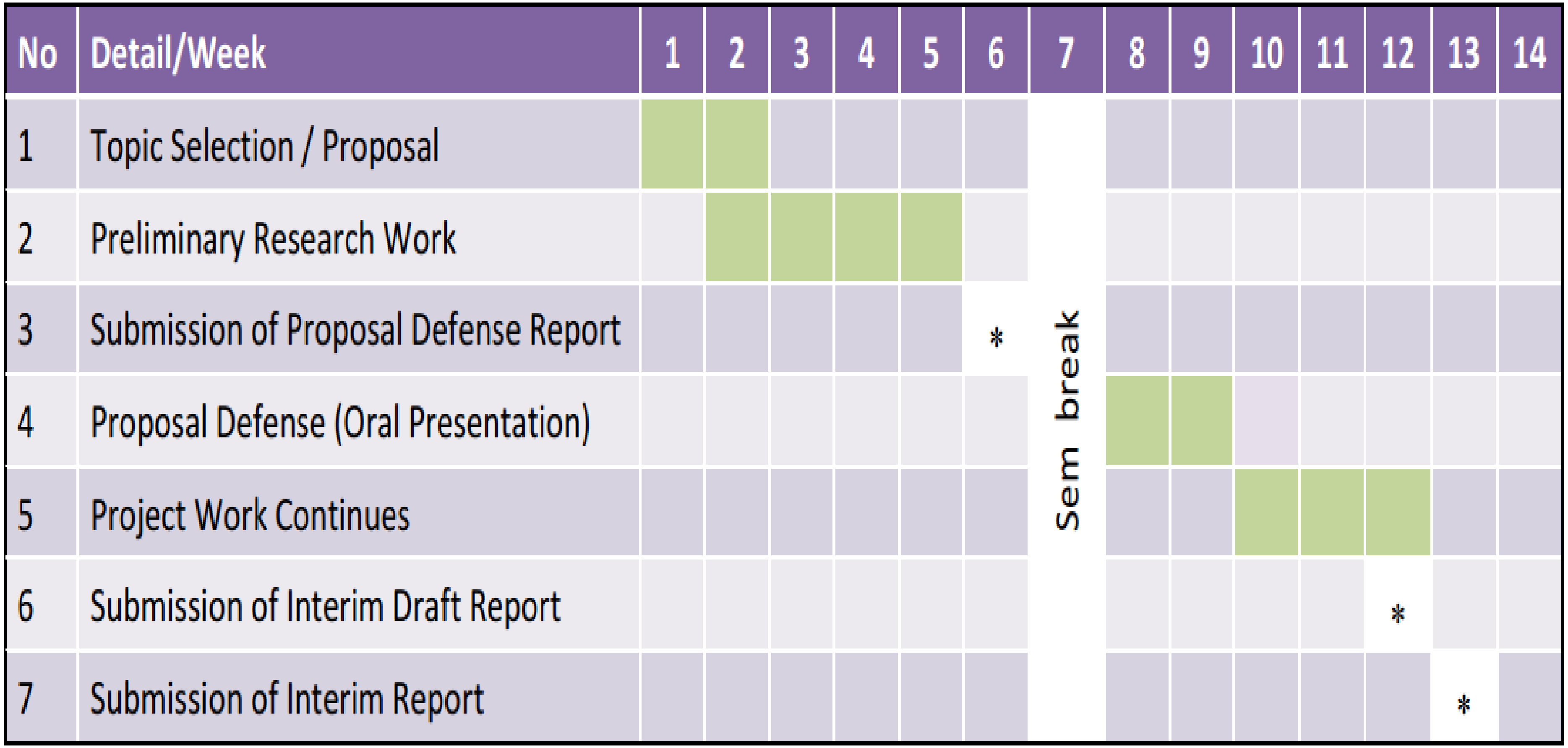
Milestone	Planned Timescale	Progress
Selection of FYP topic	Week 2	Completed
Prelim research work	Week 2 - Week 5	Completed
Submit Proposal Defense Report	Week 4	Completed
Project Work (Literature Review)	Week 2 - Week 8	Completed
Proposal Defence Oral Presentation	Week 8 - Week 9	Completed
Project Work continues	Week 8 - Week 12	Completed
Fix Methodology	Week 9	Completed
Start Pre-Lab Preparation	Week 10 - Week 14	Completed
Submit Interim Report Final Draft	Week 12	Completed

3.4.2 Key Milestones for FYP 2

Milestone	Planned Timescale	Progress
Briefing & Update on students progress	Week 2	Completed
Project Work continues	Week 1 - Week 8	Completed
Submit Progress Report	7-11-2012	Completed
Project Work continues	Week 9 - Week 10	Completed
Pre-EDX (Seminar/Poster Exhibition)	Week 11	Completed
Submit Final Report (CD & soft bound)	Week 11	Completed
Final Oral Presentation	Week 14	
Submit Dissertation (hard bound)	Week 16	

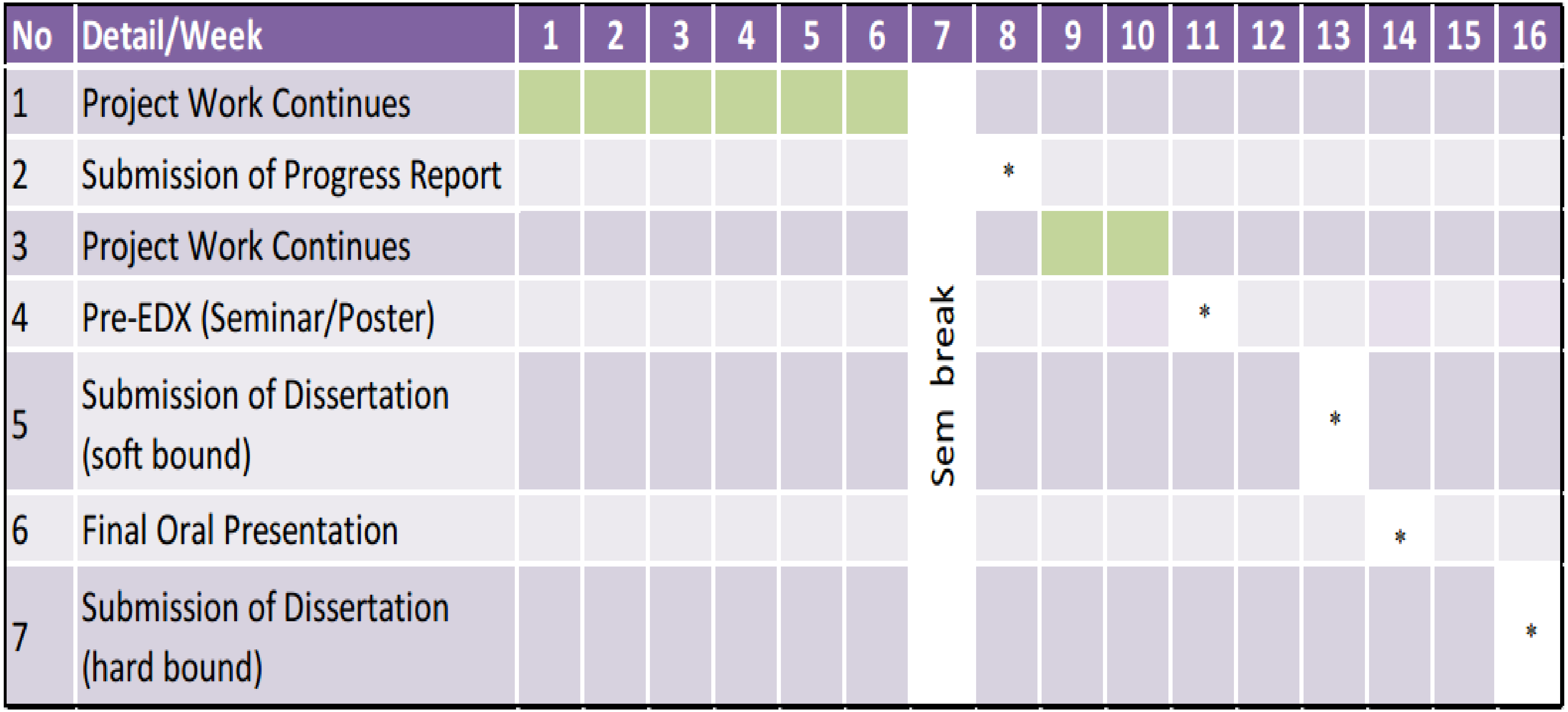
3.5 Gantt Chart

3.5.1 Gantt Chart for FYP 1



No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Topic Selection / Proposal	🟩	🟩					Sem break							
2	Preliminary Research Work		🟩	🟩	🟩	🟩									
3	Submission of Proposal Defense Report						*								
4	Proposal Defense (Oral Presentation)								🟩	🟩					
5	Project Work Continues										🟩	🟩	🟩		
6	Submission of Interim Draft Report												*		
7	Submission of Interim Report													*	

3.5.2 Gantt Chart for FYP 2



No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	Project Work Continues	🟩	🟩	🟩	🟩	🟩	🟩	Sem break									
2	Submission of Progress Report								*								
3	Project Work Continues									🟩	🟩						
4	Pre-EDX (Seminar/Poster)											*					
5	Submission of Dissertation (soft bound)													*			
6	Final Oral Presentation														*		
7	Submission of Dissertation (hard bound)																*

3.6 Tools

3.6.1 HP Micro-DSC

All the studies in this project were performed using the laboratory equipment which is HP Micro-DSC. This equipment is very user friendly and easy to operate. It can be efficiently used for thermodynamic and kinetic studies of the formation of high-pressure gas hydrate in complex fluids, suspensions and emulsion. It offers the same level of precision as classical PVT technique while much less time-consuming. In comparison, HP Micro-DSC is better because classical equipment (DSC) is limited by the pressure admitted in the vessel. It is difficult to exceed a working pressure of 100 bar.

Figure 13 below shows the internal view of equipment:

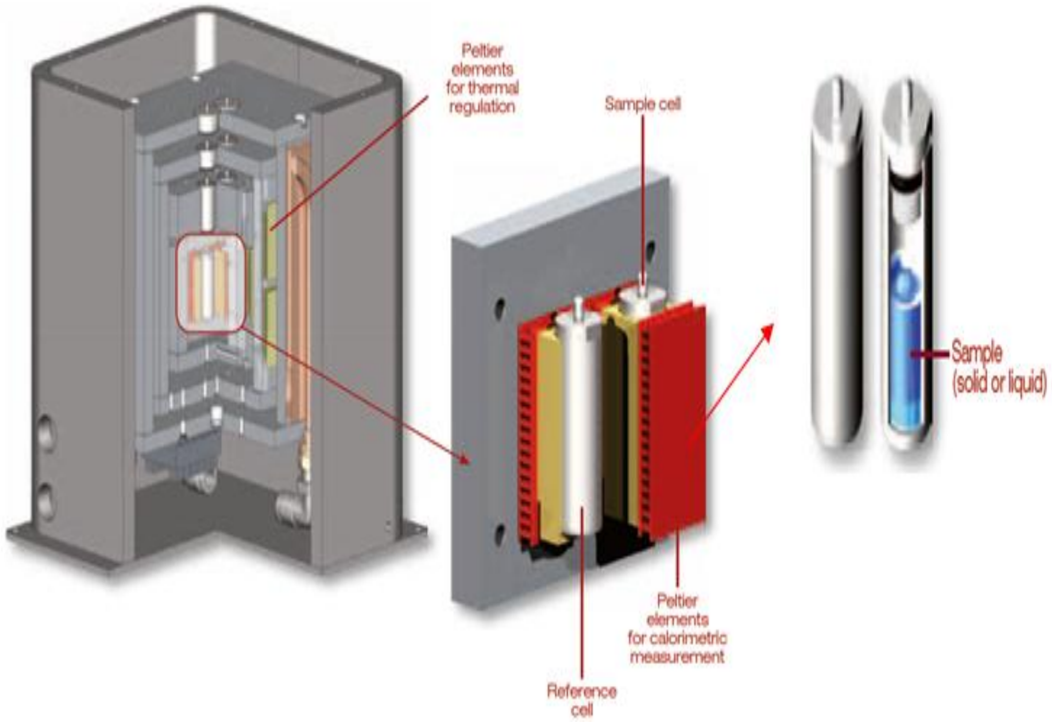


Figure 13 - Internal view of HP Micro DSC

The calorimetric furnace is made of a double aluminum wall. The experimental and reference vessels are inserted into the furnace by two cylindrical cavities. The main advantage is related to the system cooling, which is provided by Peltier effect. This system allows avoiding the handling of refrigerating fluids such as liquid nitrogen. The minimum temperature that can be reached is about -45^{o}C and the maximum temperature is 120^{o}C [20]. Heat flow measurement is based on the Calvet principle. The fluxmeters and ensure a high sensitivity and excellent level of precision to the DSC calorimeter.

This HP Micro-DSC has vessels that able to support very high pressure up to 400 bar were specially designed. They are made of alloy Hastelloy C276, which allows the analysis of corrosive fluids such as drilling fluids. The maximum working volume is 0.5mL. The screwed top is equipped with a doughnut ring coupled to an anti extrusion ring. It is welded to a thermal line. The whole system can be connected with gas by high-pressure L-curved joint. The high-pressure vessels can be re-used after a suitable cleaning.

Figure 14 below shows the specific high-pressure vessel:

Figure 14 - Specific high-pressure vessel

High-pressure vessels required a very careful handling. The high sensitivity of HP Micro-DSC calorimeter requires a meticulous cleaning of vessels between each analysis, before and after filling with sample. Humidity or finger trace on the walls or in the sealing system can lead to thermal signals of interference during the analysis.

For the case of this project experiment, pipette was used as a medium to transfer the sample solution into the vessel. The vessel has to be weight before and after filling, in order to precisely determine the mass of sample to be analyzed. The reference vessel can be empty or filled with inert material in order to compensate for the difference in heat capacity between the two vessels. The inert material can be alumina (for powder) or silicone oil (for liquid). In this project, the reference vessel is kept empty for all analysis.

Figure 15 below shows the schematic diagram of HP Micro-DSC representing the experimental setup for this project:

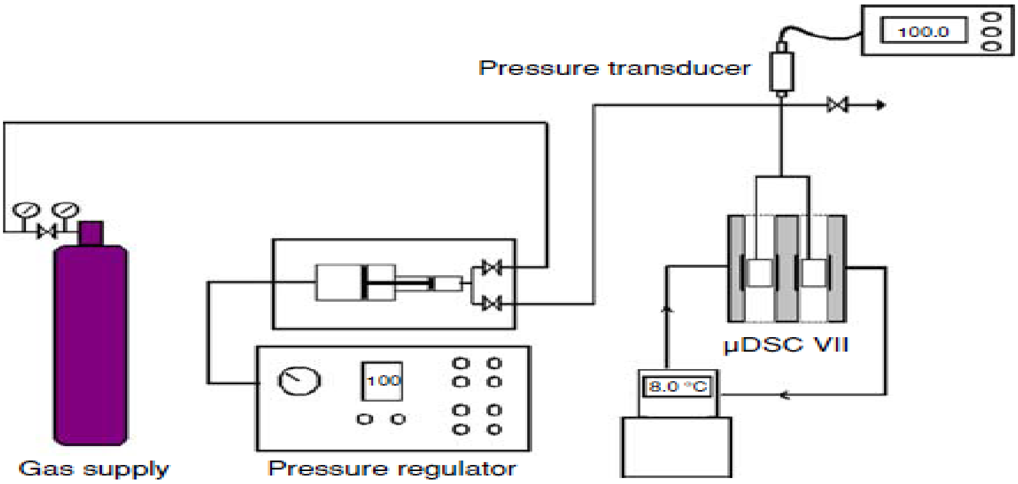


Figure 15 - HP Micro-DSC schematic diagram

The experiment was run under temperature ramping mode (non-isothermal condition). Description of high pressure experimental setup with HP Micro-DSC is as above (***Figure 15***). CO_2 gas was supply from the storage tank to the pressure regulator through small tubing. The pressure will then being regulated until 30 bar. After reaching that pressure, the pressure is kept constant. Before running the experiment, the sample prepared was weighted using the electronic mass balance around 60 mg. Then it will be injected into the sample vessel attached to high pressure vessel by using pipette. After that, the vessel was being fit into the cell cavity available at the main body.

Then, the experiment was run once the “start” button was clicked using the software in the personal computer. The experiment was kept running following the setting that being set initially.

As the experiment ended, the thermogram graph was produced [Heatflow (mW) vs Time (min)] & [Heatflow (mW) vs Temperature (^{o}C)]. Analysis of the graph obtained will be further discussed in result & discussion part.

Table 3 below represents the summary of the equipment specification:

Table 3: HP Micro-DSC specification

Temperature range	-45^{o}C to 120 ^{o}C Cooling under 0 ^{o}C requires the use of an auxiliary thermostat
Programmable temperature scanning rate (heating and cooling)	0.001 to 2 ^{o}C.min-1
RMS Noise	0.4 μW
Resolution	0.02 μW/ 0.002 μW
Cells	1 ml, made of Hastelloy C- Removable Batch, mixing batch, ampoule and high pressure
Pressure (measured & controlled)	400 bar / 5899 psi or 1000 bar/ 14600 psi requires the use of high pressure cells and gas panel
Weight	37.4 kg (82.5 lbs)
Dimensions	40 /53/58 cm (15.7/20.922.8 in)
Power requirements	230 V/ 50/60 Hz

3.6.2 Materials

CMA and was purchase from Cyotech Technology with a purity of 99%. PVP is provided by the chemical University Teknologi Petronas laboratory. Both chemical were then diluted in distilled water. Two concentrations which are 0.1 wt% and 1.0 wt% were to be produced from the dilution. Below are the formula used:

$$M_1V_1=M_2V_2$$

M= mass V=volume

For 0.1 wt% sample preparation, formula below was used:

$$\frac{0.1\text{g of sample}}{100\text{mL of distilled water}} \text{ x } 100\% = 0.1 \text{ wt}\%$$

For 1.0 wt% sample preparation, formula below was used:

$$\frac{1.0\text{g of sample}}{100\text{mL of distilled water}} \text{ x } 100\% = 1.0 \text{ wt}\%$$

Figure 16 & ***Figure 17*** shows the overview of CMA and PVP respectively

Figure 16 - Calcium Magnesium Acetate (CMA)

Figure 17 - Polyvinylpyrrolidone (PVP)

For sample preparation, several laboratory apparatus had been used:

- Mass balance (***Figure 18***)
- 100 mL beaker (***Figure 19***)
- Magnetic stirrer (***Figure 19***)
- Spatula (***Figure 20***)

Figure 18 - Mass Balance

Figure 19 - Magnetic Stirrer & Beaker 100 mL

Figure 20 - Spatula

CHAPTER 4: RESULT AND DISCUSSION

4.1 Result

After conducting several runs of experiment, below are the result produced:

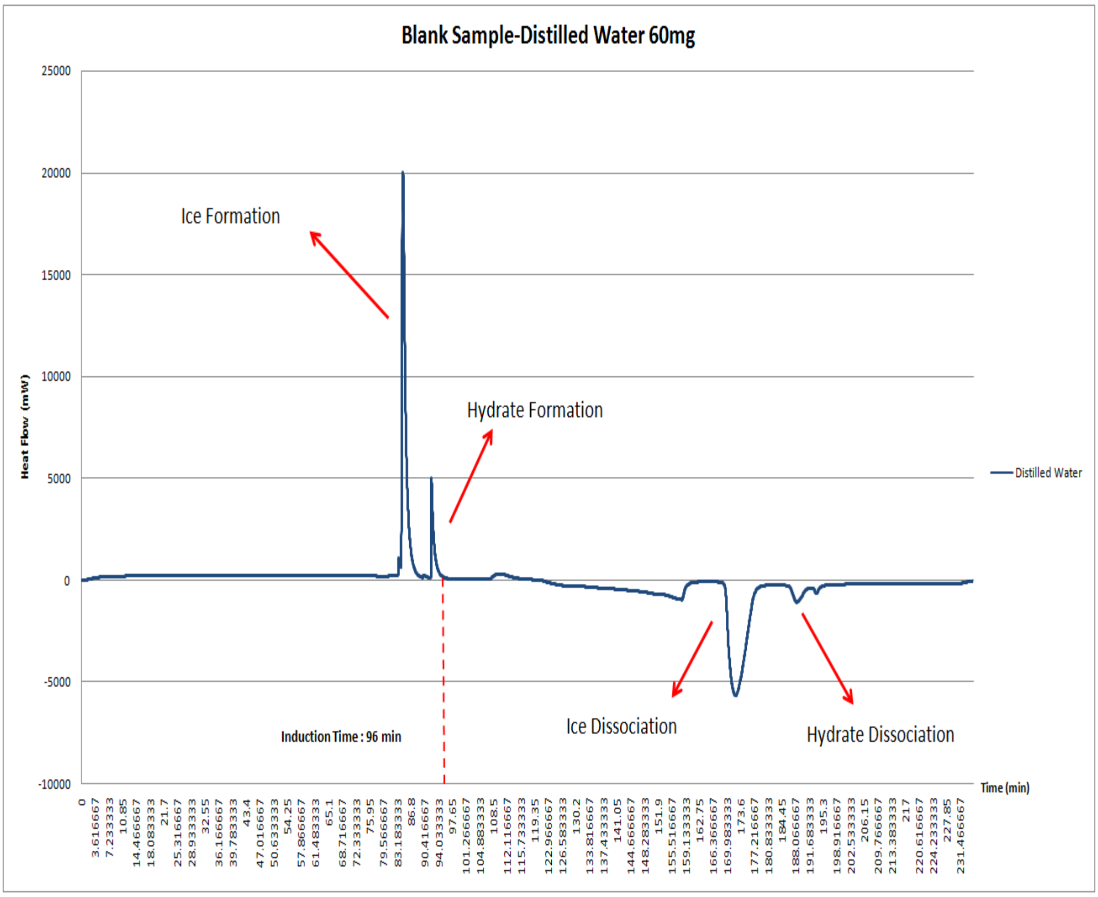


Figure 21 - Distilled water thermogram

Figure 21 above show the thermogram for distilled water. 60 mg of distilled water had been used as blank sample in this project. The first formation peak indicates the ice formation while the second peak is the hydrate formation. Both peak are actually undergoes **exothermic** reaction. In thermodynamics, the term **exothermic** describes a process or reaction that releases energy from the system, usually in the form of heat. For dissociation peak, they undergoes vice versa reaction which is **endothermic** reaction. In thermodynamics, the word **endothermic** describes a process or reaction in which the system absorbs energy from its surroundings in the form of heat.

Differentiating hydrate exotherms from ice exotherms is relatively straightforward. Hydrate formation from an immiscible guest requires contact between the water and the guest phase, in this case the vapor phase. A thin hydrate film typically forms at an interface. However, water can convert entirely to ice. Hence ice phase fraction should be much greater than that of the hydrate when forms from a gas phase guest. Due to the similar latent heats of formation, the integrated area of the hydrate exotherm is expected to be much smaller than that for the ice exotherm [21].

The main concern of this project is actually to determine the induction time of the hydrate formation. Induction time is the amount of time where the hydrate has completely formed and completely consumes all the gas needed to form stable hydrate. In the above case, the induction time for distilled water is 96 minutes. This means that the hydrate is completely formed at 96 minutes. The induction time for this distilled water will be used as a reference time for all the analysis. A delay of induction time would be expected when solution of inhibitors is used. If the inhibitor results in much longer induction time, this mean the inhibitor give a positive result and have a potential to be kinetic hydrate inhibitor.

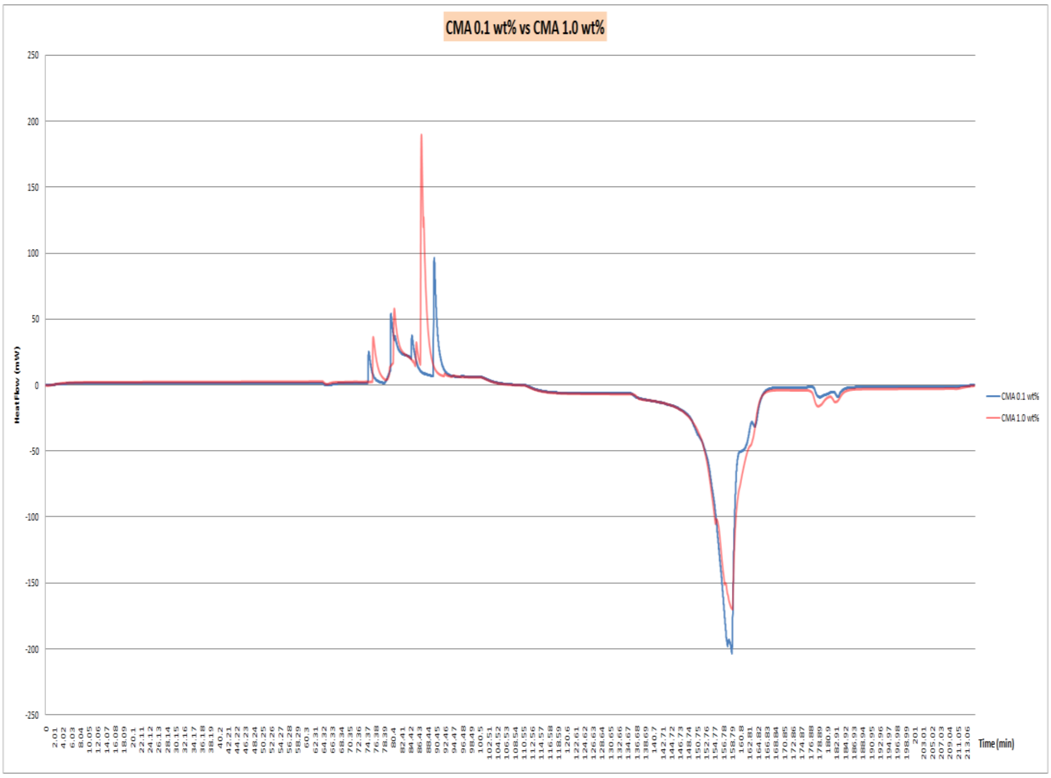


Figure 22 - Combination of CMA 0.1 wt% and CMA 1.0 wt % thermogram

Figure 22 above show the thermogram of CMA 0.1 wt% and CMA 1.0 wt %. Both of the graphs have been combined in order to ease the analysis process. From the graph, hydrate induction time can be observes and comparison can be made by referring to the x-axis which represent the time (min). CMA 0.1 wt% is represented by the red line while CMA 1.0 wt% is represented by blue line. From above graph, it shows that the induction time for CMA 0.1 wt% is **110 minutes** while for CMA 1.0 wt % is **104 minutes**. So this mean that CMA 0.1 wt% is more effective compare to CMA 1.0 wt% in delaying the hydrate induction time by 6 minutes difference.

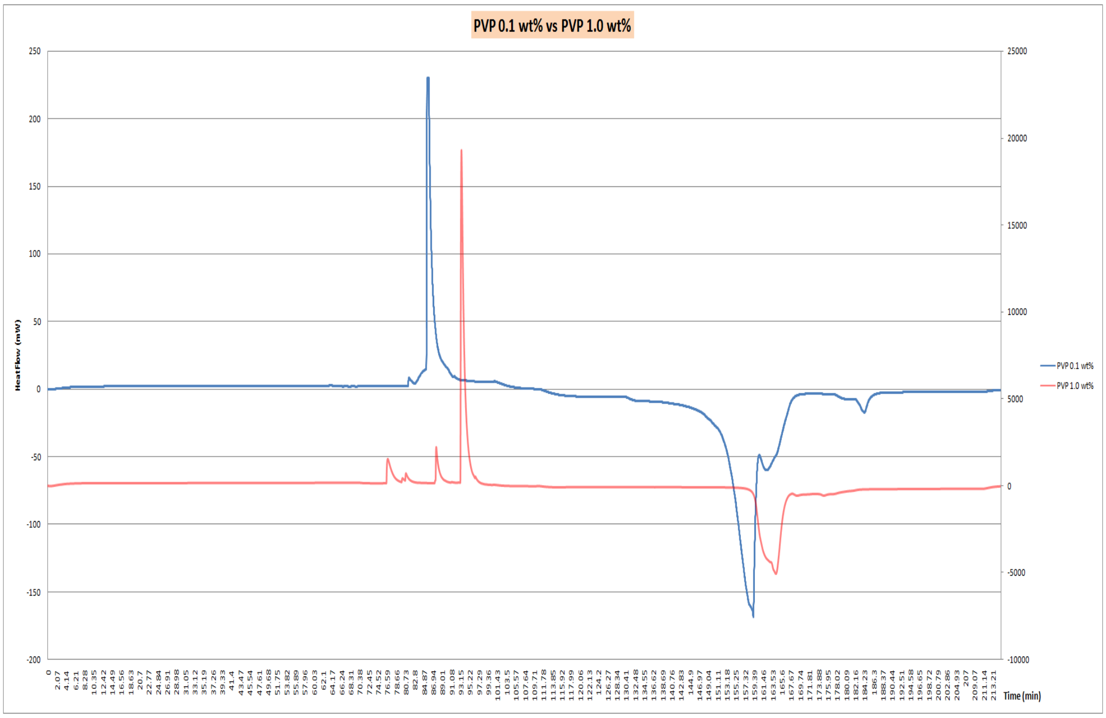


Figure 23 - Combination of PVP 0.1 wt% and PVP 1.0 wt% thermogram

Figure 23 above show the thermogram of PVP 0.1 wt% and PVP 1.0 wt %. Both of the graphs have been combined in order to ease the analysis process. PVP 0.1 wt% is represented by the red line while PVP 1.0 wt% is represented by blue line. From above graph, it shows that the induction time for PVP 0.1 wt% is **92 minutes** while for PVP 1.0 wt % is **98 minutes**. So this mean that PVP 1.0 wt% is more effective compare to PVP 0.1 wt% in delaying the hydrate induction time by 6 minutes difference.

For further analysis, those result had been compare to PVP+PEO (0.1 wt% and 1.0 wt %) result. PEO is actually stand for Poly(ethylene oxide) which act as additive in order to enhance the effectiveness of PVP in delaying the hydrate formation. The result for PVP+PEO (0.1 wt% and 1.0 wt %) was actually obtained from other FYP student whom also doing research on flow assurance.

Table 4 below show the summary of the induction time for the entire samples tested:

Table 4: Induction Time Summary

Sample	Concentration (wt%)	Hydrate Induction Time (min)
Distilled water	-	96
CMA	0.1	110
	1.0	104
PVP	0.1	92
	1.0	98
PVP + PEO	0.1	99
	1.0	103

Figure 24 below shows the bar chart produce from the data in ***Table 4***:

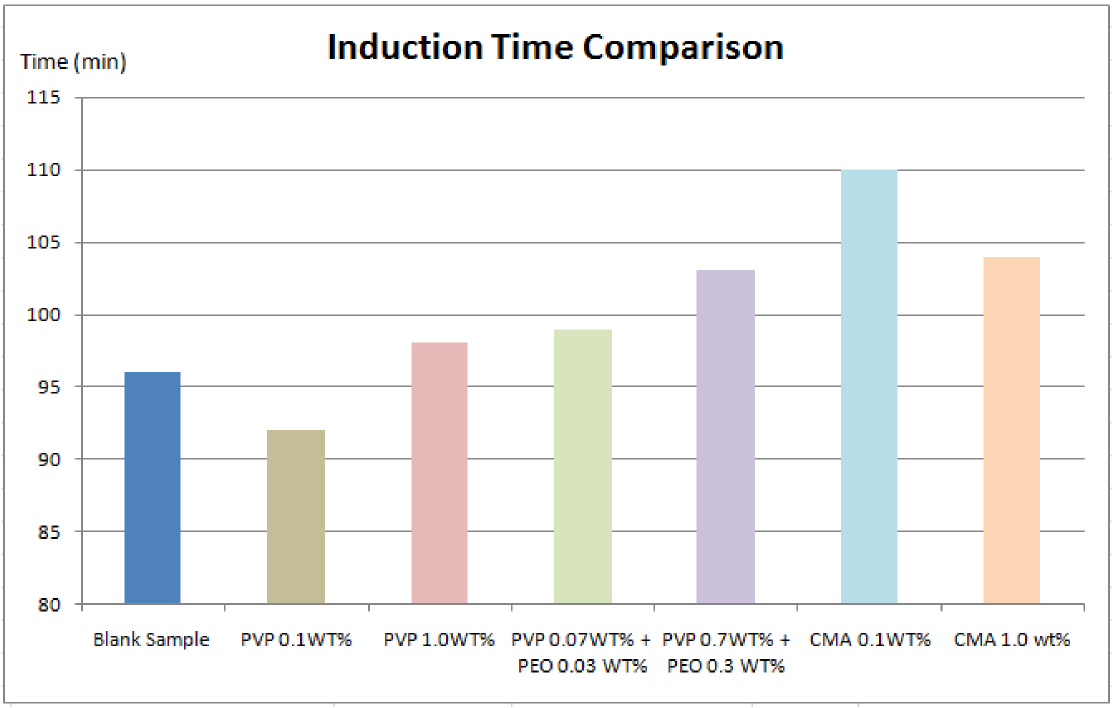


Figure 24 - Induction Time Comparison

4.2 Discussions

- From the bar chart, the most effective KHI are:

  CMA 0.1 wt% > CMA 1.0 wt% > PVP 0.7 wt% + PEO 0.3 wt% > PVP 0.07 wt% + PEO 0.03 wt% > PVP 1.0 wt% > PVP 0.1 wt%

- For PVP, the higher the concentration use, the longer the time delay for the hydrate induction time.
- Additive (PEO) thus increases the effectiveness of PVP by increasing the hydrate induction time.
- PVP at 0.1 wt% is not effective.
- For CMA, it is more effective in lower concentration (0.1 wt%) compare to higher concentration (1.0 wt%)

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The first objective this project is to study the effectiveness of PVP and CMA as KHI is also relevant and can be achieved. To study the effectiveness of these two chemical, kinetic experiment will be conducted by using HP Micro DSC equipment. This equipment is set to run at 30 bar and running in temperature ramping mode.

The experiment start with cooling process starting from 25 ^{o}C to -25 ^{o}C and then change to heating process starting from -25 ^{o}C to 25 ^{o}C. From this, graph will be created and onset temperature of hydrate formation and dissociation can be observe and further analyze. In this experiment, distilled water will be selected as “blank” sample. The result from this blank sample will be compared to PVP and CMA sample result. A delay of onset hydrate formation will be the expected result. CMA result will be compared to PVP result in order to study its effectiveness as KHI. Effectiveness of these both sample will be studied in term of induction time in different concentration of inhibitors sample.

The second objectives of this project which are to study the effective concentration of PVP and CMA as KHI is relevant and can be achieve. This is done by preparing different sets of solution concentration which are 0.1 wt% and 1.0 wt%. Comparison can be made by observing the induction time of both concentrations. It is not necessary that the higher the concentration, the more effective it will be. Sometimes, the inhibitor work very well in lower concentration. This difference is due to the characteristic of the inhibitor itself. Different inhibitors exhibit different characteristics. In this project, PVP is effective in higher concentration while CMA is effective in lower concentration.

So, throughout the experiment, it is concluded that PVP and CMA thus have potential to be effective KHI. Besides that, concept of kinetic inhibitor as low-dosage inhibitor was proven because less concentration of sample (0.1 wt% & 1.0 wt%) tested prove to be still effective in delaying hydrate induction time.

5.2 Recommendations

1. Continue the research with the Isotherms experiments in order to really prove the effectiveness of sample tested. (Isotherms mode is actually when the temperature is kept constant for certain period of time).

2. The ramped mode experiments can be test with 2-3 runs to find the optimum results.

3. Use more concentration of each sample tested such as:

   - O.3 wt%
   - 0.5 wt%
   - 0.7 wt%
   - 1.5 wt%
   - 2.0 wt%

4. Run the experiment by using introducing others hydrate formers instead of just CO_2 such as:

   - Ethane
   - Methane
   - Butane
   - Propane
   - Nitrogen
   - Hydrogen Sulphide

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Appendix I

Calcium Magnesium Acetate (CMA) MSDS

CRYOTECH CMA®
MATERIAL SAFETY DATA SHEET

1. PRODUCT NAME & DESCRIPTION

CRYOTECH CMA® Solid Commercial Deicer

MANUFACTURED AND SUPPLIED IN THE USA BY:
Cryotech Deicing Technology
6103 Orthoway
Fort Madison, IA 52627
United States

CRYOTECH CONTACT INFORMATION:
Telephone: (800)346-7237
FAX: (319)372-2662
email: deicers@cryotech.com
website: http://www.cryotech.com

2. CHEMICAL COMPOSITION

The percent compositions are given to allow for the various ranges of the components present in the whole product and may not equal 100%.

PERCENT	COMPONENT	CAS#
100%	Cryotech CMA® Solid Commercial Deicer	
CONTAINING		
96%	Hydrated Calcium Magnesium and other acetates	76123-46-1
<4.0%	Water-insoluble material	

CAS - Chemical Abstract Service Number

3. HAZARD IDENTIFICATION
(also see Sections 11 and 12)

CAUTION! - MAY CAUSE EYE IRRITATION

EYE CONTACT:
This substance is not expected to cause prolonged or significant eye irritation.
SKIN IRRITATION:
This substance is not expected to cause prolonged or significant skin irritation.
DERMAL TOXICITY:
If absorbed through the skin, this substance is considered practically non-toxic to internal organs.
RESPIRATORY/INHALATION:
If inhaled, this substance is considered practically non-toxic to internal organs. Dust, in high concentration, may cause irritation of eyes, nose and throat.
INGESTION:
If swallowed, this substance is considered practically non-toxic to internal organs.
OCCUPATIONAL EXPOSURE LIMITS:
None Identified

4. FIRST AID MEASURES

Chemical Emergency: Spill, leak, fire, or accident call
Chemtrec day or night (800)424-9300;
Outside continental USA call (703)527-3887

EYE CONTACT:
No first aid procedures are required. However, as a precaution flush eyes with fresh water for 15 minutes. Remove contact lenses if worn.
SKIN CONTACT:
No first aid procedures are required. As a precaution, wash skin thoroughly with soap and water. Remove and wash contaminated clothing.
INHALATION:
Since this material is not expected to be an immediate inhalation problem, no first aid procedures are required.
INGESTION:
If swallowed, give water or milk to drink and telephone for medical advice. Consult medical personnel before inducing vomiting. If medical advice cannot be obtained, then take the person and product container to the nearest medical emergency treatment center or hospital.

5. FIRE FIGHTING MEASURES

FLASH POINT:
Not Applicable
AUTO IGNITION:
No data available
FLAMMABILITY LIMITS (% by volume in air):
Lower: No data available
Upper: No data available
Non-flammable
EXTINGUISHING MEDIA:
Use extinguishing media appropriate for surrounding fire.
FIRE FIGHTING PROCEDURES:
Fire fighters should wear proper protective equipment, self-contained breathing apparatus with full face piece operated in positive pressure mode.
COMBUSTION PRODUCTS:
Normal combustion forms carbon dioxide and water.
NFPA RATINGS:
Health 1; Flammability 0; Reactivity 0; Special NDA:
(Least - 0, Slight - 1, Moderate - 2, High - 3, Extreme - 4)
These values are obtained using the guidelines or published evaluations prepared by the National Fire Protection Association (NFPA) or the National Paint Coating Association.

6. ACCIDENTAL RELEASE MEASURES

Chemical Emergency: Spill, leak, fire, or accident call
Chemtrec day or night (800)424-9300;
Outside continental USA call (703)527-3887

SPILL/LEAK PRECAUTIONS:
Sweep up spills and transfer to a container for disposal. See section 13.
If needed, wash spillage area with plenty of water.

7. HANDLING AND STORAGE

STORAGE:
Do not store or handle product with systems constructed of parts that have galvanized steel, zinc or brass components.
SPECIAL PRECAUTIONS:
Avoid contact with skin and eyes.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

EYE PROTECTION:
Wear eye protection if exposure is possible
SKIN PROTECTION:
No special skin protection is usually necessary. Avoid prolonged or frequently repeated skin contact with this material. Skin contact may be minimized by wearing protective clothing.
RESPIRATORY PROTECTION:
No special respiratory protection is normally required where adequate ventilation exists. However, if operating conditions create high airborne concentrations, the use of an approved respirator is recommended.
VENTILATION:
No special ventilation is necessary. However, if operating conditions create high airborne concentrations of this material, special ventilation may be needed.

9. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE:
White to off-white spherical pellet.
pH (20°C):
8-10 (10% aqueous solution)
SPECIFIC GRAVITY:
1.2 min
MELTING POINT:
No data available
SOLUBILITY:
Partially soluble in water.

10. STABILITY & REACTIVITY

HAZARDOUS DECOMPOSITION PRODUCTS:
Not applicable
STABILITY:
Stable
HAZARDOUS POLYMERIZATION:
Polymerization will not occur.
INCOMPATIBILITY:
None
SPECIAL PRECAUTIONS:
READ AND OBSERVE ALL PRECAUTIONS ON PRODUCT LABEL. KEEP CONTAINER TIGHTLY CLOSED IN ANY GENERAL CHEMICAL STORAGE AREA.

11. TOXICOLOGICAL INFORMATION

EYE IRRITATION:
The Draize Eye Irritation Score (range, 0-110) in rabbits is 8.7.
SKIN IRRITATION:
The Draize Skin Primary Irritation Score (range, 0-8) for a 4-hour exposure (rabbits) is 0.1.
This material was not a skin sensitizer in the Buehler Guinea Pig Sensitization Test.
DERMAL TOXICITY:
The dermal LD50 in rabbits is >5.0 g/kg.
RESPIRATORY/INHALATION:
The 4-hour inhalation LC50 in rats is 4.6 mg/liter.
INGESTION:
The oral LD50 in rats is greater than 5000 mg/liter.
Additional Toxicological Data: The 96-hour LC50 in rainbow trout (Salmo gairdneri) is >1000 mg/L.
The 48-hour LC50 daphinia (Daphnia magna) is >1000 mg/L. Results of a 28-day oral toxicity study in rats showed that daily doses of 1000 mg/kg of Cryotech CMA Deicer caused no significant toxicity.

12. ECOLOGICAL INFORMATION

COD (TOD):	0.75 kg O_2/kg
BOD_{20} @ 2° C:	0.40 kg O_2/kg
BOD_{20} @ 10° C:	0.67 kg O_2/kg

13. DISPOSAL CONSIDERATION

Based on information available to Cryotech Deicing Technology, this product is neither listed as a hazardous waste nor does it exhibit any of the charact-eristics that would cause it to be classified or disposed of as an RCRA hazardous waste. If product should spill or be otherwise unsuitable for normal deicing applications, it may be absorbed on suitable materials and disposed of in sanitary landfill unless state or local regulations prohibit such disposal.

14. TRANSPORT INFORMATION

Not restricted under any transport regulations.

15. REGULATORY INFORMATION

ALL OF THE COMPONENTS IN THIS PRODUCT ARE ON THE FOLLOWING INVENTORY LISTS:
U.S.A. (TSCA)
Europe (EINECS)
Canada (DSL/NDSL)
TSCA SECTION 12(b):
None of the components in this product are regulated under TSCA Section 12(b).
OSHA HAZARD CLASSIFICATION:
Hazardous Chemical (Irritant);
None of the components in this product are considered highly hazardous by OSHA.
CERCLA HAZARDOUS SUBSTANCES:
There is no CERCLA Reportable Quantity for this material.
SARA 311 CATEGORIES:

Immediate (Acute) Health Hazard:	Yes
Delayed (Chronic) Health Hazard:	No
Fire Hazard:	No
Sudden Release of Pressure Hazard:	No
Reactivity Hazard:	No

SARA 313:
None of the components in this product are subject to reporting under SARA Section 313.
CLEAN WATER ACT:
None of the components in this product are listed as Priority Pollutants under the CWA.
None of the components in this product are listed as Toxic Pollutants under the CWA.
STATE RIGHT-TO-KNOW:
This product does not contain components at levels which are required to be reported under the statutes of the following states: PA, MA, NJ
This product does not contain components known to the State of California (Proposition 65) to cause cancer and/or reproductive harm at levels which would require a warning under the statute.
WHMIS (Canada) CLASSIFICATION:
Not controlled

16. OTHER INFORMATION

ADDITIONAL HEALTH DATA COMMENT:
This Material Safety Data Sheet contains environmental, health and toxicology information for your employees. Please make sure this information is given to them. It also contains information to help you meet community right-to-know/emergency response reporting requirements under SARA Title III and many other laws. If you resell this product, this MSDS must be given to the buyer or the information incorporated in your MSDS. Discard any previous edition of this MSDS.

Latest version of this MSDS can be found at http://www.cryotech.com.

The above information is accurate to the best of our knowledge. However, since data, safety standards, and government regulations are subject to change and the conditions of handling and use or misuse are beyond our control, **Cryotech Deicing Technology, a Division of General Atomics International Services Corporation makes no warranty, either express or implied, with respect to the completeness or continuing accuracy of the information contained herein and disclaims all liability for reliance thereon.** Cryotech Deicing Technology, a Division of General Atomics International Services Corporation assumes no responsibility for any injury or loss resulting from the use of the product described herein. User should satisfy himself that he has all current data relevant to his particular use.