出國報告（出國類別：其他（出席國際會議及參訪））

出席「**2013 ISOPE** 海洋採礦及天然氣水合物討論會」及參訪德國萊布尼茲海洋科學研究中心

服務機關：經濟部中央地質調查所

姓名職稱：陳柏淳 / 技正

派赴國家：波蘭、德國

出國期間：**102** 年 **9** 月 **21** 日至 **9** 月 **30** 日

報告日期：**102** 年 **11** 月 **27** 日

摘要

本出國計畫係執行核定之 102 年度出國計畫：「參加天然氣水合物相關國際會議及實驗技術討論」。經蒐尋國際會議資料及與天然氣水合物相關研究機構洽詢後，決定參加 9 月 22 日至 26 日於歐洲波蘭甚切青市（Szczecin）所舉辦之「第 10 屆（2013） ISOPE 海洋採礦及天然氣水合物討論會」 (The Tenth (2013) ISOPE Ocean Mining & Gas Hydrates Symposium)，口頭發表論文一篇：Using Alcohol Vapor as Catalyst for Synthesizing Methane Hydrate。會後並赴德國基爾市（Kiel）的萊布尼茲海洋科學研究中心 (IFM- GEOMAR)，與中心內天然氣水合物相關研究學者會面，晤談可能合作機會，並參訪該研究中心水合物實驗設備。

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壹、目的

天然氣水合物不僅具有成為新型態天然氣能源資源的潛能，在自然環境系統演化或受人為因素干擾情形下，也是影響海底斜坡穩定性、海事工程安全性及全球氣候變遷之重要因子。經濟部中央地質調查所自 93 年起開始規劃並執行天然氣水合物的調查研究，目前正進行「能源國家型科技計畫−臺灣西南海域天然氣水合物資源地質精查及南部海域天然氣水合物賦存潛能調查」之四年期計畫。為增進對國際研究現況與進度之瞭解，並進一步規劃與調整本所計畫內容，因而規劃出國參加天然氣水合物相關研討會並參訪知名研究機構。

本出國計畫的任務為參加於歐洲波蘭甚切青市（Szczecin）舉辦之「2013 ISOPE 海洋採礦及天然氣水合物討論會」（The Tenth(2013) ISOPE Ocean Mining & Gas Hydrates Symposium），於會議中口頭發表論文一篇（Using Alcohol Vapor as Catalyst for Synthesizing Methane Hydrate）。本會議有多國研究學者針對天然氣水合物相關研究發表最新成果，另有其他關於海域礦產開發之文章發表，皆於地質調查所資源地質組之業務密切相關。會後並參訪位於德國基爾市（Kiel）的萊布尼茲海洋科學研究中心（IFM-GEOMAR）內的天氣水合物相關研究設施。近年來德國 IFM-GEOMAR 與國內「能源國家型科技計畫天氣水合物主軸計畫」合作密切，藉由參訪其總部相關研究設施並討論研究方向，可進一步加強彼此的合作關係。

貳、行程

本出國計畫行程為 102 年 9 月 21 日至 9 月 30 日，行程如下表所示：

表 1　出國計畫行程表

日期	住宿地點	預定工作內容
9 月 21 日 （星期六）	荷蘭阿姆斯特丹	赴程
9 月 22 日 （星期日）	波蘭甚切青	轉搭火車至甚切青， 下午抵達當地飯店辦理報到註冊、準備會議資料，參與開幕晚會。
9 月 23 日 （星期一）	波蘭甚切青	參與研討會
9 月 24 日 （星期二）	波蘭甚切青	參與研討會
9 月 25 日 （星期三）	波蘭甚切青	參與研討會
9 月 26 日 （星期四）	德國漢堡	參與研討會 轉搭火車至漢堡
9 月 27 日 （星期五）	德國基爾	自漢堡至基爾參訪 IFM-GEOMAR
9 月 28 日 （星期六）	荷蘭阿姆斯特丹	參訪 IFM-GEOMAR 自基爾回荷蘭阿姆斯特丹
9 月 29 日 （星期日）	荷蘭阿姆斯特丹	返程
9 月 30 日 （星期一）	荷蘭阿姆斯特丹	返程

參、過程

本次出國行程分為兩大部分。第一部分為赴波蘭甚切青市參加「第 10 屆（2013）ISOPE 海洋採礦及天然氣水合物討論會」。除聆聽會議全程內容外，亦口頭發表論文一篇，並與相關領域學者討論研究主題，建立交流管道。第二部分則在出發前先行蒐尋與波蘭甚切青市相距最近的國際知名天然氣水合物研究中心，最後擇定位於德國基爾市的「萊布尼茲海洋科學研究中心」。經聯繫獲得首肯，於研討會結束後順路拜訪中心內對天然氣水合物學有專精的研究人員，並在其引導下參訪相關研究設備。

1. 參加 2013 ISOPE 海洋採礦及天然氣水合物討論會

圖 1 會議召開場地：波蘭甚切青 Radisson 飯店

2013 年第 10 屆的 **ISOPE** (The International Society of Offshore and Polar Engineers) 於波蘭甚切青召開，會議的主題訂為「Ocean Mining & Gas Hydrates Symposium」。會議分為 14 個議程，共有來自 16 個國家總計 53 篇事先經審稿後的文章口頭發表，另外還有 5 位接受特別邀請的講者發表論文。今年此項國際研討會除持續針對深海探礦、

礦區特性、採礦工程技術及環境影響評估等主題提出最新的研究成果外，還特別對海域及永凍層的天然氣水合物相關研究做專題探討。天然氣水合物專題有多篇來自德國、日本、韓國與中國大陸的論文，本人則代表臺灣口頭發表論文一篇：「Using Alcohol Vapor as Catalysts for Synthesizing Methane Hydrate」（見附錄）

圖 2 會議場地

研討會與天氣水合物相關的論文如下所列：

1. Influence of Cation for Cage Occupancy from Small Cage Competition with Methane at Natural Gas Hydrates in Real sediments. Juwoon Park, KAIST, Korea.
2. Axial Symmetrical Thermal Conduction and Phase Transformations in THF Hydrate-Bearing Sediments. Xu Hui Zhang, Chinese Academy of Sciences, China.
3. Origin of Gases from Gas Hydrate in the Qilian Mountain Permafrost, Qinghai: Comparison of Gas Composition and Carbon Isotopes. Zhengquan Lu, Chinese Academy of Geological Sciences, China.
4. Spectroscopic Explanation of Metastablity in Gas Hydrate Formation. Dongwook Lim,KAIST,Korea.

5. Development of Ring Shear Apparatus with Permeability Measurement System for Hydrate Bearing Sediments. Hideki Minagawa, National Inst of Advanced Industrial Science and Tech,Japan.
6. Basic Study on the Permeability of Sand during Direct Shear Test. Masayo Kakumoto, National Institute of Advance Industrial Science and Technology (AIST), Japan.
7. Geotechnical Properties of Soil Samples Recovered from Eastern Nankai Trough Offshore Japan. Shin'ya Nishio, Shimizu Corp,Japan.
8. Geochemical Characteristics of the Soil above Muli Gas Hydrate Reservoir. Zhongjun Sun, Chinese Academy of Geological Sciences, China.
9. An Experimental Study of Natural Gas Hydrate in Permafrost by the Electromagnetic Method. Meixing He, Chinese Academy of Geological, China.
10. Using Alcohol Vapor as Catalyst for Synthesizing Methane Hydrate. Po-Chun Chen, MOEA, Taiwan.
11. Gas replacement in clathrate hydrates during CO2 injection – kinetics and micro-structural mechanism. Andrzej Falenty, Universität Göttingen, Germany.
12. Quantitative Raman Scattering of Guest Molecules in Gas Hydrates and Its Relevance to Gas Exchange Processes Involving N2. Junfeng Qin, Werner F. Kuhs, Universität Göttingen, Germany.
13. Validation of Seismic Methods to Detect Natural Gas Hydrates in Permafrost. Mingcai Xu, Chinese Academy of Geological Sciences, China.
14. Triaxial Behaviour of Mathance Hydrate Bearing Sand. Masayuki Hyodo, Yamaguchi Univ, Japan.
15. Monitoring System for Seafloor Deformation during Methane Hydrate Production Test. Tatsuya Yokoyama, OYO Corp, Japan.
16. Research on Marine Gas Hydrate Drilling Sampler of China. Hong Ren, Laiju Han, Junliang Xu, Zhonghua Wu, Sinopec, China.
17. Development of Large Scale Production System for Methane Hydrates. Jiro Nagao,Inst of Advanced Science and Tech, Japan.
18. Experimental Investigation on Controlling the Depressurization-induced Production Behavior from Hydrate-Bearing Sediments in 10-Meter-Scale. Taewoong Ahn, Korea Inst of Geoscience and Mineral Resources, Korea.

19. Laboratory Test to Evaluate the Performance of Sand Control Screens during Hydrate Dissociation Process by Depressurization. Jaehyoung Lee, Korea Inst of Geoscience and Mineral Resources, Korea.
20. The Lab-Scale Evaluation of Geomechanical Safety during the Production from Marine Gas Hydrate Deposits. Joo Yong Lee, Korea Inst of Geoscience and Mineral Resources, Korea.

近年來臺灣鄰近的國家，如日本、韓國與中國，皆投入大筆的經費設置天然氣水合物實驗室，藉由發展各式各樣大型的模擬器，企圖以放大實驗設備尺寸的手段脫離純科學的研究範籌，讓研究更趨近自然界真實的狀況，得到工程上實用的分析數據參數。而德國則致力於研究以二氧化碳置換出天然氣水合物裏甲烷的可行性。

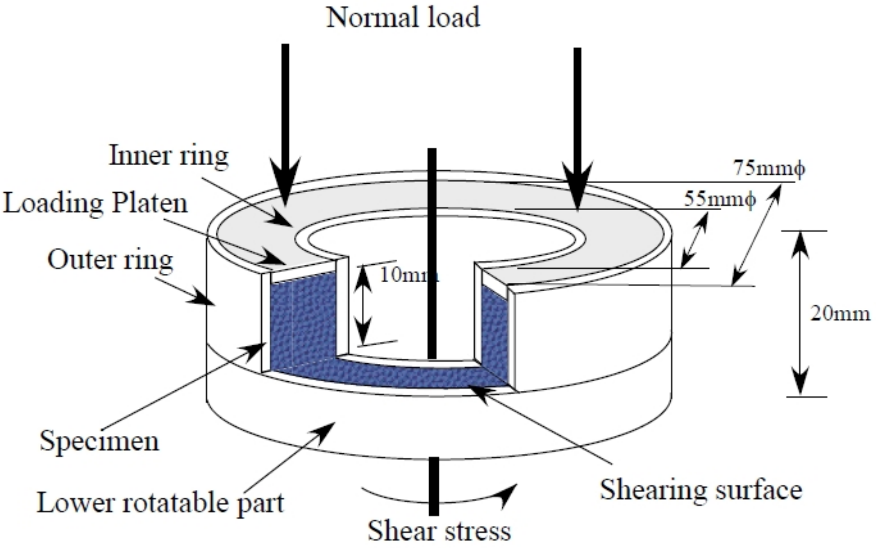
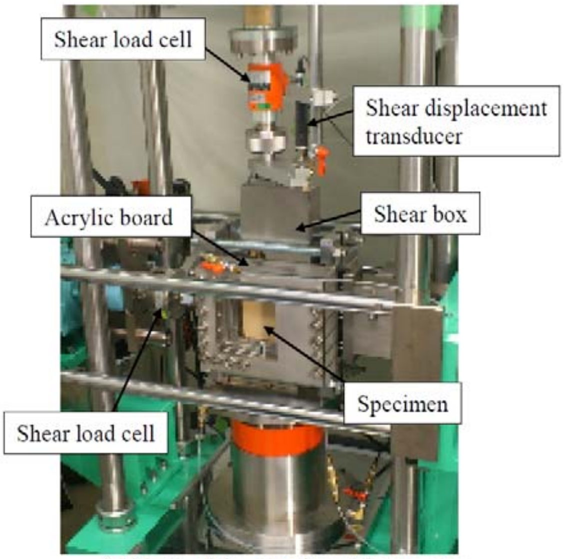


圖 3 日本北海道札幌 Methane Hydrate Research Center, National Institute of Advanced Industrial Science and Technology (AIST)所發展測試含水合物沉積物標本受環形剪力破壞時變形與滲透率變化的設備。



(b) Photo of the experimental apparatus

圖 4 日本北海道札幌 Methane Hydrate Research Center, National Institute of Advanced Industrial Science and Technology (AIST)所發展另一套測試含水合物沉積物標本受垂直剪力破壞時變形與滲透率變化的設備。

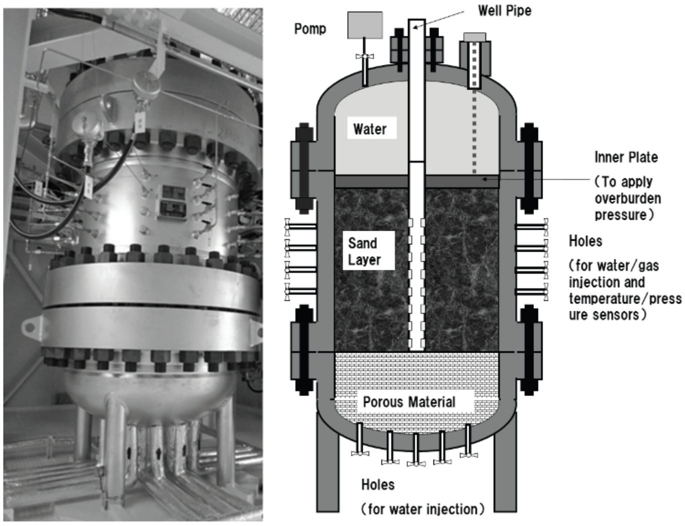


圖 5 日本北海道札幌 Methane Hydrate Research Center, National Institute of Advanced Industrial Science and Technology (AIST)所發展測試含水合物沉積物解離開發的設備。

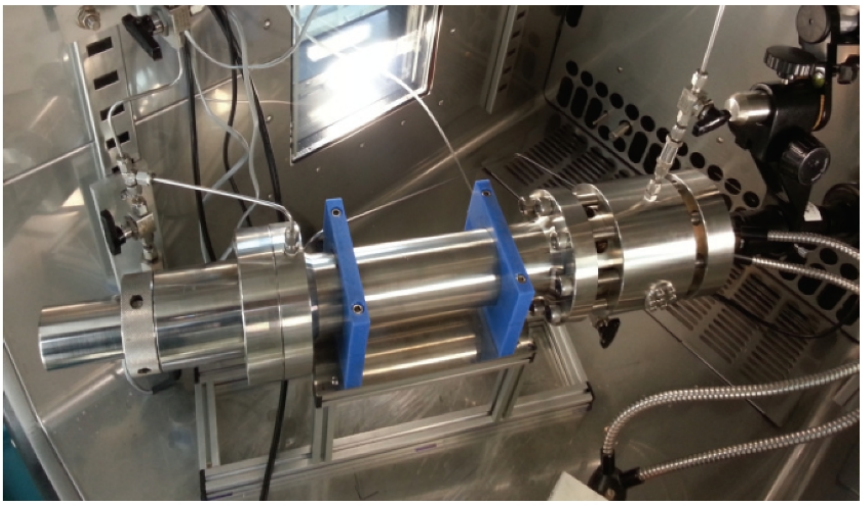


圖 6 韓國 Petroleum and Marine Resources Division, Korea Institute of Geoscience and Mineral Resources 所發展測試生產水合物時控制出砂屏幕效果的高壓設備。

2. 參訪萊布尼茲海洋科學研究中心

2.1 萊布尼茲海洋科學研究中心背景

本人此次前往德國基爾市(Kiel)的萊布尼茲海洋科學研究中心（IFM-GEOMAR），是當今世界上海洋甲烷冰研究的領航者。甲烷冰又稱為天然氣水合物（Gas Hydrate），有些人稱之為 21 世紀新能源。其研究與開發之所以受到重視，在於甲烷冰可轉換的能源據估計是全球石油、天然氣、煤等總和的兩倍以上。而德國最有名的研究機構正是位在基爾市（Kiel）的萊布尼茲海洋科學研究中心（Leibniz-Institute of Marine Science，又名 IFM-GEOMAR），距離德國北部大城漢堡約 90 分鐘的車程，鄰近區域有很多重要的海洋研究機構，諸如 Alfred Wegener Institute (AWI)極地與海洋生物學研究所，共同形成德國北部重要的海洋研究基地。

圖 7　萊布尼茲海洋科學研究中心(GEOMAR)入口

萊布尼茲海洋科學研究中心主要任務為調查研究海洋中的物理、化學、生物與地質作用，以及其與海床、大氣間的交互作用。截至 2011 年統計資料，研究中心共有員工約 750 人。其中科學研究者 400 人，有 32 人同時擔任基爾大學教授職。

萊布尼茲海洋科學研究中心可分成四大研究群，分別為：洋流與氣候、海洋生地化學、海洋生態與海洋地體動力研究群。其中，以「海洋地體動力」研究群對天然氣水合物投入最多心力，近年已發表許多篇重要論文。其研究區域廣泛，從南美洲智利、秘魯、哥斯大黎加等國近海，一直到黑海都有，從 1992 年起已經有 20 個以上的研究航次。1996 年研究中心成功地在美國奧勒岡州外海，實際鑽取到固態的甲烷冰標本，是該研究領域中很大的突破，因為他們所發展出來的技術都是能源界實際探採時所需要的。而於今年度（2013），其也利用海洋地球物理的方法，以佈放海底地震儀配合海面研究船施測的方式，瞭解海床下的地層構造及能源礦藏的分布位置。

目前該研究機構刻正執行與天然氣水合物相關的計畫有三大項：

一、 **CHRIMP**　October 2012 - February 2015　Funding Body: BMBF

Mechanism of formation of pockmarks at the southern Chatham Rise and their influences on gas hydrate stability, benthic habitat and climate.

二、 **PetroHydrate** August 2012 - July 2015 Funding Body: Private Sector

Prediction of gas hydrate accumulations in the Gulf of Mexico using PetroMod.

一、 **SUGAR II** August 2011 - July 2014

SUGAR II 計畫總負責人為 Dr. Klaus Wallmann。計畫可分為 A, B 兩大項，其下又各具 3 項子計畫：

A1: Detection and Monitoring of Gas Hydrate Deposits.

探找與監測天然氣水合物礦床

A2: Exploration and Characterization of Gas Hydrate Deposits.

調查與定性描述天然氣水合物礦床

A3: Simulation of Gas Hydrate Accumulation

模擬天然氣水合物富集成藏模式

B1: Simulation of Gas Hydrate Exploitation

模擬天然氣水合物開採

B2: Optimization of Gas Hydrate Production Technologies

優化天然氣水合物開採技術

B3: Drilling Technologies for Marine Gas Hydrate Deposits

海域水合物礦床鑽探技術開發

2.2 臺灣與萊布尼茲海洋科學研究中心交流概況

臺灣與德國萊布尼茲海洋科學研究中心的合作在近年相當密切，例如：

2009 年 11 月

國科會能源國家型計畫辦公室於臺灣大學凝態館國際會議廳主辦「臺德海域天然氣水合物調查及二氧化碳封存」研討會，邀集國內及德國萊布尼茲頂尖海洋科學家與會，希望能增進兩國於天然氣水合物調查與二氧化碳封存技術研發領域的合作。萊布尼茲研究中心的兩位學者分別給予專題演講。

1. Dr. Klaus Wallmann: 主講「二氧化碳封存技術的最新發展」。他提到德國刻正進行的 SUGAR 計畫（Submarine Gas Hydrate Reservoir）就是研究如何利用二氧化碳去取代海域天然氣水合物中的甲烷，達到獲取能源及減量溫室氣體的雙重目標。

2. Dr. Christian Berndt: 說明臺德雙方未來如何在臺灣海域進行聯合調查工作。內容包括利用德方先進的儀器設備（例如德國太陽號研究船、高解析度三維反射震測裝備等）來研究天然氣水合物的生成以及氣體如何在地層中遷移。

2013 年 3 月 31 日至 5 月 2 日

德國研究船太陽號（Sonne）順利抵臺執行西南海域研究航次，從事「天然氣水合物之甲烷資源」調查探勘。德方之領隊即為萊布尼茲海洋科學研究中心的 Dr. Christian Berndt.

本次海域調查重點分為三區：「四方圈合海脊」、「福爾摩沙海脊」與「大陸斜坡」。在航次中利用三維震測系統（P-cable）、海底電磁（OBEM）、側掃聲納（Side Scan）、即時影像採集器（TV-Grab）與熱流量測等現今最先進的海洋探勘設備進行資料蒐集以及探測區精查。藉由跨國交流增進我國天然氣水合物的調查探勘水準。

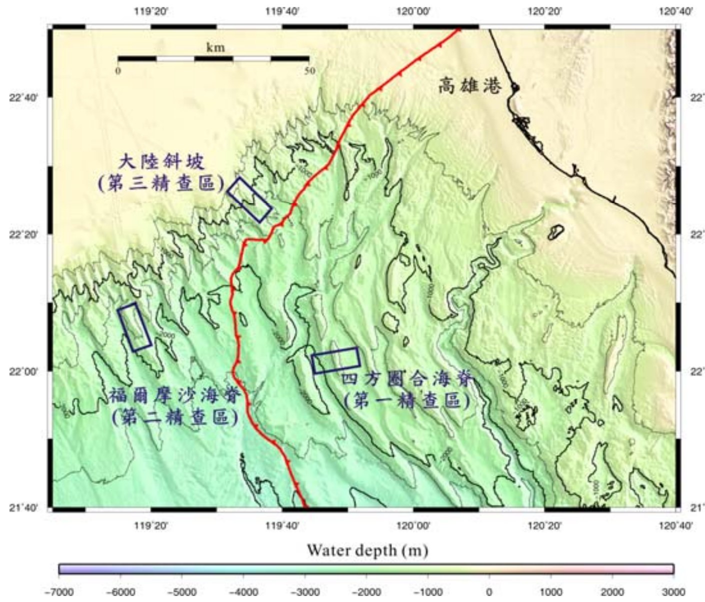


圖 8 海域調查重點區

2.3 參訪重點

此次參訪重點為前述 B2 計畫(Optimization of Gas Hydrate Production Technologies, 優化天然氣水合物開採技術）相關實驗室。先拜訪總計畫主持人 Dr. Klaus Wallmann, 討論個人在臺灣的一些研究成果，後經由其介紹負責模擬實驗室的 Dr. Matthias Haeckel，並於 Dr. Haeckel 帶領下，參觀天然氣水合物合成實驗室。

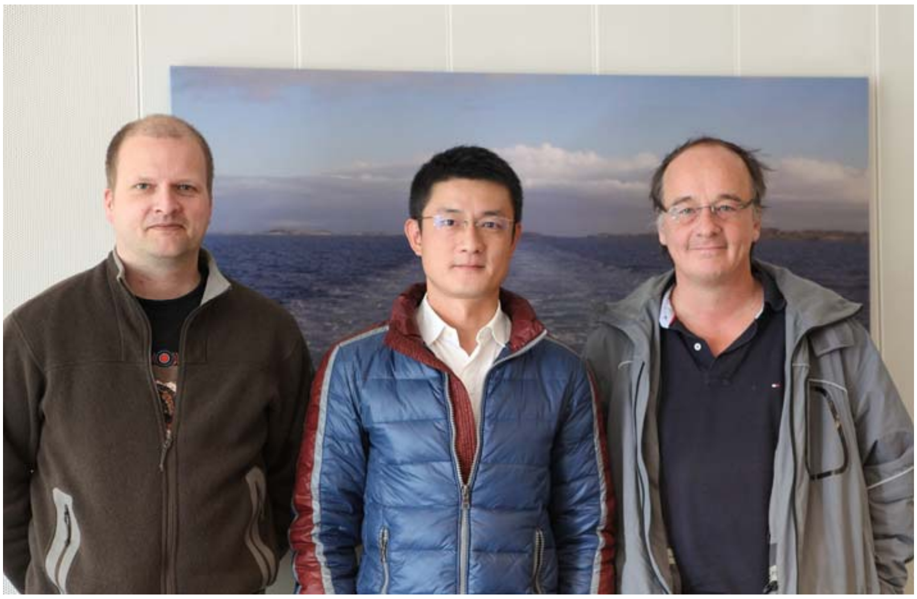


圖 9 右為 Dr. Klaus Wallmann, 左為 Dr. Matthias Haeckel

所參觀的部份，主要可以分為兩大合成系統, 分別是 NESSI (National Environment Simulator for Sub-seafloor Interactions)以及 Sapphire Reactor with NMR Microimaing System.

2.3.1. NESSI (National Environment Simulator for Sub-seafloor Interactions)

為了發展與描述水合物開發策略的特性，必須先於實驗室進行符合海底水合物礦藏處熱動力學條件的實驗。基爾 GEOMAR 於 SUGAR 計畫第一期建立了 NESSI 設備，實驗可操作溫度為 0~60℃，壓力可至 40MPa，容積則為 2000ml，可以灌注流體，以動態方式操作。

適用的流體包括：可控制溶解氣體量及鹽類濃度的水，氣態、液態或臨界態的二氧化碳以及氣態甲烷。進出管線皆加裝能偵測溫壓鹽度及甲烷、二氧化碳溶解量的偵測裝置。另也加裝了額外的拉曼感應頭，可以更進一步分析流出入液體的成分，或是另行採集樣品分析。

圖 10 NESSI 設備

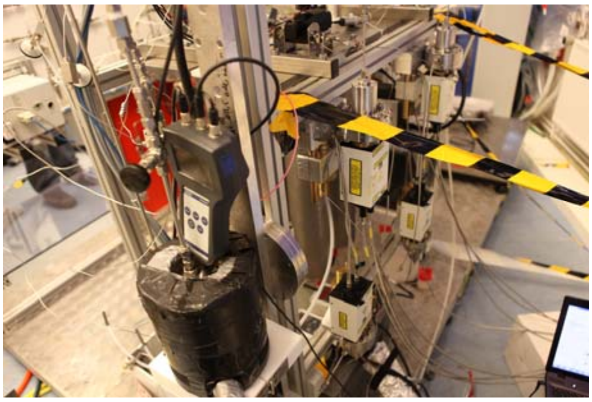


圖 11 NESSI 設備一角

2.3.2. Sapphire Reactor with NMR Microimaging System.

Dr. Haeckel 於 GEOMAR 實驗室內架設了一套 MRI (Magnetic Resonance Imaging) 磁震造影系統，利用特別設計的藍寶石管柱做為水合物反應容器。該管柱外徑 19mm，

內徑 12mm，長度 165mm。溫度由外側可通反流向高壓氣體的冷卻套控制，在管柱兩端又有額外的加溫裝置，防止水合物生成堵塞孔隙。

NMR 的機型為 Avance III 400 WB Plus，附加客製化，外徑 30mm，內徑 25mm 的 micro imaging probe，以配合加裝了冷卻套的藍寶石管柱系統。

目前初步進行的實驗是觀察 CO_2 取代水合物中 CH_4 分子的巨觀模式。實驗的基本設定條件為以粒徑 0.09~0.5mm 的石英砂填滿藍寶石管柱，充填去離子水後，將溫度設定為 8℃，甲烷壓力則設為 14MPa。當水合物形成後，用海水將殘餘的甲烷趕出，接著再打入液態 CO_2。

利用 MRI 系統，就可追蹤甲烷水合物形成的模式。例如圖 14，灰色部分代表液態水的訊號。水合物的形成致使此灰色訊號的消失。此實驗設備能夠提供天然氣水合物研究上珍貴的動力學資料。而圖 15 則顯示出氣體交換只可能在超臨界態二氧化碳可流經的區域發生。

圖 12 NMR 設備

圖 13 附冷卻套的藍寶石管柱

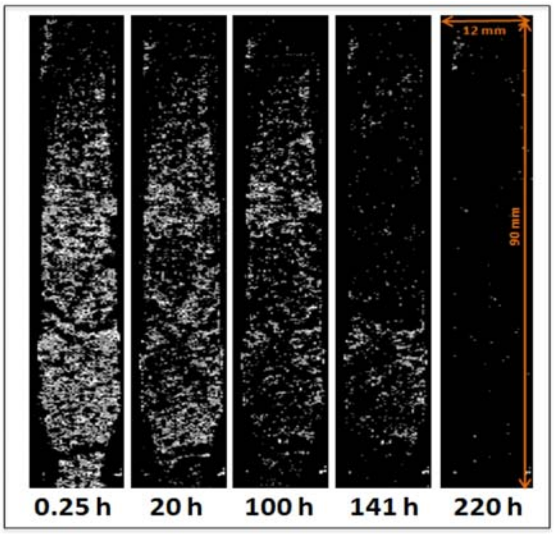


圖 14　甲烷水合物形成動態顯示

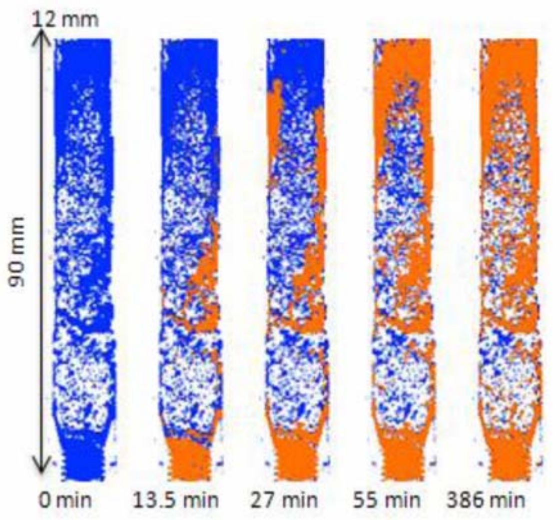


圖 15　二氧化碳取代水合物甲烷分子

2.3.3　Raman Spectrum System.

GEOMAR 實驗室內亦架設了一套拉曼光譜儀（型號：HORIBA HR800）。拉曼光譜儀可以監測具可視視窗高壓容器裏面天然氣水合物的形成、融解以及二氧化碳置換甲烷等動態變化的實驗數據。其也可以判定水合物的結晶構造（為 Structure I 還是 Structure II）或是辨別氣體是在液相、氣相或是水合物固相中，是研究天然氣水合物動力學的利器。

在行政院國家科學委員會指導下，能源國家型科技計畫項下的「天然氣水合物主軸計畫」中也委請臺灣大學化學工程學系陳立仁教授購置了一套拉曼光譜儀，並特別針對天然氣水合物研究加裝各項配件，如 GC-mass，希望將來亦能於國內開展相關研究。

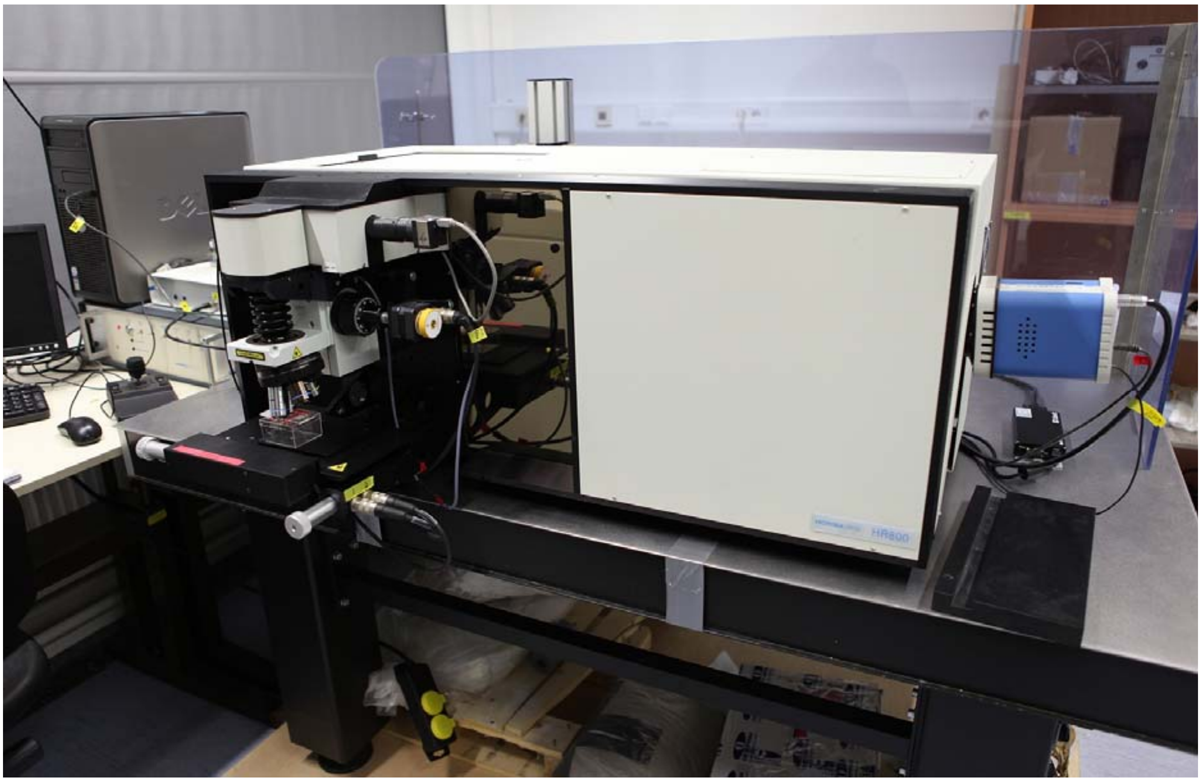


圖 16　拉曼光譜儀

肆、心得與建議

目前世界上許多先進國家，如美國、日本、加拿大、德國等，都積極進行天然氣水合物的相關研究，就連臺灣週遭的開發中國家，如中國大陸、韓國與印度等，也都已成功於所屬經濟海域鑽獲天然氣水合物標本。本年度（2013）3 月 12 至 18 日，日本於沖繩海槽（Naikai Trough）東側，本州渥美半島南方約 70 公里處，水深約 1,000 公尺的海上，利用地球號（Chikyu）率先進行全球首次的海域天然氣水合物開發測試，成功藉由解壓法（Depressurization Method）於深海底解離固態天然氣水合物，連續產氣達 120,000 立方公尺。雖然最後因為出砂的緣故暫停試驗，大體仍算成功，順利獲取大量珍貴的研究數據，目前正積極分析中。

而與日本同樣缺乏天然資源的臺灣，經過經濟部中央地質調查所彙整多年的研究調查成果顯示，西南外海的高屏斜坡及南海大陸斜坡也都可能蘊藏有大量的天然氣水合物。另依據天然氣水合物儲集系統觀念，已於 12 處天然氣水合物富集構造勘定了 17 個站位，並依據水合物可能儲量以及科學目的，將站位分成 8 處主要站位及 9 處候選站位。目前就等正式的鑽井才能有效掌握此區天然氣資源潛能及天然氣水合物賦存條件。

無論是未來生產開發自然界中的天然氣水合物礦產資源，亦或是利用水合物來發展天然氣運輸儲存等技術，都需要具備處理天然氣水合物標本的能力，也需對天然氣水合物本身的物理化學性質，以及其在沉積物中各式特性做更深入的分析與研究。而欲進行這些研究，複雜的儀器設計與先進的量測設備是不可或缺的。

受限於人力、經費與相關工業技術，與國際先進國家相比，臺灣在天然氣水合物的物理化學性質等實驗室研究工作方面一直處於相對簡單，落後的局面。在初期欠缺經驗的情況，臺灣應多至國外相關實驗室參訪，瞭解天然氣水合物相關實驗儀器設備與研究方向，並尋求機會赴德國、日本等實驗室進行合作研究事宜，待學習到相關知識、操作技巧，再於國內發展先端的研究。

附錄

Using Alcohol Vapor as Catalyst for Synthesizing Methane Hydrate

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ABSTRACT

We found that the amount of methane hydrates formed during synthesis can substantially increase, if trace alcohol vapor (methanol, ethanol or 1-propanol) is added to the Ice-Seed system during the “pressurization” stage. Among them, ethanol has the best promoting effect when the initial system temperature is around 270K. Nearly 91% of the ice seeds can be converted during this stage. Furthermore, the duration of the “heating” stage can be shortened while consuming the remaining ice. Ethanol also has similar catalytic effect for synthesizing carbon dioxide hydrate. This discovery may have practical value for the transportation and storage of natural gas.

KEY WORDS: Gas hydrate; methane hydrate; alcohol; catalyst; ice powder; synthesize; vapor.

INTRODUCTION

Natural gas hydrate (NGH) is a non-stoichiometric compound with a structure consisting of a network of H_2O molecules that are hydrogen-bonded together in an ice-like manner within which gas molecules are encaged. It can play an important role of transporting natural gas because of the ability for storing significant volumes of natural gas (Gudmundsson et al., 1994; Khokhar et al., 1998; Gudmundsson and Graff, 2003). Although there is research concentrating on how to promote or retard the formation of gas hydrates in a liquid water system by adding different additives (Makogon et al., 2000; Zhong and Rogers, 2000; Ganji et al., 2007), published reports seldom focus on how to improve the conversion efficiency of the “ice seed method" (to synthesize hydrate by slowly warming granular ice in a pressurized atmosphere of the hydrate former). “Ice seed method” can divide into pPressurization” and “heating” stages (Chen et al., 2010). We have now found that there are three kinds of alcohol vapors which can noticeably increase the conversion efficiency during the pressurization stage. This means that the heating stage for consuming remaining ice can also be shortened and save more energy.

EXPERIMENTAL SECTION

Starting Materials

Gas hydrate was formed from ultrapure methane (99.99%), and seed ice was prepared from a nearly gas free ice block made from ultra-pure deionized water. The ice block was crushed and ground followed by sieving into grain sizes ranging from 180 to 250 µm. Volatile alcohols chosen in this study are methanol, ethanol (medical-grade with 5% water) and 1-propanol.

Apparatus

The apparatus (Fig. 1) used for synthesis of methane gas hydrate (MGH) was modified from Stern et al. (1996, 2000). The system was equipped with a freezer (~253 K) within which a trapezoidal copper vessel (25.5×50.5 cm width × 51.5 cm length × 23 cm height) was set on a heating plate (25.5 × 51.5 cm). The copper vessel held a fluid bath of 95% ethyl alcohol aqueous solution, in which two pressure vessels (reservoir and reactor, both made of stainless steel with a total inner volume of 315 cm^3 and maximum pressure capacity of 140 MPa) were immersed. The sample holder was a high-density polyethylene (HDPE) cylinder (5 cm outer diameter and 4.8 cm inner diameter, with a length of 10 cm and wall thickness of 0.1 cm).

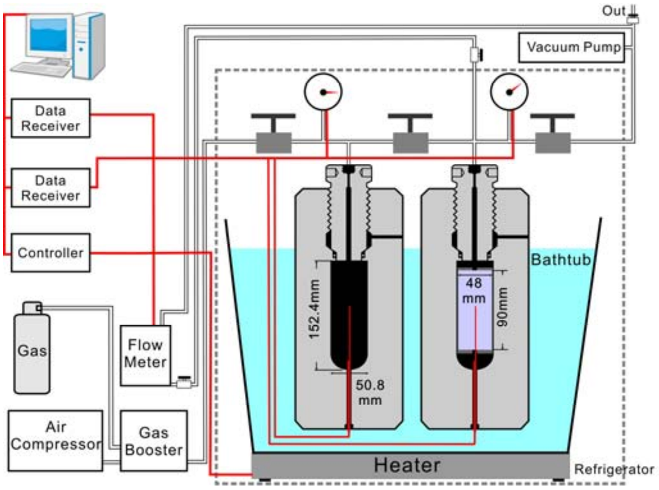

Figure 1. Experimental setup for MGH synthesis. The dashed line frame indicates the refrigerator (not to scale).

The methane pressure was increased using a gas booster (200 MPa maximum capacity) and monitored using a pressure transducer. The pressures reported were absolute pressure with an accuracy of 0.02%. Four type-K thermocouples were used to independently monitor the bath temperature, gas temperatures within both the reservoir and reactor, and mid-specimen sample temperature. The reliability of pressure and temperature data was verified by determining the P-T equilibrium boundary between methane hydrate and methane + water.

Experimental Procedures

First of all, we conducted one set of experiments to test the effect of ethanol with the same initial temperature (258.2K, Table 1). A cylindrical holder containing the packed starting ice grain aggregate (4.8 cm diameter) was capped with porous steel disks on each end and loaded into the reactor with the sample thermocouple inserted into the middle of the ice cylinder. A typical mass of 80.0 g of ice was used (Table 1). The ice was packed carefully and loosely to ~66.0% porosity. To avoid melting the ice grains, all sample handling was conducted at low temperatures in a freezer (<260 K).

For experiments with ethanol additives, we admitted 2 ml (0.63% of the reactor volume) of ethanol at the bottom of the reactor without contacting the ice directly. There is still some space between the holder and the bottom of the reactor chamber; therefore, the ethanol vapor phase rather than the liquid phase may play a more important role. Even after nearly 100% MGH samples had been made, there was still some liquid ethanol at the bottom of the reactor. The reactor and reservoir vessels were evacuated after immersing in the bath. The reservoir vessel was then charged with the desired methane pressure from a gas booster, while the reactor remained evacuated.

We started the "pressurization stage" through rapidly pressurizing the reactor vessel to 16.60 MPa by quickly opening the valve between two vessels once the gas temperature in both vessels was equal to the controlled bath temperature (T_{init}). The total duration for the “pressurization stage” was 1440 min before actively heating the system. These samples then underwent 1-4 heating cycles (Heating Stage) for completing the MGH formation. During each heating cycle, the bath temperature was raised from 258.2 K (T_{init}) to 285 K over an interval of approximately 60 min, then held at 285 K for 480 min, and followed by resetting to its initial temperature.

For another set of experiments, we individually tested three kinds of volatile additives (methanol, ethanol or 1-propanol) to compare the conversion efficiency in the pressurization stage with runs without additives at different T_{init}. The basic experimental procedure and sample preparation way of the second set was similar to the first one, except the heating stage was skipped. After kept in the pressurization stage for 1440 min, we initiated the dissociation procedure for the measurement of the MGH yield.

For the dissociation step, we rapidly vented the reactor pressure to 0.1 MPa over 10 s to destabilize the MGH and start the dissociation. The system vent was then immediately closed, while simultaneously opening the valve connecting the sample to the flow meter (Fig. 2), allowing for collection and measurement of all released methane. The cumulative weight of displaced water in the flow meter and gas collection apparatus was continuously monitored for getting the information of dissociation rate. We can get the released methane volume from the displaced water weight and then calculate the methane hydrate yield and ice conversion efficiency, since we know the starting weight of ice seed.

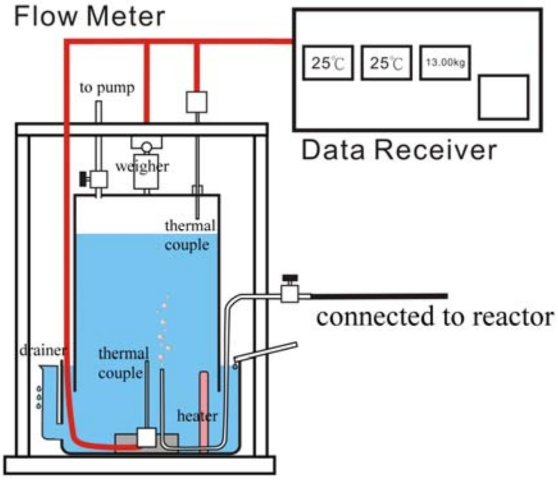

Figure 2. Flow meter for measuring the MGH dissociation rate and yield.

RESULTS

From the first set of experiments, we can clearly find that the existence of ethanol has a positive effect on synthesis performance (Table 1, Fig. 3). The sample A (without ethanol vapor as additive) did not meet a 100% conversion until the 4th heating cycle. In Fig. 3 (a1), the pressure value of the reactor dropped after each heating cycle, which meant the consumption of methane and the formation of new gas hydrates. In Fig. 3 (a2), we can notice that during every cooling process, a peak appeared in the sample temperature record. This phenomenon suggested that there was an exothermic reaction, which should be the crystallization of unreacted liquid water.

Table 1. Comparison of different synthesis procedures with or without ethanol vapor.

Sample	**Additive (2ml)**	**Heating Cycle**	**Ice (g)**	**Porosity (%)**	**T_{init} (K)**	**P_{init} (MPa)**	**P_{end} (MPa)**
A	—	1st	80.0	66%	258.2	16.60	12.93
	—	2nd	80.0	66%	258.2	12.93	12.09
	—	3rd	80.0	66%	258.2	12.09	11.67
	—	4th	80.0	66%	258.2	11.67	11.51
B	Ethanol	1st	80.0	66%	258.2	16.60	11.53
	Ethanol	2nd	80.0	66%	258.2	11.53	11.53

On the other hand, it took only one heating cycle for converting all ice seed to MGH with additive ethanol in sample B. In Fig. 3 (b1), there is no pressure difference before and after the second heating cycle which implied that there is no gas hydrate formed after the first heating cycle. We also noticed the obvious peak in temperature of the sample, shown in Fig. 3 (b2) when the bath temperature was maintained around 285 K. Since the formation of gas hydrates is also an exothermic reaction, the graph clearly demonstrates the dramatic effect of ethanol vapor on the rate of hydrate formation.

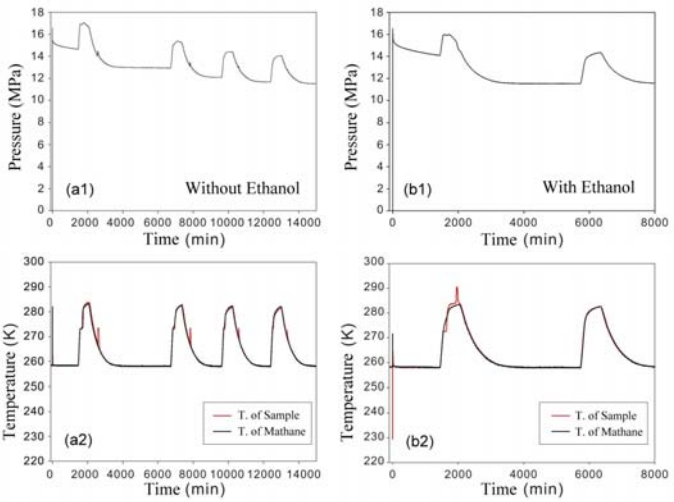

Figure 3. Comparison between different synthesis P-T paths of methane hydrates with and without ethanol.

From Fig. 3 we also noticed that the methane pressure kept decreasing with a rate greater in (b1) than in (a1) before the first heating cycle. This phenomenon highlighted the fact that ethanol could play a role even in the “Pressurization Stage”.

According to the results of previous experiments, we introduced another two alcohols, methanol and 1-propanol into the system for testing their catalyst effect during the “Pressurization Stage”. We kept the system in the pressurization stage for 1440 min, then started the dissociation procedure for the measurement of the MGH yield. We also assumed that the initial bath temperature would have obvious influence on MGH converting performance, so $T_{init.}$ is another parameter took into consideration. Fig. 4 and Table 2 present the settings and results of this set of experiments.

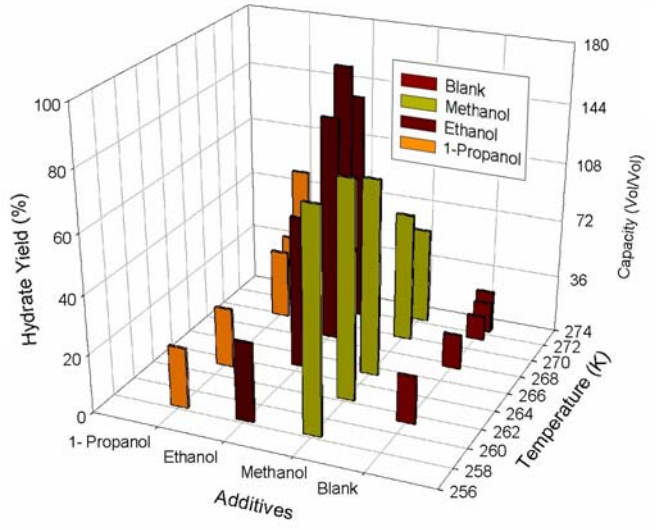

Figure 4. The yields of methane hydrate with different additives and $T_{init.}$

Table 2. MGH yields of experiments with different additives and initial temperature.

Sample	Additive (2ml)	Ice (g)	Porosity (%)	T_{init} (K)	P_{init} (MPa)	P_{end} (MPa)	Yield (%)
B1	No	40	66%	261.3	16.57	15.29	16.33
B2	No	40	66%	267.7	16.53	15.35	12.01
B3	No	40	66%	271.4	16.82	16.02	8.45
B4	No	40	66%	272.4	16.63	15.78	10.59
B5	No	40	66%	272.7	16.55	15.52	13.93
M1	Methanol	40	66%	258.3	15.88	13.76	75.00
M2	Methanol	40	66%	262.3	16.55	14.26	74.00
M3	Methanol	40	66%	265.3	16.59	13.98	67.05
M4	Methanol	40	66%	269.9	16.60	14.07	44.46
M5	Methanol	40	66%	272.4	16.57	14.50	33.21
E1	Ethanol	54.8	66%	258.3	15.91	14.71	27.03
E2	Ethanol	54.8	66%	264.7	16.53	14.99	51.90
E3	Ethanol	54.8	66%	268.5	16.60	13.96	77.18
E4	Ethanol	54.8	66%	270.2	16.65	13.41	90.95
E5	Ethanol	54.8	66%	271.7	16.51	13.93	78.09
P1	1-propanol	40	66%	258.3	16.53	15.26	20.66
P2	1-propanol	40	66%	263.2	16.56	15.22	20.54
P3	1-propanol	40	66%	269.9	16.64	15.50	23.60
P4	1-propanol	40	66%	271.4	16.64	15.34	25.39
P5	1-propanol	40	66%	272.7	16.61	15.23	46.39

Compare to blank runs, all three additives showed apparent catalytic effect on the conversion from ice seed to MGH during the “Pressurization Stage”. When the MGH yields of catalyst-free experiments were all less than 20%, it could be as high as 90.95% with the existence of ethanol vapor at 270.2 K within 1440 minutes. Furthermore, MGH yields and $T_{init.}$ showed a positive correlation in systems with ethanol and 1-propanol while methanol vapor lead to an opposite trend. It had a stronger catalytic effect when the system started with a lower initial temperature. Overall, in ice seed systems with different temperatures, suitable alcohol vapors should be chosen to achieve the best conversion results.

Based on the previous results, we conducted the third set of experiments (Table 3) for checking the effect of different initial pressures for MGH yields. In this set, ethanol was the only additive we introduced into the system and the initial system temperature fixed at 271.9 K since this setting could get the most optimal outcome of conversion. The result revealed that though we changed the value of initial pressures from 16.60 MPa to 6.57 MPa (decreased by more than 60 percent), the MGH yields, being reduced from 95.72% to 71.92% (about 25 percent), stayed preserved in a high-yield performance.

Table 3. MGH yields of experiments with different initial pressures.

Sample	**Additive (2ml)**	**Ice (g)**	**Porosity (%)**	**T_{init} (K)**	**P_{init} (MPa)**	**P_{end} (MPa)**	**Yield (%)**
EL0	Ethanol	40.0	66%	271.9	16.60	14.09	95.72
EL1	Ethanol	40.0	66%	271.2	11.72	9.09	94.81
EL2	Ethanol	40.0	66%	271.2	11.21	9.09	74.74
EL3	Ethanol	40.0	66%	271.2	10.49	7.96	88.63
EL4	Ethanol	40.0	66%	271.2	7.86	5.28	68.25
EL5	Ethanol	40.0	66%	271.2	6.57	3.89	71.92

DISCUSSION

To avoid formation of gas hydrates in aqueous solution, inhibitors such as methanol, ethanol and propanol are typically used (Mohammadi et al., 2007, 2008a and 2008b). When used in large amounts, methanol prevents hydrate crystallization by shifting the phase boundary to the lower temperature and higher pressure. (Abay and Svartaas, 2009). However, in the ice seed system, a small amount of methanol, ethanol or 1-propanol vapor could work as an efficient promoter.

By decomposing synthesized MGH, we knew that alcohol vapor didn't shift the phase boundary. In aqueous solution, NMR and dielectric studies also verified no sign of enclathration of methanol (Davidson et al., 1981). There should be other reasons rather than phase boundary shift which caused this catalytic effect. Khokhar et al. (1998) pointed out that polyvinyl-pyrrolidone, PVP, could promote the formation of sH hydrate. One of their hypothesis suggested that the morphology of formed hydrate is changed from block, ice-like hydrate to a dendritic structure in the presence of PVP. This meant that the guest molecules could keep in touch with water molecules and continuing the formation of hydrates. Whether this mechanism is the case in our system still needs further investigations.

Table 4 lists the equations related with temperature for calculating saturated vapor pressure of methanol, ethanol and 1-propanol individually. Through them, we plotted Fig. 5 to show the relationship between MGH yields and saturated vapor pressures (mmHg) at different temperatures. It seems 10 mmHg is a critical point. Once the saturated vapor pressure of alcohol was higher than 10 mmHg, the MGH yields would start reducing.

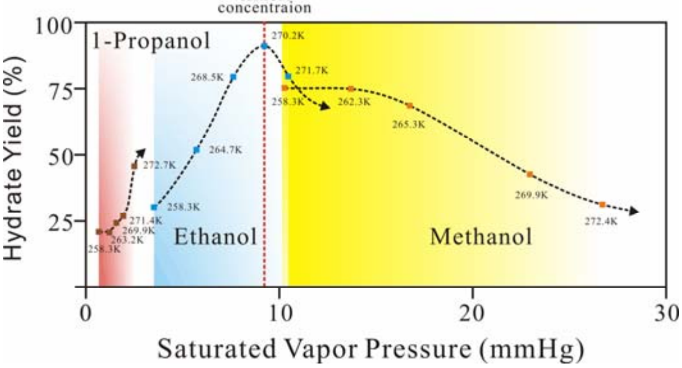

Figure 5. The relation between hydrate yields and saturated vapor pressures of alcohols.

Table 4. Equations for calculating saturated vapor pressure of methanol, ethanol and 1-propanol.

	Vapor Pressure Equation
Methanol	$P_{mmHg} = 10^{7.87863 - \frac{1473.1}{T-43.85}}$ (Lange's Handbook of Chemistry 10th ed, pp.1522-1524)
Ethanol	$P_{mmHg} = 10^{8.04494 - \frac{1554.3}{T-50.5}}$ (Lange's Handbook of Chemistry 10th ed, pp.1522-1524)
1-Propanol	$\log_e P_{mmHg} = \log_e\left(\frac{760}{101.325}\right) - 7.702226 \log_e(T+273.15) - \frac{8002.693}{T + 273.15} + 71.71697 + 3.950448\times10^{-07}(T+273.15)^2$ (Chemical Engineering Research Information Center.http://www.cheric.org/research/kdb/hcprop/cmpsrch.php Retrieved 19 May 2007.)

CONCLUSIONS

The ice seed method" can be divided into pressurization and heating stages. We found that the total amount of methane hydrates formed during the pressurization stage can increase substantially as trace alcohol vapor (methanol, ethanol or 1-propanol) is added into the ice seed system. The one that has the best promoting effect is ethanol. Furthermore, the duration of the heating stage can also be shortened while converting all remaining ice into methane hydrates.

The preliminary hypothesis for this promoting effect is that the presence of these trace gaseous alcohols is able to slow down the formation rate of hydrates and prevent the generation of impervious hydrate film covering the ice core in the early stage. Instead, the formed hydrates are permeable because of a different texture so the inner ice can keep converting into hydrates by continuously interacting with methane molecules.

The catalytic efficiency may have a relationship with the alcohol vapor pressure which changes with the temperature. According to our experimental data, each alcohol vapor tends to show its best catalytic efficiency at different temperatures when their vapor pressures are all around 10 mm Hg.

ACKNOWLEDGEMENTS

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