**Institution:** Edinburgh Research Partnership in Engineering – ERPE (Heriot-Watt/Edinburgh)

**Unit of Assessment:** B15: General Engineering

**Title of case study:** Assuring Hydrocarbon Flow with Improved Hydrate Management

**1. Summary of the impact** (indicative maximum 100 words)

ERPE research led to the following impacts in the REF2014 period:

- Extending the life of the NUGGETS field (operated by Total) by three years with an increase in cumulative production of 2% (2.8 Million Barrels of Oil Equivalent, value $150M).
- Saving $3-7M in costs associated with methanol removal from liquid hydrocarbon phase by demonstrating methanol could be removed from Natural Gas Liquids directly by molecular sieve, which played a major role in Total's decision in eliminating a de-propaniser from "methanol removal facilities", saving around £50M.
- Hydrafact: a start-up company with a turnover of £1M in 2012 and employing 8 full-time and 15 part-time staff.

**2. Underpinning research** (indicative maximum 500 words)

The key ERPE researchers throughout the period were; Bahman Tohidi (Professor), Adrian Todd (Professor), Ali Danesh (Prof)(1986-2007), Rod Burgass (Research Associate), Ross Anderson (Research Associate).

The most important outputs of the ERPE research were:-

- The ability to predict hydrate and water hydrocarbon phase behaviour using the thermodynamic modelling and experimental data generated through various research projects.[1]
- The discovery that n-propanol takes part in clathrate formation, which is contrary to the general understanding that alcohols prevent hydrate formation. Consequently, n-propanol was modelled as a hydrate-forming compound by use of a thermodynamic model.[2]
- The examination of a statistical thermodynamic model of the phase equilibria to predict the hydrate dissociation conditions of methane and natural gases in the presence of distilled water or ethylene glycol aqueous solutions.[4]

Gas hydrates form in hydrocarbon production and processing operations, causing serious operational and safety concerns. Petroleum Engineering in ERPE sought to understand and address various aspects of flow assurance and gas hydrate research, and built expertise in the field of research in Hydrate-Phase Equilibria (PVT). Areas of interest included avoiding gas hydrate, wax and asphaltene problems in petroleum production and transportation, design and testing of low dosage hydrate inhibitors, hydrate monitoring and early warning systems and the natural occurrence of hydrates in sediments.

From 1993 onwards, ERPE successfully undertook a variety of Joint Industry Projects (JIP) and Government sponsored research projects, the focus of which was to develop a method for avoiding hydrate problems in offshore oil and gas operations. These projects were partnerships of up to 20-30 industrial partners investing up to £38.5k per annum per sponsor into the research. Grants from the ESPRC supplemented the activity from the late 1990s, supporting research such as work on gas hydrates in subsea sediments [G1], and rational design & testing of low dosage hydrate inhibitors for use with offshore oil & gas production [G2], the objective of which was to use molecular dynamics computer simulation in conjunction with carefully designed experiments to identify the molecular mechanisms by which low dosage hydrate inhibitors (LDHIs) work and thereby to design and synthesise new LDHIs for use in the petroleum industry.

The Group's longest running JIP, Gas Hydrates and Flow Assurance, investigated thermodynamic issues associated with gas hydrates. This work examined the relationship between pore size, geometry, capillary pressures and gas hydrate growth and dissociation conditions in synthetic and natural sediments and the potential hazard hydrate destabilisation could pose to deep-water oil/gas

platforms, pipelines and subsea cables, and long-term considerations with respect to hydrate stability, methane (a potent greenhouse gas) release to the atmosphere, and global climate changes. In previous phases of this JIP, gas hydrate phase equilibria for various fluid systems (i.e., single, binary and multi-component systems; synthetic and real gas, condensate and oil systems) were studied, resulting in the generation of a large quantity of novel experimental data on hydrate dissociation conditions and the amount and composition of various phases under equilibrium conditions.

Over the course of the period 1993 to 2013, the team firmly established itself within the industrial and academic communities as a leader in flow assurance research, with a reputation for quality experimental work and advanced theoretical studies. Sequential JIPs have supported the generation of a large in-house library of hydrate equilibrium data, and development of the commercial hydrate predictive software such as HydraFLASH® was developed as the most accurate software for predicting hydrate and water hydrocarbon phase behaviour using the thermodynamic modelling and experimental data generated through various research projects used by major hydrocarbon production and service companies, such as Total, BP and Statoil, in planning their flow assurance strategies.

**3. References to the research** (indicative maximum of six references)
The references identified with * are the ones which best indicate the quality of the underpinning research.

[1] * Tohidi, B., Danesh, A., and Todd, A.C., "Modelling Single and Mixed Electrolyte Solutions and its Applications to Gas Hydrates", *Chemical Engineering Research and Design*, 73A pp. 464-472 (1995).
This paper contributed to the development of HydraFLASH® the most accurate software for predicting hydrate and water hydrocarbon phase behaviour using the thermodynamic modelling and experimental data generated through various research projects ISSN: 02638762. 75 Google Scholar (GS) citations. Available on request

[2] * Chapoy, A; Anderson, R; Haghighi, H; et al. "Can n-propanol form hydrate?" Industrial & Engineering Chemistry Research Volume: 47, Issue: 5, pp: 1689-1694 2008 DOI: 10.1021/ie071019e . 21 GS citations
The publication made industry aware of hydrate characteristics of n-propanol and iso-propanol and provided the necessary information for modelling using other software.

[3] Yang, J; Tohidi, B "Determination of Hydrate Inhibitor Concentrations by Measuring Electrical Conductivity and Acoustic Velocity" Energy & Fuels, 2013 Volume: 27, Issue: 2, pp: 736-742 DOI: 10.1021/ef301755q
This is the basis for HydraCHEK® (one of Hydrafact's Products) which can determine the amount of salt and hydrate inhibitor and determine the hydrate safety margin.

[4] * Haghighi, H; Chapoy, A; Burgess, R; et al. "Experimental and thermodynamic modelling of systems containing water and ethylene glycol: Application to flow assurance and gas processing" Fluid Phase Equilibria, Volume: 276, Issue: 1, Pages: 24-30 2009, DOI: 10.1016/j.fluid.2008.10.006 30 GS citations
This paper examined a statistical thermodynamic model of the phase equilibria to predict the hydrate dissociation conditions of methane and natural gases in the presence of distilled water or ethylene glycol aqueous solutions. Predictions of the developed model were validated against independent experimental data and the data generated in this work to support the reliability of the model.

[5] Mohammadi, A, Chapoy, A.,.H., Richon, D and Tohidi, B., "Experimental Measurement and Thermodynamic Modeling of Water Content in Methane and Ethane Systems ", Industrial and Engineering Chemistry Research, *2004,* Vol. 43, No. 22, pp. 7148–7162. DOI: 10.1021/ie049843f 41 GS citations
Experimental data generated in this work was compared with predictions of the HydraFLASH®

thermodynamic model as well as other predictive methods. The results of this project were used in improving and validating HydraFLASH® predictions for low water content systems.

**Grants**

[G1] EPSRC, GR/N06724/01, £212k, Tohidi, Danesh, Todd. "Rational Design & Testing Of Low Dosage Hydrate Inhibitors For Use With Offshore Oil & Gas Production" 2000–2003. The identification of the molecular mechanisms by which low dosage hydrate inhibitors (LDHIs) work to inform synthesis of new LDHIs for use in the petroleum industry.

[G2] EPSRC, EP/D052556/1, £286k, Tohidi, Anderson "Capillary controls on gas hydrate growth and dissociation in synthetic and natural porous media: PVT, NMR, Neutron Diffraction and SANS 01" 2006–2009. An examination of the relationship between pore size, geometry, capillary pressures and gas hydrate growth and the potential hazard hydrate destabilisation could pose to deep-water oil/gas platforms, pipelines and subsea cables.

[G3] EPSRC, EP/D013844/1, £297k, Tohidi, "Can CO2 hydrate formation act as a safety factor for subsurface storage of CO2?", 2006-2009. Worldwide occurrences of methane gas hydrates (comparable to total fossil fuels) inspired scientific investigation of the ways to recover this resource of low-carbon energy. The main recovery methods proposed include depressurization, thermal stimulation, inhibitor injection, or various combinations of these.

[G4] EPSRC, EP/E04803X/1, £412k, "Towards Zero Carbon Emissions: Novel Low Pressure Molecular Natural Gas/CO2/H2 Storage and Separation using Semi-Clathrates" 2008–2011. Assessment of the potential of hydrate formers through an intensive integrated experimental and theoretical study to support the global energy industry.

**4. Details of the impact** (indicative maximum 750 words)

The Centre for Gas Hydrate Research was formed in 2001 and the Centre for Flow Assurance Research established in 2007. The Centres have generated circa £10M since 2001 from industry in research projects. The data generated in numerous research projects was used in development and tuning of accurate thermodynamic modelling.

Total has extended production from the NUGGETS reservoir that was to be abandoned in 2010. So far they have produced an extra 2.8 million Barrel of Oil Equivalent (BOE) of gas increasing the recovery factor by 2% (and generating around $150M additional income at a gas price of $11 per MMBtu (Million British thermal units)). [S4, S7] They are still producing and plan to continue production for several more years. Using ERPE IP and HydraCHEK®, they have not only extended the life of the reservoir, but reduced the methanol injection drastically. Currently they have completely stopped methanol injection (from the designed 28%) and control the hydrate slurry concentration by HydraCHEK®. Reducing/eliminating the methanol injection rate has several important consequences, including; reduction of the use of expensive toxic chemicals, reduction/elimination of methanol contamination in the produced condensate and improving the management of a highly toxic and flammable compound and the associated environmental impact.

Total have also made changes to the design of methanol removal from NGL facilities, using Hydrafact test results and ERPE knowledge to demonstrate that a depropaniser could be removed from the design, saving around £50M. [S3]

Total has obtained a significant reduction in methanol injection rate from the designed 28 wt% to less than 3 wt%, saving around £1-5M per year and eliminating disposal of around 28,000 $m^3$ of methanol per year using one of Hydrafact's products, HydraCHEK®. HydraCHEK® is a lab based analytical tool that measures the concentration of hydrate inhibitor and salt in produced water samples taken from a pipeline [3]. Total state "*The C-V technique (HydraCHEK®) has allowed North Alwyn to rapidly monitor the degree of hydrate inhibition present in the NUGGETS produced waters at reception facilities, leading to an increased confidence in optimising the hydrate treatment"* [S6]

In 2005 the University decided to form a spin-out company to exploit the commercial opportunity. Hydrafact (founded in 2006) has grown during the REF period to employ 23 staff (8 full-time and 15 part-time staff) and has 3 key products, laboratory facilities, hydrate blockage management services and experimental services with a turnover of £1M in 2012.

Hydrafact has delivered more than 135 projects to 77 companies in 26 countries across a range of specialisms such as complex and unusual flow assurance challenges for the transportation of oil, gas and multi-phase products. [S8] The benefits of working with Hydrafact are described by a Senior Specialist, Flow Assurance at Statoil: "*Several… projects… related to acquisition of high quality experimental equilibrium data of fluid systems are critical for Statoil's operation. The results have been invaluable for our operation enabling Statoil to optimise our operation within the relevant area covered by these studies. It is difficult to substantiate the value of these results due to the complexity of the system. It suffices to state that without these results our operations would be non-optimal resulting in lost value in tens of millions Norwegian Kroner (hundreds of thousands of GBP) per year."* [S1]

Companies such as BP, Total, Schlumberger, Statoil and Petrobras are repeat customers that routinely commission Hydrafact to solve their flow assurance problems, increase production, extend the life of wells and fields and provide training to their own teams. All of these activities transfer knowledge developed in ERPE to the companies. As a Flow Assurance Chemist from Petrobras stated, "*Flow assurance imposes a significant challenge for our deep-water off-shore oil production developments. The knowledge and procedures created… contributed significantly to optimise the design of our subsea systems and reduce production losses due to flow assurance issues, mainly gas hydrates pipeline blockage*".[S2]

**5. Sources to corroborate the impact** (indicative maximum of 10 references)

[S1] Senior Specialist Flow Assurance, Statoil. Regarding acquisition of high quality experimental equilibrium data of fluid systems critical for Statoil's operation. The results were invaluable to enable Statoil to optimize operation within the relevant fields.

[S2] Flow Assurance Chemist, Petrobras Will confirm that Petrobras uses the research to optimise the design of subsea systems to tackle mainly gas hydrates pipeline blockage

[S3] Senior Development Engineer, TOTAL E&P UK Limited Will corroborate the impact of removal of methanol from NGL directly by molecular sieve, which played a major role in Total's decision in eliminating a de-propaniser from "methanol removal facilities", saving around £50 million.

[S4] Team Leader - Production and Site Support, Total E&P UK Ltd Will describe how the research was instrumental in extending the life of the NUGGETS and how it led to increased cumulative production of 2%+ . Will also talk about savings generated costs associated in removing methanol from liquid hydrocarbon phase.

[S5] NUGGETS Gas Field - Pushing the Operational Barriers SPE Paper 166596, available on request. DOI: 10.2118/166596-MS The paper confirms on page 10 that Total used the Hydrachek tool to inform their hydrate management strategy.

[S6] "Successful Deployment of a Novel Hydrate Inhibition Monitoring System in a North Sea Gas Field". MacPherson et al, at 23rd International Oil Field Chemistry Symposium, 2012. http://www.tekna.no/ikbViewer/Content/832455/Oil%20Field%20Chemistry%20-%20Final%20program%202012.pdf #16.

[S7] http://ycharts.com/indicators/europe_natural_gas_price Provides the rationale for the calculations on generating income through extending the life of the NUGGETS field.

[S8] www.hydrafact.com describes the products developed by the research in detail