Microwave Inhibition of Gas Clathrate Hydrate Formation

3.1.2 Objectives

This project is devoted to the development of a novel fundamental methodology to control gas clathrate hydrate formation and growth at a molecular/atomic level thus ensuring that the desired properties and flow characteristics of natural gas are achieved under industrial processing conditions.

The **principal aim** of the project is:

- to develop new models (based on statistical-mechanical theory of inhomogeneous fluids) of gas clathrate hydrate formation and growth in the presence of electromagnetic fields of GHz frequency range and to develop a novel methodology for application of these models to the manipulation of the structure and composition of processed natural gas thereby ensuring its desired thermodynamic properties and flow characteristics.

The **primary objectives** of the project are:

- to develop an experimental microwave generator-based equipment and procedures for experimental studies of gas clathrate hydrate formation and growth in the presence of electromagnetic fields of GHz frequency range; to perform experimental studies of gas clathrate hydrate formation in the presence of high frequency electromagnetic fields for various thermodynamic conditions and compositions of the natural gas and for various parameters of the electromagnetic fields (various frequencies within the GHz band, field strength);
- to generalize the Pozhar-Gubbins (PG) statistical mechanical theory of inhomogeneous fluids to inhomogeneous systems processed in the presence of high frequency electromagnetic fields;
- to develop PG-based theoretical models of (i) microwave propagation and absorption in the natural gas systems which are supersaturated with the water vapor and (ii) the dielectric properties of the natural gas systems with regard to high frequency electromagnetic wave propagation;
- to develop theoretical (statistical mechanical) models of (i) the coupling between rotational and vibrational degrees of freedom of water molecules, (ii) the dependence of the libration magnitude of water molecules on the electromagnetic wave frequency and the field strength, (iii) microwave absorption spectra of gas clathrate hydrates, (iv) electromagnetic resonant phenomena in the natural gas systems with and without hydrate formation and (v) gas hydrate formation in the presence of high frequency electromagnetic fields;
- to develop molecular dynamic (MD) codes for simulation of high frequency electromagnetic wave propagation and clathrate hydrate formation and growth in the natural gas supersaturated with water vapor;
- to validate the aforementioned theoretical models of gas clathrate hydrate formation and EMD simulations results against experimental data;
- to analyze existing industrial data on clathrate hydrate formation in gas pipe lines and to adjust the theoretical models and experimental data to specific industrial conditions; to identify the most effective, resonant electromagnetic wave bands that can be used for inhibition of clathrate hydrate formation and growth;
- to use the theoretical models and experimental results of gas clathrate formation for development of a novel, electromagnetic wave based methodology for inhibition of gas clathrate hydrate formation and growth.

3.1.3 Background & Justification for Undertaking the Project

Gas clathrate hydrates are nonstoichiometric crystalline inclusion compounds where the host lattice composed of water molecules is formed around small atoms or molecules (guests) trapped in such one-molecule cages. Existence of gas clathrate hydrates has been known since the beginning of 19^{th} century. They have been found in various environments including gas pipelines and wells, oceanic sediments, the Earth's atmosphere, etc. They form in hydrocarbon-based mixtures where water is dissolved in gaseous or liquid hydrocarbons at appropriate thermodynamic conditions corresponding to the hydrate stability pressure-temperature region. Gas hydrate crystals may grow in the aqueous phase, on a particle in the aqueous phase (“seed”), on the pipe/equipment walls or at gas-liquid interfaces if water molecules are available in sufficient amount.

The physics of the gas hydrate nucleation process is complicated and poorly understood, in spite of a growing number of gas hydrate studies and experimental data. The primary nucleation period of gas hydrates is the controlling period in the majority of hydrate formation processes. It may last for days before hydrates form; conversely, instantaneous hydrate formation sometimes occurs with no determination of the controlling variables. In many cases, for example, homogeneous nucleation may occur in the body of the fluid mixture, rather than at the gas-liquid interface. The hydrate particles may grow in the direction of the gas bubbles, indicating diffusion-controlled phenomena. As the hydrate crystals extend from the liquid interior to touch the interfacial region of the gas bubbles, catastrophic nucleation occurs on the bubble surfaces within fractions of a second. The formation and deposition of gas hydrates is influenced by a number of factors including the degree of subcooling of the mixture, heat flux, mixture flow rate, fluid properties and emulsification of the liquid phases, etc. Even for single-phase flowing systems, deposition of crystals at surfaces and in the body of the phase is not fully understood. For multiphase flows, the problem is further complicated by complex flow patterns.

The natural gas hydrate reserves are enormous. The energy contained in such hydrates is several multiples of the total fossil fuel energy reserve of the planet, and therefore, gas hydrates can be considered as a potential future energy supply. Unfortunately, gas hydrates also introduce numerous complicated technical problems to the oil and gas industry, aviation, submarine and ship operation, marine exploitation, etc. that invariably have overwhelming economic consequences. For example, the incremental cost of insulation of a 15 km submerged pipeline in the North Sea to prevent hydrate flow stoppage was in the range of 48-50 million ECUs in 1984. Gas clathrate hydrates plug blowout preventers, kill pipelines, cause gas and oil wells to be abandoned, jeopardize the foundations of offshore structures, plug nozzles, block fuel supply of engines, etc. From an environmental prospective, the release of methane from sedimentary gas hydrates enhances the greenhouse effect.

The oldest method of prevention of gas hydrate formation is gas drying. This method is very expensive, due to the enormous amount of natural gas to be dried and is also inefficient due to complications in gas production, transportation and processing. Chemical injections have also been one of the most common ways to prevent gas hydrates from forming. The use of alcohols (methanol) and glycols is well known. A large number of experimental studies have been carried out by the industry to establish the required experimental concentrations of chemical inhibitors and related calculation methods. The accuracy of these predictions are very sensitive to details of the hydrate formation process, including the amount of water in the hydrocarbons at reservoir conditions, the distribution of water and inhibitor between the different phases, water phase activity, temperature distribution within a reservoir, liquid accumulation, and the general thermodynamic state of the system under consideration. In addition, various conditions of reservoir operation (that are difficult to take into account theoretically) have tremendous impact on the hydrate formation process and the reliability of the existing methods for the prediction of hydrate formation. In recent years a significant effort has been made to develop/find effective chemical inhibitors (e.g., PVP) acting on the hydrate crystallization and agglomeration process and thereby, inhibit formation of blockages. Though such inhibitors can be used with relatively low concentrations as compared to the traditional inhibitors (e.g., alcohols), they are very active chemical compounds and/or environmental contaminants and therefore, need to be removed from the system after treatment. This significantly increases the costs associated with the new inhibitor usage. A typical offshore inhibitor injection system using a piggyback inhibitor supply line with onshore recovery costs about 10 million dollars. Another method employed in the prevention of gas hydrate formation, namely, heat tracing, is sometimes used in gas/oil industry. Again, this method is not a reliable and cost effective solution to the clathrate hydrate formation problem for other than short pipelines. In many cases it can not be used in principle (e.g., for heating submerged pipelines).

Development of new, effective technologies of gas hydrate growth prevention is firmly based on a knowledge of the properties of gas hydrates. While development of new inhibitors is a costly, but necessary enterprise today, studies of electromagnetic properties of gas hydrates have suggested an innovative approach to the gas hydrate formation problem. Experimental downhole emitters of high frequency (HF) electromagnetic fields developed in 1988 provide gas hydrate decomposition within a radius of 12 meters. This method has also been used to clean oil pipes of deposited asphalts and paraffins. Further development of this approach has led to the understanding that HF electromagnetic waves can prevent gas hydrate formation. The principle scheme of a device based on a HF microwave generator was patented in 1997, though the details of the device development, including the proper HF frequency band and suitable antenna module, are not known even today. Subsequently, experimental (inelastic neutron scattering) and molecular dynamics simulation studies confirmed that HF electromagnetic waves belonging to a wide frequency band from about 1 GHz to several THz are capable of affecting the structure of gas clathrate hydrates significantly. The measured inelastic incoherent neutron scattering spectra revealed several energy-loss peaks in the above frequency band of about two orders of magnitude in width at the lowest temperature of the measurements (5 K). These peaks become much wider at 35 K, and in some cases split or become shoulders of the widened band. Little is understood about the underlying molecular phenomena causing this change. The spectral features indicate that the encaged gas molecules interact strongly with the host lattice vibrations and their motion is damped at the highest temperature (77 K) of the measurements. Therefore, at low temperature the localized ratting vibrations of the guest molecule are coupled strongly to the host lattice vibrations. However, as a result of the absence of any theoretical description of the system, the physical mechanisms which control this coupling still remain unclear. The experimental studies were performed for very low (from 5 to 77 K) temperatures and therefore, do not provide reliable information on the frequency dependence of the vibrational and translational motions of encaged gas molecules at high temperature (263 to 283 K) and their coupling to the various degrees of freedom of the host lattice. No direct experimental studies have been undertaken regarding GHz and THz microwave propagation/absorption in gas hydrates. These and other important problems are addressed in this project.

This project is focused on detailed studies of physical mechanisms of GHz microwave propagation and absorption in the natural gas systems supersaturated with water at conditions of clathrate hydrate formation (temperatures from 263 to 283 K and pressures from 1 to 30 atm). These studies involve experimental, theoretical and molecular simulation developments.

Experimental studies will commence with two systems that mimic those possessing the ability to promote gas clathrate formation. The medium will be gaseous methane supersaturated with water vapour. One of the otherwise equivalent systems will be acted upon by HF EM waves generated by tunable, GHz microwave generators. Experimental measurements will concern (i) the dynamics of gas hydrate nucleation and crystallization in both systems, to ascertain the resonant microwave modes/bands contributing critically to formation of the gas hydrates and to investigate the resonant mode contributions to the rotation and vibration spectra of the medium and (ii) the HF microwave absorption in the medium. The experimental technique will be measurements of dielectric properties of the media and gas hydrates, optical spectroscopy and diffuse laser beam scattering. These methods are both sensitive and feasible at room temperature and high pressure conditions. Experimental studies will provide data on GHz microwave absorption spectra of CH_4-water systems and clathrate hydrates at practical temperatures and pressures.

Theoretical developments will include generalization of the Pozhar-Gubbins theory to describe transport phenomena in inhomogeneous, many particle systems in the presence of HF electromagnetic (EM) fields. This generalization will be applied both to the process of HF EM wave propagation through a particular CH_4-clathrate hydrate (solid)/fluid mixture interface (i.e. on a microscopic level), and to the process of HF EM field propagation through the entire inhomogeneous medium (fluid mixture with CH_4-clathrate nuclei), i.e. on a macroscopic level. The microscopic side of this study will be coupled to a theoretical investigation of the vibration spectra of various gas clathrate crystalline structures (including thin films, clathrate nuclei, structures containing defects, structures in the vicinity of the structural phase transition, multi-layer compounds with large number of atoms in the elementary cells, etc.). The primary goal of all theoretical studies is to identify several eigenmodes (or resonant modes) of the spectra that can be used effectively to control the gas clathrate structure formation and to identify the EM field and media characteristics that ensure simultaneously (i) long range propagation of the EM field in the medium and (ii) effective absorption of the HF EM waves by gas clathrate nuclei.

The results of these experimental and theoretical studies will be supported by intensive molecular dynamics simulations of the gas clathrate nucleation process in the presence of HF EM fields. This will (i) clarify the intermolecular interaction potential models and theoretical models of coupling between rotational and vibrational modes of water and gas molecules, and (ii) supply ultimate rotation and vibration spectra of the crystalline lattices that will be compared to the experimental and theoretical ones to ascertain the frequency band of optimal resonant absorption.

The experimental, theoretical and molecular simulation results will be analyzed together to ensure that unambiguous and detailed description of the physical processes responsible for GHz microwave control of gas hydrate formation is obtained. The outcome of this work will, in turn, provide a reliable foundation for a future GHz-microwave based, gas hydrate control technology. While gas hydrate formation control is of primary concern in this project, similar technologies and devices can be of much wider use in industry (microwave-based control of chemical and biological reactions and processes, development of new materials and energy conversion schemes, *etc*.).