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Editorial

An introduction to natural gas hydrate/clathrate: The major organic carbon reserve of the Earth

1. Existence of hydrates

Gas hydrates belong to a general class of inclusion compounds commonly known as clathrates. A clathrate is a compound of molecular cage structure made of host molecules encapsulating guest molecules. It is also considered a chemical substance consisting of a lattice of one type of molecule trapping and containing a second type of molecule (Sloan, 1998; Taylor et al., 2004). Natural gas clathrates owe their existence to the ability of H_2O molecules to assemble via hydrogen bonding and form polyhedral cavities as shown in Figs. 1 and 2.

Natural gas hydrate is a naturally occurring ice-like solid (see Fig. 3), which is made of water molecules as the cage forming host and other molecules (mostly methane) as the guest. The guest molecules, like methane or carbon dioxide, are of an appropriate size such that they fit within cavities formed by the host material. Common clathrate compounds of interest are those formed from CO_2/H_2O and CH_4/H_2O mixtures: the former for application in carbon sequestration and the latter for methane extraction.

The physical appearance of the natural gas hydrate is like other crystalline substances. At standard pressure and temperature, a methane hydrate molecule contains approximately 160 volumes of methane for each volume of water.

Until recently, methane hydrates, known to scientists for almost 200 years, have remained a scientific curiosity. It was not until the 1930's that it was realized that methane hydrate was responsible for plugging natural gas pipelines, particularly those located in cold environments. For the next 40 years, a small body of researchers investigated the physics of various clathrates, including the construction of the first predictive models of their formation. A prime focus of this work was (and continues to be) the development of chemical additives and other methods to inhibit hydrate formation.

The United States Geological Survey (USGS) estimates that there are more organic carbon reserves around the earth as methane hydrate than all other forms of fossil fuels combined (Booth et al., 1996). The Department of Energy (DOE) considers about 1% recovery of methane from the known methane hydrate reserves within the U.S. enough (over 2000 TCF) to satisfy the U.S. consumption for the next eight decades.

As it is demonstrated in the pie-chart, Fig. 4, the amount of organic carbon contained in natural gas hydrate reserves around the globe is estimated to be twice the amount contained in all fossil fuels on Earth. By fossil fuels it is meant coal, oil and conventional natural gas reserves all around the world.

According to the U.S. Geological Survey, the estimated global natural gas hydrate reserves are in the range from 100,000 to about 300,000,000 trillion cubic feet. This estimate when compared with the 13,000 trillion cubic feet of conventional natural gas reserves demonstrates the vastly more abundant natural gas hydrates around the globe.

Interest in methane hydrate as an energy resource was initially ignited in 1960s' by Russian scientists who claimed contribution from hydrates during conventional gas drilling in the Messoyakha field, Siberia. The U.S. was a leader in the 1970s' in this area. In mid-1990's, two countries, with a large energy demand but limited resources (Japan and India), began to explore the possibility of extracting methane from hydrates. The U.S. research effort got a big push in Year 2000 with the passage of the Methane Hydrate Research and Development Act. Under the Act, the U.S. DOE coordinated a five-year effort by the Federal Agencies "to promote the research, identification, assessment, exploration, and development of methane hydrate resources". Advances in the basic understanding of hydrates have occurred during these 5 years, including several hydrate-specific

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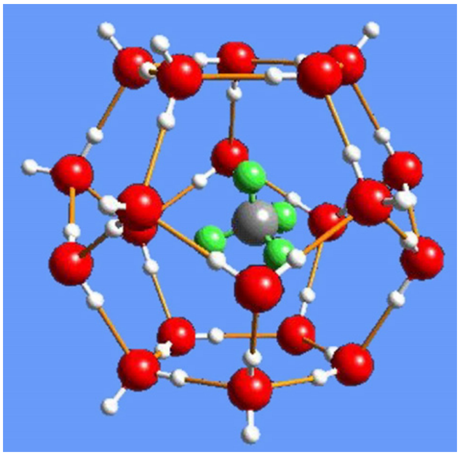

Fig. 1. The schematic drawing of one type of natural gas clathrate structure in which a methane molecule is encaged by a lattice of water molecules. (Courtesy of NETL).

expeditions in the polar region and in the deep water on the continental shelves around the world (see Fig. 5). The Methane Hydrate Research and Development Act (H.R. 1753, 2000) was extended by an amendment through 2010 as part of the Energy Policy Act of 2005.

Methane hydrates have been discovered in the subsurface in permafrost regions, but most occur in oceanic sediments hundreds of meters below the sea floor where water depths are greater than about 500 m. As it is shown in Fig. 5 natural gas hydrates have been discovered at numerous locations along continental margins as well as in the Arctic.

Many issues are under investigation by hydrate researchers around the world. These include implications on the global carbon cycle, long-term climate-change effects, seafloor stability, future energy source, hydrate formation and dissociation properties, physical and chemical properties, and global distribution of hydrate. We have attempted to represent papers reporting on the latest research in these areas. As research is progressing, it may lead to an environmentally-benign methane extraction method in a not too distant future.

2. About this special issue

This special issue is primarily dedicated to natural gas hydrate, an unconventional energy source that has the potential to supplant the world's energy supply. A thematic symposium on "Gas hydrates and clathrates" was organized during the 2005 Spring National Meeting of the American Chemical Society in San Diego, CA. The two-day symposium consisted of 28 invited speakers from industry, government, and academia discussing the latest research issues and advances in the field of gas hydrates and clathrates. Of those presented, below are the titles and authors, followed by brief summaries of the 20 papers that are included herein:

1. "Resource potential of methane hydrate coming into focus" by Ray Boswell*
2. "Natural Gas-Hydrates — A potential energy source for the 21st century" by Y.F. Makogon*, S.A. Holditch, and T.Y. Makogon
3. "Methane hydrate exploration on the mid-Chilean coast: A geochemical and geophysical survey" by Richard Coffin*, John Pohlman, Joan Gardner, Ross Downer, Warren Wood, Leila Hamdan, Shelby Walker, Rebecca Plummer, Joseph Gettrust, and Juan Diaz
4. "Growth kinetics of ethane hydrate from a seawater solution at an ethane gas interface" by John P. Osegovic*, Shelli R. Tatro, Sarah A. Holman, Audra L. Ames, Michael D. Max
5. "Effects of gas hydrates on the chemical and physical properties of seawater" by Chung-Chieng A. Lai*
6. "Effect of pressure vessel size on the formation of gas hydrates" by Scott D. McCallum, David E. Riestenberg, Olga Y. Zatsepina, Tommy J. Phelps*
7. "Raman spectroscopy of a hydrated CO_2/water composite" by Monsuru O. Gborigi, David A. Riestenberg, Michael J. Lance, Scott D. McCallum, Yousef Atallah, Costas Tsouris*
8. "Formation of HFC-134a hydrate by static mixing" by Hideo Tajima*, Toru Nagata, Akihiro Yamasaki, Fumio Kiyono, Tadashi Masuyama
9. "Investigations into surfactant/gas–hydrate relationship" by Rudy Rogers*, Guochang Zhang, Jennifer Dearman, Charles Woods

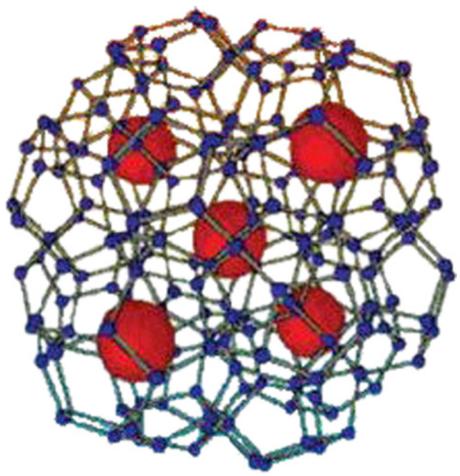

Fig. 2. Methane clathrate dual structure.