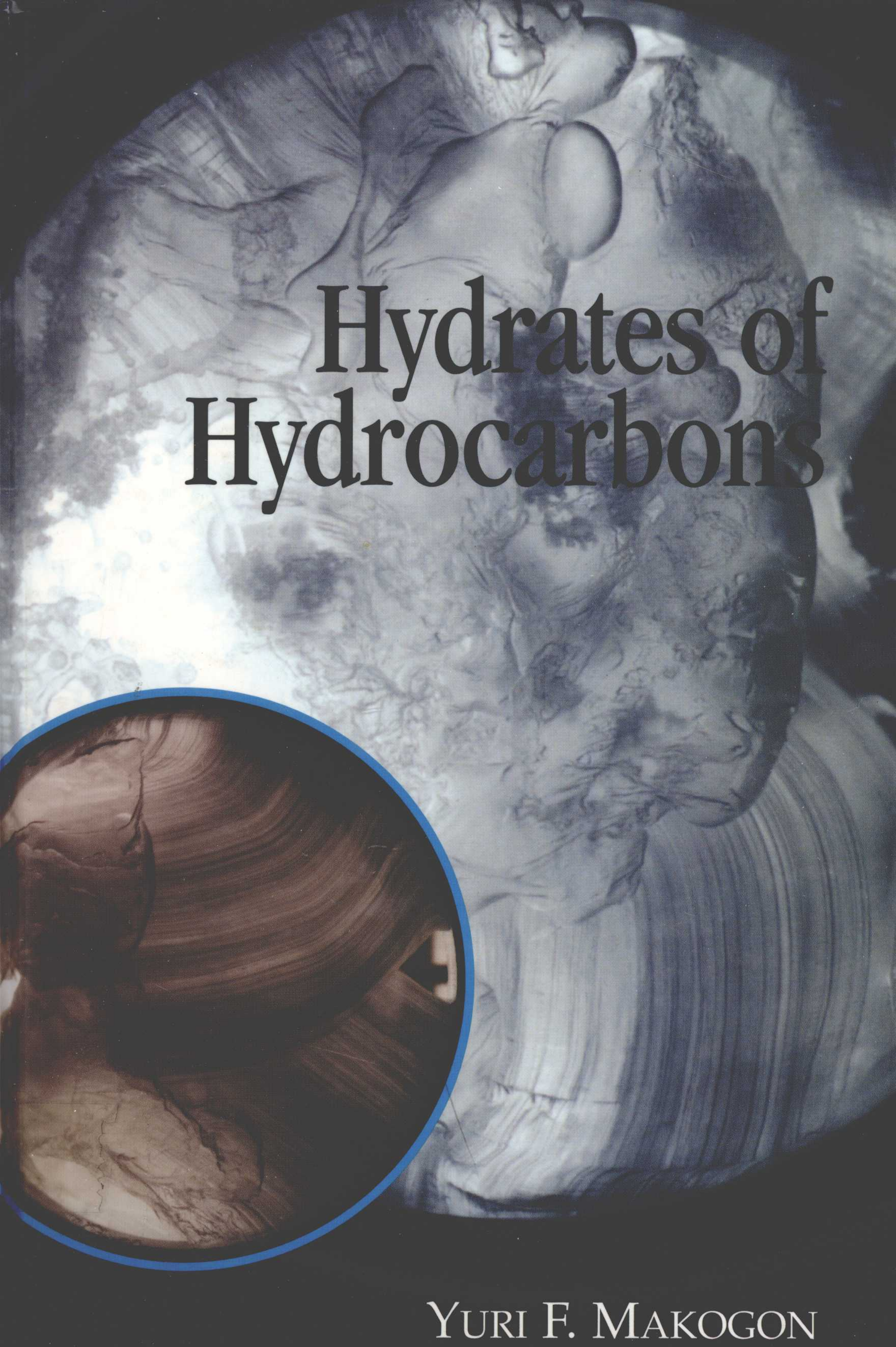
Hydrates of Hydrocarbons



Yuri F. Makogon

Hydrates of Hydrocarbons

by

Yuri F. Makogon

Russian Academy of Natural Sciences
IPNG, RAN
Texas A&M University
Dr. Wayne Dunlap, Editor

PennWell Books

PENNWELL PUBLISHING COMPANY
TULSA, OKLAHOMA

Comments, suggestions, or corrections are welcome and should be sent to:

Y. F. Makogon
Petroleum Engineering Department
Texas A&M University
College Station, Texas 77843–3116
USA

PennWell Publishing Company
1421 South Sheridan Road/P.O. Box 1260
Tulsa, Oklahoma 74101

Library of Congress Cataloging-in-Publication Data

Makogon, IU. F. (IUrii Fedorovich)
Hydrates of hyrocarbons / Yuri F. Makogon.
p. cm.
Includes index.
ISBN 0-87814-718-7
1. Natural gas—Hydrates. I. Title.
TN884.M35 1997
665.7—dc21 96-51830
CIP

Printed in the United States of America

03 02 01 00 99 98 97

ACKNOWLEDGMENTS

This monograph contains a number of general solutions of the problems on natural and technogenic gas hydrates obtained by the author and by many researchers who work in research laboratories and industry around the world. Certainly, one monograph cannot embrace all aspects of the gigantic multifaceted problem of gas hydrates. A tremendous amount of specialized literature exists on gas hydrates—several thousands of scientific papers, several dozens of serious monographs, numerous reports, etc.

I am pleased to note that in my research I not only used the published works of the majority of hydrate researchers, but also discussed the results with many of them during visits to their laboratories, in meetings at numerous scientific conferences, and by correspondence.

I am pleased to present a letter which was sent by Professor Donald L. Katz a few months before his death. From his letter it is evident how highly he valued the achievements of his students and colleagues.

The most widely known works among the specialists are *Handbook of Natural Gas Engineering* by D. L. Katz et al. (1959); *Hydrates of Natural Gases* by Y. F. Makogon (1981); *Clathrate Hydrates of Natural Gases* by E. D. Sloan (1990); *Gas Hydrates, Studies in Organic Chemistry* by E. Berecz and Balla-Achs, (1983); and *Handbook of Gas Hydrate Properties and Occurrence* by Lewin (1983). However, the requirements of theory and industry exceed by far the boundaries of the earlier published results.

Mastering of the hydrocarbon resources in the polar regions and in deep sub-sea zones has sharply increased the importance of studying both the natural and technogenic gas hydrates. Many discussions with Professors E. D. Sloan, R. Kobayashi, P. R. Bishnoi, G. D. Holder, J. M. Brooks, G. Lisichkin, Drs. D. B. Robinson, A. Malyshev, Y. Batalin, V. Fomina, L. Krasnovskaya, Y. Steklianin, L. Smirnov, M. V. Tolkachev, Y. P. Handa, H. J. Ng, V. A. Kamath, R. D. Malone, P. Notz, A. Lund, T. Austvik, B. Kvamme, T. Svartas, A. Nerheim, T. Valand, J. Monfort, Adisasmito Sanggono and many others have resulted in a need to write the present monograph with the applied character. I express my deep gratitude to all of my colleagues who helped to create this monograph in one way or another.

This monograph resulted from collaboration between the Institute of Oil and Gas Problems of the Russian Academy of Science and Texas A&M University. This monograph was sponsored by the Russian Committee on Science, New Technologies, and Education; Russian Academy of Sciences; Texas A&M University; Amoco, Brown & Root Ltd.; Conoco; Marathon; Holditch Associates; and the Minerals Management Service of the U.S. Department of the Interior.

Special thanks are directed to Professor Wayne Dunlap of the Offshore Technology Research Center who edited the translated manuscript, and who arranged the funding from Texas A&M University and others.

As the experience of translating my previous monographs indicates, it is a complicated task requiring not only knowledge of Russian and English languages, but also a deep understanding of the presented material. With this I take a special pleasure in acknowledging my son, Taras, who performed this work on a highly professional level.

Yuri F. Makogon

Department of Chemical Engineering

H. H. Dow Building
Ann Arbor, Michigan 48109-2136
313/764-2383

College of Engineering
The University of Michigan

August 16, 1988

Prof. Yuri F. Makogon
147717 Moscow
Lenin Region
Rasvilka
VNIIGAZ, USSR

Dear Professor Makogon:

It is some time since Dr. Robert Lee brought me from Toronto your recent book with your greetings and the paper on Natural Gas Hydrates. I recall our meeting at the World Petroleum Congress in 1971 in Moscow. Also, I found your earlier book on Natural Gas Hydrates very informative.

The paper you gave at Toronto was excellent in bringing out the experiences of harvesting of natural gas which occurs in hydrate form in the earth. Your work with understanding gas hydrates and the communication with U. S. investigators is commendable.

Although my experimental work with hydrates has been a small part of my total activities, I have been interested in gas hydrates for 54 years. The repressured gas fields in Michigan used for gas storage starting in 1941 were at pressures and temperatures close to those at which hydrates form. When Normal Wells oil and gas field was drilled in Northwest Territories of Canada (1943), I inquired about the reservoir temperature and pressure there below permafrost but found no hydrate conditions. It was you and your associates who found the gas hydrates present in the earth.

My health and age keep me from doing technical work these days. It is good to see the technical developments made by the oncoming generations like yourself and my former students Kobayashi, Robinson, and Holder.

With thanks and best wishes, I am

Sincerely yours,

Donald L. Katz

Donald L. Katz
A. H. White Distinguished University Professor
of Chemical Engineering, Emeritus

DLK:bd

INTRODUCTION

The percentage of hydrocarbon fuel use in the world energy balance has increased during the 20th century from 3% to 63% worldwide, and is as high as 75% in some industrial countries. Table I-1 illustrates the dynamics of population growth and energy consumption in the world during the present millennium. This table shows that the world population has increased during this period by 20.5 times, specific energy consumption has increased by 37 times, and the total consumption of energy from mineral sources has increased by 814 times. Figure I-1 presents the dynamics of population and energy consumption growth in the world during this millennium. Figure I-2 shows the structure of specific energy consumption starting in 1800 and provides a perspective for the world energy balance during the next 50 years.

It is noteworthy that the percentage of coal usage in the 1800s did not exceed 5%. It reached 50% by 1880, reached a maximum of 74% by 1925, and at the present time it is under 27%. The percentage of oil and natural gas in the world energy balance did not exceed three percent at the beginning of the century. This percentage increased to 40% by 1950 and to 66% by 1975. Currently, oil and natural gas consumption is at 63%. The role of natural gas in the world energy balance will certainly increase in future decades based on the availability of resources and environmental factors.

Potential sources of energy minerals and energy consumers in the world are distributed unevenly. The social status of countries and populations and the development rate of individual countries are determined by the availability of energy resources and the rate of their consumption. However, even in countries with vast energy resources, the rate of energy consumption and social status also depend on political stresses.

The history of Russia, whose high energy potential is recognized all over the world, is a prime example. Major stresses in the present century have slowed down social development in this country. Early in the century Russia held the lead in oil production in the world and produced more oil than the United States. However, the First World War, the 1917 Revolution, and the following Civil War left Russia far behind. Despite the fact that Russia increased its oil production and exceeded the United States in oil and gas production in 1975, Russia never reached the specific

Table I-1 World consumption of energy.

Years	1000	1500	1900	1920	1940	1960	1970	1980	1989 July	1990	1992	1993	1994	1995
World population, 10^6 p.	275	450	1617	1811	2295	2982	3635	4500	5000	5090	5240	5350	5470	5650
Energy consumption, 10^9 T.O.E.	0.01	0.14	0.9	1.50	2.25	3.55	5.57*	6.50*	7.70*	7.81*	7.79*	7.80*	7.92*	8.14*
Energy consumption per capita, T.O.E./yr.	0.04	0.31	0.55	0.83	0.98	1.19	1.53	1.44	1.54	1.53	1.49	1.46	1.45	1.44

*BP Statistical Review of World Energy, 1996.

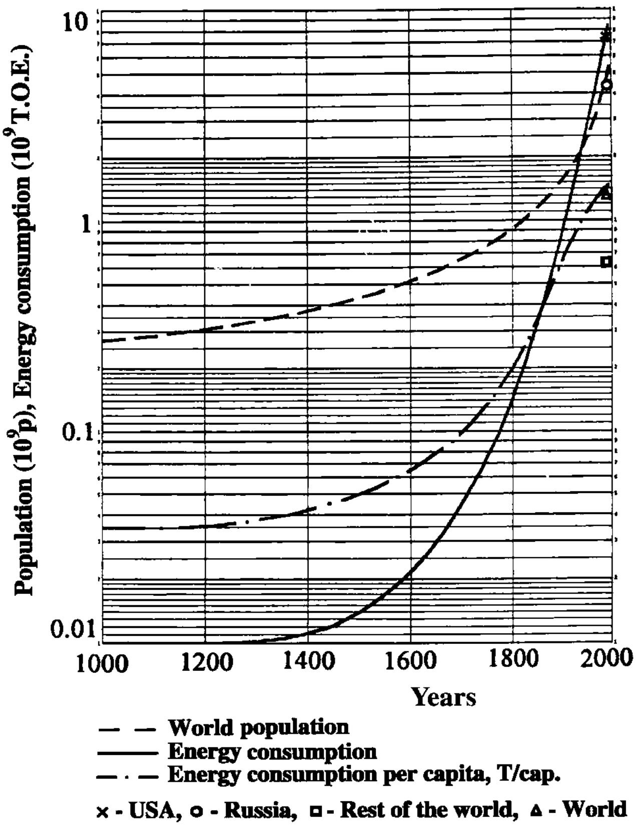


Figure I-1 World population and energy consumption.

rate of energy consumption per capita at the same rate as the United States (see Figure I-3).

Figure I-3 shows the growth dynamics of the three main energy industries in Russia: coal, oil, and gas production. There are three abrupt depressions on the production curves: the first is due to the Revolution and the Civil War; the second is due to the war with Germany, and the third is due to Perestroika in the political system.

This example illustrates dramatically that political aggression, either internal or external, is followed by destruction of economies and the degradation of a social system. In order to provide stable economic progress, mankind must find the power and wisdom to avoid political shocks and eliminate mutual claims.

Today increased rates in specific energy consumption are significantly higher than the population growth (see Figure I-1). Specific energy consumption is extremely uneven in different regions and fluctuates within a wide range from 0.1 to 7.5 tons of oil equivalent (TOE) per person

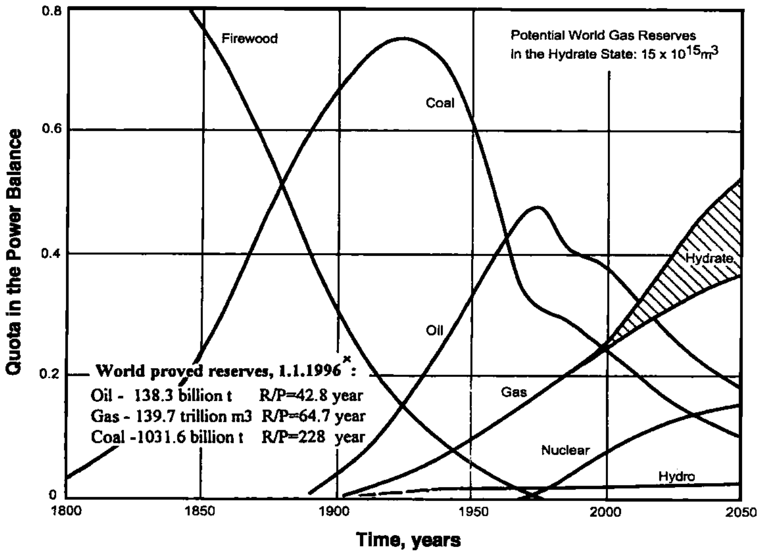


Figure I-2 World power balance dynamics.
x-BP Stat. Review of World Energy, 1996.

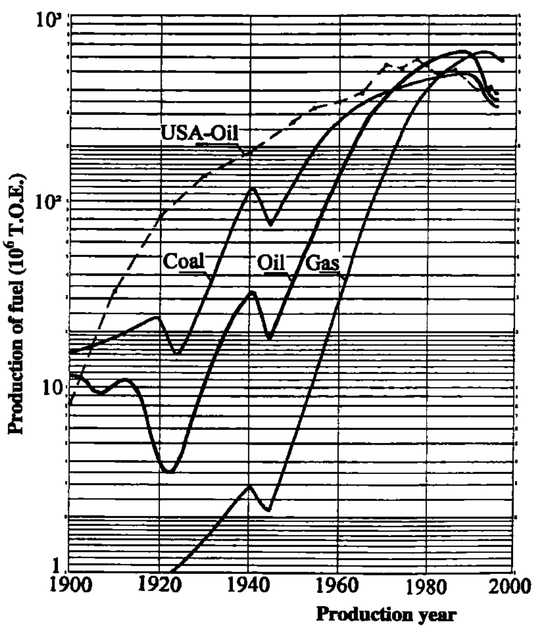


Figure I-3 Production of mineral resources in USSR.
(Oil Equivalent)—Oil = 10^7 kCal/T = 42.8 MJ/T; Gas = 0.9 × 10^7 kCal/1000 m^3 = 37.6 MJ/1000 m^3; Coal = 0.67 × 10^7 kCal/T = 28 MJ/T.

annually. Modern methods for survey and exploration of mineral energy sources allow us to determine the level of energy available for individual countries and regions in future decades. In the next 50–70 years, oil and natural gas will continue to be the main raw material for fuel and chemical industries, despite the investigation of new energy sources. So far, the share of oil in the world energy balance has reached its maximum and despite the annual increase in production oil's further role as a fuel will decrease. Active redistribution of hydrocarbon resources will take place in the world, as well as an active search for new unconventional hydrocarbon sources.

In modern conditions environmental requirements of energy sources, along with economic demands, have advanced to the forefront. Due to this the role of natural gas and unconventional hydrocarbons, sources will increase sharply. Some of the most prospective unconventional sources of natural gas are accumulations of natural gas hydrates which were proven to exist by Russian scientists in the 1960s. In 1969 a scientific discovery No. 75 was registered in the State Register of the USSR: "A Property of Natural Gases to Come into Combination with Water under Certain Thermodynamic Conditions in the Earth's Sedimentary Cover and to Form Gas Hydrate Deposits." This discovery by Russian scientists received international recognition and development.

The first gas hydrate deposits were revealed in the northern area of Siberia within the permafrost zone in the Messoyakhi and Ust-Vilyui fields. The first experience in producing gas from a gas hydrate deposit was obtained there.

Natural gas hydrates have become an exciting energy source for power engineers, space physicists, physical chemists, and other specialists over the last twenty years. Power engineers are interested in potential resources of hydrocarbon gases contained in the bowels of the earth in the hydrate state since those resources are by two orders of magnitude greater than the world's explored gas reserves.

The discovery of gas hydrate accumulations and the investigation of their properties have forced geologists to reconsider a number of principal statements on formation and conservation of oil and gas deposits both on land and offshore. Knowledge of the properties of hydrates allows us to evaluate in other contexts processes taking place in outer space. It gives us new insight into the formation of planets—particularly into the formation and dynamics of the earth's atmosphere and the ocean, as well as into the physics of comets and other space bodies.

Knowledge of the physical-and-chemical characteristics of hydrates and the processes of their formation, stable existence, and decomposition allow us to refine the impact of these phase transitions in the earth and on the thermal characteristics of the sedimentary section, ocean, and atmosphere. The volumetric properties of hydrates appear to be unique: the specific volume of water at its transition into the hydrate state increases by 26–32%, whereas at freezing the increase is just 9%. The specific volume of gas at its transition into hydrate state changes sharply.

A large number of these problems remain to be investigated in order to get a quantitative result. However, it is noted that gas hydrates cannot be neglected when solving multiple fundamental problems connected with the dynamics of our planet and other space bodies.

Investigations on natural gas hydrates are underway in several scientific laboratories around the world—Russia, the United States, Norway, England, France, Japan, Indonesia, Brazil and other countries. The existence of natural gas hydrates is a global one, and these studies represent an example of international cooperation. Studies on gas hydrates are done under the United Coordination Program. The results of these studies are discussed annually at joint conferences.

Along with fundamental laboratory studies, intensive field work is being done to reveal gas hydrate fields on land and, especially, in the world's oceans. More than 60 large gas hydrate fields have been revealed to date in oceanic sediments and eight fields on land. Explored reserves of methane in the hydrate state are over 700 trillion m^3, exceeding seven fold the world's explored gas reserves. Potential gas resources concentrated on earth in the hydrate state exceed 1.5×10^{16} m^3. Figure I-4 provides a schematic map of the gas hydrate deposit occurrences (Kvenvolden, 1994). Figures I-5 through I-8 present the gas hydrate fields discovered on the North American Continent and in the seas of the USA.

An important concern is the economical feasibility of the development of gas hydrate deposits. There is an erroneous opinion among some specialists that in the regions abundant in natural gas resources, investing in the study of hydrates, surveys, and development of gas hydrate deposits is not appropriate. Unfortunately, the natural distribution of these energy resources is uneven. There are some regions low in mineral resources. The energy distribution of Russia's Far East, for example, is principally different from Western Siberia. Revealing hydrocarbons in the hydrate state and putting them into an energy balance of individual regions may radically change energy supply to industry and municipal consumers.

Despite some definite scientific achievements in hydrate studies, the basic properties of hydrates and hydrate-saturated porous media such as acoustic, electrical, thermophysical, thermomechanical, volumetric, and others remain practically unknown.

Preliminary results on the study of the acoustic properties of hydrates allowed us to design the means to reveal hydrate deposits in oceanic sediments and revealed the majority of hydrate occurrences known to

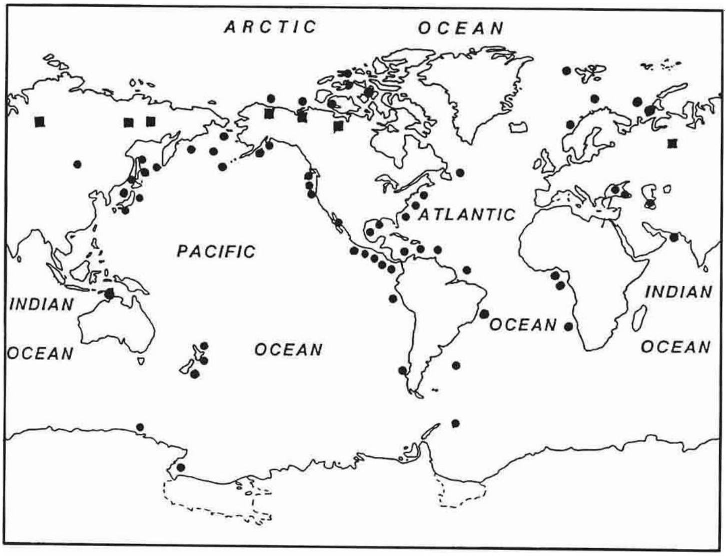


Figure I-4 Map of worldwide locations of gas hydrates occurrences in on-shore (■) and offshore (●) sediments.

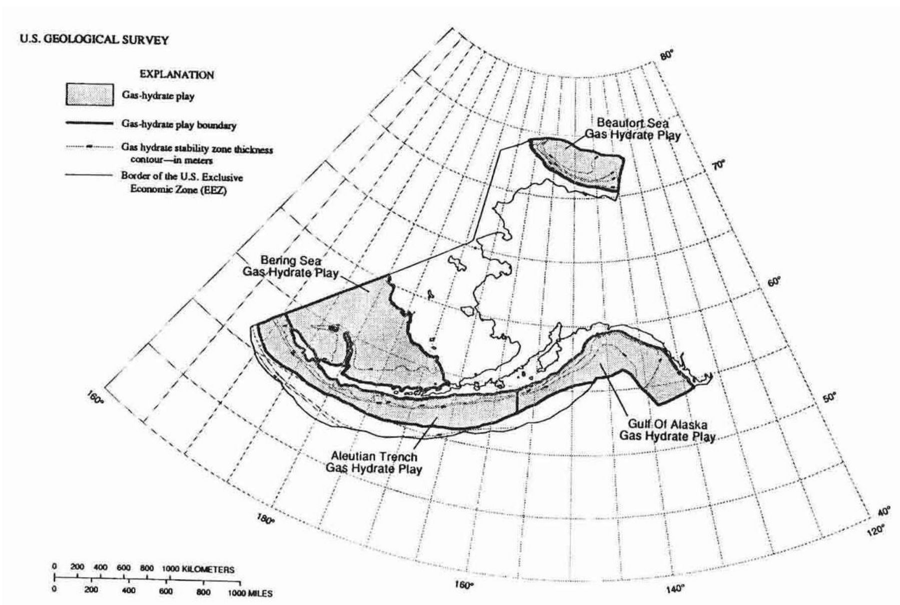


Figure I-5 Map of the Beaufort Sea, Bering Sea, Aleutian Trench, and Gulf of Alaska gas hydrate plays (Collett et al., 1994).

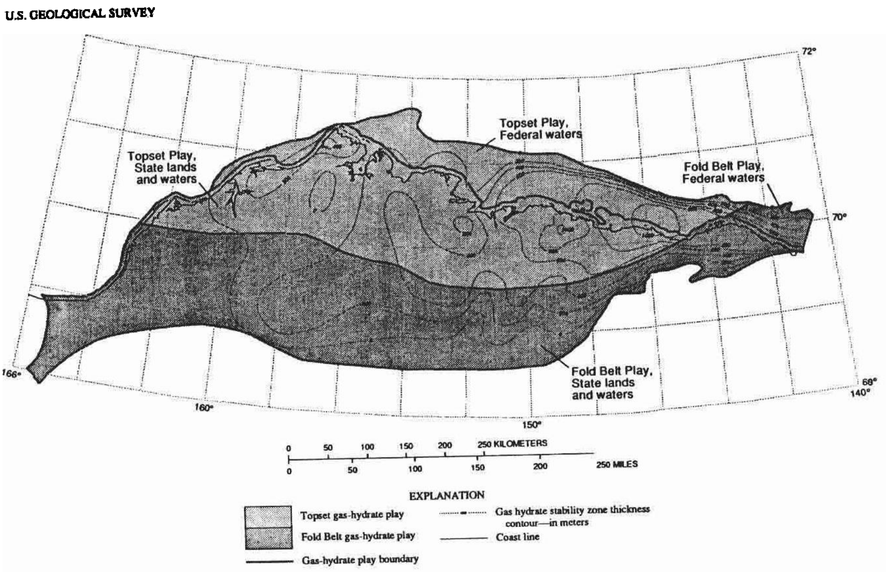


Figure I-6 Map of the Alaska topset and fold belt gas hydrate plays (Collett et al., 1994).

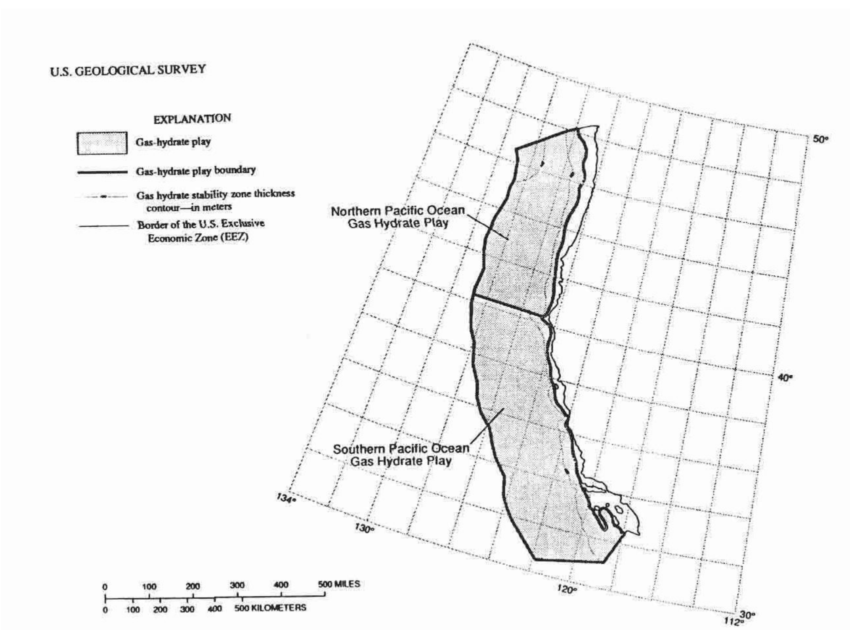


Figure I-7 Map of the Northern Pacific Ocean and Southern Pacific Ocean gas hydrate plays (Collett et al., 1994).

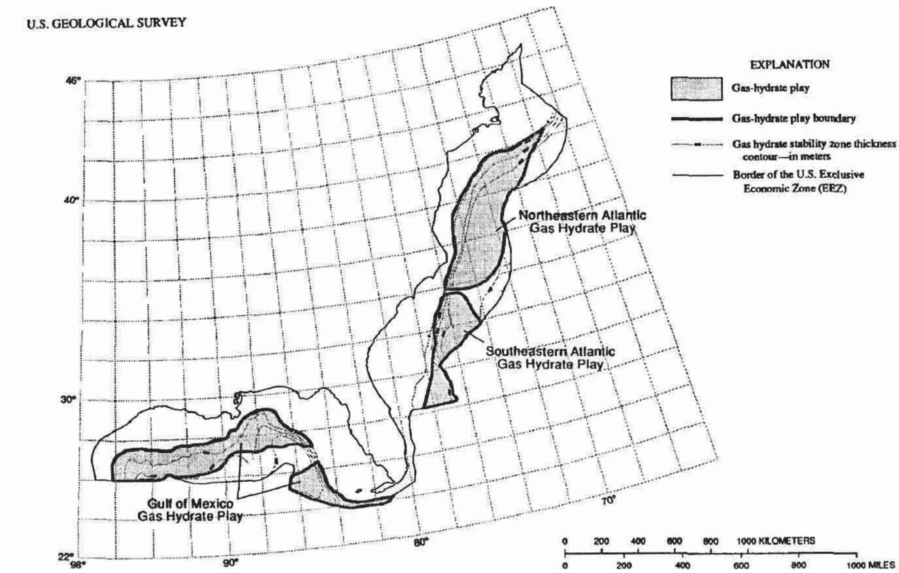


Figure I-8 Map of the Northeastern Atlantic Ocean, Southeastern Atlantic Ocean, and Gulf of Mexico gas hydrate plays (Collett et al., 1994).

date. However, the knowledge of seismoacoustic characteristics of gas hydrates does not allow us to determine the hydrate saturation of sedimentary layers in the zone of hydrate formation. For this, expensive wells must be drilled with core sampling and the full suite of logging.

Investigation of electrical properties of gas hydrates, and the processes of their formation and dissociation will allow us to develop highly efficient remote methods of outlining gas hydrate accumulations using aerial or satellite mapping.

Thermophysical properties of gas hydrates have been examined inadequately, within a very narrow temperature interval and for a limited number of hydrates.

The most difficult to examine are the thermomechanical and volumetric properties of hydrates. Absence of data on these properties has already resulted in a number of serious accidents in different parts of the world during construction and operation of wells in hydrate-saturated intervals of sedimentary rocks. It is important to know these properties of hydrates when designing, constructing, and operating offshore engineering installations.

Studies on properties of gas hydrates have made it possible to formulate the basic propositions of the influence of natural gas hydrates on the ecological situation on our planet. Natural gas hydrates stabilize the thermal regime of the sedimentary section on one hand, and actively affect the dynamics of the ozone layer, greenhouse effect, and the earth's climate on the other.

Without revealing in detail the basic theses of the gas hydrates problem we would like to note that although hydrates were studied for over two centuries, the extent to which their properties have been determined is still in a primitive state, most notably at very high pressures and low temperatures. The basic technological features of hydrate formation and decomposition processes as well as kinetics and morphology of crystal hydrates have also been poorly studied. This considerably lowers the possibility for creating radically new technologies based on gas hydrate processes.

At the present time, fundamentally new instrumental methods and means of investigations have been developed for studies of gas hydrate properties and kinetic processes, which achieve new scientific and practical results.

Many problems of technogenic gas hydrates exist parallel with those of natural gas hydrates, complicating production, transportation, and processing of gases and volatile liquids. A regular trend can be seen in the example of gas hydrates—science solves only topical problems. Gas hydrates were first obtained in 1778, however, until the 1930s they were of no industrial interest. With the advance of hydrocarbon production and pipeline transportation, when formation of hydrate plugs resulted in emergency shutdowns of gas supply, hydrates came under study in the context of developing an effective means of their prevention and control. After the discovery of natural gas hydrates in the 1960s, they were studied in the context of gas production from hydrates and putting their resources into the energy balance. Unique properties of hydrates provide a basis for new efficient technologies.

Modern study of crystalline hydrates has two clear directions—technogenic and natural gas hydrates. Technogenic gas hydrates form in the technological system during production, transportation, processing, and storage of various gases and liquids having high vapor pressures. The goal of these studies is to create effective methods of prevention of hydrate formation and to develop new technologies utilizing gas hydrate properties.

Study of the natural gas hydrates pursues the goal of in-depth understanding of the genesis and properties of the natural hydrates. Based on this understanding, the following effective techniques are created:

- revealing and mastering the natural gas hydrate accumulations;
- assessment of hydrate influence on engineering constructions in hydrate formation intervals; and
- effect of hydrates on regional ecological situations and global changes.

CONTENTS