SAVONIA

Development of Natural Gas Hydrate

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Abstract

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Abstract

At present, the energy crisis is becoming more and more serious. At the same time, the extensive use of coal and oil has caused serious environmental pollution problems. People are urgently developing new energies, to replace the traditional energy, which has low pollution or even no pollution. Talking about the energy, people immediately think of the coal, oil or natural gas, but seldom think of the “ice”. However, since the 1960's, people have found a burning “ice” in the permafrost and the depth of the ocean. This kind of "combustible ice" in geological field is called natural gas hydrate.

This thesis will focus on introducing the development of natural gas hydrate, composition of natural gas hydrates, the formation of natural gas hydrates, the development history of natural gas hydrates and exploration and development method of natural gas hydrates. One of the most important parts is to introduce five exploration methods and six kinds of development technology. The development of technology contains three traditional development technologies and three new development technologies.

This thesis also introduces the environmental problems in the development process of natural gas hydrate.

Keywords
Natural Gas Hydrate, New Energy, Environmental Pollution, Development Technology, Low Pollution

CONTENTS

SYMBOLS AND ABBREVIATIONS

$M \cdot n\ H_2O$	Chemical formula of natural gas hydrate
CH_4	methane
CO_2	carbon dioxide
C_2H_6	ethane
C_3H_8	propane
C_4H_{10}	butane
N_2	nitrogen
H_2S	hydrogen sulfide
DSDP	Deep Sea Drilling Project
OPD	Ocean Drilling Program
GHSZ	gas hydrate stability zone
US	United States
H_2O	water
O_2	oxygen
$CaCO_3$	calcium carbonate
$Ca(HCO_3)_2$	calcium bicarbonate
BRS	bottom simulating reflector
VAMP	structures with abnormal velocity and amplitude

1 INTRODUCTION

Energy is very important for the economic and social development. Energy is needed everywhere. Petroleum energy and coal energy have been used for over 100 years. However, these two main energy resources will be exhausted with the continuous consumption of energy. At the same time, due to the extensive use of the two energies, there are series of environmental problems in the world, especially in China. The rapid development of economy accompanied by huge energy consumption has made China a net importer of energy. China becomes a most seriously polluting country in the world. Although China vigorously builds hydroelectric power stations, nuclear power stations, wind power stations, solar power stations and so on, it still is unable to meet the needs of economic development and energy demand of a large population. So, in order to resolve the energy problem and environmental pollution problem, people must vigorously develop renewable energy and clean energy.

Nowadays, all countries are actively developing new energy, including solar energy, wind energy, nuclear energy, tidal energy, bio energy and geothermal energy and so on. In addition, this also includes natural gas hydrate. This energy is not well known to the public because it has not fully entered the commercial development stage. However, this new energy development has become an important research subject for many countries. Because scientists believe this new energy sources will become main energy in 21st century. Not only because of the natural gas hydrate reserves is great, but also because of natural gas hydrate is a kind of clean energy. Natural gas hydrate is same as natural gas. It just produces carbon dioxide and water vapor after combustion. This will greatly reduce the impact on the environment.

This thesis will focus on a deeper research of the development of natural gas hydrate in the world. The development of natural gas hydrate had been researched about 50 years. At the present stage, there are many methods to explore the natural gas hydrates, include geophysical prospecting, geochemical exploration, by typomorphic mineral exploration and by earth-observation system and so on. Through these methods it is found the identification marks (geological sediment sampling, boring sampling, deep sea exploration and so on) of natural gas hydrate, and then, we will know the distribution of the natural gas hydrate. After finding the distribution of the natural gas hydrates, we need to ensure based on the mining environment are which mining method is the best. For example, we use thermal activation method extraction if there are resources. Because the method needs an injection into the hot fluid heating in the natural gas hydrate layer and promote the natural gas hydrate break down in to water and natural gas hydrate. We can use CO_2 displacement method when we have more CO_2 (use the carbon dioxide by industrial emissions). Other methods (Pressure releasing method, Inject chemical agents, High energy gas fracturing technique, Slurry mining) will be researched in detail in this thesis. Actually, although there are many methods to develop the

natural gas hydrate. However, the principle of the methods is similar. The first thing is to decompose the natural gas hydrate, and then extract the natural gas.

2 SUMMARY OF NATURAL GAS HYDRATE

Natural gas hydrates look likes ice, but they are convenient to use, have high combustion value, and are a clean and non-polluting energy. It is a kind of non-stoichiometric crystalline clathrate compound (at high pressure, carbon atom can attract hydrogen atoms because of electronegativity of the carbon atom and formed clathrate compound) formed by natural gas and water under the condition of low temperatures and high pressure.

Chemical formula of natural gas hydrate is

$$M \cdot n\, H_2O \qquad (1)$$

Where *M* is gas molecules in the hydrate and *n* is hydration number, also called water molecule number. (Zhang 2008, 19.)

Natural gas contains many ingredients. For example, It includes some homologue (includes CH_4, C_2H_6, C_3H_8 and C_4H_{10}), CO_2, N_2, H_2S and so on. CH_4 (Methane) is the ingredient to form the natural gas hydrate. If the methane is more than 99% in the natural gas hydrates, it is called methane hydrate. (See Fig.1).

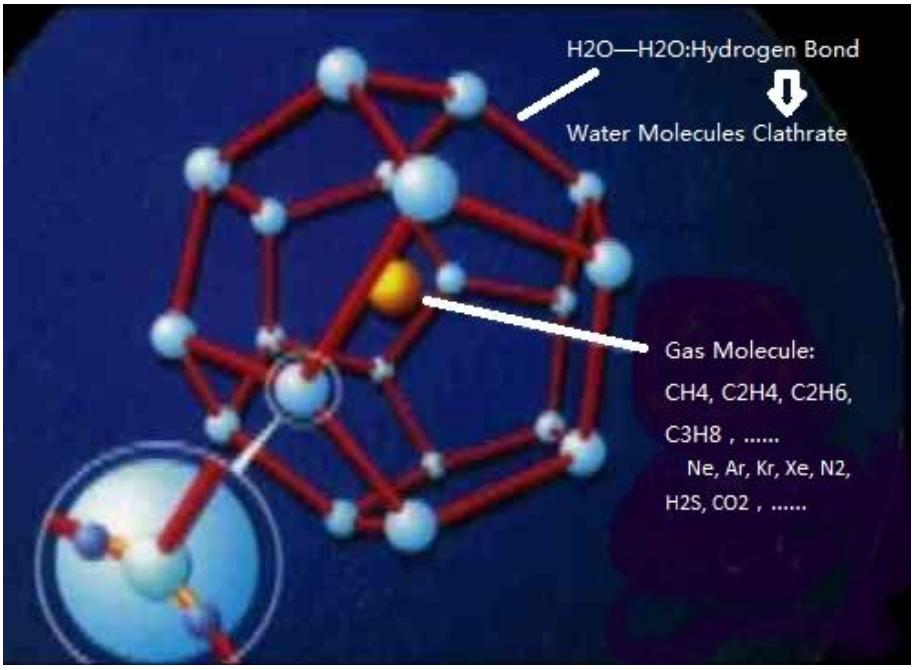

Figure 1. Chemical molecular structure of natural gas hydrates (Cishan 2007.)

Under standard situations, one unit volume natural gas hydrate can resolve up to 164 unit volume natural gas (See Fig.2). It is high combustible and has a low flash point because of much CH_4

included in the natural gas. Under the same conditions, energy generated by burning natural gas hydrate is more than coal, oil, natural gas. It does not produce exhaust gas or residues after combustion of natural gas hydrate. So, natural gas hydrate is a kind of clean energy in the future, and it allows people to avoid the most problems of pollution.

Thermochemical chemical equation of natural gas hydrate:

$$CH_4 \bullet 8\ H_2O + 2\ O_2 \rightarrow CO_2 + 10\ H_2O \qquad (2)$$

Reaction condition is ‘combustion’. (Zhang 2008, 20.)

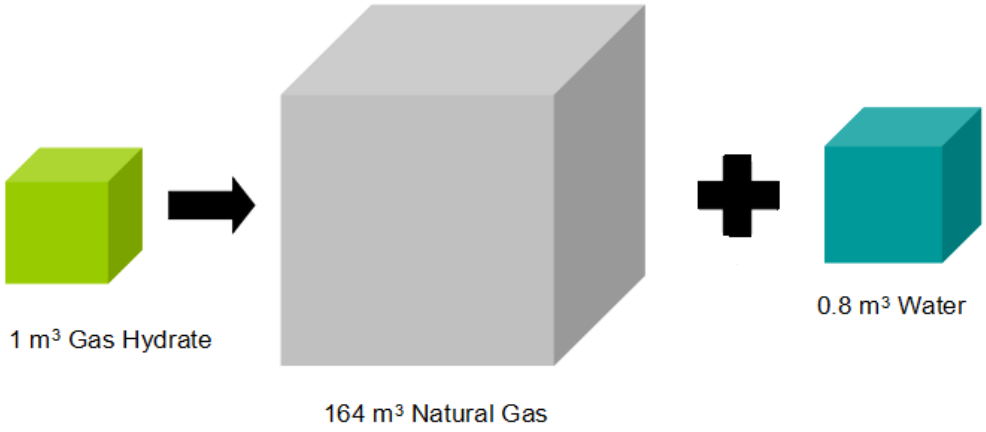

Figure 2. The composition of natural gas hydrate

About the physical properties, density of natural gas hydrate is close and slightly smaller than the density of the ice. Shearing coefficient, electrolysis constant and thermal conductivity are smaller than ice. Sound wave propagation velocity of natural gas hydrate is bigger than gas-containing sediment and saturated water sediment, and neutron porosity is smaller than saturated water sediment. These differences are theoretical basic to recognize natural gas hydrate by geophysical exploration methods. (Zhang 2008, 21.)

2.1 Formation of natural gas hydrate

The formations of natural gas hydrate in two different environments include sea environment and terrestrial environment.

2.1.1 Formed in the ocean

The formation of natural gas hydrate is a natural gas molecule wrapped water molecules. There are three conditions to form the natural gas hydrate: temperature, pressure and raw material.

First, the temperature cannot be too high. It means that the natural gas hydrate easily resolves when the temperature is higher than 20℃. However, under the sea temperature is usually maintained at 2 ℃ to 4 ℃. So, the sea temperature is most suitable for formation of natural gas hydrate.

Second, the pressure need be large enough. At 0 ℃, only at 30 atmospheric pressures the natural gas hydrate can be generated. The depth of the ocean easily guarantees 30 atmospheric pressures. The pressure is bigger, and the natural gas hydrate is more difficult decomposition if the pressure increases.

At last, the raw materials are natural gas molecules. The organic matter in the seabed and the submarine sediments of paleontology corpse will be decomposed to methane or other gas by bio-transformation. These processes can produce enough gas. Then the natural gas hydrate crystal will be formed through the combined action by temperature, pressure, gas and bio-transformation in the seabed strata of porous media. So, natural gas hydrate is distributed in all the oceans of the world.

2.1.2 Formed in the continent

The natural gas hydrates also can form in beds of sandstone or siltstone of continental rocks, but the depth must be less than 800 m. Sampling results pointed out that the formation of the natural gas hydrate is by mixed heat, the gas of microbial decomposition and the heavier hydrocarbons can be selectively decomposed. This kind of pattern exists in Alaska and Siberia.

3 DEVELOPING HISTORY OF NATURAL GAS HYDRATE

The developing history of natural gas hydrate has existed more than 200 years. At first it was discovered in laboratory. After about 150 years, it was found in natural environment. After that, people began to study how to develop and reserve the natural gas hydrate.

3.1 Exploration and discovering history

Developing and discovering of natural gas hydrate experienced a long process. In 1810, the natural gas hydrate was discovered in the laboratory. In 1960, the natural gas hydrate was found in a natural environment, almost 150 years after it was discovered in the laboratory.

More than two centuries' many scientists had researched kinds of natural gas hydrate and various physical and chemical properties. The extensive and fruitful studies include natural storage condition, formation condition, stock assessment, exploration and development methods, etc. Now many scientists are still to explore and research natural gas hydrate, because the natural gas hydrate is likely to be the main resource of energy in the following 1000 years. (Zhang 2001, 3.)

3.1.1 Exploration and discovering history around the world

In 1810, natural gas hydrates was discovered for the first time in the laboratory. (Wang 2012, 33.)

In 1934, the former Soviet Union found the natural gas hydrate in the blocked natural gas pipeline. The pipe was blocked by the natural gas hydrate. This discovery caused the former Soviet Union people attach importance to the natural gas hydrate. (Wang 2012, 33.)

In 1965, the former Soviet Union found natural gas hydrate mineral reserves for the first time in the permafrost of West Siberia, and caused the attention of many scientists in different countries. (Wang 2012, 33.)

In 1969, the USA began to prospect natural gas hydrate. (Wang 2012, 33.)

In 1970, the Soviet Union began commercial exploitation of the natural gas hydrate mineral deposits. (Wang 2012, 33.)

After that, in the same year, Deep Sea Drilling Project (DSDP) implemented deep-sea drilling in continental margin of the eastern USA. They found many more bubbles from the cold sediment cores, and the processes continued for hours. However, at that time, the marine geologists were

very puzzled. They knew the bubbles were caused by the hydrate decomposition after a period of time, and in fact, the sediment cores were hydrate. (Wang 2012, 34.)

In 1971, the USA scholar Stoll first found natural gas hydrate in deep sea drilling cores, and formally proposed the concept of "natural gas hydrate". (Wang 2012, 34.)

In 1974, the former Soviet Union found ice crystal samples of natural gas hydrate in depth of 1950 meters of Black Sea. (Wang 2012, 34.)

In 1979, DSDP's 66th and 67th deep-sea drilling were implemented in the Gulf of Mexico. They gained 91.24 meters hydrate core of natural gas. Thus it was verified the existence of natural gas hydrate deposits for the first time under the sea. (Wang 2012, 34.)

In 1981, DSDP uses "Glomar Challenger" (See Fig.3) drilling vessel to take three feet long hydrate core from the bottom of the sea. (Wang 2012, 34.)

Figure 3. Glomar Challenger (Kepu 2006.)

In 1991, the U.S. department of energy organized the "America is national symposium on natural gas hydrate". (Wang 2012, 34.)

In 1992, the 146th voyage of Ocean Drilling Program (OPD) got the natural gas hydrate core in the Oregon. In the same year, Japan began to pay attention to the natural gas hydrate and completed investigation and evaluation of natural gas hydrate in the waters surrounding Japan. However, Germany was the first country to excavate natural gas hydrate. (Wang 2012, 34.)

In the winter of 1995, during the OPD's 164th voyage implemented a series of deep-sea drilling at Blake ridge and gained a lot of hydrate core. For the first time it was proved that the deposit has commercial development value. (Wang 2012, 34.)

In 1997, ODP team for the first time finished the direct measurement and seabed observation for hydrate by submarine in the Carolina Sea. In the same year, OPD has made natural gas hydrate cores when they implemented deep-sea drilling on Canada's West Coast. At that point, DSDP and OPD found 10 accumulations of natural gas hydrate: Peru trench slope, Central America trench slope (Costa Rica, Guatemala and Mexico), Atlantic sea of southeast USA, two sea areas of Japan, Alaska offshore and Mexico bay and so on. (Wang 2012, 35.)

In 1998, natural gas hydrate was regarded as strategic energy of national development and it was included in the national long-term plan. (Wang 2012, 35.)

In the same year, Japan cooperated with Canada. They were drilling for natural gas hydrate in northwest Canada and got 37 meters hydrate cores from the underground 890 ~ 952 meters deep. That drilling depth was 1150 meters and it was first drilling in the high latitude permafrost zone for research natural gas hydrate. (Wang 2012, 35.)

In 1999, Japan mined some natural gas hydrate in Shizuoka Prefecture Omaezaki offshore. (Wang 2012, 35.)

From 2000, on research and exploration of natural gas hydrate was entering the peak period. There were at least 30 countries and regions involved and USA's plan was the most perfect. The reason is that the President's Commission on Science suggested the research and development of natural gas hydrate. Many members of congress introduced bills to support development of natural gas hydrate. Therefore, every year the financial allocation for natural gas hydrate research was more than ten millions dollars in the United States. (Wang 2012, 35.)

There are 19 countries establish a research institute to research and sample the samples of marine geology. 50 technical personnel drive a ship from the east coast of USA to prospect submarine natural gas hydrate. The 7 layers cabins of the exploration ship are equipped with advanced experimental equipment. The equipment in the ship can be used to study sedimentology, paleethnology, petrology, geochemistry, geophysics, etc. (Wang 2012, 35.)

3.1.2 Exploration and discovering history in China

As the largest developing country in the world, the problem of energy shortage is very prominent in China. There is a large gap between supply and demand of oil and gas resources in China. The development trend of Chinese crude oil trade manifest is more and more relying imported crude oil. (Zhishi 2014.)

From 1993, China has moved from being a net exporter of oil to become the world's second-biggest importer, relying on foreign sources for 40% of its demand. (ECO Chinese network 2014.) In 1999, China imported more than 40 million tons of oil. China imported about 70 million tons oil in 2000. In 2009, China imported crude oil and petroleum products account to 0.24 billion tons, the imports were 2.6 times more than in 2000. (See Fig.4) However, net crude oil imports reached 0.269 billion tons, net crude oil foreign degree of dependency increased to 56.6%. In 2013, China imported 0. 282 billion tons crude oil, 4.03 percent rise to year-ago levels. (Wang 2012, 37.)

China is already a big importer of energy sources because of energy sources imports were larger and larger. In 2009, China imported coal about 0.126 billion tons, the imports were 60 times more than 212 million tons in 2000. In 2009, China became a net importer of coal on an annual basis for the first time since reliable records have existed. (FT Chinese network 20.04.2010.) Due to the expansion of energy demand, the trend of import will continue. (See Fig.4) So, there is an urgent need to develop new energy resources to meet the needs of its growing economy in China.

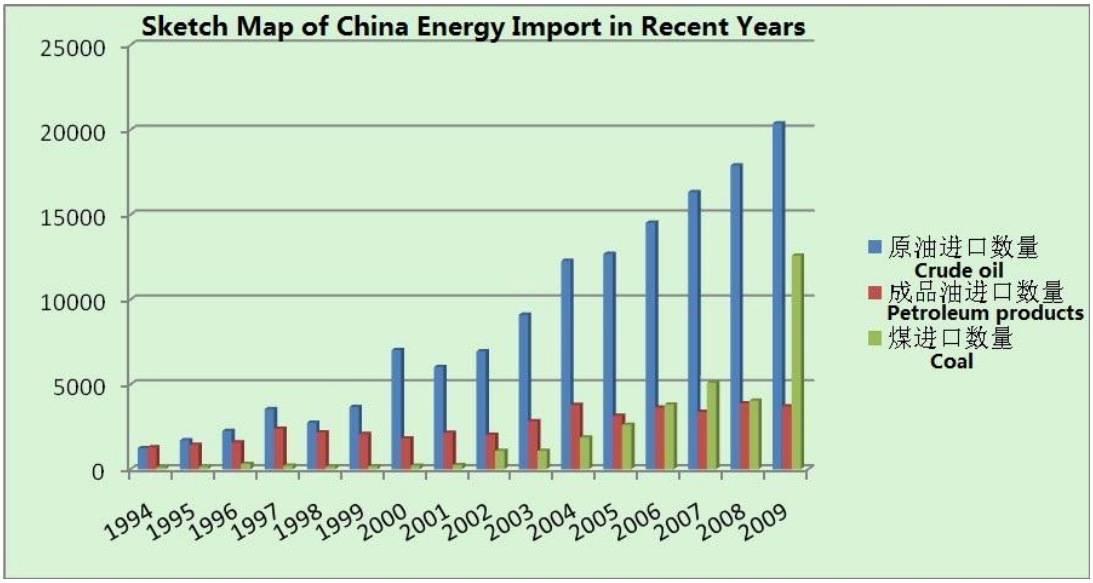

Figure 4. Sketch map of China energy import in recent years (Cnfol.com 09.09.2010.)

In 1999, in the National Development and Reform Commission, the Ministry of Finance and other national departments support, the Ministry of Land and Resources integrated all aspects of

outstanding scientific engineers and technicians to officially launched survey of natural gas hydrate resources. So far, China Geological Survey has carried out 40 times comprehensive investigations of natural gas hydrate in Pearl River Estuary basin, completed 45800 kilometers high resolution multi-trace seismic surveying and 36800 kilometers multi-beam surveying, 7100 kilometers sub-bottom profiling surveying, seabed geology sampling at 1480 stations and measuring seafloor heat flow at 222 stations. (Wang 2012, 39.)

On April 14th, 2005, Geological Museum of China collected the first discovery of natural gas hydrate carbonate rock sample. China found the largest natural gas hydrate distribution area; its area is about 430 square kilometers. (Zhishi 2014.)

In the morning of May 1st, 2007, China's first successful sampling in the northern south China sea and confirmed that the northern South China Sea was especially rich in natural gas hydrate resources. This marks the Chinese natural gas hydrate investigation level has entered advanced ranks in the world. China is the fourth nation getting the hydrate physical samples.

In September 2009, China Geological Department published that they observed the new energy of environmental protection natural gas hydrate in the Qinghai Tibet Plateau. They expected the new energy will put in to use after a decade or so. That was first time found the natural gas hydrate has found in Chinese region. In Qinghai Tibet Plateau the prospective reserves of natural gas hydrate at least amount to 350 tons oil. (Zhishi 2014.)

In 2013, China marine geology science and technology personnel first time drilled high purity natural gas hydrate samples in Pearl River Estuary Basin of Guangdong coast, and they knew the reserves of natural gas hydrate by drilling. The main features of the natural gas hydrate samples were with shallow burial depth, large thickness, high enrichment and types. The controlling reserve is about 100 billion cubic meters to 150 billion cubic meters, equivalently a large scale conventional natural gas mine. (Zhishi 2014.)

In 2014, the eighth session of the international natural gas hydrate Conference was opened in Beijing and it was sponsored by the Chinese geological survey and China Academy of Sciences. (Zhishi 2014.) Reporters learned China plan to implement drilling of natural gas hydrate in China Sea. This will effectively promote the China’s natural gas hydrate exploration and development process and may trigger off "revolution" of Chinese energy development and utilization.

According to the China’s strategic planning, from 2006 to 2020 is a survey phase, from 2020 to 2030 will be development and trial production phase, and during 2030 and 2050, China will enter commercial production of natural gas hydrates.

3.2 Distribution of natural gas hydrate

Natural gas hydrate increasingly attracted attentions of scientists and governments around the world. Because natural gas hydrates is an important energy resource in the 21st century. Since the 1960s, the Deep Sea Drilling Program (DSDP) and Ocean Drilling Program (ODP) carried out a large number of deep-sea drilling marine geological investigation and geophysical exploration and directly or indirectly found the natural gas hydrate in many places of the seabed. (360doc 03.11.2011.)

Since the 1980s, in the developed countries had invested much money carried out investigation and evaluation of natural gas hydrate on mainland or in international sea area. USA, Japan, Canada and India had developed the exploration and development of natural gas hydrate in the state plan.

3.2.1 Distribution of natural gas hydrate around the world

At present, scientists have found 116 potential natural gas hydrate origins in the world (See Fig.5). (Tang 2003, 192.) The main distribution of natural gas hydrate are in the Gulf of Mexico, the Caribbean Sea, the continental margin of the eastern South America, the continental margin of Western Africa, the Blake Ridge of eastern US coast, the Bering Sea, the Okhotsk sea, the Kuril Trench, the Okinawa trough, the Japan sea, the Nankai Trough, the Sulawesi Sea, sea area of northern New Zealand, the Central America trough, the California offshore, the Peru trough, the Gulf of Oman, the Antarctica's Ross Sea and Weddell Sea, the Arctic's Barents sea and Beaufort Sea, the Black Sea and Caspian Sea.

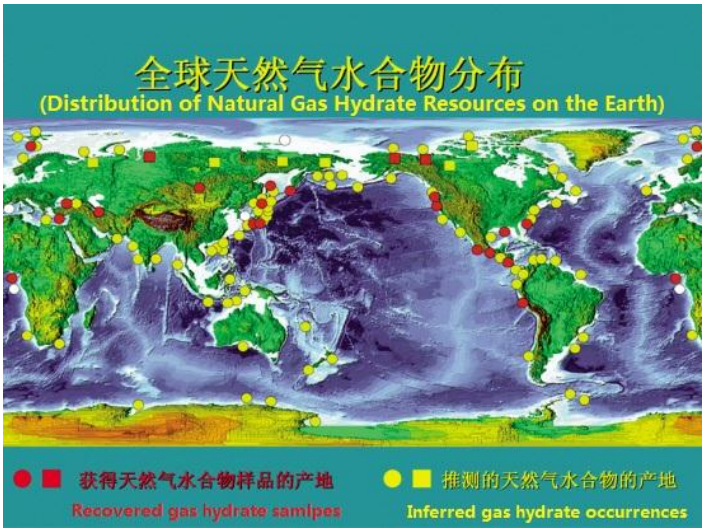

Figure 5. Distribution of natural gas hydrates resources on the earth (Hudong 02.02.2014.)

Natural gas hydrate resources mainly exist in groove-arc-basin systems, continental slope systems, marginal basins and the deep-sea basins. In addition, it also includes spreading basin and permafrost region of Arctic. (Wang 2012. 53-54.)

In the Arctic region, the natural gas hydrate exists in the underground between 200 meters and 1100 meter. The temperature will be kept at between -8 ℃ and 13 ℃ in this range. The temperatures ensure that the natural gas hydrates cannot decompose. At the same time, the Arctic region grew a large number of vegetation and paleontology in the 2.5 million years ago. The organic matter and the sediments of paleontology corpse will be decomposed into methane or other gas by bio-transformation. These processes can produce enough gas. (See Fig.6)

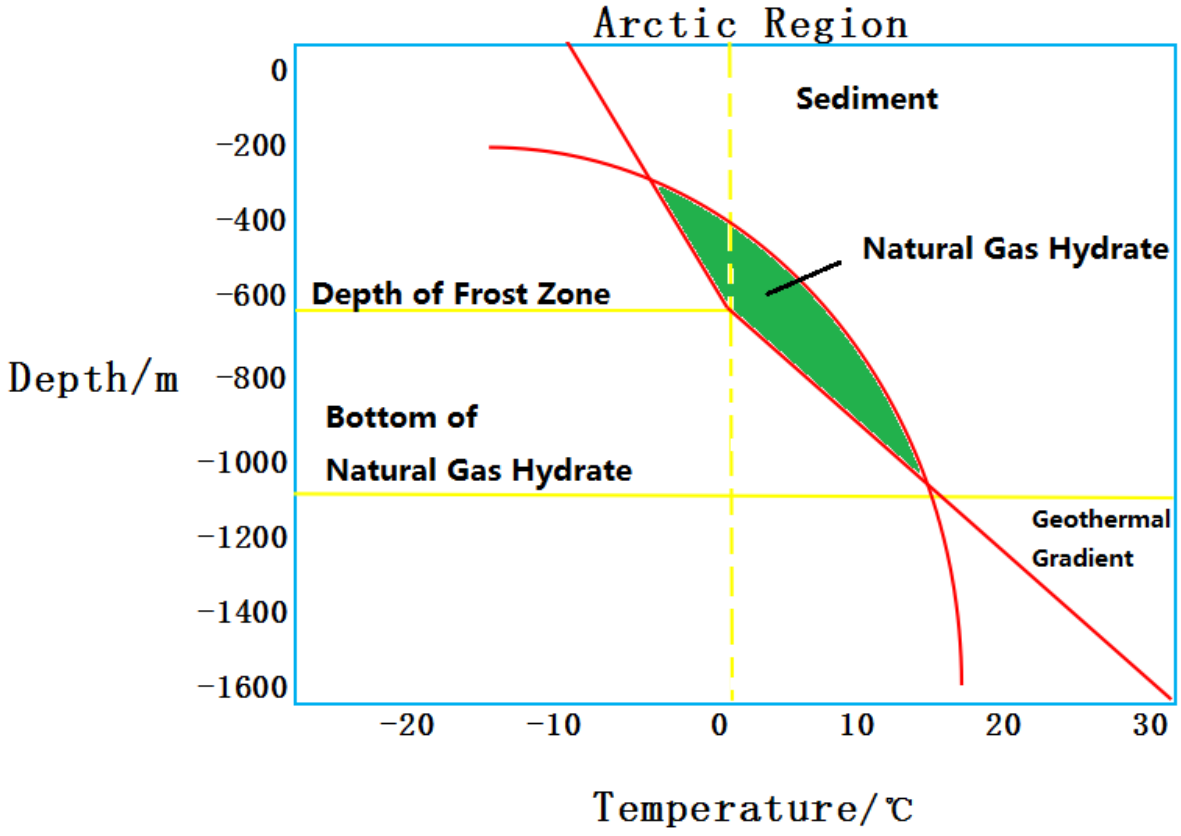

Figure 6. Arctic Region

85% area of the Atlantic, 95% area of the Pacific and 96% area of the Indian Ocean are rich in natural gas hydrates.

In the marine environment, natural gas hydrate mainly exists under the sea level from 1200 meters to 1500 meters (because of crustal movement, the natural gas hydrate also can exist under the sea level from 400 meters to 1200 meters). In this depth range, the pressure is large enough, the

temperature is lower than 20 ℃, the temperature is generally maintained at between 2 ℃ to 17 ℃℃. And the organic matter will be decomposed to methane or other gas by bio-transformation. This is why the natural gas hydrate distributes under the marginal sea. (See Fig.7)

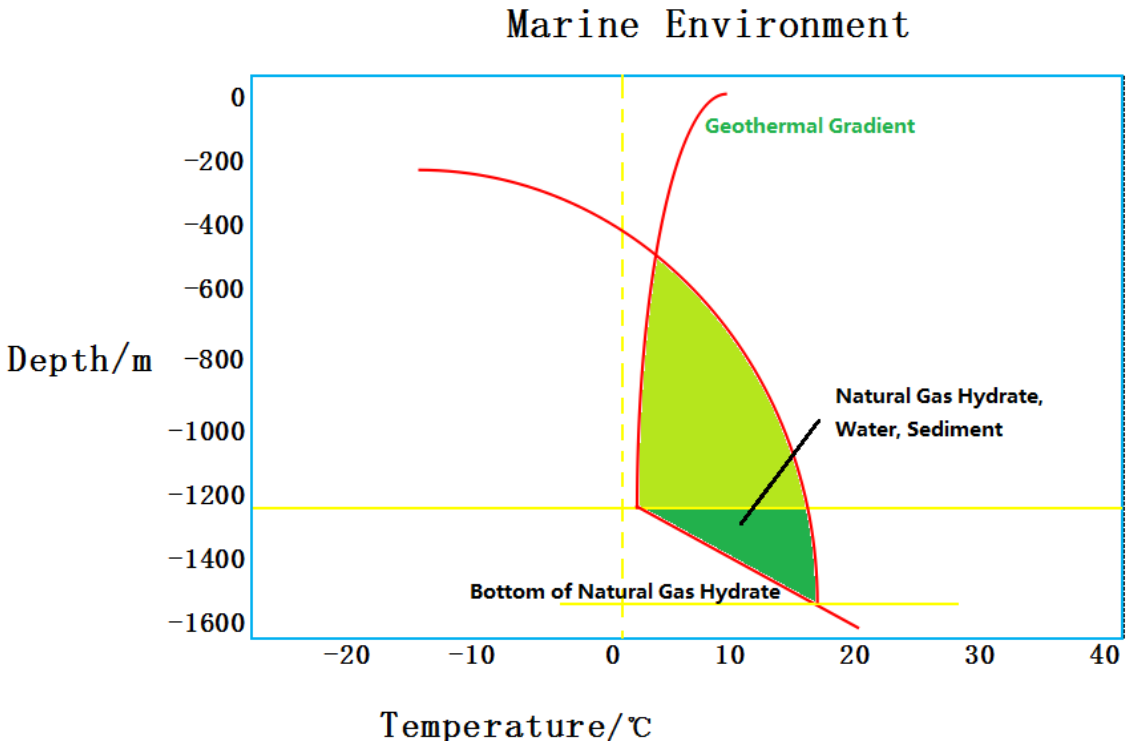

Figure 7. Marine Environment

3.2.2 Distribution of natural gas hydrate in China

In China, the natural gas hydrate mainly distribute in the South China Sea, East China Sea, Tibet plateau permafrost and the Dongbei permafrost. (See Fig.8) According to the rough estimate, the deposits are 64.97x1012 m^3, 3.38x1012 m^3, 12.5x1012 m^3 and 2.8x1012 m^3 in the four areas. (Zhishi 2014.) Chinese had got the physical samples natural gas hydrate in the Shenhu waters and Qilian Mountains.

Figure 8. Distribution diagram of nature gas hydrate in China (JNTV 03.02.2014.)

In 2012 and 2013, the main exploration work of natural gas hydrate was pre-exploration in the Shenhu Waters. (See Fig.9)

Figure 9. Distribution of natural gas hydrates in South China Sea (Hexun 28.05.2012.)

3.3 Reserves of natural gas hydrate

The natural gas hydrate exists widely in the world. Natural gas hydrates are mainly distributed in the permafrost regions, the scope of the seabed, slope and land-based. However, because of the different standards, there are big different estimations of the natural gas hydrate reserves. On the other hand, because of the deepening research on natural gas hydrate, the measuring values of natural gas hydrate reserves are changing. (See Fig.10)

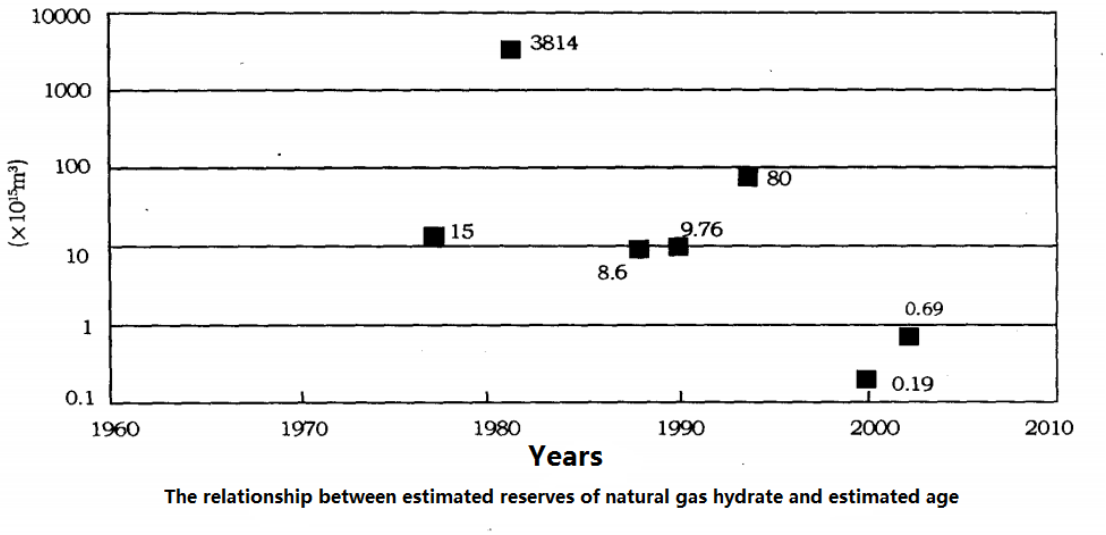

Figure 10. Relationships between estimated reserves of natural gas hydrate and estimated age (Xu 2010, 3.)

3.3.1 Reserves of natural gas hydrate around the world

The reserves of conventional natural gas resources are consumed too fast, they will be exhausted after about 50 years. The energy crisis makes the humans worried. However, the proven reserves of natural gas hydrate have more time than the reserves of coal, oil and natural gas.

According to the evaluation results, the areas of natural gas hydrate are about 40 million square kilometers in the sea-bed. This means that the area cover more than 25% ocean area. People have found 116 natural gas hydrate areas in the word. The reserves are bigger than conventional natural gas fields. On the other hand, 27% land area has conditions to form natural gas hydrate. Natural gas hydrate reserves alone can support people for the next 1000 years.

3.3.2 Reserves of natural gas hydrate in China

In China, the natural gas hydrates are mainly distributed in the South China Sea, East China Sea, Tibet plateau permafrost and the Dongbei permafrost. The reserves are 64.97x1012 m^3, 3.38x1012 m^3, 12.5x1012 m^3 and 2.8x1012 m^3 in the four areas. (Zhishi 2014.)

4 EXPLORATION METHOD

There are many methods to explore the natural gas hydrate. It includes geophysical prospecting, geochemical exploration, typomorphic mineral method, authigenic and sedimentary mineralogy and by earth-observation system.

4.1 Identification marks

People discern directly natural gas hydrate minerals by geological sediment sampling, boring sampling, deep sea exploration, BSR and VAMP. (Xu 2014, 17-22.)

4.2 Geophysical exploration method

Many physical properties of rock can be used for geophysical prospecting. It includes density, magnetic conductivity, electrical conductivity, elasticity, thermal conductivity and radioactivity. Geophysical exploration method includes gravity prospecting, magnetic prospecting, electrical prospecting, seismic prospecting, geothermal exploration and nuclear prospecting. (Zhishi 25.05.2014.)

Seismic prospecting technology (See Fig.11) and well logging technology are main methods of geophysical prospecting method. Scientists can determine the location of natural gas hydrate by seismic exploration technology. Scientists can determine the depth of natural gas hydrate by well logging technology.

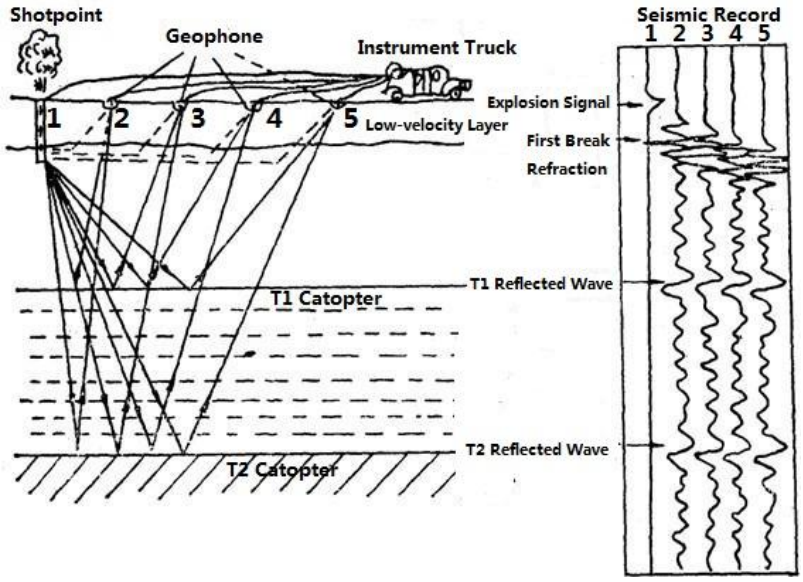

Figure 11. Seismic exploration techniques (Image 2013.)

4.3 Geochemical exploration method

Geochemical exploration method mainly measures the chemical properties of natural substances. The natural substances are rock, gossans, soil, water, sediments, ice deposits, plant or gas. Scientists need to measure the levels of the element in the natural substances. (Zhishi 12.03.2013.)

Geo-chemical exploration is a new exploration method. It includes an organic chemistry method, a fluid geochemistry method and a stable isotope chemistry method. Because the natural gas hydrate easily decomposes with the changes of the temperature and pressure. Geochemical anomalies of natural gas form in shallow seabed sediments. The anomalies can indicate the locations of natural gas hydrate. Besides, scientists can ensure the genesis of the natural gas by the carbon isotopic composition. (Zhishi 2013.)

4.4 Typomorphic mineral method

Scientists can find the mineralogy phenomenon by typomorphic mineral. Mineralogy phenomenon is typomorphic mineral assemblage, typomorphic mineral species and typomorphic characteristics. (Zhishi 18.11.2013.)

Scientists can discern the existence of natural gas hydrate by carbonate, sulfate and sulfide. For example, carbonate will be easily sedimented after the decomposition of natural gas hydrate. Then scientists can measure the special isotope in the carbonate. The special isotope can prove the existence of natural gas hydrate. (Zhishi 18.11.2013.)

4.5 Authigenic and sedimentary mineralogy

Since 1990s, authigenic carbonate mineral and natural gas hydrate are found in same places. So people began to connect the distribution of natural gas hydrate and authigenic carbonate mineral. The output of authigenic minerals means the existence of natural gas hydrate. (Zhishi 08.2014.)

4.6 Earth-observation system

Earth observation systems are very important in many fields of human life and production. It can provide accurate and detailed information to humans. The information includes physical, chemical and biological. At present, many countries and organizations are developing and using earth observation systems. (Zhishi 2013.)

The systems collect information and analyze data in the fields of atmospheric gas composition, geological structure and crustal movement, and ecosystem health and so on. The three platforms of the earth observation system are ground and sea, remote sensing, seafloor observatory network. (See Fig.12)

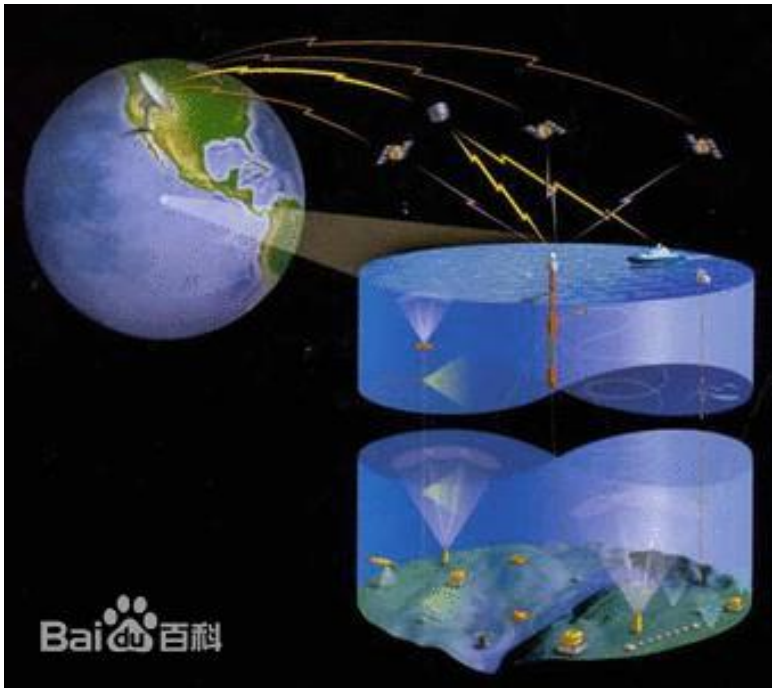

Figure 12. Earth- observation systems (Zhishi 25.12.2013.)

The new earth observation systems can reflect the information of natural gas hydrate (such as solid natural gas hydrate seepage) in remote sensing image. Then people can find the natural gas hydrate mineral resources.

5 EXTRACTION TECHNOLOGY

Scientists need consider how to decompose natural gas hydrate (change the temperature and pressure). Then people can exploit the natural gas. Several exploitation methods for tapping natural gas hydrate have been suggested, such as thermal activation, pressure releasing, chemical inhibitor, replacement and slurry mining. (English Dict 2014.)

5.1 Traditional mining method

Traditional mining methods are themal activation method, pressure releasing method and injecting chemical agents.

5.1.1 Thermal activation method

Thermal activation method means heating the gas hydrate layer. The temperature of natural gas hydrate layer exceeds its balanced temperature. Then the natural gas hydrate decomposes into natural gas and water. (See Fig. 13)

The chemical equation is:

$$M \cdot n\ H_2O \rightarrow M + n\ H_2O \quad (3)$$

Where *M* is gas molecules in the hydrate and *n* is hydration number, also called water molecule number. (Zhang 2008, 22.)

Or

$$CH_4 \cdot 8\ H_2O \rightarrow CH_4 + 8\ H_2O \quad (4)$$

Reaction condition is ‘heating’ (Zhang 2008, 22.)

This method underwent some developmental course. At first, this method injected hot fluid (the steam, hot water, hot brine or other thermal fluid) into the natural gas hydrate layer. Afterwards, people began use fire flooding heating (exploit heavy oil), down-hole electromagnetic heating and microwave heating. (See Fig.13) Thermal activation mining method can realize the recirculation heating, and the speed is fast. The continuous improvement of heating mode promotes the development of thermal activation mining method. (Xu 2014, 24-35.)

However, thermal activation methods will lose quantity of heat. Especially in the permafrost area, scientists have not solved the problems of low efficiency. So the thermal activation method should be further improved before being a practical application.

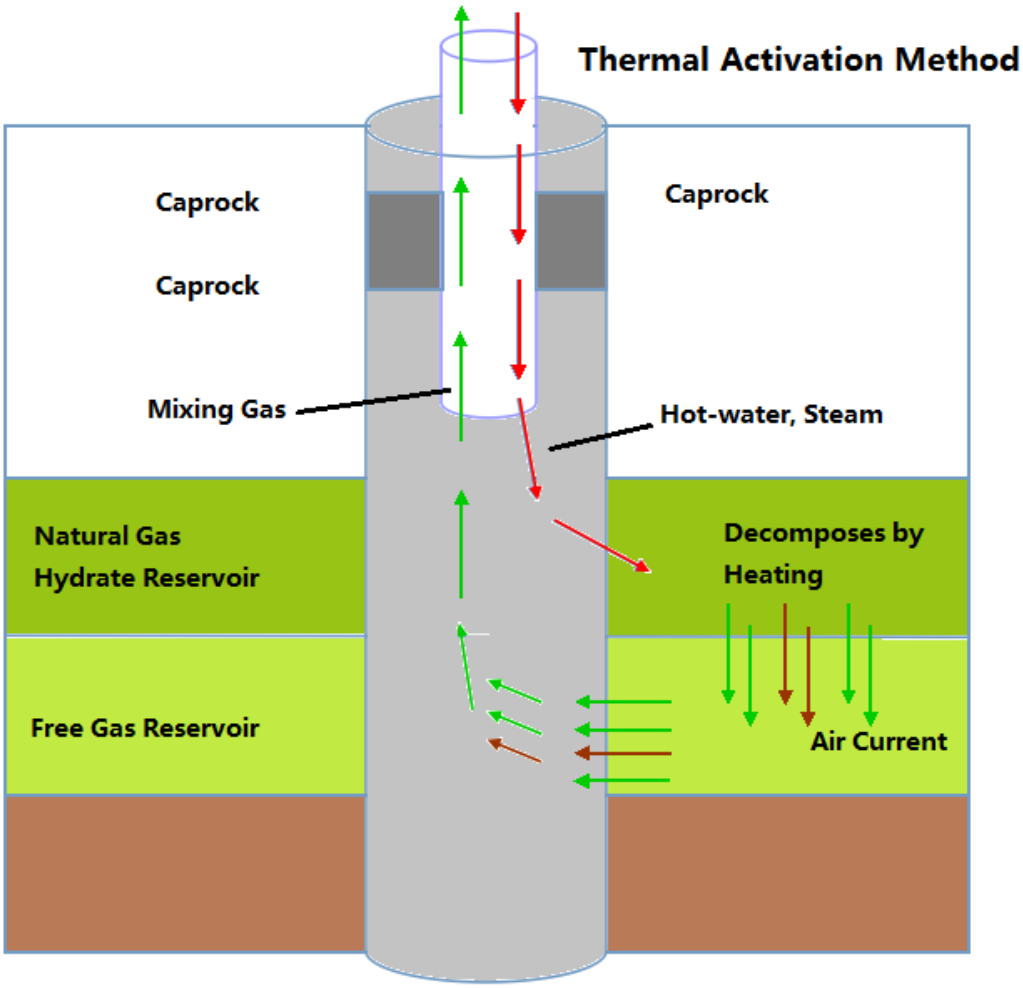

Figure 13. Thermal activation method

5.1.2 Pressure releasing method

The pressure releasing method is carried out by reducing the pressure of natural gas hydrate layer. Then the natural gas hydrate will be decomposing. There are two ways to release pressure. First, we can use the low density drilling mud technology. Second, we can use an equipment to pump out the free gas if there are free gases or other fluid under the natural gas hydrate layer. (Xu 2014, 36-40.) (See Fig.14) Pressure releasing method is without continuous excitation. So the method is low cost. It is fit to large area mining. It is a most promising technique to exploit natural gas hydrate. The pressure releasing method has a disadvantage. The natural gas hydrate layer must be near the boundary of boundary temperature and pressure balance.

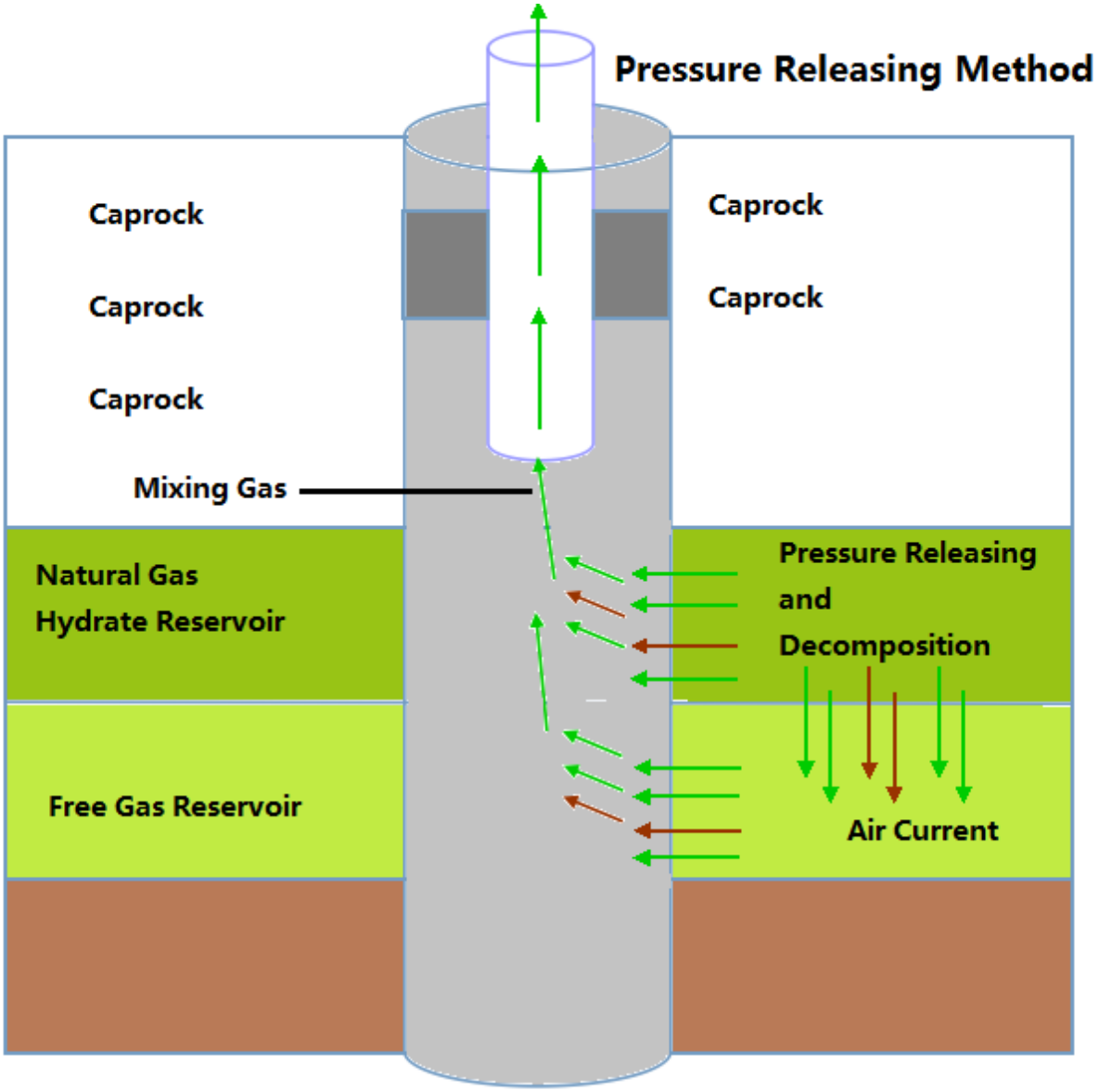

Figure 14. Pressure releasing method

5.1.3 Inject chemical agents

We can inject some chemical agents (such as salt water, methanol, ethanol, ethylene glycol and glycerol etc.) to the natural gas hydrate layer. The chemical agents will change the chemical equilibrium condition. The natural gas hydrate will decompose into natural gas and water. (See Fig.15) (Xu 2014, 45.) The method is slower than the thermal activation method and its cost is high, but the initial energy input is less.

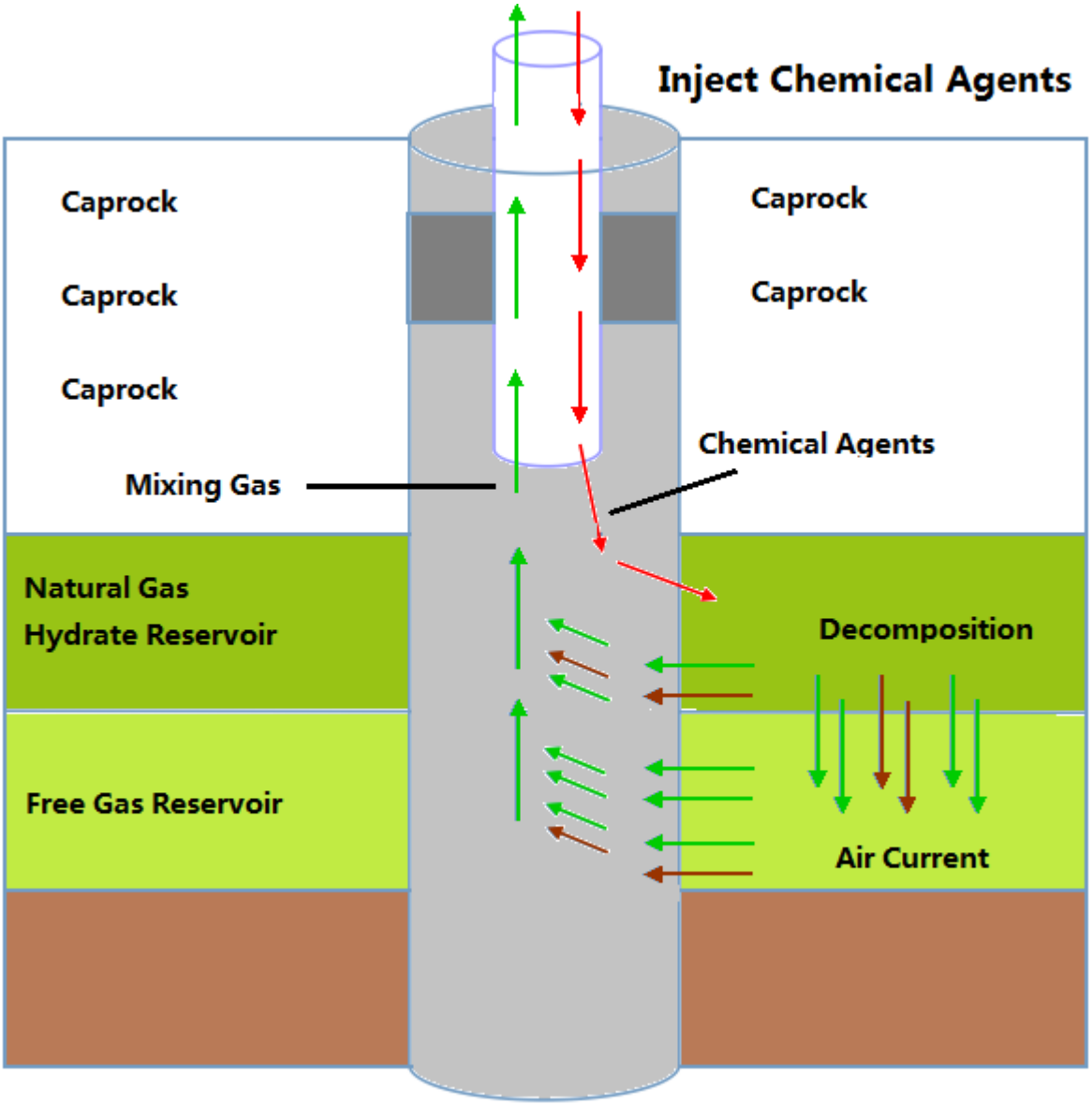

Figure 15. Inject chemical agents

5.2 New mining method

The new mining methods include slurry mining, the high energy gas fracturing technique and displacement by CO_2.

5.2.1 Displacement by CO_2

Recently, some scholars put forward the CO_2 replacement mining, which is named as the CO_2 displacement method. This is a replacement reaction. The CO_2 replaces the CH_4 in the natural gas hydrate (See Equation 5). (See Fig.16) The advantage of this method can absorb the CO_2 in industrial emissions. (Xu 2014, 50-63.)

The chemical equation is:

$$CH_4 \cdot nH_2O + CO_2 \rightarrow CO_2 \cdot nH_2O + CH_4 \quad (5)$$

As with the above method to produce 8 tons methane, about 22 tons carbon dioxide is needed. Because:

$$CH_4 \cdot nH_2O + CO_2 \rightarrow CO_2 \cdot nH_2O + CH_4$$

1 1 1 1

44 16

M 12 t

So, M = 44*8t/16 = 22 t

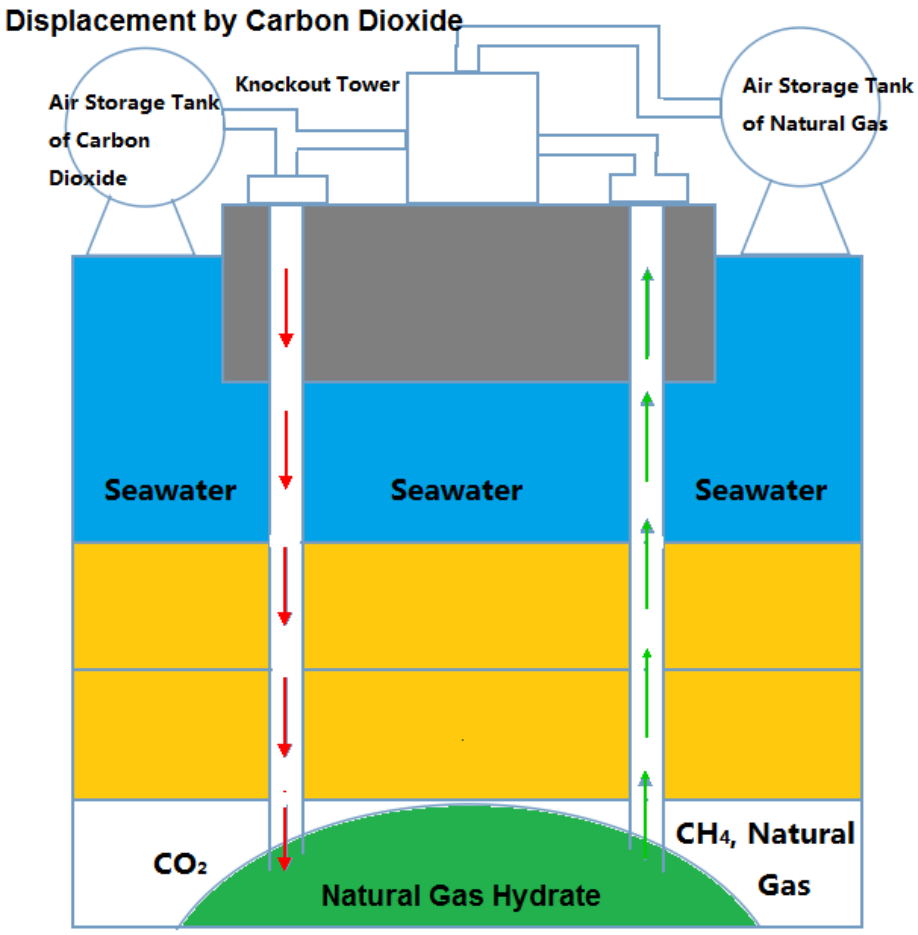

Figure 16. Displacement by carbon dioxide (CO_2)

5.2.2 High energy gas fracturing technique

The basic principle of high energy gas fracturing is the usage of gunpowder or propellant combustion. (Xu 2014, 66-72.) Generating pulse loading and controlling the pressure can raise the rate. Then the high temperature and high pressure gas are released in wall rock. The radial crack system is fractured. Although removing the organic stemming near well bore, the flow conductivity is raised obviously.

5.2.3 Slurry mining method

The slurry mining method is developed from the solid mining method. (Xu 2014, 75-80.) First, the natural gas hydrate is moved to the shallow parts. The natural gas is decomposed by the controlled decomposition (natural gas hydrate is decomposed into CH_4 and water). Then we can gain the natural gas.

6 INFLUENCE OF NATURAL GAS HYDRATE DEVELOPMENT FOR ENVIRONMENT

Scientists believe that natural gas hydrate is the main energy in 21st century when the mining technology has a breakthrough. However, the environmental problem is a severe challenge for the humans. The development and usage of natural gas hydrate have some impacts on the development process. The most common impacts are the greenhouse effect, submarine landslide and the destruction of marine ecological environment.

6.1 Greenhouse effect

Natural gas hydrate reserve is great. Its main component is CH_4. CH_4 is an important link in the global carbon cycle. It plays an important role in the carbon exchange in the lithosphere, the hydrosphere and atmosphere. CH_4 is an important part in the atmosphere, although its content is just 0.00015% in the air, the greenhouse effect of methane is stronger than CO_2, about 21 times than CO_2. (Zhang 2001, 30.) Some CH_4 will be released into the atmosphere in the mining process of natural gas hydrate. There is no doubt that the greenhouse effect will be increasing. Along with the global warming, the natural gas hydrate will have spontaneous decomposition. The atmospheric greenhouse effect will be further intensified. This is a “chain reaction”.

6.2 Submarine landslide

Submarine landslide is caused by earthquake, volcano eruption and sediment rapid accumulation as well as the slope body excessive tilt. However, the decomposition of natural gas hydrate also can cause submarine landslides. (Qi 2004, 81.) The decomposition of natural gas hydrate can produce large amounts of gas. The gas is released in the rock pores, so the strata structure and the degree of consolidation will be changed. This cause the submarine landslide or debris flow under. However, the natural hydrate occurrence zone mainly in the continental shelf and continental slope area. The human’s marine engineering is also in the region. The submarine cable laying and maintenance, offshore oil and gas drilling engineering, marine fisheries and others will be threatened.

6.3 Destruction of marine ecosystem

Methane gas often occurs following this chemical reaction:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (6)$$

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2 \quad (7)$$

The reactions will reduce the oxygen level in the seawater. Some aerobic biological community will be dying and even cause the species extinction. On the other hand, the CO_2 content will increase in seawater. Too much CO_2 will cause the degeneration of organic reefs. The marine ecosystem will suffer a great destruction.

7 DEVELOPMENT PROSPECT OF NATURAL GAS HYDRATE

According to the analysis of the latest data, the latest estimate of natural gas hydrate reserves is reduced clearly. It is not two times more than the total resources of coal, oil and natural gas, but the total reserves of natural gas hydrates are still the equivalent of oil and gas resources in the world. Natural gas hydrates have great development prospect.

With the increase of population growth and GDP growth, the energy consumption will be increasing. At the same time, human should reduce the CO_2 emissions and thus reduce the devastating effect of atmosphere. This will reduce the using of core and improve the rate of natural gas in the primary energy consumption structure. Natural gas hydrates will become the first disposable energy after 20 years. Natural gas hydrate will become the most popular energy fuels in the middle of 21st century. (See Fig.17)

From Figure 17, we can see that the consumption of natural gas hydrates has increased gradually from 2000. Expected in 2040, the consumption of natural gas hydrates begins to increase rapidly, and natural gas hydrates will become the main energy source for human from 2056. The coal will be depleted in 2040. (See Fig.17)

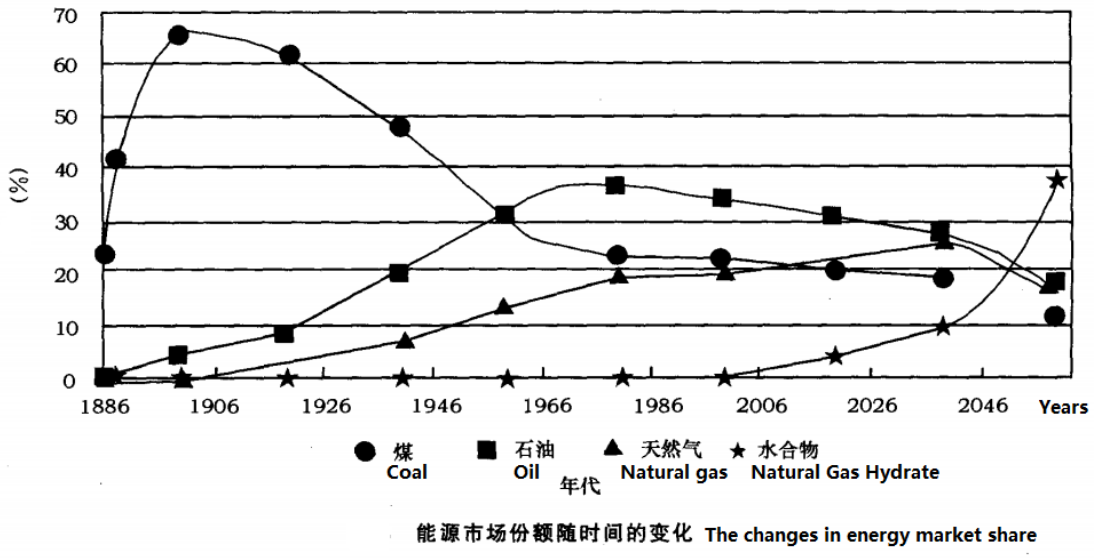

Figure 17. The changes in energy market shares (Mohitpour M. 2002, 668.)

The demand of energy in 21st century has become increasingly urgent. At present, the exploitation of natural gas hydrates is too difficult. However, we believe that natural gas hydrates will contribute to the sustainable development of society, economy and environment with the progress of science.

8 CONCLUSIONS

My supervisor recognized my thesis topic in February 2014. I back to China in May 2014. Then I started thework of data collection. I recorded the important information in the process of data collection.

I choose nine books, and searched the important knowledge by computer. Much knowledge was studied by myself. So I studied much knowledge in the process. I think the knowledge of extraction technology and exploration methods are very important for me.

The goal of thesis is the development of natural gas hydrate. This thesis introduces the extraction technology, exploration methods, distribution, the history and the influence of natural gas hydrate.

Nowadays, with the shortage of conventional energy and the increase of population growth, people have to search a new energy. The natural gas hydrate is an important energy in future. It is clean energy and the reserve is so big. So the natural gas hydrates have great development prospect. According to the China's strategic planning, from 2006 to 2020 is a survey phase, from 2020 to 2030 will be development and trial production phase, and during 2030 and 2050, China will enter commercial production of natural gas hydrates.

People discern directly natural gas hydrate minerals by geological sediment sampling, boring sampling, deep sea exploration, BSR and VAMP. The exploration methods includes geophysical prospecting method, geo-chemical exploration method, typomorphic mineral method, authigenic and sedimentary mineralogy method and by earth-observation system. The extraction technology includes thermal activation method, pressure releasing method; inject chemical inhibitor method, displacement by CO_2, high energy gas fracturing technique and slurry mining method. There are many methods of identification, exploration and extraction. However, each method has advantages and disadvantages. For example, the thermal activation methods will lose quantity of heat. But the method can realize the recirculation heating, and the speed is fast. The advantage of displacement method can absorb the CO_2 in industrial emissions, but some area (Tibet plateau permafrost) cannot provide enough CO_2. So, combine various methods and adjust measures to local conditions are the best method.

Influences of natural gas hydrates are greenhouse effect, submarine landslide and destruction of marine ecosystem. However, at some level I still believe that the development and using of natural gas hydrate will do more good than harm. It will be an important energy in future and it is conducive to the development of human society.

REFERENCES

Literature

Lu Hongfeng. 2011.08. South China Sea gas hydrates sediment mineralogy and geochemistry
China: Science Press.

Mohitpour M. 2002. The development prospect of gas pipeline and gas supply
Beijing: Chinese Petrochemical Press

Qi Xuegui. 2004. Progress in study of natural gas hydrate
China: Chinese Journal of Nature

Tang Yong. 2003. Relationship between the Okinawa trough seismic, fault and natural gas hydrate
China: Marine Geology Press

Wang Yitian. 2012. Developing history of natural gas hydrate
China: Energy Press

Xu Junliang. 01.04.2014 Primary Research on Key Technology for Deepwater Gas Hydrates Drilling and Sampling, First edition
China: Petroleum Industry Press

Xu Wenshi. 10.2010 Natural Gas Geoscience
China: Environment Science Press

Zhang Jinchuang. 2001. Resources and environmental significance of natural gas hydrate
China: Chinese Energy Press

Zhang Shuquan. 2008. Organic Chemistry
China: Education Press

Internet Sources

360doc 03.11.2011 (Distribution of natural gas hydrate around the world)
http://www.360doc.com/content/12/0322/16/880941_196665958.shtml
[Accessed 12.07.2014]

Cishan.sznews.com 2007 (Figure 1 Chemical molecular structure of natural gas hydrates)
http://cishan.sznews.com/tech/content/2007-07/03/content_1299760.htm
[Accessed 03.06.2014]

Cnfol.com .09.09.2010 (Figure 4 Sketch map of China energy import in recent years)
http://news.cnfol.com/100909/101,1588,8398278,02.shtml
[Accessed 31.07.2014]

ECO Chinese network 2014 (China become the world's second-biggest importer)
http://www.ecocn.org/portal.php
[Accessed 20.07.2014]

English Dict 2014 (Slurry mining)
http://www.chazidian.com/dict/slurry mining/
[Accessed 20.08.2014]

FT Chinese network 20.04. 2010 (A market re-emerges)
http://www.ftchinese.com/story/001032244/ce
[Accessed 08.09.2014]

Hudong Baike 02.02.2014 (Natural gas hydrate)
http://tupian.baike.com/a4_78_50_01300000927307132188501734828_jpg.html
[Accessed 22.07.2014]

Hexun.com 28.05.2012 (Figure 9 Distribution of natural gas hydrate in South China Sea)
http://news.hexun.com/2012-05-28/141836085.html
[Accessed 11.08.2014]

Image.baidu.com 2013 (Figure 11 Seismic exploration techniques)
http://image.baidu.com/i?tn=baiduimage&ct=201326592&lm=-1&cl=2&fr=ala1&word=%B5%D8%D5%F0%BF%B1%CC%BD%CA%BE%D2%E2%CD%BC
[Accessed 15.08.2014]

JNTV.cn 03.02.2014 (Figure 8 Distribution diagram of nature gas hydrate in China)
http://life.ijntv.cn/top/2014-02-03/271204.html
[Accessed 08.08.2014]

Kepu.ccut.edu.cn 2006 (Figure 3 Glomar Challenger)

http://kepu.ccut.edu.cn/100k/read-htm-tid-10828-fpage-2.html
[Accessed 13.07.2014]
Zhishi 2014(Natural gas hydrate)
http://baike.baidu.com/view/83115.htm?from_id=599540&type=syn&fromtitle=可燃冰&fr=aladdin
[Accessed 20.07.2014]

Zhishi 12.03.2013 (Geo-chemical exploration)
http://baike.baidu.com/view/256496.htm
[Accessed 19.08.2014]

Zhishi 18.11.2013 (Typomorphic mineral)
http://baike.baidu.com/link?url=yqSzQ5qIuW9riFE4OVRR2s1tBxzXWTFhlQg_utyzWhyAF0td7X_WNiHySYrjVitTTJpFa0CZ3wIR58tfmsQVnK
[Accessed 19.08.2014]

Zhishi 25.12.2013 (Figure 12 Earth- observation systems)
http://baike.baidu.com/view/3814227.htm?fr=aladdin
[Accessed 19.08.2014]

Zhishi 25.05.2014 (Geophysical prospecting)
http://baike.baidu.com/view/27690.htm
[Accessed 15.08.2014]

Zhishi 08.2014 (Authigenic and sedimentary mineralogy)
http://baike.baidu.com/view/543669.htm?fr=aladdin