# Methane hydrates

## Special ice

At the beginning of the Nineties, in marine geology research environments, word began to spread about a particular substance present under the ocean floor: it was the first information on methane hydrates that had up to then received scarce attention because they were considered not much more than a mere geological curiosity and lacking any commercial value.
The so-called biogenic methane is released during decomposition processes of organic matter and accumulates within sediments where it may concentrate and eventually rise towards the surface. If the surface is a sea bed, the gas that is released mixes with the cold water of the deep sea and forms a sort of 'ice'. The water molecules crystallize forming a 'cage-like' structure inside which methane molecules are trapped. On freezing, the water squeezes the gas and the mixture's density increases greatly. Chemically, methane hydrates are made up of a molecule of methane and 6 molecules of water ($CH_4 6H_2O$) and belong to the 'clathrate' family, that comprises compounds whose crystalline solids occur when water molecules form cells closed in a 'cage-like' structure. For this process to take place, two simultaneous factors are necessary: a low temperature (-15°C) and high pressure all around (20 bar, that corresponds to a sea depth of a little less than 200 m), in addition to an abundant supply of methane and water molecules, of course.

## Where do you find them?

Due to the particular conditions required for these compounds to form and remain stable, their presence is limited to three environments: ocean floors, terrains covered by permafrost and the deeper polar ice.
The conditions that are more favourable to the formation of methane hydrates are to be found on a large scale beneath the sea beds at depths ranging from 300 to 3,000 – 4,000 m. Above this depth the pressure is not sufficient for the formation of methane hydrates and below it instead, there are optimal pressure and temperature conditions but the organic matter that originates methane is scarce: in other words, at this depth, the 'raw material' is absent. It is for this reason that methane hydrate deposits seem to concentrate along the continental slope that divides the continental platform from the deep abyssal plains: here great amounts of sediments accumulate that are often rich in organic matter and slide from the continents towards the open sea along the slopes. However, if the temperatures are very low, methane hydrates can form at lower pressures, as, for example, on shallower sea beds (in polar regions) or in the frozen soil covered with permafrost found in vast regions of Alaska and Siberia.
The greatest amount of methane hydrates, however, are found in the oceans. They occupy the porous spaces in the sediments for a thickness of several hundreds of metres. At deeper levels within the sediments where the temperature increases due to the geothermal gradient, the methane hydrates dissociate into water and methane gas and, as in the case of normal deposits, they constitute a sort of 'crust' that envelops methane in its gaseous state.

## An original behaviour

Methane hydrates, made as they are of ice 'cages' that trap gas molecules, are stable compounds only when simultaneous very low temperature and high pressure conditions occur. If the temperature increases or the pressure decreases, the ice melts and methane is released in its gaseous form: methane hydrates, at room pressure and temperature, survive for only a couple of seconds. It is for this reason that to collect a sample of this substance is very difficult because, on bringing it to the surface, the majority of the methane is lost and only a minor part can be recovered in solid form. This characteristic is one of the main limitations to the extraction of methane stored in this way and also one of the possible sources of serious environmental hazards connected to its exploitation.
Methane hydrate ice found under the ocean floors can melt for various reasons, but the main one is surely the increase in the water temperature. The release of methane in its gaseous form brings about the formation of gas bubbles that expand on rising, and on reaching the surface they scatter in the atmosphere. This gives rise to a characteristic bubbling

of the waters where the phenomenon is taking place.

## Methane: a 'clean' fuel

Among fossil fuels, currently methane seems to be the one that will be exploited more and more in the near future, thanks to its relative abundance and thanks to the fact that it is relatively 'clean'. Its molecule is made up of 4 atoms of hydrogen and one of carbon ($CH4$): on burning, it is the hydrocarbon that releases the smallest amount of carbon and it is for this reason that it is less harmful for the environment. Its $CO2$ emissions are 25% lower than petrol, 16% lower than Liquid Propane Gas, 30% lower than diesel and 75% lower than carbon. Its capacity to form ozone is 80% less than petrol and 50% less than diesel and Liquid Propane Gas. Moreover, the combustion emissions do not contain carbonaceous residues, benzene and microscopic dusts (PM10), contrary to petrol and diesel oil. Among all the fossil fuels, methane is surely the most 'ecological'. The use of methane is expected to increase greatly in the near future.
The natural gas reserves that are of 'geological' origin are estimated to be sufficient for 60-70 years and they are mostly concentrated in the areas surrounding the Persian Gulf. (vedi speciali e sezione Energia)
Much smaller amounts are currently obtained from waste products of zooculture, with the use of anaerobic digesters that enable the production of methane from animal sewage. Other small quantities can be obtained from self-produced methane in abandoned carbon mines; here, this naturally produced gas is tapped and at the same time is prevented from dispersing in the surroundings.

***Immense reservoirs***

Methane hydrates could be the energy source of the future. A cubic metre of methane hydrates can contain from 160 to 180 m3 of methane gas.
It has been calculated that beneath the ocean floor and in areas of permafrost more than 100,000 million billion cubic metres of methane are present, trapped in the form of hydrates. Some estimates state that the 'reservoirs' contained in the permafrost of Alaska and Siberia are 5 x 1013 m3 while those contained beneath the ocean floor are 5-25 x 1015 m3. The amount that can be exploited could be at least two orders of magnitude greater than the amount of methane present on the planet and could supply about twice the amount of energy that can be obtained from all the fossil fuel deposits known to date.

## Energy of the future?

The exploitation of such quantities of natural gas is not possible today: present day technologies are not yet able to collect the hydrates so as to extract the gas, without losing it in the environment.
The first problem that has to be solved is that of finding the deposits. The research for methane hydrates utilizes geophysical methods that make use of the particular property of layers rich in hydrates to reflect seismic waves. Appropriate systems (usually compressed air 'cannons', for investigation in the sea) provoke the propagation of seismic waves that, passing through the rocks beneath the sea floor, are reflected at particular levels (the so-called Bottom Simulating Reflectors). This phenomenon occurs also for levels rich in hydrates: the so-called 'seismic profiles' are thus obtained and are real 'ultrasound scans' of the rocks that make up the sea floor. Italy is in the forefront in this type of research that is carried out by the Istituto Nazionale di Oceanografia e Geofisica Sperimentale (National Institute for Oceanography and Experimental Geophysics) with the research ship, OGS-Explora.
The second problem is that not much is known about these compounds: currently studies continue both for scientific research purposes and for commercial reasons. The GEOMAR Institute of Kiel, one of the major institutes of marine research, has created a laboratory in which the temperature and pressure conditions required for the conservation of methane hydrates have been recreated: in this way they can be studied in a laboratory at controlled conditions. Other research institutes, like the Brookhaven National Laboratory (USA), are carrying out experiments regarding the creation of these substances in a laboratory.
As far as commercial research is concerned, in March 2005, an expedition set out, financed by the American Energy Department and by the oil company, Chevron-Texaco. During the 35 days spent in the Gulf of Mexico, hydrate samples,

collected with the additional aid of mini submarines at a depth of 1,300 m, were studied. Laboratory tests will enable us to understand in what way the methane trapped in ice can be released, recovering the maximum amount possible without losing it in the environment: extractive technologies, in fact, will have to consider the separation and collection of the gas directly in the sediments. However, commercial researches are taking giant steps in this field: the American Energy Department has already started a research programme that could result in the commercial production of methane from hydrates starting from as soon as 2015.

## Hydrates and climate changes

Methane is much more opaque to infrared radiation than $CO_2$ and consequently it produces a greenhouse effect 20 times greater than that of carbon dioxide. It is a gas whose effect on the atmosphere is much more dangerous than that of $CO_2$: its effects are not very important because, at the moment, it is found in very limited quantities. Geological evidence in Antarctic ice cores show, however, that periods when the climate was warmer are always associated to increases in the methane concentration in the atmosphere.
The exploitation of methane hydrates potentially creates the risk of releasing great amounts of methane, either accidentally or as an undesired consequence of the extractive process. What must be avoided is that the exploitation of this enormous energy source should happen in an irresponsible way: the release of great quantities of methane could cause an increase in the greenhouse effect and, consequently, a warming of the oceans. This would bring about the melting of great amounts of hydrates beneath the ocean floor, in the land covered with permafrost and in the polar ice causing a further release of methane: this would trigger off a series of processes whose final effects are difficult to foresee. Man's contribution to the greenhouse effect as a result of the burning of all the fossil fuels available, would be of 'only' 200 billion tonnes of $CO_2$: nothing, when compared to the possibility that hydrates could release 10,000 billion tonnes of methane 'spontaneously'!
Moreover, when hydrates are absent, the sediments of continental slopes are made up of loose and unstable elements. Therefore it is likely that the melting of hydrates could trigger off landslide phenomena, even on a large scale, in the areas where extraction is taking place.

## A look at the past

Some geological evidence proves that there have been climatic 'crises' on a large scale that have modified the distribution of creatures living on Earth. Recent geological and paleontological researches seem to indicate that in at least one of these crises the role played by methane hydrates could have been very important.
55 million years ago, between the Paleocene and the Eocene, on our planet a climatic and environmental catastrophe of enormous proportions took place, known to researchers as the Paleocene-Eocene Thermal Maximum (PETM).
The global warming, that involved the whole planet, brought about migrations of animals on the mainland from subtropical zones to higher latitudes, while 70% of the creatures living on the ocean floor died out. As a consequence of conditions that have not yet been understood (but probably a result of a period of intense volcanic activity) the oceans got warmer provoking the release of enormous quantities of methane from the ocean floor that then entered the atmosphere. The amount of gas is in the order of billions of tonnes released in the time interval of a couple of millenniums, or perhaps, even a few centuries. The melting of the hydrates made the continental slopes unstable and these, sliding and falling, released more methane creating a cyclic process that was self-powered for a period that lasted between 80,000 and 200,000 years.
The greenhouse effect that the released methane triggered off, heated the oceans more and more, bringing about the release of other methane and a reduction of the oxygen dissolved in sea water causing serious damage to sea life. In the Nineties, the analysis of marine sediments and of their paleontological content has led to estimate the rise in temperature of the oceans as having been around 8-10°C. This resulted in a modification of both oceanic and atmospheric circulation bringing about intense climate modifications and the extinction of numerous forms of life.
Other 'crises' of this kind are documented in the geological history of the Earth, for example, 250 million years ago, in the

Permian or at the beginning of the Jurassic. For these events that are so far back in time, there are no geological proofs to indicate a relationship with methane hydrates. In a more recent past, instead, the analysis of ocean sediments and the study of the presence of bacteria that feed on methane show that in different parts of the world, the warmest spells of the last glacial period always correspond to the presence of great quantities of methane, released from beneath the sea floor (70,000 to 12,000 years ago).
Some scientists who are studying the problem of global warming, fear that an increase in temperature on our planet can in turn trigger off a sudden release of the methane contained in the hydrates.

***Other consequences***

Now that methane hydrates have been discovered, they are proving to be present on sea floors in enormous quantities. As already mentioned, some researchers suppose that it is the very methane hydrates that act as the 'adhesive' that allows the stability of the sediments that are deposited along the continental slopes. Therefore the rapid melting of methane hydrates would have the immediate effect of destabilising the sediments that have accumulated along these slopes. This could set off underwater landslide phenomena, even on a vast scale, that could in turn bring about the propagation of anomalous waves.

## What can be done?

What is known about methane hydrates, about their behaviour and their distribution along with the geological data of the past, suggest caution in the race to utilize these compounds for the production of methane. The exploitation of these enormous energy reserves could temporarily solve many energetic problems and help in the difficult transition phase between the utilization of fossil fuels and the use of renewable energy sources. However, the environmental risks connected to an indiscriminate exploitation that does not respect the environment seem very high. Commercial exploitation must therefore be postponed till when state of the art technologies can protect us from the most serious risk: the release of great quantities of methane into the sea and the atmosphere.
Moreover, the possible risk of triggering off great underwater landslides on a vast scale must not be forgotten.
The presence of compounds with such particular and unstable characteristics, that are so sensitive to the slightest variation in temperature keeps us on guard as far as man's contribution to the greenhouse effect is concerned: it is true that geological data show that climate changes on a large scale and environmental and climatic 'crises' at a planetary level have occurred in the geological past without any involvement on man's part, but our behaviour could give a decisive contribution to sparking off these processes that, once started, could prove to be irreversible.