Icy sponges filled with natural gas may be the next source of the world's energy

Fuel from the ocean floor

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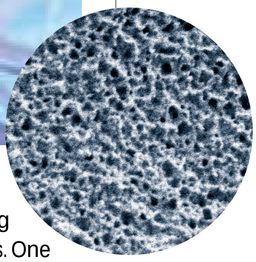
The detector bank of the high resolution powder diffractometer D2B

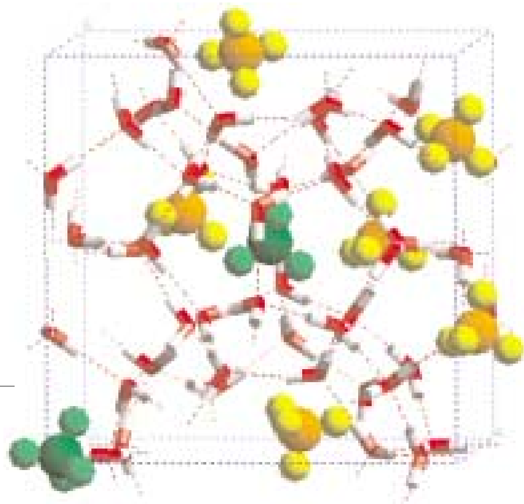


An electron micrograph of methane hydrate showing its sponge-like structure

Industrialised countries are constantly searching for new sources of fossil fuels. One potential candidate are gas hydrates found on the ocean floor and in arctic regions. These crystalline compounds consist of networks of water molecules in which are caged small gas molecules – methane, for example.

People have known of gas hydrates, also called clathrate hydrates, for almost 200 years, but it was only a few decades ago that they were discovered in Nature – and in great abundance! In fact, marine sediments probably contain 10,000 billion tonnes of methane hydrate – considerably exceeding sources of coal, oil and gas (methane, of course, is natural gas). Methane hydrates are therefore likely to be of major economic importance, once we know how to extract them safely.

Gas hydrates are also interesting for other reasons. They can cause blockages in gas pipelines. Hydrates containing carbon dioxide could be used to trap the gas at the bottom of the ocean thus reducing levels in the atmosphere; in fact, it is likely that water on Mars is largely stored as carbon dioxide hydrate. Air hydrates found in the deeper parts of polar ice sheets reveal how the composition of air has changed over the past million years.



The structure of methane hydrate. Methane molecules occupying small and large cages are shown in green and yellow respectively

Not surprisingly, there is intense research interest in gas hydrates. One important aspect is to understand how their stability changes with pressure and temperature. Gas hydrates exist only at high pressure and/or low temperatures – as are found at depths of several hundred metres in the sea or in permafrost regions. Experiments on gas hydrates, therefore, have to be done under similar conditions. This has proved extremely challenging and has meant that a number of properties of gas hydrates have not been well established.

How stable are gas hydrates?

For this reason, our research group at the University of Göttingen decided, a few years ago, to investigate the stability of gas hydrates. We first prepared the hydrates as polycrystalline materials containing large and small 'cages' (below left). Since the constituent atoms are lightweight, neutron powder diffraction (see Introduction, p.4) is the ideal technique to study them.

One of the major unknowns is how the filling up of the large and small cages with gas molecules depends on pressure and temperature. We had assumed that it obeyed a well-established thermodynamic theory but it had never been rigorously proven. Using the D2B instrument at ILL, we were able to test the theory by following the changes in composition of several gas hydrates with increasing pressure.

We found that although the theory predictions were broadly followed, there were deviations in all cases, and in some cases the theory failed completely. We were very surprised to find that the large cages in the nitrogen hydrate contained two nitrogen molecules, violating one of the basic assumptions of the theory, although it can be modified to allow for this double occupancy. In other cases such as the carbon dioxide hydrate, the behaviour was quite different, and the theoretical description has to be changed considerably. These findings are extremely important to chemical engineers developing techniques to handle gas hydrates. We also looked at the compressibility of gas hydrates, which is important in detecting them using seismic profiling of the ocean floor.

Neutron techniques will continue to probe these and other questions such as unravelling how their fascinating structures form and decompose. ■

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