Design and Construction of an X-ray Diffraction Cell for Hydrate Studies at Elevated Pressures

This work describes the setup and operation of an X-ray diffraction (XRD) cell for hydrate studies at elevated pressures (hereon we call it “high-pressure cell” for convenience). Most hydrate XRD measurements have been performed at low temperatures to ensure hydrate stability at atmospheric pressure. As a result, extrapolation has been required to determine hydrate volume at in situ conditions. With high pressure capabilities, however, this system can extend current structural knowledge without extrapolation, leading to less error in predictive modeling and a more accurate view of in situ hydrates. The cell has both low- and high-temperature capabilities, operating from 77 to 300 K using liquid nitrogen boil-off as a means of refrigeration, and can maintain pressures from 14 kPa to 7 MPa. Preliminary measurements of carbon dioxide hydrates at in situ conditions have been obtained and lattice parameters are comparable to those in the literature.

KEY WORDS: diffraction; hydrates; in situ; X-ray.
While valid, these measurements may not accurately simulate in situ conditions, possibly leading to erroneous results when models are extrapolated to higher formation temperatures. Although neutron diffraction studies at elevated temperature and pressure exist, the availability of such equipment makes these measurements prohibitively expensive. Thus, a definitive in situ hydrate structural measurement using X-ray diffraction, a much less expensive alternative, is desirable.

In addition to the data extrapolation problems, measurements in this laboratory have experienced substantial condensation on the low-temperature cell window and sample surface. Not only did this interfere with the overall quality of the diffraction patterns obtained, but also limited the amount of structural information that could be acquired about the hydrates. To solve these problems, an XRD cell was custom designed to allow hydrate study at in situ conditions in this work.

2. CELL DESIGN

Several requirements need to be satisfied in order for such a cell to function properly:

• It must be able to contain a pressure of approximately 6.9 MPa to simulate in situ conditions.
• It must allow for the passage of cobalt X-radiation.
• It must contain enough sample surface area to give strong diffraction signals.

Beryllium (Be) is a natural choice to meet the above requirements as it is strong, transparent to X-rays, and easy to joint with support structures. A cylindrical Be tube is chosen as the basic construction to hold pressure. Another advantage of the cylindrical shape is that the X-rays will have constant attenuation at different angles.

To determine the dimensions of the beryllium cell, two factors had to be considered: design of the X-ray sample holder, and pressure holding capability.

As shown in Fig. 1, the X-rays are attenuated twice by passing in and out of the cell through the tube wall (incoming X-ray and diffracted X-ray). Therefore, to have the X-ray counter, get at least 30% (an arbitrary value) of the intensity compared to an open sample, we need