

Crystallite Size Distributions of CH₄-CO₂ Gas Hydrates from Diffraction Data

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For gas hydrates, classical techniques to determine crystal sizes fail, since they are notoriously hard to handle due to their instability. Nevertheless, crystal sizes of gas hydrates are of fundamental interest regarding the extraction of CH₄ for energy purposes and the sequestration of CO₂ to store this dangerous greenhouse gas. Using the full potential of natural gas hydrates requires a precise understanding of its physical and mechanical properties and therefore a good estimation of gas hydrate crystal sizes and crystallite size distributions (CSD). Determining crystal sizes using X-rays provides a fast, quantitative, and non-destructive method with relatively low experimental effort.

Aim of the project is to focus on the gas exchange of CH₄ with CO₂ and its changes to crystal size, especially, whether the gas exchange mechanism destroys the crystal structure. Therefore, a sample series of mixed CH₄-CO₂ gas hydrates in different exchange stadia (1 day, 3 days, and 7 days) was produced. Ground synthetic CH₄ hydrate as the starting material was filled into quartz glass capillaries (0.8 mm diameter, 50 mm length) and set under pressure of pure CO₂ gas at 277 K for the specific duration. Temperature and pressure conditions were kept constant over the whole duration of the experiments. Before and after the experiment, samples were stored in liquid N₂.

Every CSD measurement consists of an image series taken at consecutive ω -steps to find the maximum intensity of every crystallite that cannot be obtained from one single diffraction image. The measurement was carried out over a ω -range from 2° with a step size of 0.02° and an exposure time of 30 s/step. The synchrotron experiments were performed at beam line P02.1 with a beam energy of 60 keV ($\lambda = 0.20713$ Å). The data was collected with a Perkin Elmer XRD1621 detector. During measurements, the samples were cooled constantly by a nitrogen system to temperatures around 100 K. A Lake Shore (Cryotronics Inc.) controller was used to stabilize the sample temperature.

Base of the CSD determination using X-rays is a new method called “Fast Quantitative Diffraction” [1, 2]. Every crystallite in a powdered sample diffracts the incoming beam under Laue condition with an intensity proportional to the size of the crystal. The new method extracts the intensity of every diffraction peak along one concentric Debye-Scherrer ring on the 2D detector image. Every single extracted intensity-value can be related to a crystal size with the help of the calibration material LaB₆ with known crystal size and intensity distribution. A so-called spotty diffraction pattern is important for extracting single crystal intensities out of a 2D detector image. Full powder Debye-Scherrer rings cannot be used.

The results of the present work indicate that the gas exchange CH₄ to CO₂ does not destroy the crystal lattice of the gas hydrate structure. For CH₄-CO₂ mixed gas hydrates, mean crystallite sizes in the range of 2.7 μm to 8.3 μm were determined with the “Fast Quantitative Diffraction” method. All CSD follow an almost symmetric Gaussian distribution. An increasing crystal size is observed for an increasing gas exchange time from 0d to 3d most likely due to particle coarsening processes (Figure 1). For the 7d sample this trend does not continue, possibly due to less analyzed reflections. The averaging of crystal sizes for the reflections (320) and (330) (in mean and median values), which were analyzed in all four hydrate samples measured with synchrotron radiation, includes the 7d sample in this trend for mean crystal sizes (Figure 2).

Crystallite sizes obtained in this work were in agreement with the scarce observations of single crystals from scanning electron microscopy pictures [3]. Where scanning electron microscopy could only give information of crystals exposed at the surface, using X-rays now provides information of the bulk of the sample. The new “Fast Quantitative Diffraction” method was developed to obtain information on crystallite size distributions of gas hydrates but can be easily applied to other polycrystalline materials.

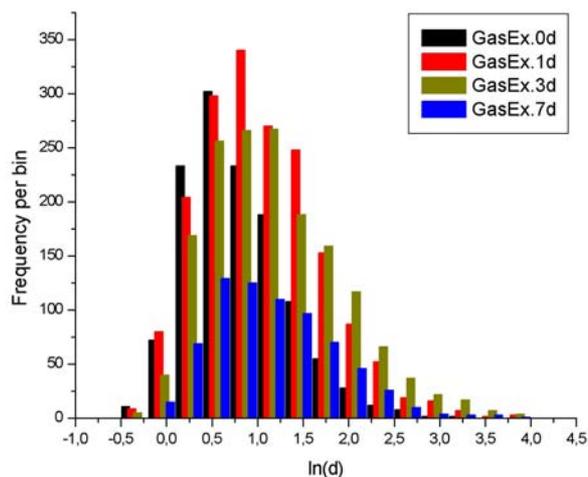


Figure 1: Logarithmic CSD of reflection (330) for the pure methane hydrate (0d) and every duration of gas exchange.

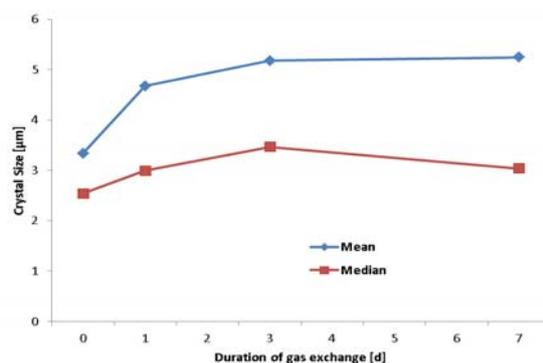


Figure 2: Trend of Mean and Median crystallite sizes with increasing duration of gas exchange.

A publication of these results for the journal American Mineralogist is in preparation.

References

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