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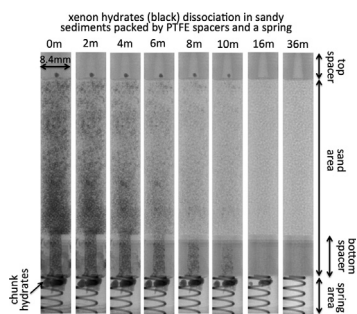
Surface area controls gas hydrate dissociation kinetics in porous media

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GRAPHICAL ABSTRACT



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ABSTRACT

This study integrates X-ray radiography and 3D computed tomography (CT) to measure xenon hydrate dissociation kinetics in a porous medium (sand) through depressurization at the quasi-isothermal condition. Before dissociation, we use X-ray CT to measure hydrate volume and surface area in the sand and find $[\text{hydrate volume}]^{2/3}$ is a linear approximation of hydrate surface area regardless of differences in hydrate specific area. During dissociation, we use X-ray radiography to quantify the evolutions of hydrate volume and dissociation rate. We find $[\text{hydrate volume}]^{2/3}$ (i.e., hydrate surface area) is a linear metric of hydrate dissociation rate. Additionally we observe two circumstances when dissociation rate is not linear with $[\text{hydrate volume}]^{2/3}$. First, above a critical hydrate saturation of 35–45%, hydrate dissociation rate initially stays constant and then decreases with $[\text{volume}]^{2/3}$. Second, the dissociation rates of patchy hydrates in large pores initially stay constant and are significantly slower than hydrates in small pores with the same sizes. Since methane hydrates in nature are patchy and heterogeneously distributed, the new knowledge will facilitate modeling of hydrates production with a simple metric of dissociation rate (i.e., $[\text{volume}]^{2/3}$) and constraints of hydrate saturation and pore size.

1. Introduction

Methane hydrate dissociation in marine sediments and permafrost is a kinetic process that not only provides an opportunity to exploit a large amount of clean energy but also poses a threat to global change [1–3]. Similar to other types of mineral dissolution/dissociation in geological porous media, gas hydrate dissociation is controlled by heat and mass transfer [4,5] and interfacial reaction [6–8]. Heat and mass transfer

rate can vary in porous media as a function of permeability [9], relative permeability [10,11], tortuosity [12] and pore-throat aspect ratio [13,14]. Interfacial reaction rate depends on interfacial area in both the aqueous solution [15,16] and the porous media [17–19] and this relationship varies with mineral morphology [20,21]. One unanswered question is that how the secondary pore structure within minerals (e.g., micro-pores within hydrates in sediments [22,23]) affects reaction rate.

Kim et al. [24] proposed a kinetic model to describe hydrate

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dissociation rate in a batch reactor without the presence of porous media:

$$-dn/dt = k_d A_s (P_e - P) \quad (1)$$

where $-dn/dt$ is the dissociation rate in mole/time, k_d is the reaction constant and an Arrhenius-type function of temperature, A_s is the surface area of hydrates, and $(P_e - P)$ is the pressure driving force, which is the difference between the equilibrium pressure (P_e) and the outlet gas pressure (P). The assumption is that hydrates are a fixed number of equal-size spheres (hereafter spherical morphology) dissociating at the same rate, which prescribes A_s is linear with hydrate volume to the power of $2/3$ [hydrate volume] $^{2/3}$. Methane hydrate depressurization experiments in batch reactors [24–26] and sand [27,28] found that the dissociation reaction constant changes from study to study by orders of magnitude. However, neither these dissociation experiments in sand [27,28] nor any other study has directly measure hydrate surface area in porous media to validate the spherical hydrate morphology assumption.

In situ monitoring of reaction and flow in geological porous media can be achieved with imaging techniques across scales. For instance, 3D X-ray CT studies show that acidic fluid injection enlarges pore structure and connectivity and enhances permeability in carbonate rocks [19,29]. Furthermore, 2D microfluidic studies show that salt precipitation/dissolution changes pore connectivity and stress state at a timescale of seconds [30,31]. However, neither of the two methods can simultaneously achieve 3D tomography and a time resolution of seconds, which are essential for measuring kinetic processes in porous media, such as gas hydrate dissociation in sediments.

In this study, we conduct one dissociation experiment by depressurization of xenon hydrate-bearing sand. By integrating micro-focus X-ray radiography and CT, we are able to resolve dissociation rates in space at a timescale of seconds. The measurement of hydrate surface area before dissociation with CT allows us to study how surface area controls dissociation rate and directly validate the spherical hydrate morphology assumption in porous media. Furthermore, we show how the spatial variations of hydrate saturation and pore size affect hydrate dissociation kinetics in porous media. Our new observations provide insight to methane hydrates dissociation in nature.

2. Materials and methods

Fig. 1 shows the setup for xenon hydrate formation and dissociation within an X-ray μ CT scanner. Xenon hydrate is similar to methane hydrate due to the same clathrate hydrate structure [32,33]. The strong X-ray attenuation of xenon hydrate facilitates phase segmentations of CT images [22,34,35]. Sand is packed between spacers inside an aluminum sample vessel and is subjected to an axial stress of 100 kPa by a stainless steel spring. The mean grain size is $711 \mu\text{m}$ and its permeability is 387 D ($3.82 \times 10^{-10} \text{m}^2$) [36].

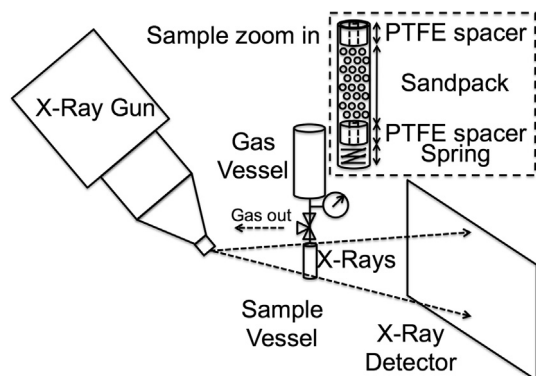


Fig. 1. Schematic of hydrate growth and dissociation within an X-ray micro-CT scanner.

Before xenon hydrate formation, the sandpack is partially saturated with deionized water (initial water saturation of $\sim 30\%$) at atmospheric pressure. Xenon hydrate formation starts as soon as xenon gas enters the sample vessel (see Fig. 1) at a room temperature of 23°C and an initial pressure of 2.84 MPa. After 75 days of xenon hydrate growth, xenon gas pressure decreases to 1.69 MPa (higher than the equilibrium pressure of 1.56 MPa at 23°C and no presence of salt [37]). Prior to dissociation, we take a full CT scan and segment it to obtain the 3D distribution of xenon hydrate in the pore space. The CT scanning parameters are 150 KV, $346 \mu\text{A}$, 250 ms exposure time, 0.5 mm copper filter and a resolution of $49.79 \mu\text{m}$. We use simple threshold methods in segmentation, of which thresholds are chosen either automatically using built-in algorithms in ImageJ [38,39] or chosen manually.

We start hydrate dissociation by opening the idle valve (Fig. 1) directly to the atmospheric pressure at room temperature of 23°C . Since it is an open system (vented gas is not collected), hydrate volume cannot be calculated from gas pressure using mass balance equations. During the 40 minutes of hydrate dissociation, we take 126 consecutive X-ray radiographs (same energy and scan parameters) to record changes inside the sample vessel, which cannot be captured with full CT scans due to time resolution constraints. The sampling rate is 3.15 radiographs/second. Each of these 126 radiographs is an average of 4 consecutive frames at a speed of 4 frames/second. Hence, the time resolution of each radiograph is 1 s and the maximum time resolution of dissociation rate measurements is 1 s too. The X-ray attenuation coefficients of xenon hydrate are one to two orders of magnitude higher than those of water, xenon gas and sand [40,41]. In particular, xenon hydrate dissociation contributes 95% to the radiograph grayscale number change within the sample vessel, which is in comparison to the 5% contribution from the pressure decrease of xenon gas (see Fig. 2). Hence, it is valid to assume the linearity between the grayscale number in X-ray radiographs of the sample vessel and the volume of xenon hydrate. This linear interpolation is constrained by the hydrate volume measured before dissociation with CT and zero volume afterwards. With the measurement of hydrate volume versus time, we calculate hydrate dissociation rate from dividing hydrate volume difference by time difference.

We define Damköhler number (Da) as the timescale of flow and diffusive heat transfer divided by the timescale of chemical reaction [18]. When Da is $\ll 1$, the effect of flow and diffusive heat transfer on the reaction is negligible; hence, reaction is limited by interfacial reaction (surface area) [8]. We estimate Da in this experiment is < 0.001 because of the high permeability of sand (387 D) and the small size and the high aspect ratio of the aluminum sample vessel (inside length: 7.3 cm, inside diameter: 0.84 cm). Therefore, the dissociation experiment stays roughly isothermal (23°C) and the effects of gas flow and diffusive heat transfer can be neglected. This work focuses on how hydrate surface area, saturation and pore size affect dissociation kinetics.

3. Results and discussion

3.1. Radiographs during hydrate dissociation

Fig. 2 shows X-ray radiographs at a few selected times during xenon hydrate (black) dissociation in the pore space. Within the sand area above the bottom spacer, the initial heterogeneous hydrate distribution gradually becomes homogeneous during dissociation. In the bottom spacer, hydrates in the annulus between the spacer and the wall (black veil-like pixels, better seen together with hydrate surface rendering in Fig. 3c for sand9 & sand10) dissociate faster than hydrates within the sand. Of the spring area, the chunk hydrates in the top half persist for a much longer time than the helical hydrates in the bottom half and the pore-filling hydrates in the sand area. These observations on hydrates dissociation are consistent with silicate mineral dissolution experiments that show the dissolution rate at low temperature increases with

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