

퇴적물 내의 하이드레이트 생성/해리 메커니즘과 탐사 및 개발생산에의 적용

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Hydrate formation/dissociation mechanisms in sediments and their implications to the exploration and the production

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Key words : gas hydrate, sediments, thermodynamics, production, exploration

Abstract : The thermal signature of nucleation process is characterized by the induction time, the degree of supercooling, and the equilibrium temperature depression. The initiation of nucleation presents stochastic characteristics. The factors that affect nucleation are mechanical impact, ionic concentration, mineral surface characters, and pore size.

Hydrate-bearing sediments behave mechanically like other cemented sediments. The data set has important implications for the calibration and interpretation of geophysical measurements and downhole logs collected in gas hydrate provinces, providing particular insight for the interpretation of P- and S-wave data and resistivity logs. In addition, laboratory formation history and ensuing pore-scale spatial distribution likely have a more pronounced effect on the macroscale mechanical properties of hydrate-bearing sediments

1. Introduction

Gas hydrate is a crystalline compound consisting of guest gas molecules encaged in water molecules. In nature, gas hydrates occur in the sediments of permafrost regions and continental margins, and methane is the most common guest molecule. The stability of gas hydrate depends on temperature, pressure, salinity, and other factors (e.g., soil characteristics). The difficulty of maintaining recovered natural samples at in situ temperatures (usually 0 to ~25°C) and fluid pressures (typically 5 to 25 MPa) has been one of the key challenges in studying natural gas hydrate-bearing sediments. At the same time, the analysis of measurements obtained in hydrate-bearing provinces during borehole logging or exploration geophysical surveys (e.g., seismic prospecting) has been limited by

the lack of high-quality calibrations of physical properties on synthetic laboratory samples with well-characterized lithology, hydrate saturation, and confining pressures.

The kinetics of hydrate formation has been studied to elucidate inhibiting or promoting mechanisms in hydrate formation. Natural gas hydrates form in seafloor and permafrost sediments. The role of mineral surfaces and pore characteristics on gas hydrate formation has been investigated in previous studies. The purpose of this study is to further address the understanding of hydrate formation/dissociation in sediments and its implication to hydrate exploration and production through theoretical and experimental investigations.

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2. Experimental Study

2.1 Hydrate nucleation experiment

The prepared specimens are submerged in the cooler. The system is equilibrated at 5°C for 1~2 hours. Then, the temperature of the cooler is gradually lowered at 0.1 °C/min of cooling rate to the target temperature: T= -5°C for 9°C supercooling tests and T= -10°C for 14°C supercooling tests. The cooling rate has minor effect on the nucleation rate: An order of magnitude increase of cooling rate lowers the mean nucleation temperature by 0.6 to 2°C. The cooler and specimen temperatures are monitored every 5 minutes. Tapping is performed only for the mechanical disturbance study. All other tests are conducted at the normal background vibration within the cooler.

The soils selected for this study are kaolinite (RP2 and SA1), precipitated silt, crushed silt, precipitated calcium carbonate (PCC), and ground calcium carbonate (GCC). RP2, randomly-shaped kaoline, is smaller than hexagonally shaped SA1. Crushed silt is an angular, low specific surface silt-sized soil. Precipitated silt consists of silt-size aggregations with extensive inter-particle pore networks and high specific surface. The irregularly shaped GCC particles are bulkier than the very uniform and rice-shaped PCC particles.

2.1 Physical property measurements

The electrical and mechanical (high-strain and low-strain) properties are measured in fully saturated, homogeneous sediments containing synthesized THF hydrate. Effective confining pressures of up to 2 MPa, sediment properties that span most of the range represented in natural marine sediments (grain sizes of 1 to 100 µm), and gas hydrate concentrations of 0% to 100% in pore space. Electrical resistivity, and real permittivity in the 200 MHz to 1.3 GHz range; such low-strain mechanical properties as P- and S-wave velocities, dynamic bulk modulus, and volume change during phase transformation. Experiments were

conducted with an oedometer and a newly constructed high pressure cell. To the greatest extent possible, measurements were automated and recorded digitally, and care was taken to demonstrate reproducibility of the results, to calibrate equipment, and to maintain close temperature control on specimens.

Four distinct homogeneous sediments used for this study are: Ottawa sand, precipitated silica flour, crushed silica flour (silt), and kaolinite (clay). The sediments were chosen to represent an ordered progression from grain sizes of 120 µm (sand) to ~1 µm (clay) and specific surface ranging from ~10⁻⁴ m²/g (sand) to ~35 m²/g (clay).

3. Experimental Results

3.1 Hydrate nucleation experiment

The thermal signature of nucleation process is characterized by the induction time, the degree of supercooling, and the equilibrium temperature depression. The initiation of nucleation presents stochastic characteristics. The factors that affect nucleation follow.

- Mechanical impact facilitates the initiation of nucleation and reduces the induction time when the strain rate exceeds a threshold level. Vibration does not affect the equilibrium temperature and does not prevent the stochastic nature of nucleation (yet it reduces its randomness).

- Salts do not affect the induction time considerably. However, salts depress the equilibrium temperature during phase transformation as the water activity is lowered, and ion exclusion leads to diffusion limited nucleation.

- Nucleation is favored in the presence of mineral surfaces.

- The character of mineral surfaces affects the induction time but it does not change the equilibrium temperature during phase transformation.

- Mineralogy and surface roughness are the most important particle characteristics to prompt the initiation

of nucleation on mineral surfaces. Particle size plays a secondary role.

- Pore size causes a significant depression in equilibrium temperature in fine grained sediments.

- Hydrate formation gradually invades the porous network, starting at large pores and advancing into the small ones. Therefore, the equilibrium temperature is gradually depressed during hydrate formation in sediments.

3.2 Physical property measurements

Laboratory formation history and ensuing pore-scale spatial distribution likely have a more pronounced effect on the macroscale mechanical properties of hydrate-bearing sediments than differences between THF and methane hydrates themselves. Nevertheless, the analysis of results gathered with THF hydrate-bearing sediments as a proxy for methane hydrate-bearing sediments should still take into consideration the inherent differences between these hydrates, particularly with regard to kinetics.

4. Conclusions

The thermal signature of nucleation process is characterized by the induction time, the degree of supercooling, and the equilibrium temperature depression. The initiation of nucleation presents stochastic characteristics. The factors that affect nucleation are mechanical impact, ionic concentration, mineral surface characters, and pore size.

Hydrate-bearing sediments behave mechanically like other cemented sediments. The data set has important implications for the calibration and interpretation of geophysical measurements and downhole logs collected in gas hydrate provinces, providing particular insight for the interpretation of P- and S-wave data and resistivity logs. In addition, laboratory formation history and ensuing pore-scale spatial distribution likely have a more pronounced effect on the macroscale mechanical

properties of hydrate-bearing sediments

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