

## Experimental Verifications of Abnormal Chlorinity appearing in Natural Deep- Sea Gas Hydrate

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### ABSTRACT

The chloride anion is known to be the most abundant salt ion in sea water. At the regions such as ODP Sites 1249 and 1250 the highly enriched chloride concentration is observed in a zone extended from near the sediment surface (~1 mbsf) to depths about 25 mbsf. Here, we designed the in-situ electric circuit system for measuring chloride concentration within reliable accuracy. In the cylindrical cell the 5-10 tubes having holes on the wall and electrodes were equipped around clay mixture. The open holes were made to regulate to a certain degree the interface area between methane gas and clay sample. As may be anticipated, the chloride concentration abnormally increased under fast rate condition for forming methane hydrate, but no noticeable concentration change was detected under relatively low rate. In fact, the present experiment seems to be a lot deficient to investigate the ion diffusion and moreover does not fully reflect the real deep-sea floor condition, but the meaningful results for describing the abnormal salinity enrichment might be drawn. The physical effects of chloride anions on surface morphologies of methane hydrate formed in the sediments were additionally examined with the Field Emission-Scanning Electronic Microscope (FE-SEM).

*Keywords:* gas hydrates, chlorinity, chlorinity enrichment, clay, SEM

### NOMENCLATURE

.FE-SEM field emission – scanning electron microscope  
MMT montmorillonite

### INTRODUCTION

Numerous methane hydrate studies covering both macroscopic and microscopic approaches have recently been conducted for a variety of purposes and with some notable successes. *Yeon et al.* suggested the possible reasons for predominant sI natural gas hydrate in the deep sea through the analysis of structure transitions driven by external

guest molecules. For journal see [1]. *Lee et al.* reported the swapping mechanism between external carbon dioxide and pre-existing methane hydrate with efficiency about 64%. For journal see [2]. The swapping and replacement phenomena occurring between the mixture of carbon dioxide and nitrogen and methane hydrate were also examined, resulting in the replacement yield up to 85%. For journal see [3]. The formation kinetics and phase equilibria of carbon dioxide hydrate in the deep ocean sediments are likely to be quite suppressed in unfavorable direction. For journal see [4]. The salts including chloride anion in

general act as the kinetic inhibitor and shift the PT pattern toward the more harsh condition, but unfortunately the actual salt effects on methane hydrate formation in MH sediments have been rarely investigated in the related fields. For journal see [5] and [6]. At the summit of hydrate ridge (ODP Site 1249 and 1250) the pore fluids were found to be highly enriched in dissolved chloride at the zone that extends from near the sediment surface (~1mbsf; meter below sea floor) to depths of 25mbsf. For conference proceeding see [7]. At some other regions the higher chlorinity than sea water level were also detected. See journal [8]. *Torres et al.* described that the transport of methane as free gas through the gas hydrate stability zone might induce the chloride concentration to be substantially enriched, using the one-dimensional transport-reaction model. See the journal [9]. However, the proper experimental approaches have not yet been attempted that reveal the significant role of surrounding methane hydrate formation conditions on the chlorinity enhancement. Particularly, in the present work, we design the in-situ electronic circuit system for measuring the chloride concentrations. We also tried to figure out the physical effects of chloride anions on surface morphologies of methane hydrate using the Field Emission-Scanning Electronic Microscope (FE-SEM).

## EXPERIMENTAL

For in-situ analysis we assembled the simple electronic circuit especially to measure the concentrations of chloride anion. The voltage drop is expressed by the following equation,

$$V_{total} = V_{sample} + V_{resist}$$

$$V_j = I_j \cdot R_j$$

When the ion concentration increases, the corresponding sample resistivity decreases accompanied with high voltage drop. The electrodes are placed in the high-pressure resistance cell with caution of perfect sealing. As the first test, we measured the voltage drops for two samples of aqueous 3.5 and 7.0 NaCl wt% solutions without adding clay material and found that the lower salt concentration exhibits the higher voltage drop and equivalently resistance. For real application, the suitable calibration was carried out to determine the relationship between chloride concentration and voltage drop, particularly, at 274K (Figure 1(b)), which appeared to be almost linear for the sample of Na-

montmorillonite (Na-MMT) 50wt% + NaCl + water in the range of 1-10 wt% NaCl. At each concentration the 20~30 times measurements were repeated within the error range of  $\pm 0.03V$ . The displacement between two electrodes was kept to be 1 cm and the measurement time was 3-5 seconds. This isotherm data can be reasonably well applied for temperature range of 270~277 K without any loss of accuracy. The present approach for precise ion-level determination is expected to provide considerable experimental advantages such as ready accessibility, reliable reproducibility, in-situ analysis, and little consumption of chloride anion during short time of measurement. In the high pressure resistance cell the sample collections with time are not favorable. The designed experimental procedure is as follows. First, we prepare the 50 wt% clay swollen with water during 1-2 hours and this sample was then ground until the viscous gel-like phase appeared at room temperature. The well dispersed suspension needs to maintain for reliable analysis because it allows the water-intercalated clay to be more homogenous even in highly complex structure. The clay sample was directly placed in the high pressure resistance cell roughly up to one third height, bending the sensing terminals of electrodes to be located at several key positions of clay mixture. The 5-10 tubes having holes on the wall were vertically equipped around clay mixture and electrodes in the cell. Here, the holes were made to regulate to a certain degree the interface area between methane gas and clay sample. We also observed that the highly viscous clay sample cannot pass through small holes, otherwise the clay comes in the tube and plugs the passage. The aqueous 3.5 NaCl wt% (600 mM) aqueous solution was charged onto the clay sample, avoiding to be penetrated in the holes. The cell temperature was maintained at 275-276K, pressurizing with CH<sub>4</sub> gas until the pressure reaches 100bar (Figure 2).

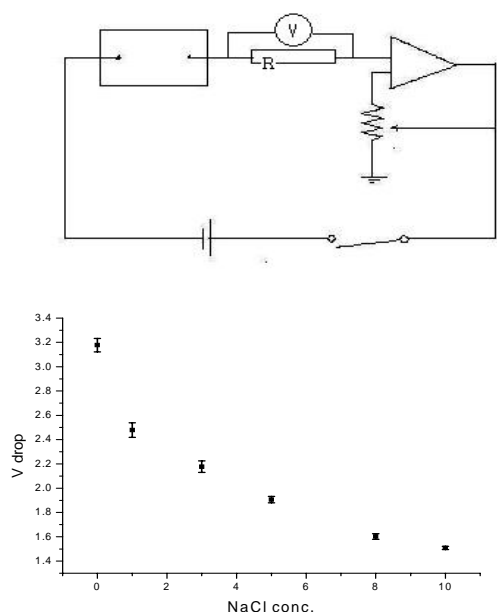


Figure 1 The Scheme of electric circuit for measuring chlorinity (a) and calibration data at 274K (b).

The FE-SEM (S-4700: HITACH) samples were prepared at 153K with 2 min etching and 80sec Pt coating at 40mA, and the measuring voltage was 10kV at 123K. The Wyoming-type montmorillonite (Wyoming, SWy-2, Wyoming, USA) was obtained from the Source Clays Repository of The Clay Minerals Society. At first, the clay samples were finely sieved and placed in a desiccator to prevent water uptake, but we used the natural samples than contain the admixture in order to eliminate the possible alteration of their inherent properties. For the sample preparation, the CH<sub>4</sub> gas was supplied by Special Gas (Korea) and had a stated purity of 99.98 mol%. Deionized water with an ultrahigh purity was supplied from Merck (Germany) and NaCl of 99.8% purity was from Ridel. All materials were used without further treatment.

## RESULT AND DISCUSSION

The Wyoming-type clay suspension in which methane hydrate forms is highly viscous with thixotropic property, while the rheological behavior of cheto type-montmorillonite follows the Newtonian fluid. During experiments we observed that the Wyoming-type clay is not well-mixed above 60 clay wt% and on the contrary the cheto-type montmorillonite is well-suspended,

facilitating methane hydrate formation in the clay interlayer space even at high

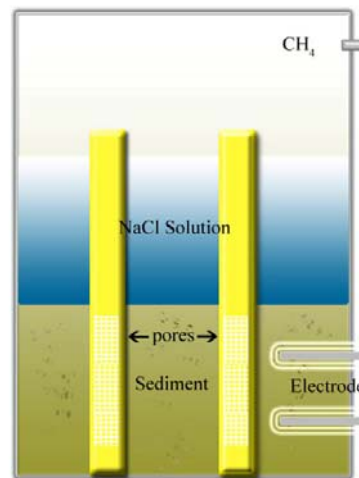


Figure 2 Design of high pressure reactor cell

clay concentration. The clay sample is charged into the in-situ high pressure cell with/without tubes and with/without aqueous NaCl solution at the upper level. Directly after methane supply the voltage drop was checked and calibrated according to the NaCl concentration as shown in Figure. 3. At the beginning of methane hydrate formation we observe that the considerable amount of chloride anions are excluded from solid hydrate phase within a short interval and accumulated in the sediment phase. The resistance and voltage drop quite rapidly decreased during the first 7 hrs and then slowly increased. On the other hand, the chlorinity pattern is just reversed, reaching the maximum of 1400mM after 7 hours, then slowly decreases because of the inversion of diffusion rate and eventually stabilized at the approximate value of 1150mM. The decrease of MH formation rate is closely linked to that of chloride exclusion rate, causing the accumulated chlorides to be directly diffused out by concentration gradients and finally reaching stable state. The notable feature arising from ion migration and diffusion is that the original level of chloride concentration can be never recovered once the methane hydrate initiates to form. We of course realize that the sediment-rich phase under the real deep sea floor appears to be highly viscous and thus enhances the chloride concentration.

The tubes were inserted in the clay samples to divide the MH formation system into three parts; the tube hole for allowing the passage for methane gas to flow in, the interface between methane gas

and clay sample at which the MH formation initially occurs and the clay sample part through which the methane gas is diffused to form the MH. Again, it is noted that the change of chloride concentration is continuously checked in the in-situ state according to the variation of interfacial area. The non-contacting surface of tubes must be of course inactive for the MH formation and readily controlled to regulate the directly contacting clay-methane area. The open contacting area on the tube wall varied to observe its effect on chloride concentration in clay sediments and the results are shown in Figure 4. The chlorinity increased with the contacting area over the entire time range and the maximum chlorinity level varied from 950mM to 1300mM. At the present stage it seems not reasonable to argue the meaningful and consistent proportionality between the contact area and chlorinity except to note that the maximum chlorinity tends to increase with the contact area. It took 10-15 hrs for the chlorinity to reach the maximum, depending on the contact area. The chlorinity increasing rate was quite fast up to the maximum, then slowly decreases and stabilized to the higher concentration than the initial one. The consistent chlorinity behavior for various clay contents implies that the MH formation leads to more concentrated ion level nearby ocean water. However, as anticipated, on the quite limited contact area on tube wall, the noticeable chlorinity change was not observed only showing 20 mM increase compared with the initial NaCl concentration of 620mM. The more actively the MH forms, the more the chloride is excluded out and its concentration is increased. Accordingly, the high chlorinity is not any more abnormal as long as the MH formation progresses steadily in certain sites of the deep-ocean MH sediments. *M.E. Torres et al.* reported that methane transport in the gas phase; not dissolved phase; have to exist for remarkable chloride accumulation like the situation of site 1249 of Cascadia margin off Oregon. For journal see [9]. The enrichment of chloride about 1000 mM was well described with their transport reaction model; scenarios 2 and 3. The present data appears to be consistent with this model results with an allowable range that the continuous methane gas injection promotes significant chloride enrichment in pore water. Although the kinetic constant vs. sea water depth can't be fully examined with the present simple cell, the following features seem to be noticeable. First, the significant amount of

chloride anion is accumulated at the initial stage, after 10 hrs keeping the much higher chloride concentration than the original sea water level. Second, the chloride level depends largely on the injected methane gas rate. We particularly note that the chloride exclusion seems to be almost impossible to occur at low MH formation rate in spite of continuous methane gas supply. The provisional outcome coincides somewhat with the scenario 1 of *Torres et al.*. For journal see [9].

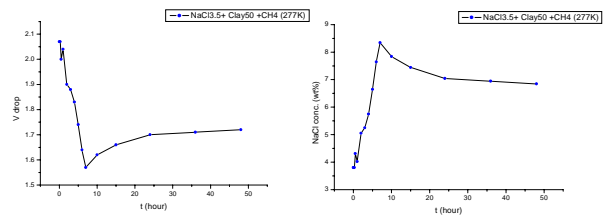


Figure 3 Measured voltage drop vs. methane hydrate formation time (a), and NaCl conc. vs. methane hydrate formation time (b)

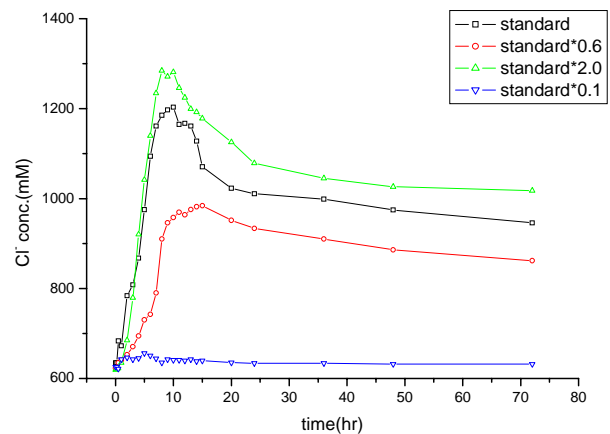


Figure 4 Chloride accumulations with various interface area.

In the present experimental system the direct contact between salt water and clay was not achieved and thus we could not draw any valuable conclusion regarding the principal role of the dissolved methane on MH formation and salinity in sediments. However, as can be seen in Site 1249, the effect of dissolved methane appears to be much smaller than that of directly supplied methane gas. Accordingly, the present approach might nearly reflect the real deep ocean surroundings, even though we didn't consider the dissolved methane. We also didn't consider the following; the sediments and upper water phase

were in the fixed state without providing any mobility and thus the vertical flow in the real sediment layer that affects on the flush-out of chlorinity could not be seriously considered. The rate of upward fluid flow ( $u_0$ ) is known to vary in the range of 0-10 cm year<sup>-1</sup>, which is equivalent to 0.001 cm hr<sup>-1</sup>. This vertical flow effect seems to be negligible. The present experimental system needs to be modified for the key phenomena influencing the chloride level to be more clearly seen. The methane gas bubbles go upward through sea water and thus must be distinguished from solely existing methane gas phase. These two different methane supply methods provide their own effective contact area, which might greatly alter the real MH formation kinetics. The second is the degree of compactness in the sediment layer. The porosity of the real sediments at the Site 1249 is reported as 0.6 to 0.7 beyond about 40 mbsf. Nevertheless, the artificial sediment of Na-MMT + NaCl aqueous solution is too compact for methane gas to diffuse out deeply into the clay sediments to the radial direction. We thus expect that the well formed methane hydrate exists just adjacent the tube. Most of chloride concentrations were measured at this part. Moreover, the massive methane hydrate and trapped bubble structure were found in the less compact sediments, but were never observed in the present experimental surroundings. In the near future we hope to solve these problems and approach the real deep-sea conditions.

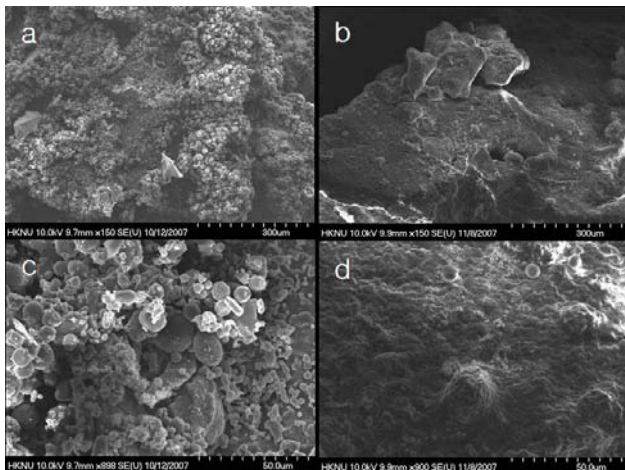


Figure 5 SEM images of Na-MMT 50wt% + Methane hydrate with 3.5wt% NaCl (a), (c) and without NaCl (b), (d).

The swelled sediments of 50wt% Na-MMT with 50wt% water exhibit high viscosity as shown in

fig. . The viscosity of the mixture of 50wt% Na-MMT and 50wt% NaCl aqueous solution has much lower than that without NaCl. We checked that difference of physical properties with. Analyzing surface morphologies of 50wt% Na-MMT + methane hydrate with pure water obtained from the FE-SEM we observe the clay-MH mixture consisting of spheres having the radii of about 5-10µm and the pictures are shown in Figure 5(a) and (c). On the contrary, no sphere-like clay-MH particles were not observed under sea-level salt phase containing specific amount of NaCl. Rather, it looks like bulky and slightly bendy. The layer structured Na-MMT contains in itself the movable Na<sup>+</sup> cations in the interlayer and thus the morphological difference of both clay-MH mixtures is supposed to be significantly affected by the sodium cations from NaCl. The chloride anions exhibit strong electro-negativity that might affect the morphology of clay sediments with alkali or alkali earth cations. Another possibility is that the secondary bonding between chloride anions and interlayer cations strongly builds up, which contributes for the clay sediments to aggregate together. Up to now the chloride anion has been considered just as a chemical inhibitor, but the unique surface morphology implies that the chloride anions in the deep sea sediments also may play a key role to promoting methane hydrate formation. It suggests a critical effect of chloride anions on hydrate morphology in the sediment layer.

## CONCLUSION

Even though the chloride anion is the most abundant in the ocean, it has only been recognized as a chemical inhibitor for methane hydrate formation. In this study, we developed the in-situ electrical circuits for chloride measurements and set up the experimental verification system. We might conclude that the chlorinity in the sediment layer is not fixed at the settled value, but is closely associated with methane hydrate formation. Next, the chloride concentrations considerably increased with the hydrate formation rate. The present results don't fully match with the real deep-sea data, but to some extent demonstrates the abnormal salinity enrichment pattern. According to surface morphology, the aggregated pattern was clearly detected in the case of sediments with chlorides of sea level.

## ACKNOWLEDGEMENT

Funding for this research was provided by the Korean International Ocean Drilling Program (K-IODP) 2007 in by Korea Institute of Geoscience and Mineral Resources.

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