SEPARATION AND RECOVERY OF CO_2 FROM EXHAUSTED GAS BY HYDRATES

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ABSTRACT

Hydrates have the peculiar crystal structure that one guest molecule is surrounded with a cage composed by water molecules. These water molecules are connected by the hydrogen bonding each other, but there is no chemical bonding between the guest molecule and the water molecules. In this paper I will show the possibility of hydrate's application to solve environmental problems. The cage-like structure of hydrates can be utilized as an environmental pollutant gas separation method since in mixture hydrates the molar fraction of components in a hydrate phase is different from that in a gas phase. Firstly properties of hydrates concerning with the separation technology are summarized concisely. Potential function between the water molecules and the guest molecule is calculated for CO2, N2 and O2. And hydrate-gas equilibrium in CO2-N2-O2 mixture is predicted. Then, based on these data, the separation technology with hydrates is demonstrated.

INTRODUCTION

Hydrates have been classified as one of clathrate compounds and show the peculiar structure that one gas molecule exists in the cage composed by water molecules. The molecule in the cage is called a guest molecule and many kinds of gas molecules like argon, oxygen, nitrogen, xenon, carbon dioxide, nitric monoxide, sulfur dioxide, and hydrogen sulfide may become a guest molecule. The forming condition of hydrates is generally in low temperature and high pressure, and this condition is different with the type of the guest molecule.

Recently, the separation technology that uses the functional material having recognition ability of molecules has been attracting many attentions. For instance, Crown ether, shown in Fig.1, can recognize and capture a molecule that fits the molecular space of the crown ether. This property of the crown ether can be utilized in the separation technology. In that case recognition and capture of the molecule are carried out based upon the molecular size. On the other hand, hydrates have the recognition ability based upon the potential energy between the guest molecule and water molecules in addition to the ability based upon the molecular size.

In this paper I take the possibility of hydrates as the functional material having the molecular recognition ability and report the result of applying this ability of hydrates to the separation of the carbon dioxide from the exhausted gas. Firstly the properties of hydrates concerning separation are introduced and the separation process using hydrates is explained. Then in relation to the molecular recognition ability of hydrates, the potential functions between the guest molecule and water molecules are presented for each guest molecule of carbon dioxide, oxygen or nitrogen. Some examples of the phase equilibrium calculation that can be used to recover carbon dioxide from the exhausted gas are shown. Lastly experimental apparatus demonstrating this technology is introduced and some experimental results are shown.

HYDRATES

Fig.2 shows models of the cage composed by water molecules and Table 1 indicates structural properties and geometric constants of the cage. Water molecules occupy summits of the polygon and are connected by the hydrogen bonding each other. And each cage contains one guest molecule. Though there are many kinds of molecules that can be held in the cage, some restrictions exist to be contained in the cage. At first, the size of the molecule must be proper to be inside of the cage because the diameter of the cage is constant and fixed. In other words, hydrates have the molecular recognition ability depending on the molecular size. And the molecule whose size is extremely smaller than the cage size cannot make hydrates. Next, it is necessary not to make the hydrogen bonding between water molecules. Table 2 shows guest molecules that make hydrates and their van der Waals diameter.

SEPARATION BY HYDRATES

Each cage of hydrates contains one guest molecule, but considering bulk hydrates, there is no need for all guest molecules to be same. In other words, mixture hydrates exists. Mixture hydrates means the situation that different kinds of molecules are scattered in hydrates cages. Mixture gas that consists of many components shown in table 2 can form mixture hydrates.

The separation technology by hydrates is based on the fact that molar fraction of components in the hydrate phase is different from that in the gas phase. Fig 3 illustrates this situation conceptually. In this case, the gas phase contains same number of black molecules and white molecules but the hydrates phase includes lager number of black molecules. That is to say, the stability of the hydrate cage is different according to the type of the guest molecule.

Fig.4 expresses the situation illustrated in Fig.2 by a diagram. This figure is also conceptual. In this figure a vapor line and a hydrate line are drawn. By utilizing this figure we can design the separation process. For instance, the dotted line in this figure indicates that the vapor in which the molar fraction of black molecules is 0.5 forms hydrates at pressure P_1 and that the molar fraction of black molecules in the hydrates phase is 0.79. When dissolving these hydrates, you can obtain the vapor in which the molar fraction of black molecules is 0.79. The dashed line shows that the vapor in which the molar fraction of black molecules is 0.79 forms hydrates at pressure P_2 and that the molar fraction of black molecules in hydrates phase is 0.95. By same procedure in the former case, dissolving these hydrates, you can recover the vapor in which the molar fraction of black molecules is 0.95. The repeating process between forming and dissolving hydrates is necessary to separate mixture gas by hydrates.

MOLECULAR RECOGNITION BY HYDRATES

Molecular recognition of hydrates is carried out by two mechanisms. One is based upon molecular size and the other is based upon the difference of the potential function between the guest molecule and water molecules. Let assume that mixture gas is composed by carbon dioxide, oxygen and nitrogen, in this case each molecule can be clathrated in the cage as shown in Table 2. So next factor of the separation is the difference of potential functions among these three components. Fig.5 shows potential functions between the guest molecule and water molecules for carbon dioxide, oxygen and nitrogen. It is obvious from this figure that the depth of the potential well with carbon dioxide is deep comparing with that of oxygen and nitrogen. This fact suggests that the carbon dioxide molecule is easier to be captured in the hydrate cage than other two components.

To design the separation process for the mixture of carbon dioxide, oxygen and nitrogen, the phase equilibrium diagram for CO_2-N_2-O_2 mixture is necessary. After removing NOx and SOx, main components of exhausted gas are nitrogen, carbon dioxide, oxygen and water. Hydrate phase equilibrium calculation was carried out for the exhausted gas of this component. Fig.6 and Fig.7 demonstrate results of the phase equilibrium calculation based upon the van der Waals and Platteeuw theory. If the molar fraction of carbon dioxide in the exhausted gas is 0.12, carbon dioxide is separated and recovered by two steps of forming and dissolving hydrates.

EXPERIMENTAL APPARATUS AND RESULTS

Fig.8 illustrates the experimental apparatus. The high-pressure vessel was made by sus303 and its diameter was 150mm. The molar fraction of mixture gas was controlled by mass flow meters. The mixture gas was pressurized by a booster pump then introduced to the vessel. Hydrates were made by the spray method. Pressurized water was jetted out from a nozzle. Temperature was measured by platinum resistance thermometers and pressure was gauged by a pressure transducer. The molar fraction of the mixture gas and hydrates was measured by a gas chromatograph.

Table 3 shows one example of experimental results. Obviously the molar fraction of carbon dioxide in the hydrate phase is higher than that in the gas phase. But there is a gap between theoretical predictions and experimental results.

CONCLUSION

Properties of hydrates concerning with the separation were briefed. Potential function between the water molecules and the guest molecule was calculated for carbon dioxide, oxygen and nitrogen. And hydrate-gas equilibrium in CO2-N2-O2 mixture was predicted. Then, based on these data, the separation technology with hydrates was demonstrated.

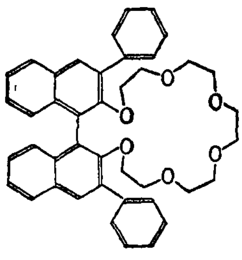

Fig.1 Crown ether

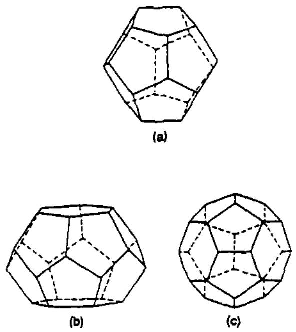

Fig.2 Cages of gas clathrate hydrates
(a) small cage. (b)(c) large cage

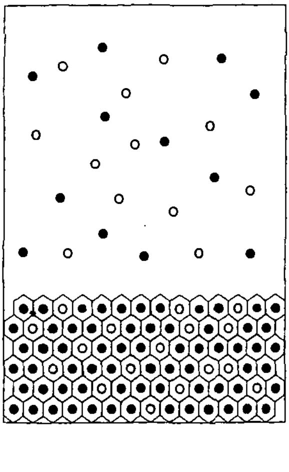

Fig.3 Mixture hydrates with vapor phase

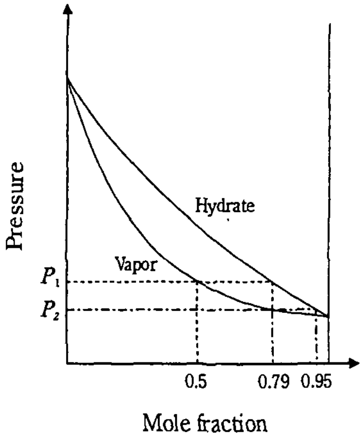

Fig.4 Hydrate-Vapor Equilibriun

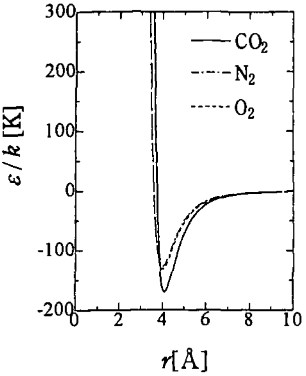

Fig.5 Potential function for the gest molecule

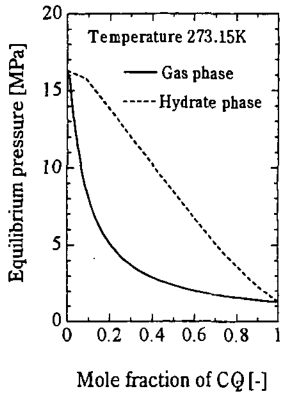

Fig.6 Phase equilibrium for CO_2-N_2-O_2 mixture hydrate where N_2:O_2 is constant at 97.7:2.3

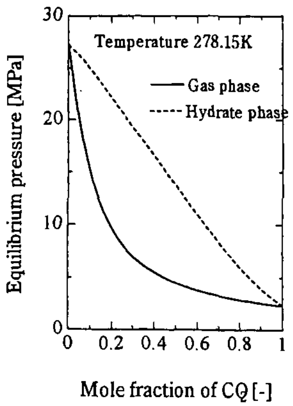

Fig.7 Phase equilibrium for CO_2-N_2-O_2 mixture hydrate where N_2:O_2 is constant at 97.7:2.3

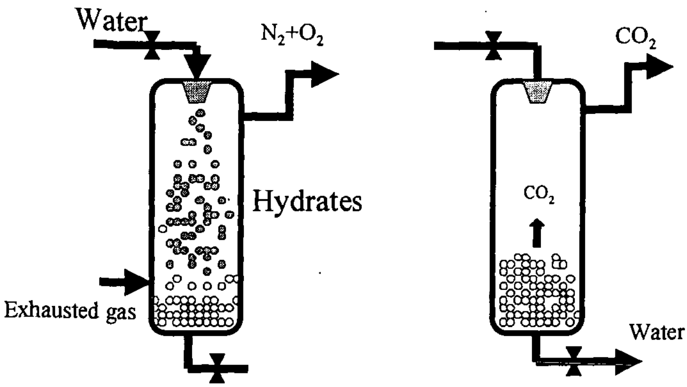

Fig.8 Experimental apparatus

Table 1 Geometry of cages

Crystal structure	I		II	
Cavity type	Small	Large	Small	Large
Description	5^{12}	$5^{12}6^{2}$	5^{12}	$5^{12}6^{4}$
Average cavity radius [nm]	0.395	0.433	0.391	0.473
Coordination number	20	24	20	28
Number of cavities per water molecule	1/23	3/23	2/17	1/17

Table 2 Guest molecules that make hydrates

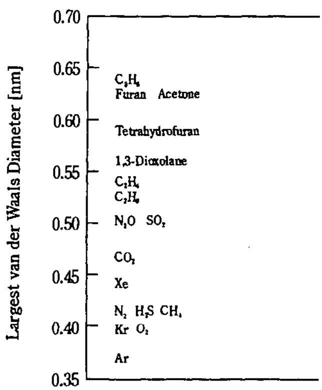

Table 3 Experimental results

Temperatuer:276.75K	Pressure:9.33MPa		
	N_2	O_2	CO_2
Injection port (control of MFC)	50.0%	20.0%	30.0%
Measurement of gas component before injection	51.1%	21.1%	27.9%
Collection port (measurement of gas chomatogroph)	41.8%	19.1%	39.1%