

## Spectroscopic investigation, cage occupancy, and gas storage capacity of hydroquinone clathrates formed with H<sub>2</sub>S-N<sub>2</sub> and COS-N<sub>2</sub> binary gas mixtures

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**Abstract**—The objective of this investigation was to determine whether hydroquinone (HQ) can form clathrate compounds with two sulfides (hydrogen sulfide (H<sub>2</sub>S) and carbonyl sulfide (COS)) at their diluted concentrations. Hydroquinone samples obtained at ambient temperature and at two pressures (40 and 80 bar) for binary gas mixtures consisting of H<sub>2</sub>S-N<sub>2</sub> and COS-N<sub>2</sub>, were analyzed using solid-state <sup>13</sup>C NMR and Raman spectroscopy. An elemental analyzer was also used to obtain quantitative information regarding the kind and amount of gas captured in the solid samples. Results show that H<sub>2</sub>S can be concentrated within the solid clathrate from H<sub>2</sub>S-containing gas, while COS is little captured after reaction with the COS-containing gas. This suggests that the HQ clathrate can be used to remove H<sub>2</sub>S, and that selective separation can be achieved when two sulfides of H<sub>2</sub>S and COS coexist. On the basis of the calculated cage occupancies of the gas components in the solid clathrate, the enclathration preference of the gas components used in this research was found to be the order of H<sub>2</sub>S > N<sub>2</sub> > COS.

Keywords: Clathrate, Coal Gas, Hydrogen Sulfide, Carbonyl Sulfide, Desulfurization

### INTRODUCTION

Globally, coal is the principal fossil fuel for electric power generation because its abundance and wide distribution [1]. The proportion of electricity produced using coal is around 40% globally and more than 50% in the U.S. [2]. Because exclusive use of renewable and nuclear energy sources is unable to meet the worldwide energy production requirements, even though researches to expand their usages have been reported recently [3-6], fossil fuels, in particular, coal, will remain primary energy sources for some time [7]. The main concern regarding coal utilization is the environmental impact due to its relatively higher release of pollutants than with other fuels. Anthropogenic CO<sub>2</sub> emission is considered to cause global warming, and coal alone accounts for about 70% of Europe's CO<sub>2</sub> emission from power generation [7]. Currently, the integration of carbon capture and storage (CCS) technologies for power generation plants is being investigated as a path to sustainable energy production. In particular, ultra-supercritical pulverized coal combustion (USC) and integrated gasification combined cycle (IGCC) technologies represent the most promising solutions for CO<sub>2</sub>-free power generation using coal [7].

In addition to CO<sub>2</sub>, other pollutants, including sulfur, should be removed appropriately to satisfy stringent regulations. Coal contains a considerable amount of sulfur in the form of sulfides, which are

toxic and corrosive to equipment and pipelines. Almost one-half of the cost of producing clean gasified coal is attributable to gas purification, and of this a major expense is associated with sulfide removal and its conversion to elemental sulfur (e.g., the Claus process) [8]. The sulfides in coal include hydrogen sulfide (H<sub>2</sub>S), the primary gas-phase, with carbonyl sulfide (COS) and carbon disulfide (CS<sub>2</sub>) as the secondary sulfur species [2]. Anthropogenic H<sub>2</sub>S and COS account for about 50% and 10%, respectively, of the total amounts in the atmosphere [9]. Nowadays, removal of such sulfides is handled mainly by adsorption, absorption, and membrane technologies. For adsorption, metal oxides in the forms of pure oxide, solid mixtures of metal oxides that react with sulfides, or mixtures of an inert oxide with a solid reactant have been investigated, especially at high temperatures [10]. The addition of an inert solid was reported to stabilize the metal oxide against its reduction to the metal form and/or volatilization [11]. Metal oxides are normally used at high temperatures, which condition is convenient for connection to subsequent processes or equipment without severe energy loss [2,12]. For absorption, amine compounds such as diethanolamine (DEA) and methyldiethanolamine (MDEA) are widely used as absorbers. Some researchers have reported the removal efficiency of sulfides and reaction kinetics using absorbers [13,14]. However, amine compounds can absorb CO<sub>2</sub> as well, which leads to reduction of the net power output from the fuel as much as 1% [8]. Sulfide removal with an immobilized liquid membrane, and with activated carbon, has also been reported [8,15,16].

While the conventional technologies above have been adapted for a variety of gas separation processes, a novel concept using clath-

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rate compounds was also proposed. Clathrate compounds are non-stoichiometric solid crystals formed by enclathration of gaseous guest molecules in cage-like structures of hydrogen-bonded polar host species. Gas hydrates, the host of which is water, are a popular example of the clathrate compounds [17]. Gas hydrates can store a huge amount of gas in a unit volume of the solid phase, and can be applied to selective separation/concentration of a specific component from gas mixtures because the formation conditions are differentiated, mainly depending on the size of the gas molecules. Kang and Lee reported hydrate-phase equilibria of binary ( $\text{CO}_2 + \text{N}_2$ ) hydrates, and proposed hydrate-based  $\text{CO}_2$  separation from flue gases [18]. In addition, phase equilibria and modeling work has been reported for various systems [19-21]. Although a hydrate-based process can be clean because only water is involved, its condition of formation is near the freezing point of water, requiring energy consumption for cooling and thereby additional energy cost. Furthermore, vapor water can contaminate the removed gases after regasification by dissociating the formed hydrate. To overcome such disadvantages, Lee et al. used hydroquinone (HQ) as a host and reported dry synthesis of clathrate compounds for various gases [22,23]. Because HQ is the solid phase at the room temperature, it does not need any cooling energy to form the clathrate compound, nor contaminate regasified gases due to its low vapor pressure. In addition, they also performed spectroscopic measurements to identify preferential or selective capturing of specific components from gas mixtures by the HQ clathrates [24,25].

In this study, we used the HQ clathrate to evaluate potential applications to separate or concentrate two sulfides,  $\text{H}_2\text{S}$  and  $\text{COS}$ . Although both  $\text{H}_2\text{S}$  and  $\text{COS}$  have been reported to form clathrate compounds with water and HQ as hosts [26-29], the present investigation has a two-fold novelty. First, we investigated the potential application of a clathrate-based process with a dry synthesis method to sulfide removal. Because dry HQ powders without any solvent are used to form the clathrate compound, the reaction is much easier to handle. Secondly, because previous studies were mainly reported from an academic perspective using pure sulfides as guest species, they cannot be applied to practical processes dealing with dilute sulfides (in the range of a few percent). In this report, we used two sulfides diluted with  $\text{N}_2$  to help in designing a practical process dealing with dilute sulfides. Therefore, we investigated clathrate formation and guest storage at dilute concentrations of 5 mol%  $\text{H}_2\text{S}$  and 3 mol%  $\text{COS}$  (balanced with  $\text{N}_2$ ). The results from experiment and calculation in this study can be used as fundamental information for designing a clathrate-based sulfide separation process.

## EXPERIMENTAL SECTION

### 1. Materials

Hydroquinone (HQ, purity 99 mol%, from Sigma-Aldrich Chemicals Co.) was used as a reagent without further purification. Two gases (5 mol%  $\text{H}_2\text{S}$  and 3 mol%  $\text{COS}$ ), both balanced with  $\text{N}_2$ , were purchased from Daemyoung Special Gas. Co. (Republic of Korea). These gases were used for reactions without further treatment.

### 2. Sample Preparation

HQ clathrate compounds were prepared by adding pure HQ to a high-pressure cell. The cell with an internal volume of  $20 \text{ cm}^3$  was

made of 316 stainless steel. A reservoir attached to the cell was used to compensate for the pressure drop during the reaction, and thus keep the experimental pressure constant during clathrate formation. Before charging into the reactor, approximately 5.0 g of HQ was finely ground with a size  $<45 \mu\text{m}$  to enhance reactions between the solid and the gas phases. The reaction cell was purged to remove the residual gases and pressurized to the desired pressure at ambient temperature with the experimental gases. A digital pressure indicator (Heise, ST-2H) was used to monitor the system pressure in the cell. After the formation completion for 14 days, the pressure gases were slowly released from the cell and the samples were collected for spectroscopic analysis. To determine that there was clathrate formation and details of guest enclathration, the collected samples were analyzed using solid-state  $^{13}\text{C}$  nuclear magnetic resonance (NMR), Raman spectroscopy, and elemental analysis.

### 3. Solid-state $^{13}\text{C}$ NMR

For solid-state  $^{13}\text{C}$  NMR, an Agilent DD2 400 MHz spectrometer was used. The  $^{13}\text{C}$  NMR spectra were collected at ambient temperature by placing samples within a 1.6 mm magic-angle spinning (MAS) probe and recording at a spinning rate of 20 kHz. The pulse length of the proton was  $2 \mu\text{s}$  and a phase repetition delay of 10 s under proton decoupling was employed. The downfield carbon resonance peak of adamantane assigned a chemical shift of 38.3 ppm at 300 K was used as an external chemical shift reference.

### 4. Raman Spectroscopy

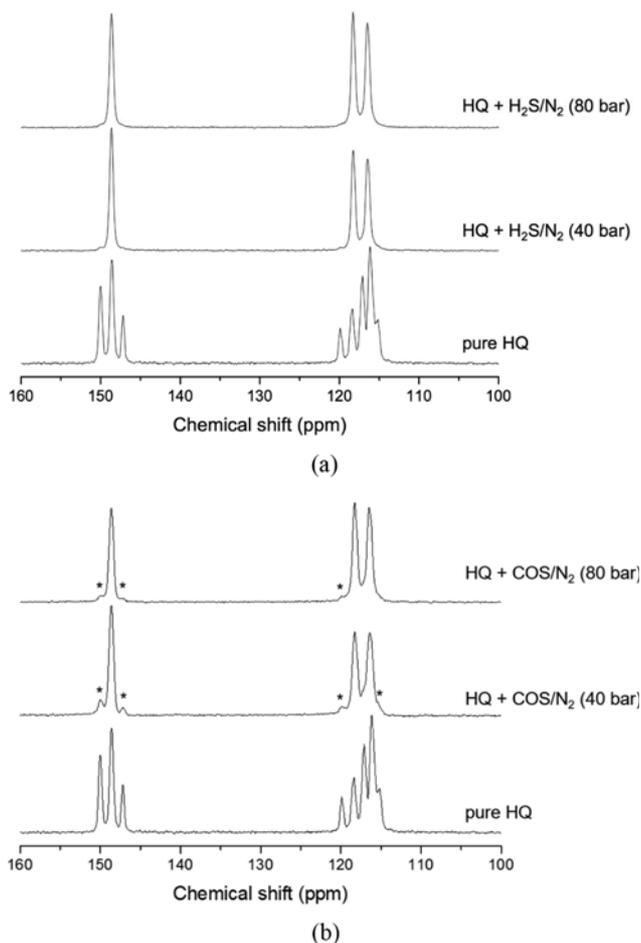
A dispersive Raman spectrometer (Horiba Jobin Yvon, Lab-RAM ARAMIS model) with a 460 mm focal length monochromator and air-cooled charge-coupled device (CCD) detector was used to identify the guest inclusion. An Ar-ion laser emitting a 514 nm line with 40 mW of power was used as the excitation source. All the Raman spectroscopic measurements were conducted at ambient temperature.

### 5. Elemental Analysis

The chemical content (C, H, N, S, and O in the HQ samples) was determined by using an elemental analyzer (Thermo Scientific, Flash 2000 Series). Approximately 3.0 mg of each sample was analyzed with the dynamic flash combustion method with a thermal conductivity detector (TCD). From ten repeated measurements, the experimental results of the elemental analysis were found to be in good agreement with the theoretical value of pure HQ with deviations of less than  $\pm 1.0\%$ . All the analytic instruments were located in the Analysis Center for Research Advancement of the Korea Advanced Institute for Science and Technology (KAIST, Daejeon, Republic of Korea). All the measurements were performed at ambient temperature and atmospheric pressure right after the sample collection in the center to minimize possible sample decomposition or sample modification. More detailed experimental procedures are given in previous reports [24,30].

## RESULTS AND DISCUSSION

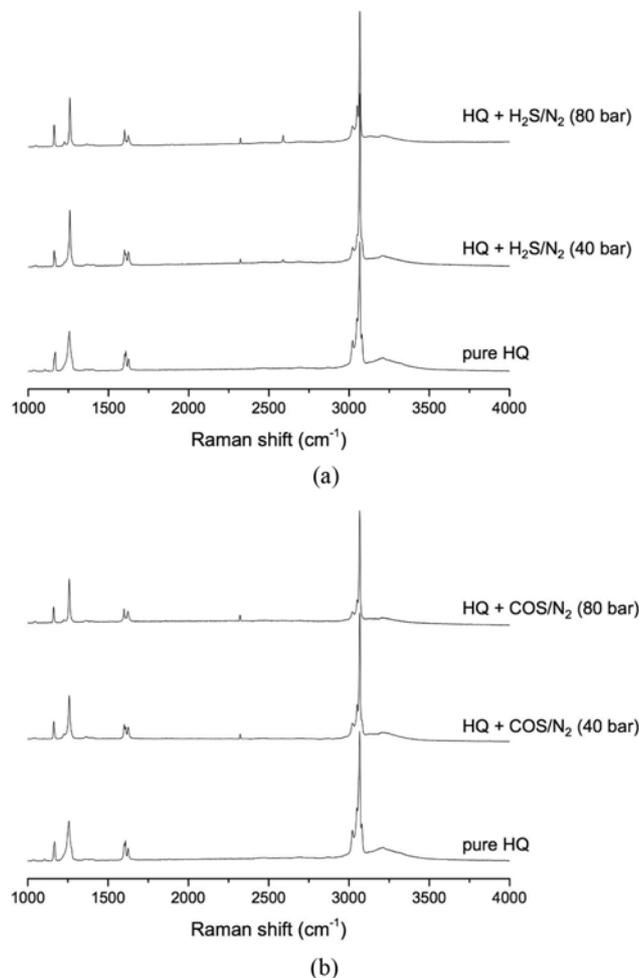
Solid-state  $^{13}\text{C}$  NMR spectra were collected for the samples reacted with 5 mol%  $\text{H}_2\text{S}$  and 3 mol%  $\text{COS}$ , and then compared with those of un-reacted pure hydroquinone (HQ) (Fig. 1). As can be seen in the figure, pure HQ shows two groups of atomic signals at around 150 ppm and 120 ppm corresponding to hydroxyl-substituted and



**Fig. 1.** Solid-state  $^{13}\text{C}$  NMR spectra of hydroquinone samples before ( $\alpha$ -form) and after reactions ( $\beta$ -form) with (a) 5 mol% H<sub>2</sub>S+balanced N<sub>2</sub> and (b) 3 mol% COS+balanced N<sub>2</sub> at 40 and 80 bar and ambient temperature. All the spectra were obtained at ambient temperature and atmospheric pressure. Asterisks around the observed carbon signals after the reactions indicate the residual (or unreacted) pure ( $\alpha$ -form) hydroquinone.

non-substituted carbon atoms. These are consistent with the  $\alpha$ -form crystal pattern of pure HQ [29,31]. However, those signals were arranged more clearly, after reaction with both gases, to represent the  $\beta$ -form crystal of HQ clathrates [31]. Such changes can be observed for all the samples prepared. In addition, the difference between two non-substituted atomic signals was found to be  $\Delta=1.79$  ppm, which agrees well with previous reports [23,31]. Some samples, especially, those reacted with COS, show shoulders around the hydroxyl-substituted carbon signal that indicate the presence of unreacted residual HQ ( $\alpha$ -form). However, reactions were almost completed because the intensity of such shoulders was relatively low.

Although the clathrate formation was identified in the  $^{13}\text{C}$  NMR spectra, it is not clear whether H<sub>2</sub>S and COS were captured because there was no carbon atom in the molecule (for H<sub>2</sub>S) and no additional peak was detected (for COS). To identify the guest behavior better, the same samples were analyzed using Raman spectroscopy (Fig. 2). Un-reacted pure HQ showed in-plane bending mode of



**Fig. 2.** Raman spectra of hydroquinone samples before ( $\alpha$ -form) and after reactions ( $\beta$ -form) with (a) 5 mol% H<sub>2</sub>S+balanced N<sub>2</sub> and (b) 3 mol% COS+balanced N<sub>2</sub> at 40 and 80 bar and ambient temperature. All the spectra were collected at ambient temperature and atmospheric pressure.

C-H bond and stretching mode of C-O and C-C bonds at 1,150 and 1,250 cm<sup>-1</sup>, respectively. In addition, strong signals of C-H stretching mode were found at 3,000 cm<sup>-1</sup>, while a broad signal at about 3,200 cm<sup>-1</sup> indicates the stretching mode of the O-H bond. The above characteristics show good agreement with previous reports for pure HQ [23,32]. After reaction with sulfide-containing gases, the Raman spectra showed some changes. The shapes and intensities of the Raman peaks at 1,150, 1,250, and 1,600 cm<sup>-1</sup> changed, and additional peaks were detected in the range 2,200-2,600 cm<sup>-1</sup>. The former represents the conversion of HQ crystal structures from its pure form ( $\alpha$ -form) to the clathrate compound ( $\beta$ -form), which matches previous reports [23,32]. The latter could be direct evidence showing enclathration of the gas components. Considering previous reports and the experimental gases used, a peak signal at 2,200 cm<sup>-1</sup> corresponds to the N-N bond of N<sub>2</sub> molecules [23,33]. Moreover, the other signal at 2,550 cm<sup>-1</sup> can be assigned to the H-S bond of H<sub>2</sub>S molecules [34]. However, signals showing the enclathration of COS cannot be observed, even though strong absorption should be shown between 2,500 and 3,000 cm<sup>-1</sup>

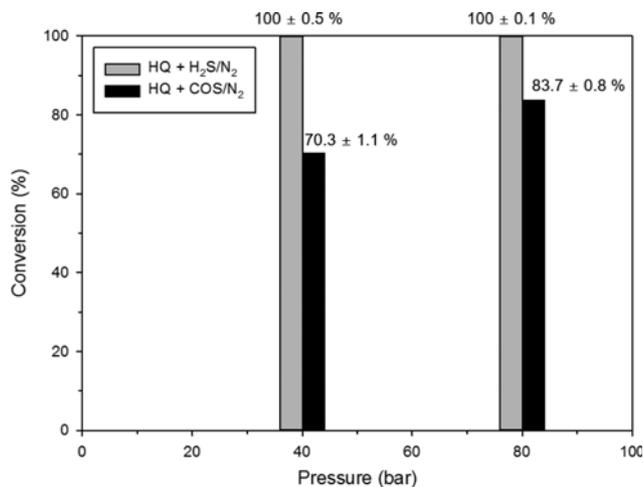


Fig. 3. Conversion yields of hydroquinone (HQ) clathrates after reactions with 5 mol% H<sub>2</sub>S+balanced N<sub>2</sub> and 3 mol% COS+balanced N<sub>2</sub> at 40 and 80 bar and ambient temperature. Grey and black bars represent the values for HQ samples from H<sub>2</sub>S- and COS-containing gases, respectively.

[35]. This suggests that only a very small amount of COS, less than the instrument resolution, was captured, or that those peaks overlapped the strong C-H stretching peaks.

To obtain quantitative information regarding the captured gas components, numerical analysis of the NMR spectra and elemental analysis were performed. Fig. 3 and Table 1 show that the reaction conversion depended on the sulfides and pressures used. Because NMR signal intensities are inherently proportional to the amount of corresponding atoms, the relative amounts of the  $\alpha$ - and  $\beta$ -forms obtained in the NMR spectra can be used to calculate the conversion yields. First, using the NMR spectra for pure HQ obtained from ten repeated measurements, the area ratio of the hydroxyl-substituted carbon atom was found to be 1 : 1.55 : 0.44 (AAD $\leq$ ±2.1%) with Lorentzian peak deconvolution [30]. This ratio was used to calculate the peak area for the  $\alpha$ -form HQ, when the mixed  $\alpha$ - and  $\beta$ -forms were identified from the <sup>13</sup>C NMR spectra. As shown in the graph, all the samples prepared with H<sub>2</sub>S-con-

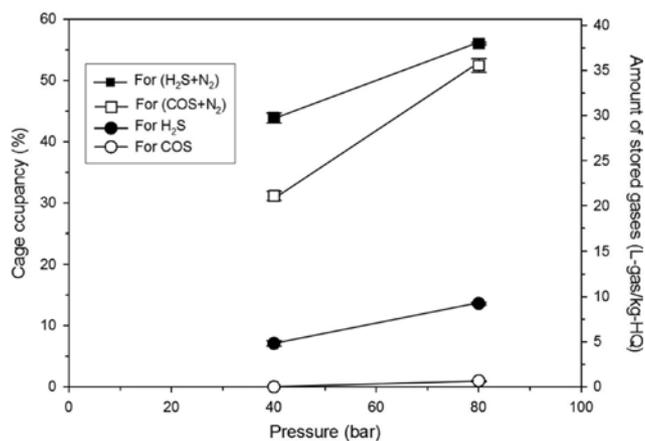


Fig. 4. Cage occupancies and stored amounts of gas components in hydroquinone clathrates after reactions at 40 and 80 bar and ambient temperature.

taining gas show full conversion (100%) regardless of the experimental pressure. However, the conversion yields after reaction with COS-containing gas were found to be (70.3 and 83.7) % at (40 and 80) bar, respectively. This means that 29.7% and 16.3% of the HQ powders remained intact after reaction at the corresponding pressures. In addition, the cage occupancies by gas components are calculated on the basis of the elemental analysis. The theoretical formula of the HQ clathrate is 3HQ·xGas (0 $\leq$ x $\leq$ 1), meaning maximum 1 mol of gas can be captured in a cage formed by 3 mols of HQ. The cage occupancy in Fig. 4 and Table 1 represents the percentage of cages occupied by gas molecules. As plotted in the figure, few COS molecules were captured regardless of the experimental pressure, while H<sub>2</sub>S molecules from the gas-phase were found to be concentrated in the solid clathrate. In other words, N<sub>2</sub> is captured better than COS, while H<sub>2</sub>S is more readily captured than N<sub>2</sub>. Accordingly, the capture preference in the clathrate compound is reflected on the order of H<sub>2</sub>S>N<sub>2</sub>>COS. Even though both H<sub>2</sub>S and COS are reported to react with water and HQ to form clathrate compounds [27-29], the low enclathration observed in this study is mainly attributed to the low partial pressure of COS.

Table 1. Conversion yields, cage occupancies and storage capacities of gas components calculated from the analytic measurements

	5 mol% H <sub>2</sub> S		3 mol% COS	
	40 bar	80 bar	40 bar	80 bar
Conversion yield (%)	100±0.5	100±0.1	70.3±1.1	83.7±0.8
Cage occupancy (%):				
N <sub>2</sub>	36.8±0.7	42.4±0.1	31.1±0.3	51.5±1.3
H <sub>2</sub> S	7.1±0.5	13.6±0.2	-	-
COS	-	-	0.0±0.1	1.0±0.1
Total	43.9±1.2	56.0±0.3	31.1±0.4	52.5±1.4
Storage capacity (L/kg HQ):				
N <sub>2</sub>	25.0±0.5	28.8±0.1	21.1±0.2	34.9±0.9
H <sub>2</sub> S	4.8±0.3	9.2±0.1	-	-
COS	-	-	0.0±0.1	0.7±0.1
Total	29.8±0.8	38.0±0.2	21.1±0.3	35.6±1.0

While the relatively larger COS molecules (compared to the other components) would require higher pressure to be enclathrated, they could not be captured in the clathrate cages because the experimental pressure (or partial pressure of COS) used in this study seemed insufficient. The small amount of COS (around 1.0%) detected at the highest pressure (80 bar) also supports such explanation. Assuming the cage occupancy conditions discussed above, about 5-9 L of H<sub>2</sub>S could be stored in 1 kg of HQ, at standard temperature and pressure (STP).

## CONCLUSIONS

A novel concept for the use of HQ clathrates for removal of sulfides from various energy gases was evaluated. HQ samples reacted with 5 mol% H<sub>2</sub>S-containing, and 3 mol% COS-containing, gases were analyzed using a solid-state <sup>13</sup>C NMR and Raman spectroscopy. Numerical analysis of the NMR spectra and an elemental analyzer were also used to obtain quantitative information. Results show that H<sub>2</sub>S can be concentrated in the solid HQ clathrate (approximately 5-10 L of H<sub>2</sub>S (at STP) in 1 kg of HQ assuming the obtained cage occupancies), while N<sub>2</sub> rather than COS is mainly captured after reaction with the COS-containing gas. The enclathration behaviors identified in this study suggest that a concentration/removal process of H<sub>2</sub>S could be achieved by forming HQ clathrates. However, because COS is not captured virtually into the clathrate compound, combination with a pre-hydrolysis of COS into H<sub>2</sub>S may be necessary to remove COS using the clathrate-based process. We will next study reaction kinetics and enclathration behavior in the presence of other gas components (ternary [H<sub>2</sub>S+COS+N<sub>2</sub>] and quaternary [H<sub>2</sub>S+COS+N<sub>2</sub>+CO<sub>2</sub> (or CO)] gas mixture to describe coal gas and synthesized gas), and provide more detailed information to develop a clathrate-based process for removal of sulfides from various energy gases.

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