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Desulfurization Characteristic by Molten Alkali Carbonates at High Temperature

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Abstract

In order to remove H_2S and COS in the gasified gas, produced by coal gasifires (e.g. IGFC) at high temperature, molten alkali carbonates (MAC) consisting of Na_2CO_3 and K_2CO_3 were applied as solvent. Before the removal experiments, the optimum experimental conditions were estimated in terms of the chemical equilibrium calculations. After that, the removal experiments of H_2S and/or COS by the molten alkali carbonates were conducted in alumina tube furnace, varying the furnace temperature. As a result, H_2S and COS were completely removed by the molten alkali carbonates. The concentrations of both H_2S and COS in the clean-up gas became less than the detection limit of FPD gas chromatograph. Additionally, the regeneration tests at high temperature of used MAC following the removal tests were conducted by introducing CO_2 as a regeneration agent into the reaction tube to form Na_2CO_3 and K_2CO_3. The regeneration tests for Na_2S and K_2S in solid phase in the CO_2 atmosphere, using a thermo-gravimetric analyzer, were also carried out. Under the present experimental conditions, it was hard to regenerate the used MAC.

Keywords: Gas clean-up, Desulfurization, Gasified gas, Molten alkali carbonate

1 INTRODUCTION

Coal gasification has been recognized as one of clean and effective technologies to produce CO and H_2, which can be used for power plant, heat generation or as a synthesis precursor[1]. In the field of power generation for electricity, particularly, coal gasification will play a role for a future promising technology since it can improve the net thermal efficiency and decrease CO_2 emission all at once.

In the coal gasification process, sulfur content in coal is converted mainly to H_2S and COS.

When the coals with high sulfur content are gasified, however, H_2S and COS are contained in the gasified gas. If the gasified gas is directly used as the fuel for fuel cells or synthesis gas (H_2 and CO) for chemical materials, H_2S and COS may affect subsequent processes of the gasifier. Therefore, H_2S and COS in the gasified gas should be removed almost completely[2]. In the application of coal gasification integrated with fuel cell, more strictly removal of H_2S and COS is needed due to their poisonous effect to the anode of fuel cell. Currently, clean coal technology is a main issue in the field of power generation technology in the world. Japanese government is now developing an important project named coal Energy Application for Gas, Liquid, and Electricity (EAGLE). This system combines fuel cell (FC) with generation turbine (GT) and steam turbine (ST), which is called triple combined cycle. This triple combined cycle improves net efficiency over 53% and reduces CO_2 emission 30%, compared to pulverize coal-fired boilers (PCF)[3].

This EAGLE system needs to install cold gas cleanup system in order to satisfy the tolerance limits of fuel cell. Therefore, the synthesis gas must be heat-exchanged at the gas/gas heater (GGH). The cooled down gas is, then, desulfurized in a Methyldiethanolamine (MDEA) absorber. The clean synthesis gas, which exits the MDEA absorber at approximately 313 K, is heated to approximately 473 K by a steam heater and GGH, and is supplied to the gas turbine. Although the cold gas cleanup system is currently applied, the hot desulphurization system favors to increase the net thermal efficiencies[4]. Because removing sulfur compounds at high temperature can result in a gain of 6 % in the overall efficiency for a typical power generation system[5, 6]. Therefore, it is necessary to develop the suitable desulfurization technologies at high temperature.

The development of reliable methods to remove sulfur compounds in the coal gasified gases at high temperatures, instead of practical wet scrubbing techniques that operate at around 323 K, is one of the important technological advances. Therefore, this study proposes one of the removal technologies of H_2S and COS in the gasified gas at high temperature, using molten alkali carbonates (MAC), consisting of Na_2CO_3 and K_2CO_3 as solvent.

2 EXPERIMENTAL CONDITIONS AND PROCEDURES

Before the removal and regeneration experiments, the optimum experimental conditions were analyzed in term of chemical equilibrium calculation. After that, the removal experiments of H_2S, COS and their mixed gas (H_2S+COS) by the molten alkali carbonates are conducted. Figure 1 shows the experimental apparatus used in this study. The furnace, which is 24 mm inside diameter and 500 mm length, made from alumina. Molten alkali carbonates with composition of 43 mol%-Na_2CO_3 and 57 mol%-K_2CO_3 inserted into the furnace is electrically heated at a designed temperature. H_2S and COS gas are introduced into the furnace. The product gas is introduced into an FPD gas chromatograph to analyze H_2S, COS and SO_2 concentrations. Following the removal tests, the regeneration tests are conducted by changing introduced gas from sulfuric gas to CO_2 as the regeneration agent. In order to investigate regeneration characteristic of Na_2S and K_2S in solid phase in the CO_2 atmosphere, regeneration tests by using a thermo-gravimetric analyzer are carried out.

3 RESULTS AND DISCUSSIONS

3.1. Chemical Equilibrium Calculations

The chemical equilibrium calculations were conducted by using chemical reaction and equilibrium software with extensive thermochemical database[7]. The initial conditions for chemical equilibrium calculation for H_2S and/or COS removal process are shown in Table 1.

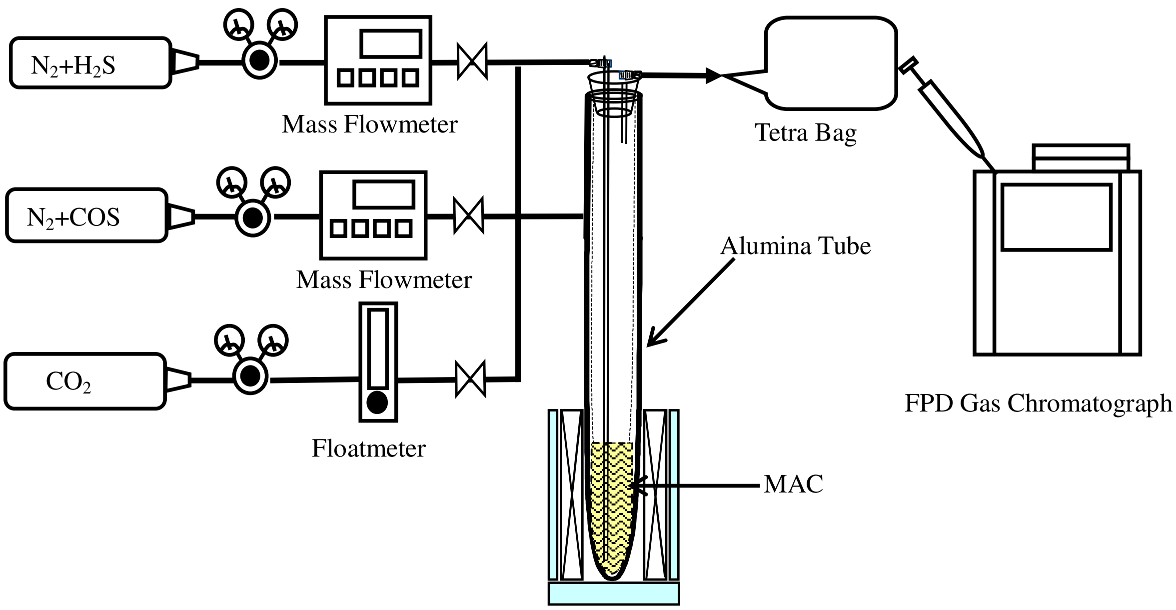

Figure 1 Experimental Apparatus for Removal and Regeneration Tests

Table 1 Initial Conditions for H_2S and/or COS Removal Process Simulations

Components	Mole		
	H_2S	COS	Mix
N_2	99.76	99.76	99.52
H_2S	0.24	--	0.24
COS	--	0.24	0.24
Na_2CO_3	11.3		
K_2CO_3	14.8		

Figures 2, 3, and 4 show the results of chemical equilibrium calculation of removal process of H_2S, COS and their mixture, respectively. These results suggest that, even at high temperature, the concentration of gaseous sulfur compounds would be zero. Based on this calculation, the removal temperature was determined as 1173 K. Figures 2, 3, and 4 also suggest that the main products of removal process are Na_2S and K_2S.

In order to know the simulation characteristic of Na_2S and K_2S regenerations, their chemical equilibrium calculations were also carried out. Table 2 shows the initial conditions for Na_2S and K_2S regeneration simulations. Figures 5 and 6 show results of chemical equilibrium calculation of regeneration process for Na_2S and K_2S, respectively. In this calculation CO_2 is introduced as the regeneration agent. These results show that Na_2S and K_2S mainly convert to M_2CO_3 at 773 K (M: Na or K).

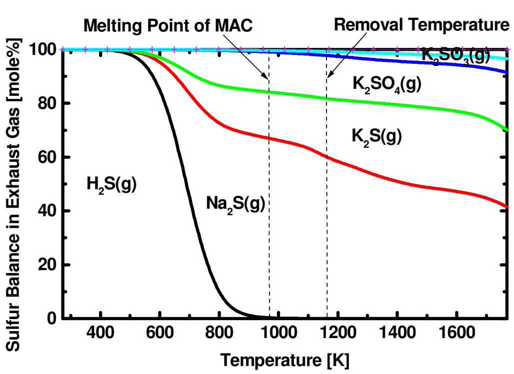

Figure 2 Chemical Equilibrium Calculation of H_2S Removal

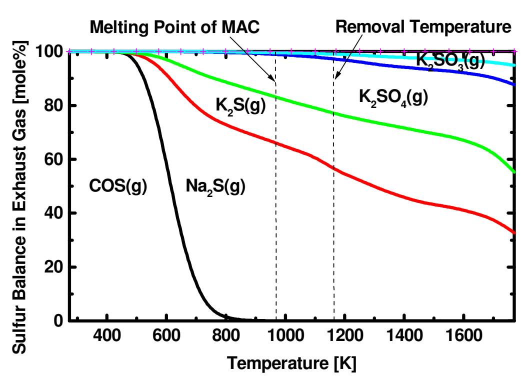

Figure 3 Chemical Equilibrium Calculation of COS Removal

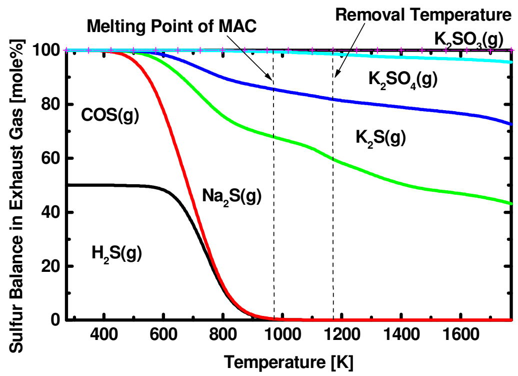

Figure 4 Chemical Equilibrium Calculation of Mixed Gases (H_2S+COS) Removal

Table 2 Initial Conditions for Na_2S and K_2S Regeneration Simulations

Components	Mole	
	Na_2S Case	K_2S Case
Na_2S	1	--
K_2S	--	1
CO_2	4	

3.2 Removal Tests

Table 3 shows the initial conditions for H_2S and/or COS removal tests. Figures 7, 8, 9 and 10 show result of H_2S, COS and SO_2 concentrations in the product during the H_2S and COS removal tests at 1173 K and 1053 K, respectively. From these figures, H_2S, COS and SO_2 concentrations detected become smaller than the detection limit of FPD gas chromatograph. Consequently, sulfur species are completely captured by the MAC to form Na_2S and K_2S mainly. Based on the experimental and chemical equilibrium calculations, the following reactions could be occurred in this removal process (l: liquid, g: gas, c: condensed).

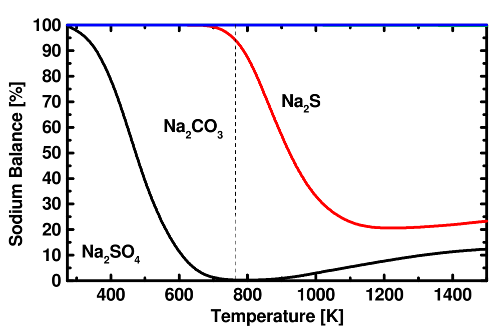

Figure 5 Chemical Equilibrium Calculation of Na_2S Regeneration

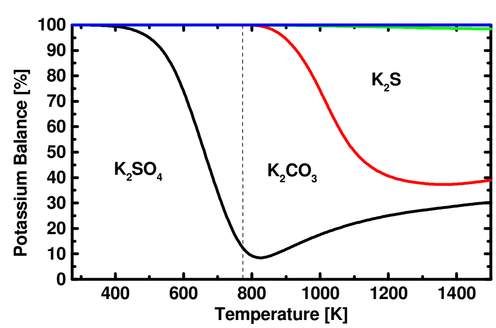

Figure 6 Chemical Equilibrium Calculation of K_2S Regeneration

$$M_2CO_3(l) + H_2S(g) \rightarrow M_2S(c) + H_2O(g) + CO_2(g)$$
$$M_2CO_3(l) + COS(g) \rightarrow M_2S(c) + 2CO_2(g)$$

Table 3 Experimental Conditions for Removal Tests

	H_2S Case		COS Case	
Temperature [K]	1173	1053	1173	1053
H_2S Initial Concentration [ppmV]	502		---	
COS Initial Concentration [ppmV]	---		505	
Flow rate [l/min]	0.7			
MAC amount [g]	26.7	32.4	26.7	32.4
Experimental time [min]	160	180	160	180

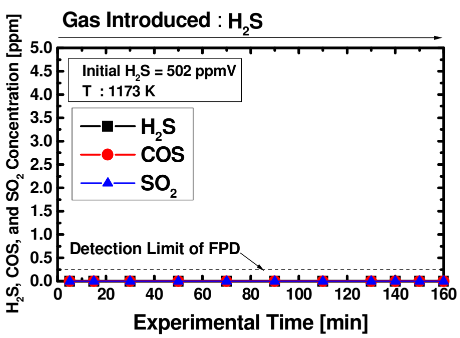

Figure 7 Result of H_2S Removal at 1173 K

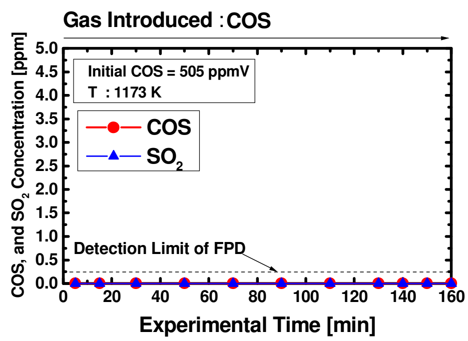

Figure 8 Result of COS Removal at 1173 K

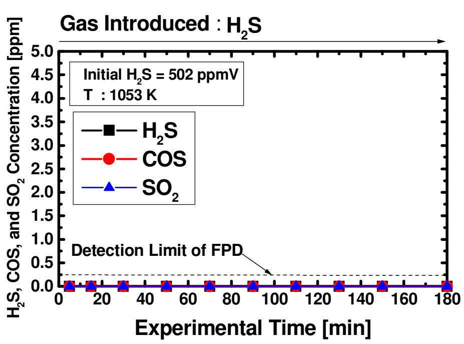

Figure 9 Result of H_2S Removal at 1053 K

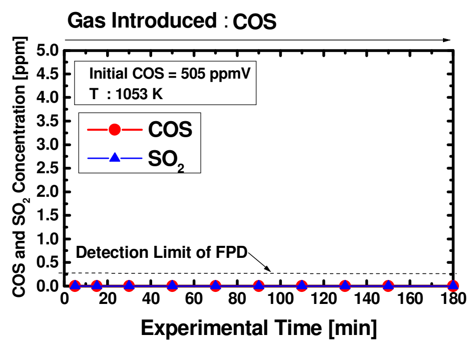

Figure 10 Result of COS Removal at 1053 K

3.3 Regeneration tests

Figures 11 and 12 show results of the regeneration test after the H_2S and COS removal tests at 1173 K, respectively. When the reactant is changed to CO_2 with the flow rate of 1 l/min, only a small amount of COS is produced. It means that the regeneration process will be hardly performed at high temperature.

According to the equilibrium calculation result of Figs. 5 and 6, the optimum regeneration temperature seems to be 773 K. Therefore, the regeneration tests for Na_2S and K_2S are conducted in the CO_2 atmosphere by the thermo-gravimetric analyzer. Figures 13 and 14 show results of the regeneration tests at 773 K for Na_2S and K_2S, respectively. Comparing both the figures, Na_2S can be regenerated more easily by CO_2 than K_2S. During this regeneration test, a few ppm of COS gas was detected in the product gas. However, the sulfur balance was not sufficient. Therefore, the following reactions would occur during the regeneration.

$$M_2S(s) + CO_2(g) \rightarrow M_2CO_3(s) + COS(g)$$

$$M_2S(s) + CO_2(g) \rightarrow M_2SO_4(s) + \text{others}$$

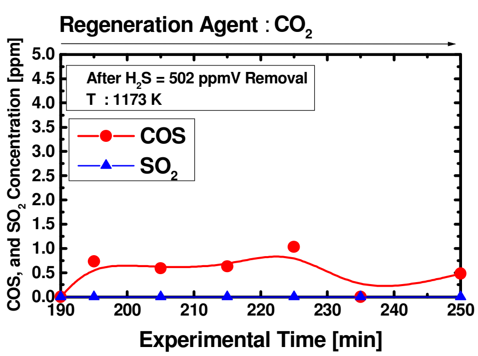

Figure 11 Result of Used MAC Regeneration Test following H_2S Removal

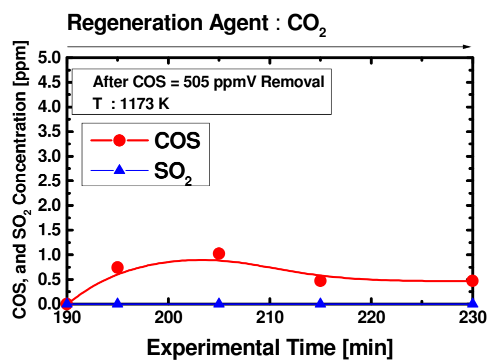

Figure 12 Result of Used MAC Regeneration Test following COS Removal

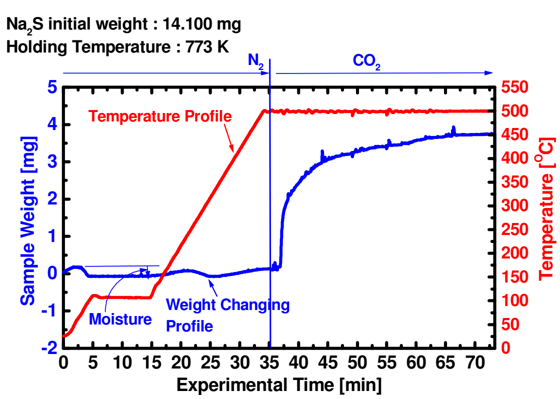

Figure 13 TG Result of Na_2S Regeneration in CO_2

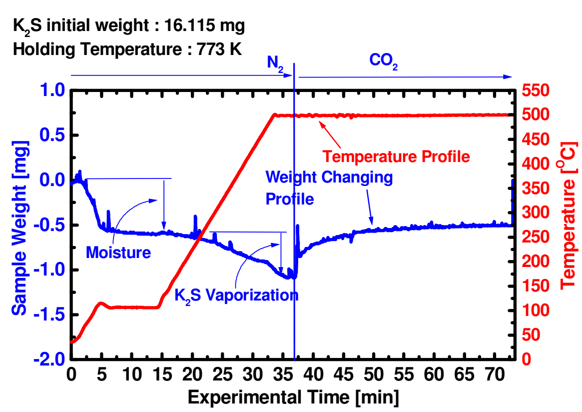

Figure 14 TG Result of K_2S Regeneration in CO_2

4 CONCLUSIONS

Desulfurization characteristics by molten alkali carbonates (MAC) were studied experimentally, using alumina tube furnace. Chemical equilibrium calculations were carried out prior to the H_2S and/or COS removal experiments. Additionally, regeneration tests of used MAC were also carried out. The main results obtained are summarized below.

1. Chemical equilibrium calculations for H_2S and/or COS removal process show that, even at high temperature, the concentration of gaseous sulfur compounds become zero.
2. Molten alkali carbonates (MAC) can be applied as a liquid solvent to capture gaseous sulfur compounds in the gasified gas even at high temperature. The following reactions could be occurred in this removal process (l: liquid, g: gas, c: condensed):

   $M_2CO_3(l) + H_2S(g) \rightarrow M_2S(c) + H_2O(g) + CO_2(g)$

   $M_2CO_3(l) + COS(g) \rightarrow M_2S(c) + 2CO_2(g)$
3. The regeneration of the used MAC is difficult under the present experimental conditions.

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