

Hot Gas Desulfurization and Regeneration Characteristics with Molten Alkali Carbonates

S. Raharjo, U. Yasuaki, R. Yoshiie, and I. Naruse

Abstract—Pollutant H_2S and COS are emitted during gasification process of coals with high sulfur content. If the gasified gas is used as the fuel for fuel cells or synthesis gas for chemical materials, H_2S and COS in the gasified gas should be removed almost completely. The development of reliable methods to remove gaseous sulfur in the gasified gases at high temperature, instead of a practical wet scrubbing technique, and to regenerate the used sorbent, is one of the important technological advances. Therefore, this study proposes a novel technology on hot gas desulfurization by using molten alkali carbonates (MACs), consisting of $43Na_2CO_3$ and $57K_2CO_3$ as a solvent. As a result, H_2S and COS were completely removed by the molten alkali carbonates at high temperature. The sulfur balance analysis of used MACs proved that it can completely capture H_2S and COS . Regeneration experiments of used MACs conducted by using thermogravimetric analyzer and gas chromatography-flame photometric detector (GC-FPD) also showed that Na_2S as one of the main components of used MACs can be around 80% regenerated at 650K by using CO_2 as regeneration agent.

Index Terms— Hot Gas Desulfurization, Molten Alkali Carbonates, Gaseous Sulfur, Regeneration Agent

I. INTRODUCTION

Coal gasification has been emerging as one of clean and effective technologies to produce synthesis fuel gases consist of CO and H_2 , which can be used for power plant, heat generation or as a synthesis precursor [1]. Many research interests are focused on the possibility to increase the overall efficiency of the system. The development of higher efficient hot gas desulfurization (HGD) system instead of current cold-type system is one of the challenging topics of research. Currently, integrated gasification fuel cell combined cycle (IGFC) under EAGLE project in Japan uses conventional cold gas clean-up system to remove H_2S and COS in order to satisfy the tolerance limits of fuel cell. Although the cold gas clean-up system is currently applied, the hot gas desulfurization (HGD) system is more favourable due to a

gain of around 6 % in the overall efficiency for a typical power generation system [2], [3]. Therefore, it is necessary to develop the suitable hot gas desulfurization technologies at around gasification temperature ($900^\circ C - 1200^\circ C$).

It has been an encouraging task to develop certain sorbents for hot gas desulfurization process, which have superior reactivity with gaseous sulfur, stability at high temperature, and character of low-cost regenerable materials. Todd H. Gardner et al. reported that H_2S catalytic partial oxidation technology using activated carbon catalyst possesses the ability to reduce total sulfur (H_2S+SO_2+COS) levels to below 20 ppmv at temperature less than $145^\circ C$, otherwise, the sulfur products began to over-oxidize and COS formation become significant if the gasification temperatures were set over $145^\circ C$ [4]. No-Kuk Park et al. investigated the capability of zinc-based sorbents for hot gas desulfurization including zinc oxide, natural zeolite, Fe_2O_3 , and CaO . They found the concentration of H_2S in the effluent gas is almost zero, although, these sulfidation and regeneration could be performed only at $480^\circ C$ and $580^\circ C$ [5]. M. Pineda et al. stated that zinc ferrites exhibit a high reactivity in the sulfidation process but still at temperature range lower than gasification temperature, $600^\circ C$ to $650^\circ C$ [6]. Moreover, in multicycle tests they showed a progressive decay of sulfidation reactivity [7], loss of sorbent efficiency [8], and degradation of the mechanical properties [9]. W.F. Elsevier et al. simulated and experimented zinc-based sorbents containing zinc oxide supported on a titanium dioxide for high temperature intensive desulfurization. However, in the subsequent sulfidation-regeneration cycles, they only managed to keep the desulfurization temperature at $500^\circ C$ or $600^\circ C$ [10].

Still low operating temperature is the most common problem in current development of hot gas desulfurization (HGD) system. Most of previous studies in hot gas desulfurization have been focused on desulfurization processes based on non-catalytic gas-solid phase reaction between gaseous sulfur and appropriate metal oxide sorbents, in which the sorbents must be kept in solid form. Therefore, many limiting factors are experienced due to the poor physical properties of solid form of sorbents at higher temperature. Meanwhile, research on hot gas desulfurization utilizing liquid solvent so that gas-liquid phase reaction takes place instead of gas-solid phase reaction is still scarce in number. By applying such idea, the problems associated with the physical degradation of solid sorbent because of high temperature operation can be eliminated. In addition, gas-liquid phase system will enhance the desulfurization reactions. In this present study, the molten alkali carbonates

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(MACs) containing Na_2CO_3 and K_2CO_3 are used as solvent for hot gas desulfurization. The operating temperature is set over the melting point of the binary eutectic salt in order to get the sorbent in molten phase.

In recent years, molten alkali carbonates have been recognized as coal gasification catalyst, which offer several important advantages particularly in lowering gasification temperature that will reduce the severity of gasification process [11]. In addition, molten alkali carbonates also give advantages associated with gas cleaning system, which can act as solvent for gaseous sulfur as well as liquid media for capturing ash contained in gasified gas. In order to study the characteristics of molten alkali carbonates as desulfurizer at high temperature and the probability to regenerate used molten alkali carbonates, chemical equilibrium calculations and laboratory experiments were performed in this study.

II. EXPERIMENTAL PROCEDURE

A. Molten Alkali Carbonates

Li_2CO_3 , Na_2CO_3 and K_2CO_3 are recognized as eutectic salt catalysts in coal gasification process. By using the eutectic mixtures of salts that show good activity as individual compound, the melting temperature can be lowered possibly with still better activity and reaction rate due to the improved dispersion of the molten catalyst during reactions [12]. In this study, Na_2CO_3 and K_2CO_3 with the molar ratio of 43:57 are chosen as solvent for hot gas desulfurization due to their low melting point and inexpensive price. The alkali salts were physically mixed at room temperature based on their mole ratio and inserted into the reaction tube. Before experiments, the mixed alkali carbonate was heated over its melting points (973K) in reaction tube so that it becomes molten alkali carbonates. The physical properties of MACs can be seen in Table I below.

Table I. Physical properties of MACs

Substances	Melting Point (K)	Density (g/m^3)	Viscosity (mPa.s)
43(mol%) Na_2CO_3 & 57(mol%) K_2CO_3 (MACs)	973	1.93	--
Na_2CO_3	1123	1.973	4.06
K_2CO_3	1164	1.89	3.01

B. Chemical Equilibrium Calculation

Chemical equilibrium calculations are conducted prior to the experiments in order to determine the optimum condition for experiments. Initial conditions for calculation are carefully compiled by considering necessary compounds including in reactions. The chemical equilibrium calculations were conducted by using chemical reaction and equilibrium software with extensive thermochemical database, HSC Chemistry version 5.1 from Outokumpu Research Oy. The software enables the user to simulate chemical reactions and processes on the thermochemical basis. However, experimental works are needed to verify the results, because the software does not take kinetic phenomenon into account. Usually, thermochemical calculations at least show what is physically possible and impossible, which is highly valuable information when making plans for experimental study [13]. The initial conditions of chemical equilibrium calculation for

desulfurization with MACs are displayed in Table II below.

C. Hot Gas Desulfurization and Regeneration Experiments

Hot gas desulfurization experiments are carried out for confirming the results which are indicated by the chemical equilibrium calculations. Fig. 1 shows the experimental apparatus used in this study. The reactor which is made from alumina has an inside diameter of 24 mm and length of 500 mm. Solid mixed alkali carbonates were inserted into the bottom of the reactor. 502 ppmv H_2S and/or 505 ppmv COS nitrogen base gases were connected to the alumina pipe inlet system as the sources for gaseous sulfur pollutants.

Table II. Initial conditions of chemical equilibrium calculation for desulfurization with MACs

Components	Mol	
	H_2S Case	COS Case
N_2	99.76	99.76
H_2S	0.24	--
COS	--	0.24
Na_2CO_3	11.3	
K_2CO_3	14.8	

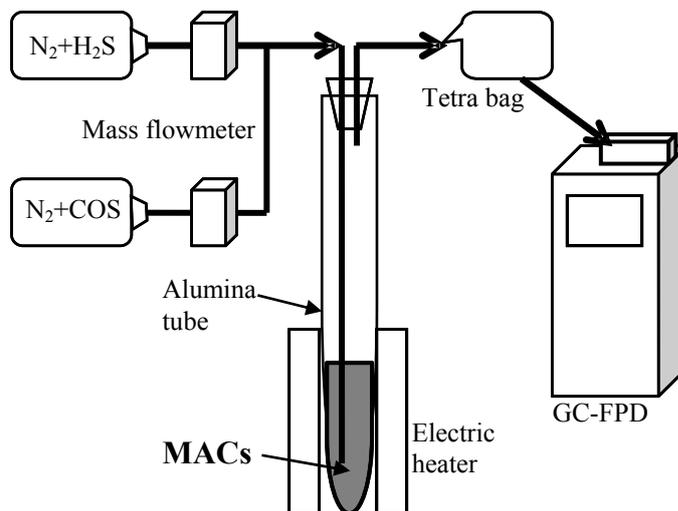


Fig.1. Experimental Apparatus for desulfurization with MACs

First of all, alumina tube was heated by using electric kanthal heater into the experimental temperature (1053 K or 1173K). At this temperature, the phase of alkali carbonates changes to liquid which is called molten alkali carbonates (MACs). Then, N_2 gas was introduced prior to 0.7 L/min gaseous sulfur in order to clean inside furnace. The gaseous sulfur was introduced into the molten alkali carbonates through alumina pipe inlet, which has the diameter of 3.6 mm. The tip of alumina pipe inlet was positioned 20 – 30 mm under the surface of the MACs to inject the gaseous sulfur. This condition gives the time for contacting between bubble gas and molten alkali carbonates around 0.2 s and the surface area for contacting of one bubble is around 314 mm^2 . During desulfurization experiments, the outlet gas was collected with tetra bag and introduced into a gas chromatograph (GC) Shimadzu 14B with flame photometric detector (FPD) equipped with Shimalite AW-DMCS-ST 25% (3M x 3MM I.D.) column for analyzing the concentrations of H_2S , COS and SO_2 simultaneously. At the end of desulfurization

experiments, a small amount of used MACs (MACs containing captured sulfur) was sampled for sulfur content analysis by using EMIA Horriba EF-120 sulfur analyzer

Considering the importance of sulfur mass balance in desulfurization experiments, blank tests were also carried out by flowing simulated gaseous sulfur (H_2S and COS in nitrogen base gas) into the reactor without molten alkali carbonates at high temperature (1173K). Experimental conditions for blank tests and desulfurization experiments are shown in Table III and Table IV, respectively.

Table III. Experimental conditions for blank test

	H_2S Case	COS Case
Temperature (K)	1173	
H_2S Init. Conc.(ppmv)	24	---
COS Init. Conc.(ppmv)	---	24.85

Table IV. Experimental conditions for desulfurization experiment

	H_2S Case		COS Case		Mix. Case
Temp. (K)	1173, 1053		1173, 1053		1173
Initial Concent. (ppmv)	502		505		$H_2S:251$ $COS:253$
Flow rate (l/min)	0.7				
MACs amount (g)	27	32	27	32	26

In this present study, in order to know the regeneration characteristics of used MACs, the probability to convert Na_2S as one of the main components of used MACs into Na_2CO_3 is also studied by chemical equilibrium calculation and regeneration experiments. $Na_2S \cdot 9H_2O$ (sodium sulfide nanohydrate) was used as the sample to study the Na_2CO_3 regeneration characteristics by using thermogravimetric Analyzer (TGA-51) Shimadzu and GC-FPD Shimadzu 14B. The weight changing of the sample during experiment was analyzed by the TGA-51, while the exit gas composition was analyzed by the GC-FPD. The nitrogen introduced prior to CO_2 was to remove the crystal water and moisture of sample since it is not pure sodium sulfide. CO_2 as regeneration agent was introduced after the temperature of reactor reaches its regeneration temperature. Table V, the initial conditions of chemical equilibrium calculation, shows that CO_2 is simulated as regeneration agent for Na_2CO_3 regeneration from Na_2S , while Table VI displays the experimental conditions for regeneration experiment.

Table V. Initial conditions of chemical equilibrium calculation for regeneration of used MACs

Components	Mol
CO_2	12
Na_2S	1

Table VI. Experimental conditions of regeneration experiment

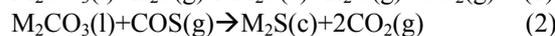
Atmosphere	$N_2 \rightarrow CO_2$
Sample	$Na_2S \cdot 9H_2O$
CO_2 flowrate (ml/min)	150
Temperature increasing rate (K/min)	20
Regeneration temperature (K)	573, 650, 773, 873

III. RESULTS AND DISCUSSION

A. Chemical Equilibrium Calculation of Desulfurization Process

Figures 2, 3 and 4 show the results of chemical equilibrium

calculation for desulfurization process of H_2S , COS and mixture case (H_2S+COS), respectively. These results suggest that molten alkali carbonates have the capability of capturing gaseous sulfur above their melting point (>973 K). From these figures, the concentration of gaseous sulfur compounds decreases to zero at high operating temperature. It seems that gaseous sulfur reacts with alkali carbonates to form mainly alkali sulfides (Na_2S and K_2S) according to the following reactions.



(M: Na and K, l: liquid, g: gas, c: condensed)

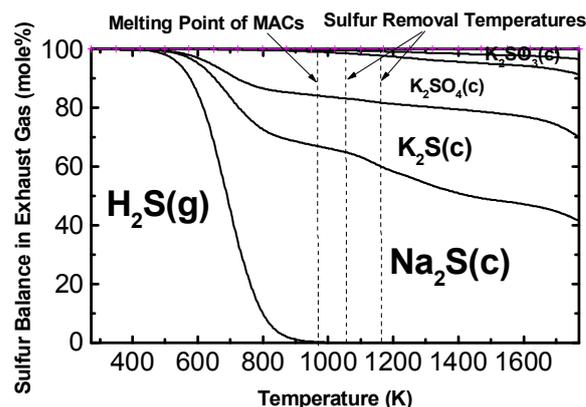


Fig. 2. Chemical equilibrium calculation results of MACs for H_2S removal

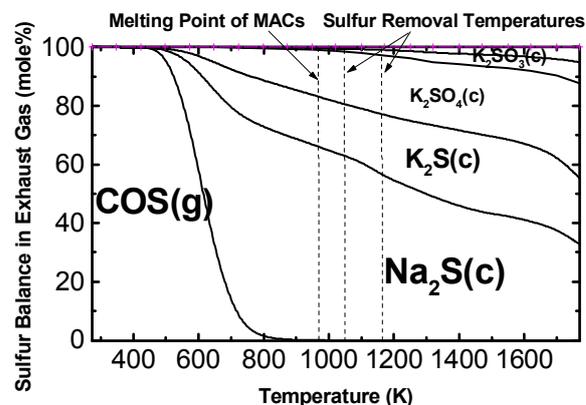


Fig. 3. Chemical equilibrium calculation results of MACs for COS removal

B. Hot Gas Desulfurization Experiments

Figure 5a and 5b show the result of H_2S blank test at 1173K its sulfur balance analysis, respectively. These figures show that sulfur exists in the form of H_2S (around 24 %) and SO_2 (around 73 %), at high temperature. It means that some introduced H_2S might be oxidized to SO_2 at high temperature by the residual air inside tube and in fine pores inside the surface of the tube. But, the total amount of sulfur species is sufficient enough (around 97%), which means there is no reaction with the surface of reactor.

Fig. 6a and 6b show result for COS case blank tests and its sulfur balance analysis at high temperature, respectively. Since the unbalance of 12% is negligible, the sulfur balance is sufficient. At high temperature, some COS might be oxidized into SO_2 (50.6%) by the similar reason of H_2S case. The sufficient sulfur balance of these blank tests suggest that there is no reaction or deposition of sulfur species on the

surface of reactor at high temperature.

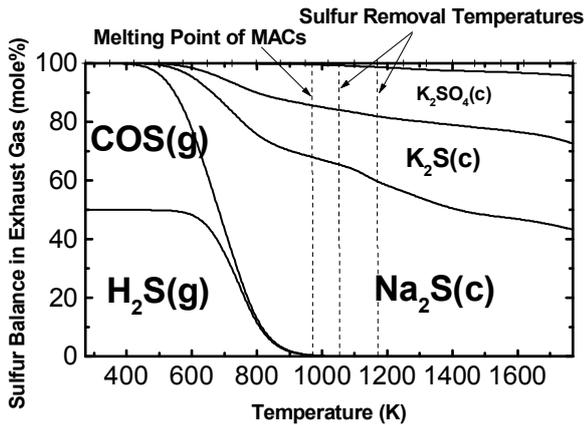
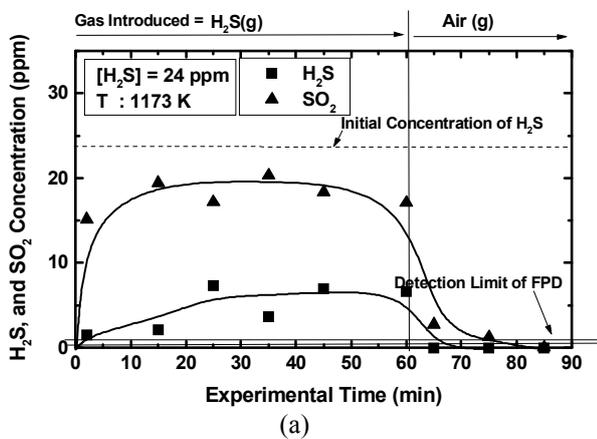
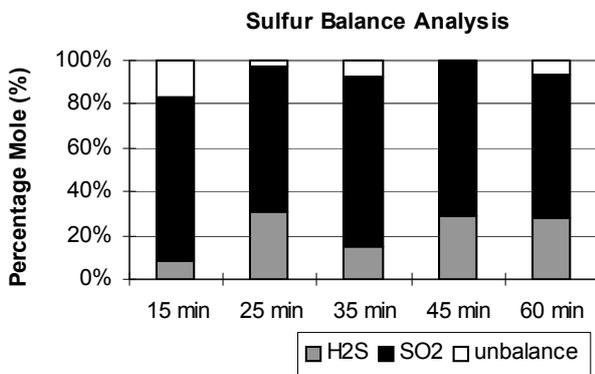


Fig. 4. Chemical equilibrium calculation results of MACs for Mixture case removal



(a)

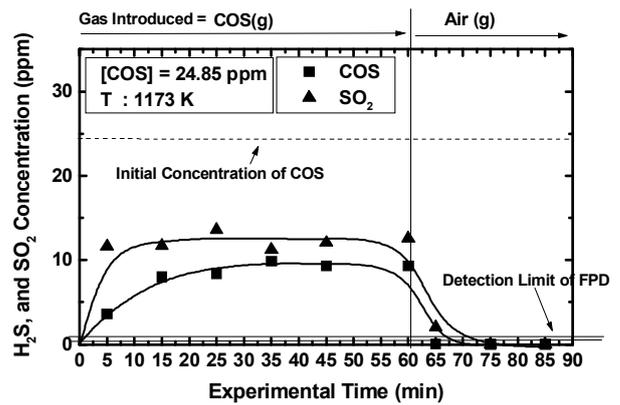


(b)

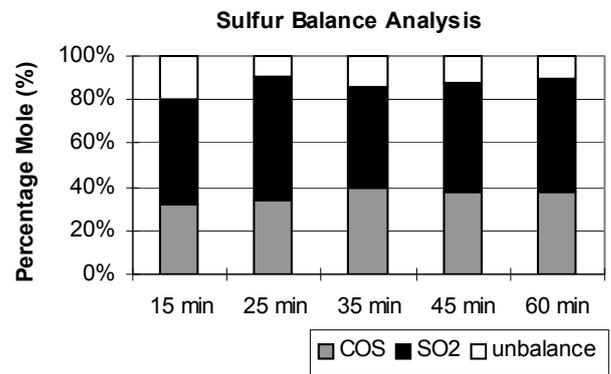
Fig. 5. Blank test at 1173K for H₂S case: (a). test result; (b). sulfur balance analysis

Fig. 7a, 7b and 8a, 8b show results of H₂S and COS desulfurization experiments at 1053 and 1173K, respectively. The mixture case of desulfurization experiment result was shown in Fig. 9. Around 500 ppmv of H₂S, COS or their mixture was introduced into molten alkali carbonates (MACs) furnace during each desulfurization experiment. These results show that H₂S, COS and SO₂ concentrations in outlet of MACs furnace became smaller than the detection limit of GC-FPD for all cases, which meets the acceptable limit of fuel cell application (<1 ppmv). Consequently, sulfur species was completely captured by the molten alkali carbonates to form M₂S mainly. In order to prove that the

sulfur species was completely captured, the sulfur material balance analysis was carried out on used MACs.



(a)



(b)

Fig. 6. Blank test at 1173K for COS case: (a). test result; (b). sulfur balance analysis

C. Sulfur Balance Analysis of Used MACs

In order to confirm the sulfidation reactions as expressed by reaction 1 and 2, which elucidate the formation of alkali sulfide (M₂S) in used molten alkali carbonates during desulfurization experiments, the sulfur material balance analysis were carried out. Fig. 10 shows the sulfur material balance in used molten alkali carbonates. These were calculated fraction of sulfur captured by the MACs based on the total amount of gaseous sulfur fed into the reactor during the tests.

The total amount of gaseous sulfur was calculated based on the fed gaseous sulfur concentration, its flowrate and experimental time. In order to get the sulfur balance analysis result, the calculated total amount of gaseous sulfur is compared to the laboratory analysis on sulfur captured by MACs (used MACs) using Horriba EMIA EF-120 analyzer.

Fig. 10 elucidates that the missing sulfur (unbalance) is only around 8%. This value is in the range of missing sulfur showed by the results of blank tests which explained that the missing sulfur ranges from 2.5% – 12%. As the small amount of missing sulfur can be negligible, however, this sulfur material balance analysis in used molten alkali carbonates can be an important proof that the gaseous sulfur was completely captured by the molten alkali carbonates at high temperature. This sulfur species reacts with alkali carbonates to form alkali sulfides (M₂S) mainly as expressed by reaction 1 and 2.

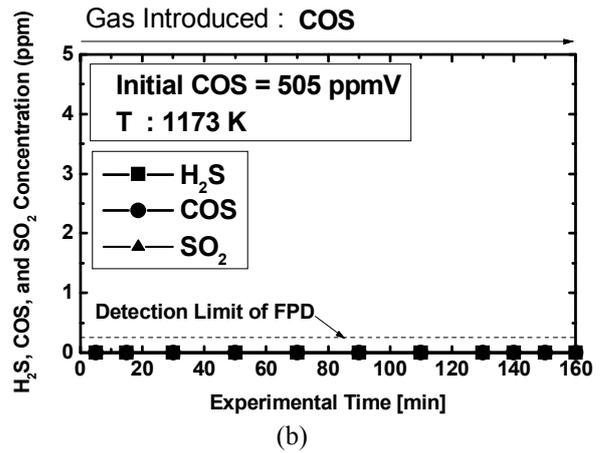
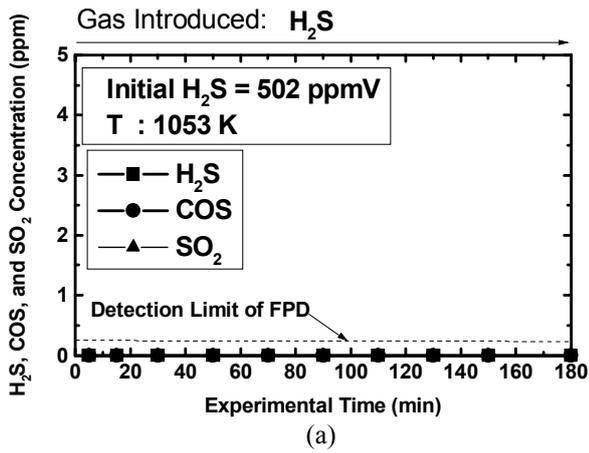


Fig. 8. Concentration of S Compounds in the exit gas for COS desulfurization case: at (a) 1053K; (b) 1173K

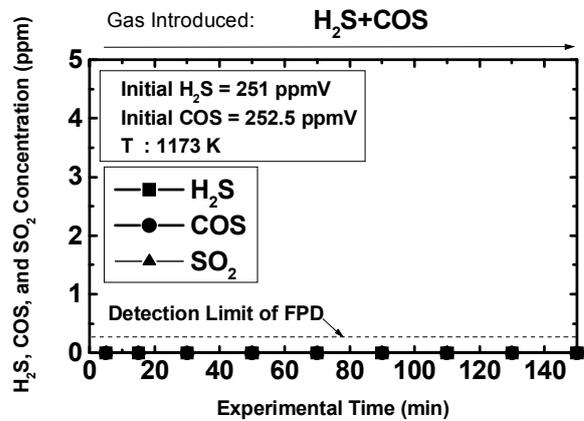
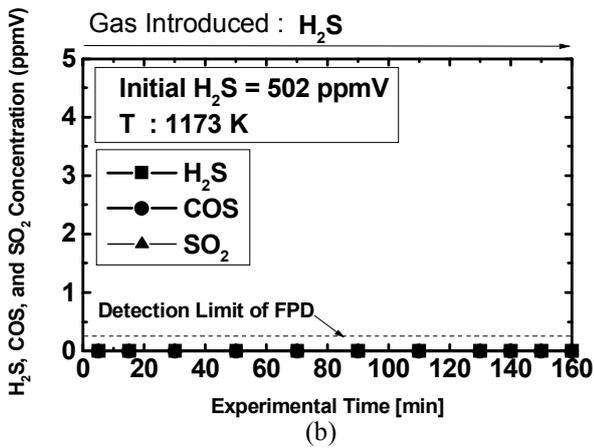


Fig. 7. Concentration of S Compounds in the exit gas for H_2S desulfurization case: (a) at 1053K; (b) at 1173K

Fig. 9. Concentration of S Compounds in the exit gas at 1173K for Mixture desulfurization case

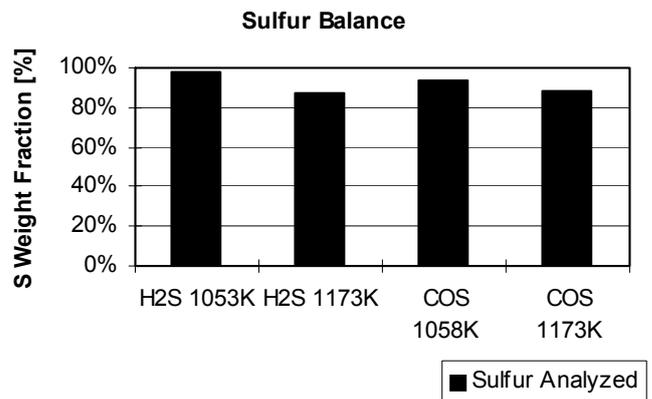
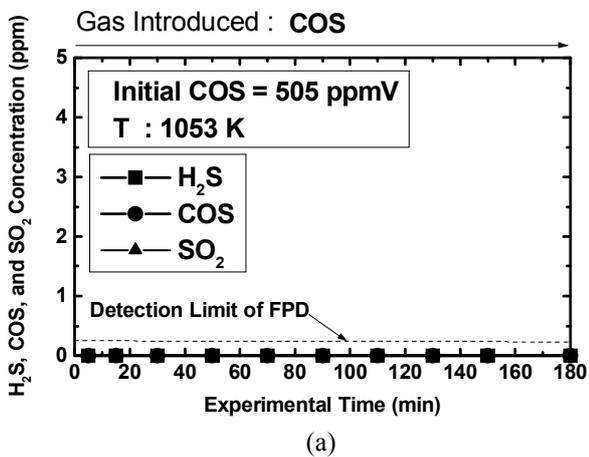


Fig. 10. Sulfur material balance analysis in used MACs

D. Regeneration Characteristics of Used MACs

Desulfurization simulation and experiment results suggested that the main compounds of used MACs are Na_2S and K_2S . The possibility to regenerate used MACs will give additional advantage in utilization of MACs as gasification catalyst and gas cleaning agent as well. In regeneration process, these alkali sulfides are converted back to M_2CO_3 (alkali carbonates). According to result of chemical equilibrium calculation as displayed in Fig. 11 for Na_2S case, CO_2 as regeneration agent can be used for converting Na_2S into Na_2CO_3 at temperature range of 500K to 900K. The

reaction mechanism for this process can be suggested as follows:



Based on the result shown in Fig. 11, regeneration experiments by using thermogravimetric analyzer and GC-FPD were carried out at 573K, 650K, 773K and 873K.

Fig.12 (a), (b), (c) and (d) display the results of TG during regeneration experiments. The decreasing weight of sample from point A to B under nitrogen atmosphere shows the weight loss of crystal water and moisture contained in the sample. There figures also shows the increasing weight of sample after introducing CO₂ as regeneration agent at 573K, 650K, 773K and 873K, respectively.

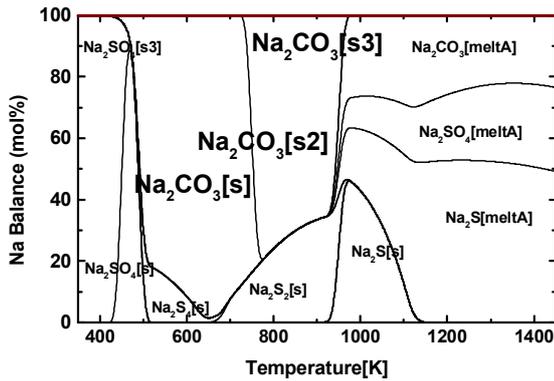


Fig. 11. Chemical equilibrium calculation for regeneration experiment for Na₂S case

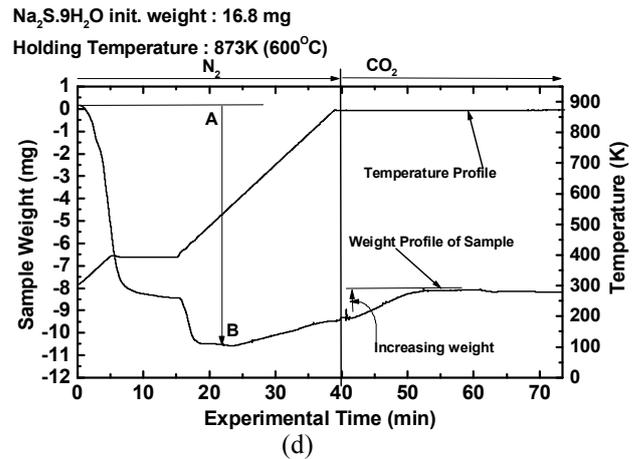
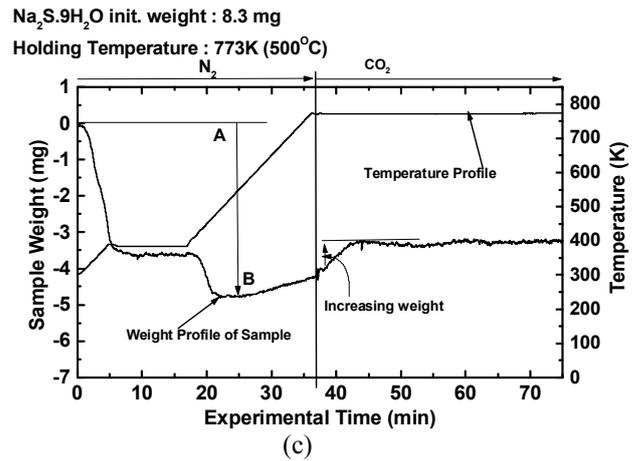


Fig. 12. Regeneration experiment results by TG at: (a) 573K; (b) 650K; (c) 773K; (d) 873K

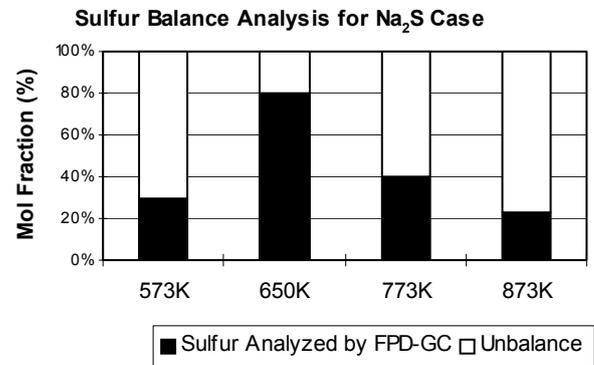
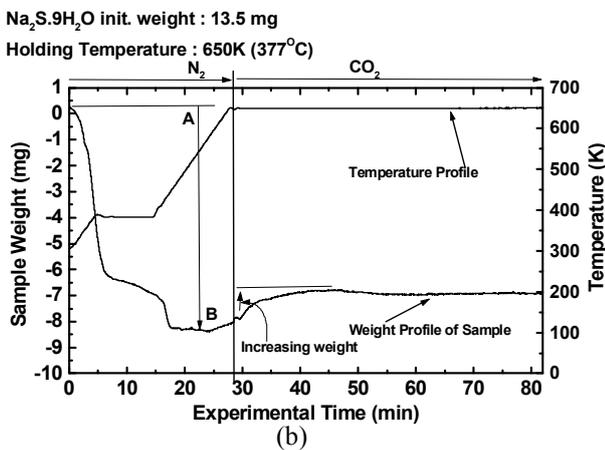
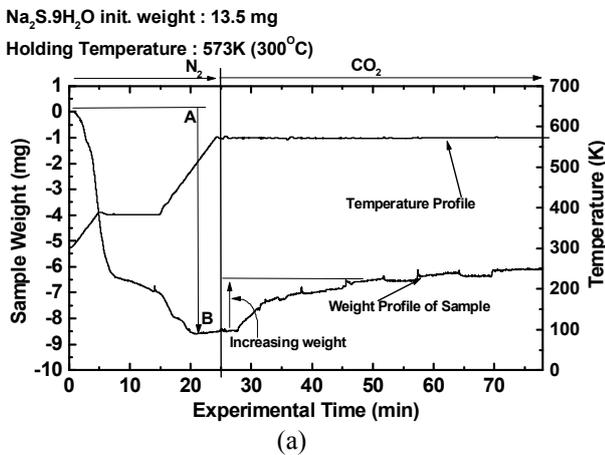


Fig. 13. Sulfur balance analysis of regeneration experiments by TG

The increasing weight of sample indicates the formation of certain compound, which has molecular weight heavier than Na₂S, which is expected to be Na₂CO₃. The exhaust gas from TG was also sampled during CO₂ atmosphere by tetra bags, which are then analyzed by GC-FPD. Their results were calculated as sulfur balance analysis as shown in Fig. 13. It shows the mol fraction of gaseous sulfur analyzed by GC-FPD compared to the net mol of Na₂S sample at 573K, 650K, 773K and 873K experimental temperatures. According to these results, regeneration process at 650K released gaseous sulfur around 80% of the net mol Na₂S, which means around 80% Na₂S was probably converted to Na₂CO₃. Regeneration process at 650K seems to be the optimum operational temperature among others for Na₂S

regeneration case. Therefore, these results suggest that it is possible to regenerate Na_2CO_3 from Na_2S by using CO_2 gas as regeneration agent at 650K.

IV. CONCLUSIONS

In this present study, binary alkali carbonates ($43\text{Na}_2\text{CO}_3, 57\text{K}_2\text{CO}_3$), heated over their melting point, were employed as solvent in alumina reactor for hot gas desulfurization experiments. Chemical equilibrium calculations indicated that the molten alkali carbonates have the capability for completely removing gaseous sulfur above their melting point ($>973\text{ K}$), which can be confirmed with desulfurization experiments at 1053K and 1173 K. Sulfur material balance analysis in used molten alkali carbonates also showed the good agreement with the above results. Thermogravimetric results of regeneration experiment and sulfur balance analysis show that Na_2S as one of the main compounds of used MACs can be sufficiently converted to Na_2CO_3 by using CO_2 gas at 650K.

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