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Regeneration and Durability of Advanced Zinc Ferrite Sorbent for Hot Coal Gas Desulfurization

Key word: desulfurization, zinc ferrite, regeneration, coal derived gas

Introduction

We have been developing a hot coal gas desulfurization technology to improve thermal efficiency in coal gasification power generation system and simplify the coal gas cleaning system. We already developed the iron oxide honeycomb sorbent, which removed sulfur compounds (H_2S, COS) to less than 100 ppm [Watanabe et.al.1988, Nakayama et al.1996, Shirai et al. 2001, Shirai et al 2002]. However, in an integrated coal gasification molten carbonate fuel cell (IG-MCFC) power generation system that has higher efficiency than IGCC, it is necessary to reduce sulfur compounds level to less than 1 ppm.

We select zinc ferrite as a prime candidate desulfurization sorbent and prepared the advanced zinc ferrite sorbent that is able to protect carbon deposition from coal derived gas. It was shown that the sorbent removed sulfur compounds to less than 1ppm at 673K to 773K [Shirai et al.1998]. Now, we already have the honeycomb-shaped sorbent used in a fixed bed desulfurization system. In order to put zinc ferrite sorbent in practical use, we need to

durability of the sorbent .

Objective

In this study, we investigate the regeneration characteristics, desulfurization performance after regeneration and the durability of zinc ferrite sorbent in the desulfurization / regeneration cycles.

Approach

Zinc ferrite sorbent is used repetitively by means of the desulfurization / regeneration cycle shown in **Fig.1**. In this desulfurization system, the regeneration conditions are important. Regeneration reaction is shown Eq.(1).

$$ZnS + 2/(1-y)Fe_{1-y}S + (3+2/(1-y))O_2 = ZnFe_2O_4 + (1+2/(1-y))SO_2 \quad 1-y=0.91 \quad 1.0 \quad (1)$$
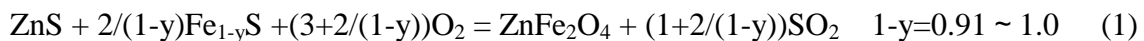
This reaction is influenced by temperature, O_2 concentration and SO_2 concentration. O_2 concentration is set at 1.5% to protect the sinter of the sorbent, because the reaction is exothermal and raises the temperature. In this study, we do not investigate the influence of O_2 concentration.

In the other hands, in our fixed bed desulfurization system shown in **Fig.2**, the sorbent is regenerated with O_2 containing regeneration gas made of air and recycle gas from sulfur recovery unit. O_2 concentration of the regeneration gas is controlled by SO_2 containing recycle gas. The regeneration gas contains SO_2. From these reason, we study on the influence of temperature and SO_2 concentration on the characteristics of regeneration using a laboratory scale fixed bed reactor apparatus. Also, we conduct the 40 cycle's test in this apparatus.

Project Description

Zinc ferrite sorbent preparation and property

We use iron nitrate, zinc nitrate, and added silica sol and urea to these nitrate solution. Next, we got hydroxide and silica mixture with urea. This mixture is calcinated and Fe_2O_3-SiO_2 powder under 200μm, is prepared. These prepared oxide powders is mixed and kneaded with titan oxide, some binder and water. Cylindrical sorbent is molded out of these kneaded powder and calcined. In our experience, we used crashed sorbent which diameter is 1-1.4mm (**Fig.3**). The property of the sorbent is shown in **Table 1**

Experiment

A laboratory scale fixed bed reactor apparatus is shown in **Fig.4**. Experiments were carried out using this apparatus where 60g of the sorbent were packed. Desulfurization is performed

with 1%-H_2S containing gas at 723K, 0.98MPa, until outlet H_2S+COS concentration becomes the same concentration of inlet gas. In this experiment, Sulfur absorptive capacity was investigated. A simulated coal gas composition was 7.5vol%-H_2 20vol%-CO   5vol%-CO_2 5vol%-H_2O N_2-balance. The regeneration was performed in the temperature range of 623K to 873K with 1.6% -O_2 and 0-0.2% SO_2 containing gas. After regeneration, the sorbent was reduced and some residual sulfur was released as SO_2. After reduction, desulfurization was performed with H_2S containing at 723K, 0.98MPa, again.

After regeneration and reduction, the sorbent was taken from a fixed bed reactor and put in another apparatus, which could measure H_2S and COS concentration below 1ppm, and removal performance below 10ppm of the regenerated sorbent was evaluated 1%-H_2S containing gas at 723K, 0.98MPa.

Results

Regeneration characteristics

The change of released SO_2 during regeneration using non-SO_2 containing gas is shown in **Fig.5**. The change of SO_2 concentration is shown with the ratio of outlet SO_2 concentration $C_{SO2,out}$ to theoretical released SO_2 concentration $C_{SO2,th}$ calculated from Eq.(1). Dimension less time is the ratio of elapsed time to theoretical time calculated from Eq.(1), O_2 concentration, gas flow rate, sorbent weigh, zinc ferrite content in the case that regeneration reaction depends on O_2 supplying rate. In this result, outlet SO_2 concentration became higher as the regeneration temperature rose, and was almost the same to theoretical released SO_2 concentration at 873K.

The change of released SO_2 during regeneration using SO_2 containing gas is shown in **Fig.6**. The change of SO_2 concentration is shown with the ratio of outlet SO_2 concentration $C_{SO2,out}$ to the sum of theoretical released SO_2 concentration $C_{SO2,th}$ calculated from Eq.(1), and inlet SO_2 concentration $C_{SO2,in}$. At 723K and 873K, SO_2 concentration became lower as the sorbent was regenerated, and at the end of regeneration, SO_2 concentration was lower than inlet SO_2 concentration. These results suggest that regenerated sorbent absorbs SO_2 contained in inlet gas.

The regeneration ratio R_{reg}, which is the molar ratio of released SO_2 to absorbed H_2S, is shown in **Fig. 7**. In the case of using non-SO_2 containing gas, the regeneration ratio became higher as the temperature rose. However, in the case of using SO_2 containing gas, the regeneration ratio was lower than that of using SO_2 containing gas, and became lower as the temperature rose. These results show that SO_2 containing in inlet gas has a strong influence on the regeneration. We request a higher efficient sulfur recovery method.

Desulfurization characteristics after regeneration

Sulfur absorptive capacity ratio QS/QS_{ini} at 723K after regeneration is shown in **Fig. 8**. The capacity ratio is the ratio of absorbed H_2S QS_{ini} at the first desulfurization to absorbed H_2S QS after regeneration. In our fixed bed system, the sorbent is reduced before desulfurization to decompose the residual sulfur compounds (Sulfate) and some sulfur is released as SO_2. The sulfur absorptive capacity ratio is higher than the regeneration ratio shown in Fig. 7. The change of the capacity ratio is almost the same to that of the regeneration ratio.

Fig. 9 shows the H_2S removal characteristics below 10ppm. 1ppm breakthrough time of the regenerated sorbent with non-SO2 containing gas at 723K was as same as that of fresh sorbent. 1ppm breakthrough time of the regenerated sorbent with non-SO_2 containing gas at 873K, was shorter than that of the regenerated sorbent at 723K, although the sulfur absorptive capacity ratio of the regenerated sorbent at 873K was higher than that of the regenerated sorbent at 723K. In the case of using SO_2 containing gas, 1ppm breakthrough time of all regenerated sorbents were shorter than fresh sorbent, because as shown in Fig.7, the sulfur absorbing capacity ratio $QS/QSini$ was lower than that of using non SO_2 containing gas.

The relationship between 1ppm breakthrough time t_{1ppm} and the sulfur capacity ratio is shown in **Fig.10**. 1ppm breakthrough time depended on the sulfur capacity ratio on the regenerated sorbents at 623K and 723K. However, at 873K, 1ppm breakthrough time did not depend. **Fig.11** shows the relationship between specific surface area of regenerated sorbents and regeneration temperature. Specific surface area decreased as the temperature rose. This result shows that the decrease of 1ppm breakthrough time of the sorbent regenerated at 873K is cause by the decrease of specific surface area. In addition, this desulfurization study suggests that the suitable regeneration temperature is 723K in the temperature range of 623K to 873K.

The sorbent durability

We already conducted the 20 cycle's desulfurization test. This result showed that the sulfur absorptive capacity decreased and did not become stable [Kobayashi et al.1997]. In this study, the 40 cycle's desulfurization test was conducted. The breakthrough curve up to 40 cycles is shown in **Fig.12**. As the cycle increased, the breakthrough time became short, but the profile of the breakthrough curve was as similar as that of first cycle. This result suggests that H_2S absorptive rate is stable, and the sulfur absorptive capacity decrease. The change of the sulfur absorptive capacity ratio is shown in **Fig.13**. The sulfur absorptive capacity of the sorbent decreased until approximately 20th cycle and after that, the capacity became stable. Moreover, as shown in **Fig.14**, the sorbent was able to reduced sulfur compounds level to less than 1ppm

after 40th cycle.

Application

The experimental results suggest we should regenerate the zinc ferrite sorbent with lower SO_2 concentration gas at 723K and the sorbent keeps the removal level of 1ppm in the long-term use. We think the desulfurization process is simplified and heat loss becomes lower in IGCC and IG-MCFC.

Future Activities

We will investigate the desulfurization characteristics of the honeycomb-shaped sorbent and the influence of HCl on the desulfurization performance. The honeycomb-shaped sorbent will be evaluated with actual coal gas in the bench scale gasification unit.

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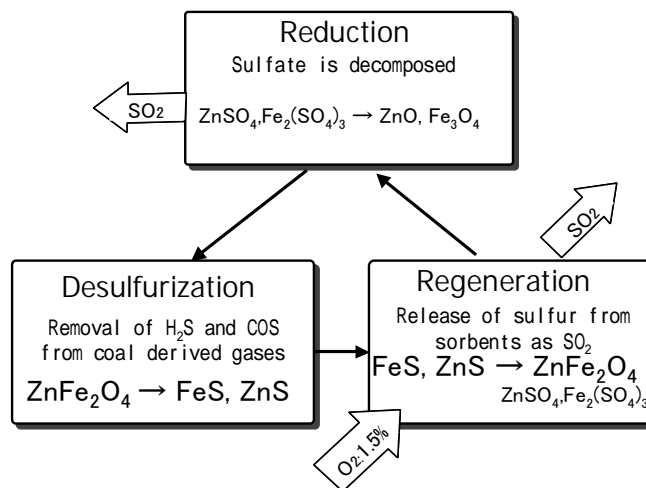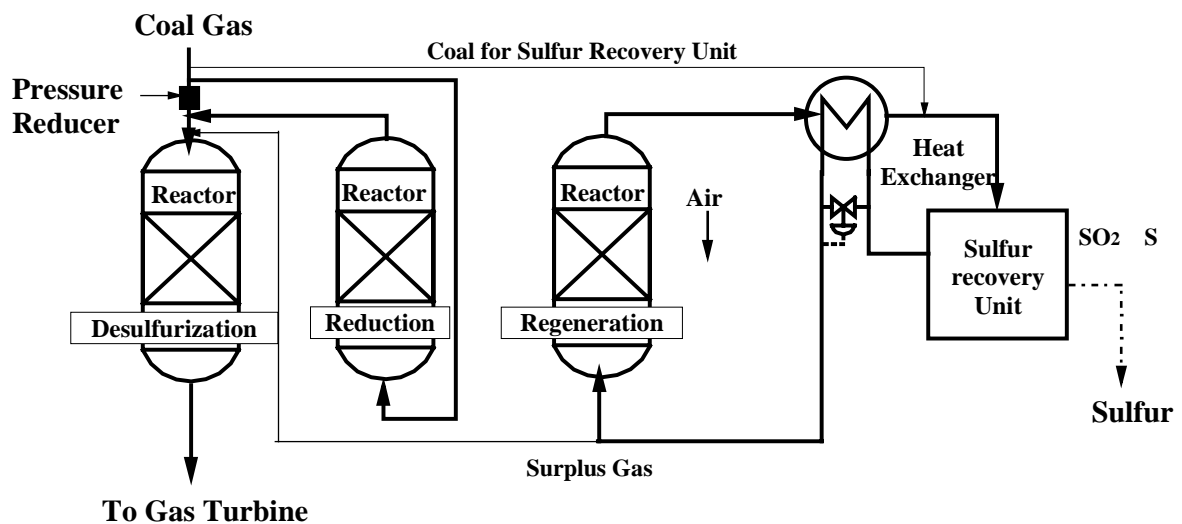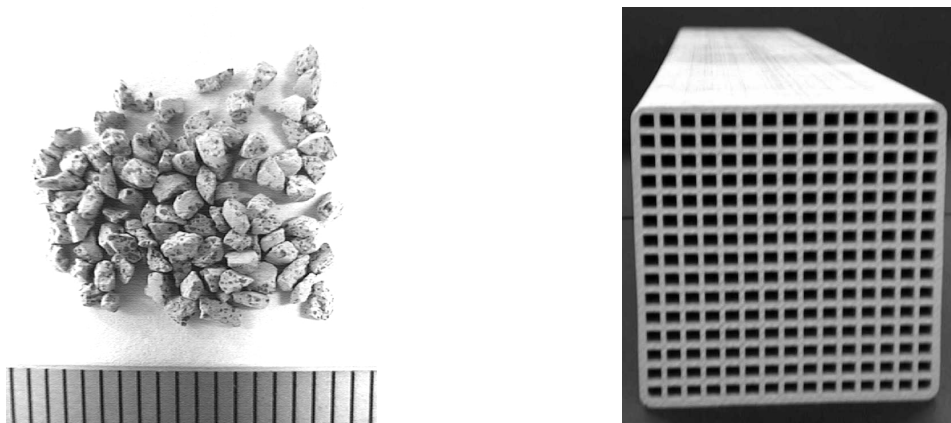
Fig.1 Reaction cycle of zinc ferrite sorbent

Fig.2 Fixed bed desulfurization system

Crashed sorbent (1-1.4mm)   Honeycomb shaped sorbent

Fig.3 Zinc ferrite sorbent

Table.1 Properties of zinc ferrite sorbent

Composing powders	Content [wt%]		MS_{th}[*1]	Sp_S[*2]	Vp[*3]
	Fe	Zn	[mol/kg]	[m²/g]	[cm³/g]
$ZnFe_2O_4$-SiO_2+TiC	8.9	5.3	2.40	32	0.35

*1 Estimated sulfur absorbing amount

*2 BET specific surface area

*3 Pore volume under 5μ m

1. Mass flowmeter 2. Water pump
3. Evapolator   4. Pre-heater
5. Reactor   6. Electric heater
7. Thermocouple
8. Backpressure valve
9. Gas cooler
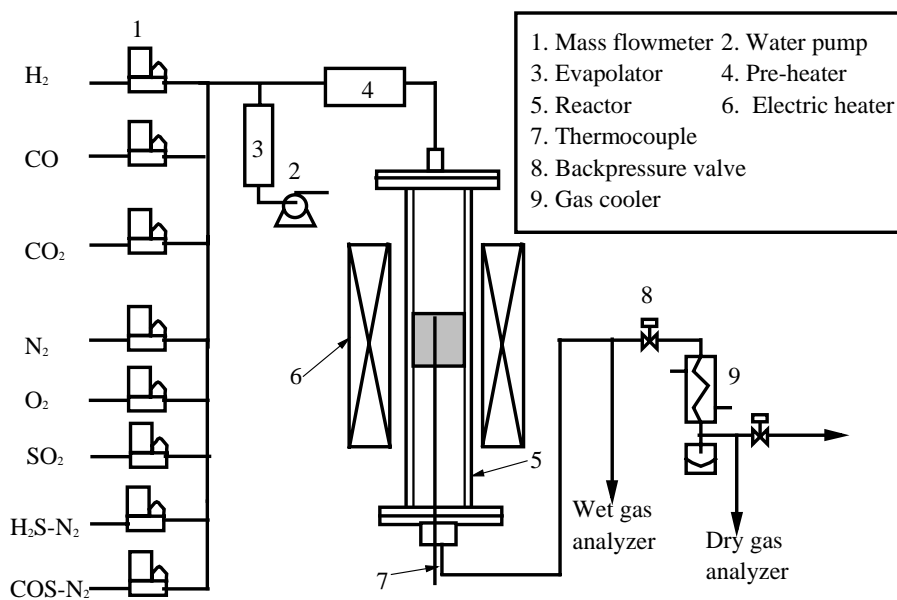
Fig.4 Fixed bed reactor equipment
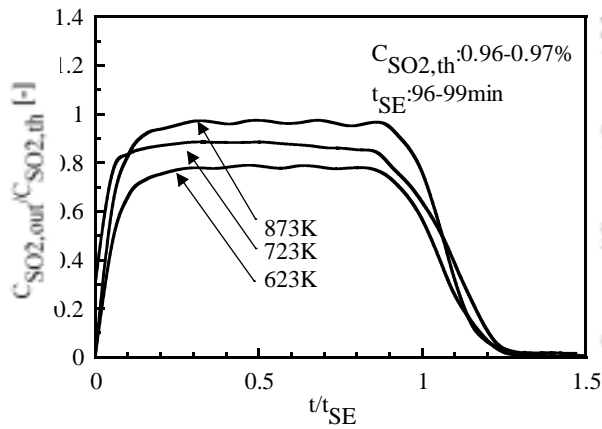
Fig.5 Characteristics of released SO$_2$ during regeneration with non-SO$_2$ containing gas
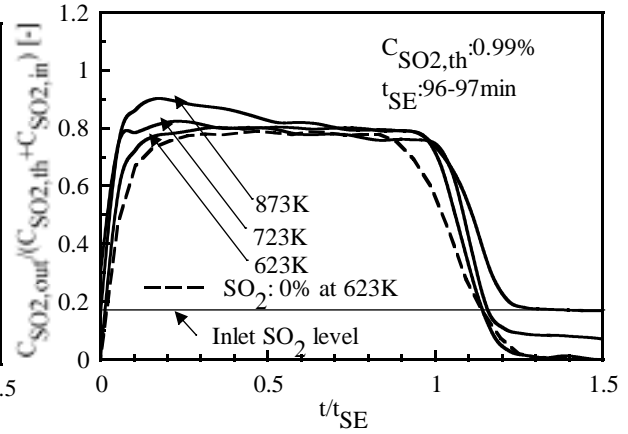
Fig.6 Characteristics of released SO$_2$ during regeneration with 0.2%-SO$_2$ containing gas
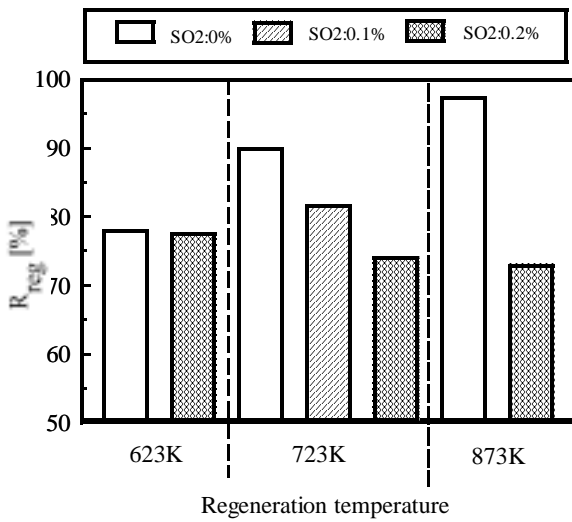
Fig.7 Regeneration ratio at each temperature
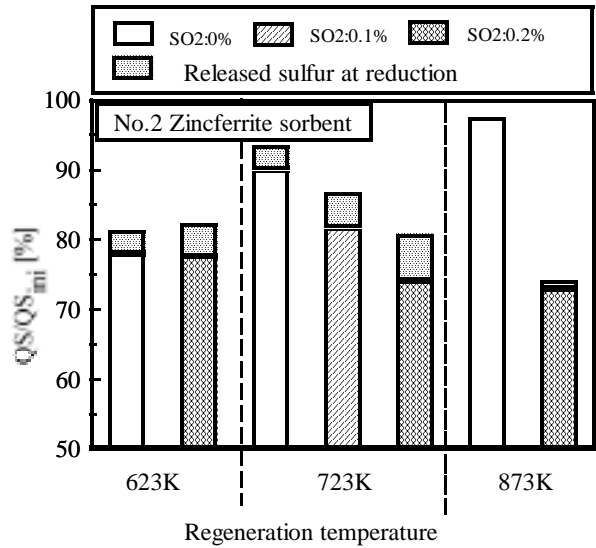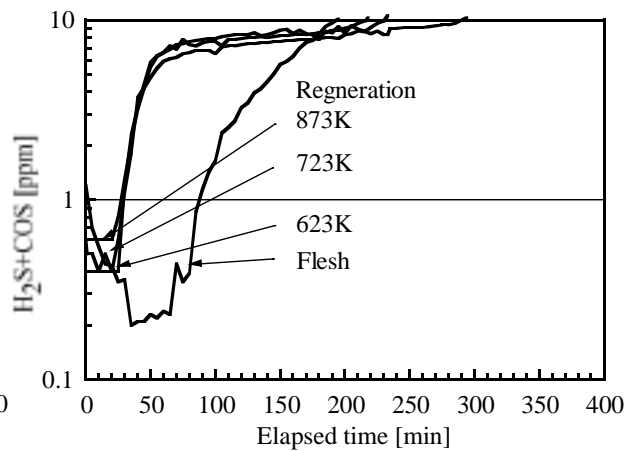

Fig.8 Sulfur absorptive capacity ratio after regeneration
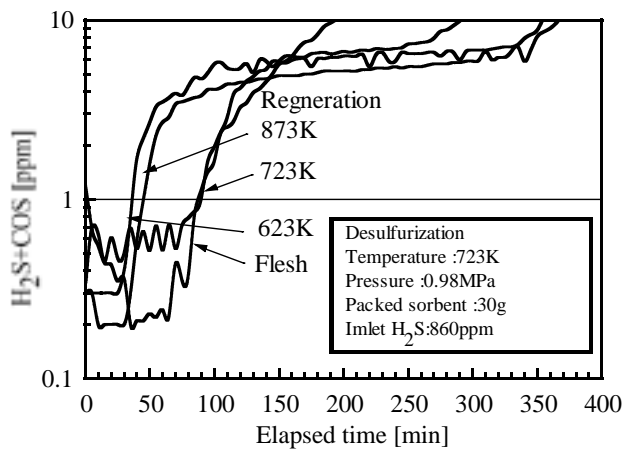
1) Regenerated sorbent with 1.6%-O$_2$ gas

2) Regenerated sorbent with 1.6%-O$_2$ and 0.2%-SO$_2$ gas
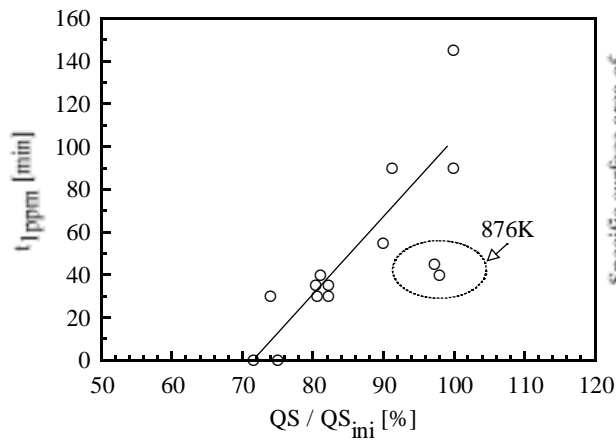
Fig.9 Sulfur compounds breakthrough characteristics below 10ppm

Fig.10 Relationship between 1ppm breakthrough time and sulfur absorptive capacity ratio
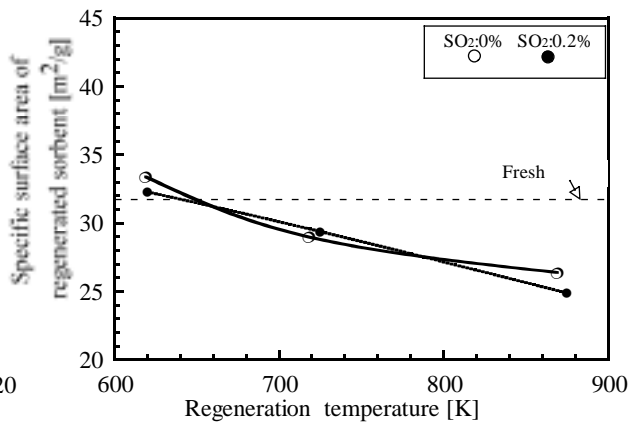
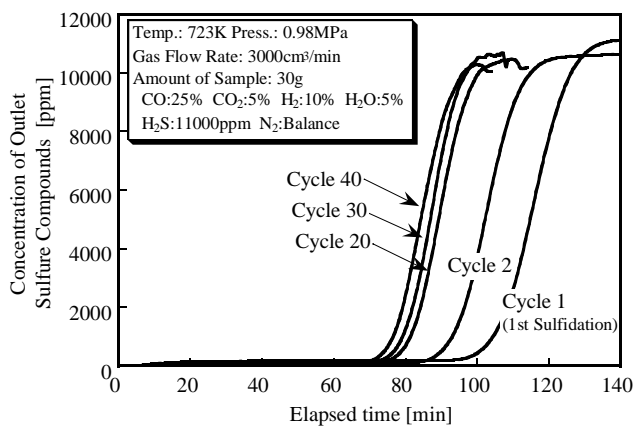Fig.11 Relationship between Specific surface area and regeneration temperature

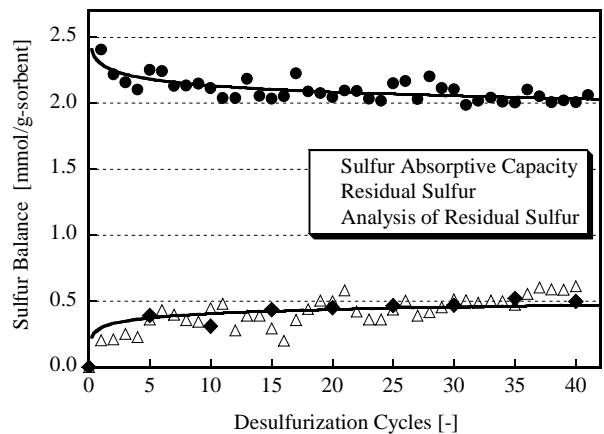Fig.12 Breakthrough curve during each cycle

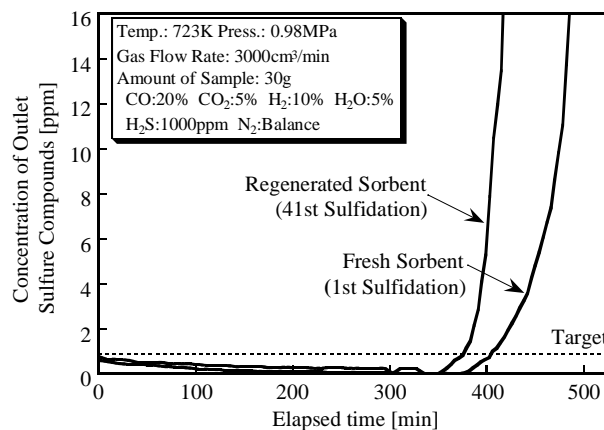Fig.13 Change of Sulfur absorptive capacity and residual sulfur

Fig.14 Comparison between 1ppm breakthrough time of fresh sorbent and that of spent sorbent after 40th cycle