

## The Utilization of Waste Seashells for H<sub>2</sub>S Removal

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**Abstract :** The waste seashells were used for the removal of hydrogen sulfide from a hot gas stream. The sulphidation of waste seashells with H<sub>2</sub>S was studied in a thermogravimetric analyzer at temperature between 600 and 800°C. The desulfurization performance of the waste seashell sorbents was experimentally tested in a fixed bed reactor system. Sulfidation experiments performed under reaction conditions similar to those at the exit of a coal gasifier showed that preparation procedure and technique, the type and the amount of seashell, and the size of the seashell affect the H<sub>2</sub>S removal capacity of the sorbents. The pore structure of fresh and sulfided seashell sorbents was analyzed using mercury porosimetry, nitrogen adsorption, and scanning electron microscopy (SEM). Measurements of the reaction of H<sub>2</sub>S with waste seashells show that particles smaller than 0.631 mm can achieve high conversion to CaS. According to TGA and fixed bed reactor results, temperature had influenced on H<sub>2</sub>S removal efficiency. As desulfurization temperature increased, desulfurization efficiency increased. Also, maximum desulfurization efficiency was observed at 800°C. Desulfurization was related to calcinations temperature.

**Keywords :** waste seashells, hydrogen sulfide, desulfurization, sorbents

### Introduction

The reactions of hydrogen sulfide with various metal oxides have been investigated extensively in connection with the desulfurization of coal gas to be used in advanced power generation cycles.<sup>1)</sup> Although hydrogen sulfide removal can be carried out at ambient temperatures by established liquid absorption processes, desulfurizations by reaction with metal oxides at high temperatures can improve considerably the economics of power generation. Thermodynamic calculations have shown that the oxides of the metals Ca, Fe, Co, Cu and Zn can be used as sulphur sorbents to be applied for high-temperature coal gas desulphurization.<sup>2-4)</sup> On basis of these metals, many sorbents have been developed. One can roughly discriminate between synthetic sorbents, which are relatively expensive but have a long lifetime, and natural sorbents which are cheap but possibly are less stable. Sorbents that belong to the category of natural sorbents are iron ore, limestone and seashells, either in raw or calcined form. Borgwardt and Roach, and more

recently Illerup *et al.*, examined the reaction between limestone and H<sub>2</sub>S. Borgwardt and Roach concluded that limestone conversion extents of more than 25% can only be obtained with very small limestone particles (<10 μm).<sup>5)</sup> In agreement with that, Illerup *et al.* found that bigger limestone particles (360-1500 μm) only show satisfactory sulphidation rate at CO<sub>2</sub>-pressures low enough to allow calcined limestone in coal gas clean-up processes may offer the advantages.<sup>6)</sup>

The objective of this study is the evaluation of the desulfurization performance of seashell sorbents in a fixed bed reactor. Seashell sorbents were tested under reaction conditions that are typical for hot coal gas streams. Experiments were carried out to study the parameters that affect the H<sub>2</sub>S removal ability of a seashell sorbents. In addition to the sulfidation experiments, the pore structure of reacted and sulfided sorbents was analyzed.

### Materials and Method

Four samples of seashell (oyster, clam, short-necked clam and hard shelled mussel) and limestone were the solid reactants of this study. A Norelco intermittent diffractometer employing Ni-filtered Cu radiation was used for qualitative chemical analysis of the components present in a sample. X-ray powder

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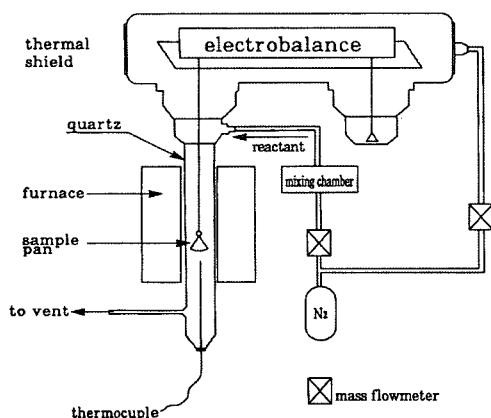
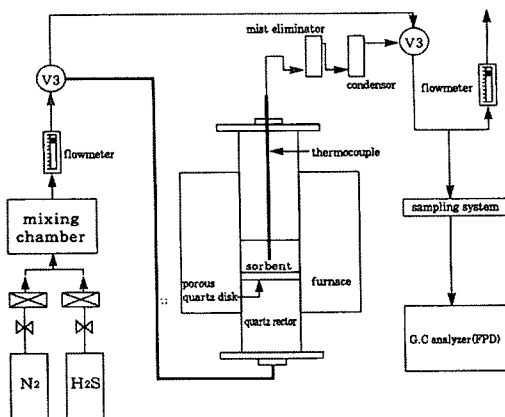


Fig. 1. Schematic diagram of the experimental apparatus.



diffraction patterns were obtained in a  $2\theta$  range of  $25\text{--}40^\circ$ , which enabled detection of various phases. Seashell sorbents were examined by an ETEC Corporation electron microscope operating at 20 kV with resolution of 70 Å. A Perkin Elmer thermogravimetric analyzer (TGA7) interfaced through an analog-to-digital converter to a computer served to measure the sample weight continuously. The quartz housing and flow path of the TGA were modified so that the system could accommodate corrosive gases such as  $\text{H}_2\text{S}$ . A gas flow of 30 ml/min was used for both the protective  $\text{N}_2$  backflow and the feed. A  $\text{N}_2$  gas was used for reduction runs, a 3%  $\text{H}_2\text{S}$  in  $\text{N}_2$  mixture was used for sulfidation runs. Typically, a 45 mg sample of particles, 10/100 mesh, was employed.

The reactor consist of a quartz tube of 1/8 inch i.d. and 8 inch length loaded to a bed height of 4 inch with a sorbent granules (10/100 mesh). The reactor tube was mounted vertically inside an electric furnace, and the bed temperature was monitored by a K-type thermocouple moving inside a quartz thermowell concentric to the reactor tube. In a typical sulfidation run, sea shell sorbents was exposed to feed gas containing 99%  $\text{N}_2$  and 1%  $\text{H}_2\text{S}$ , at a constant temperature of  $600\text{--}800^\circ\text{C}$ . Feed gas rate of a  $200\text{ cm}^3/\text{min}$  (STP) were typically used.

### Results and Discussion

The desulfurization performance of seashell depends on the nature and physicochemical properties of

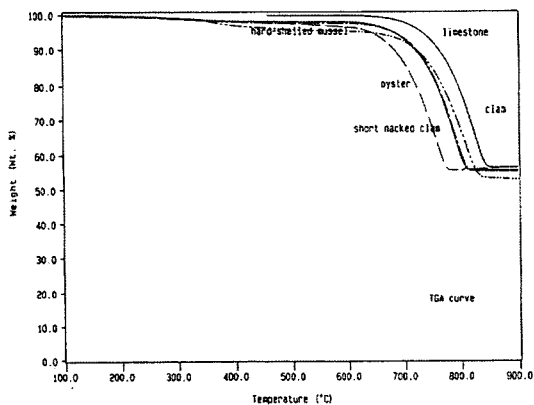


Fig. 2. Thermal gravimetric analyzer (TGA) profile of sea-shells and limestone calcination.

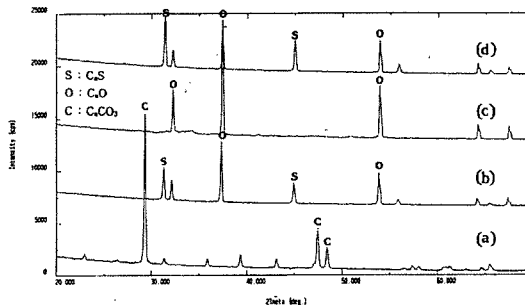
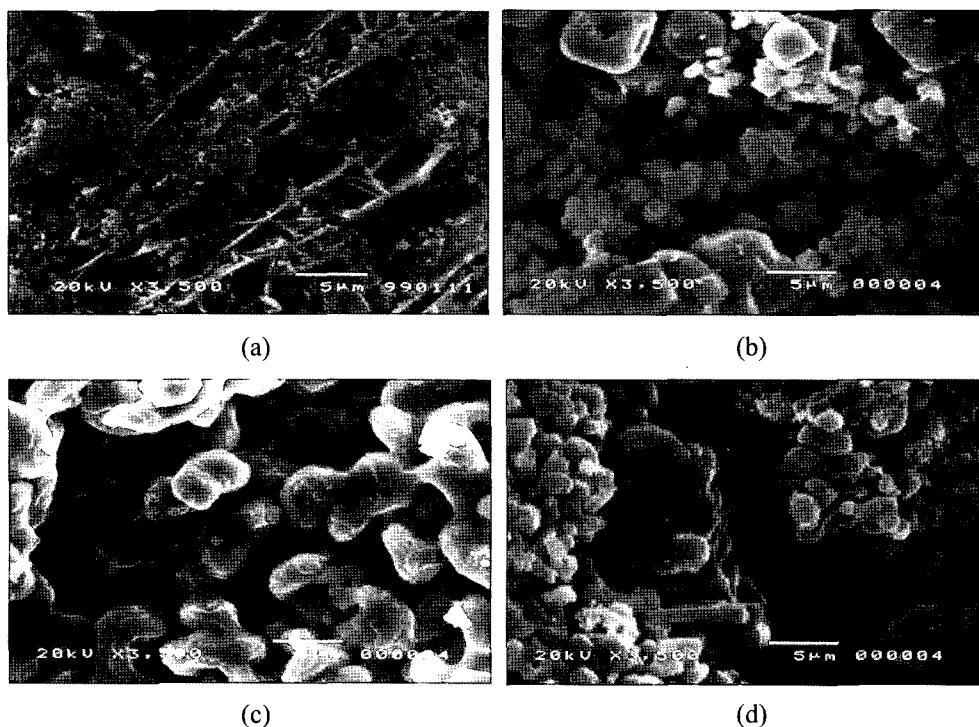


Fig. 3. XRD diagram of oyster; (a) Natural, (b) After sulfidation at uncalcined, (c) Calcined, (d) After sulfidation at calcined.

the sorbents and the composition of the reactive gas. Limestone and waste seashells were mostly



**Fig. 4.** SEM micrograph of oyster; (a) Natural, (b) After sulfidation at uncalcined, (c) Calcined, (d) After sulfidation at calcined.

consisted of CaCO<sub>3</sub> and rest of components were similar. As shown in the Fig. 3, final calcinations temperature were completed at 780°C, 850°C for oyster, natural limestone respectively. Another waste shell were calcinated at 810-830°C.

XRD (Simens D500) analysis to identify major components before and after calcination and product CaS, showed that maximum intensity peak of precalcinated samples mostly consist of CaCO<sub>3</sub> were occurred 2θ was 31°. In the case of the samples after calcinations, CaCO<sub>3</sub> was converted into CaO, so this was observed at 37°. After sulfurization maximum intensity peak of CaS was observed at 32°.

As shown in the Fig. 4, the scanning electron

microscopy (SEM) picture a we took of the center of partially sulfided oyster treated at 610-830°C under H<sub>2</sub>S during 30 min show that the sulfur atoms are relatively homogeneously distributed around all the pores, even in the core of the oyster particle. The sulfide ions surround the pores but are not present in the core of the individual CaCO<sub>3</sub> grains forming the particle. This proves that H<sub>2</sub>S has not been prevented from diffusing deep into the particle.

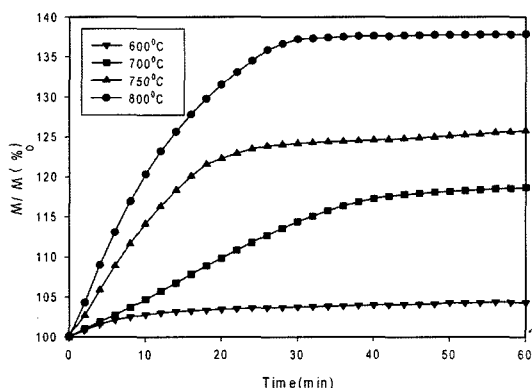
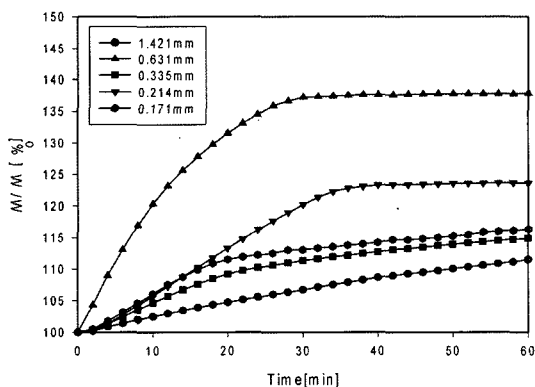
According to SEM/BET analysis were investigated pore distribution and surface area of particles. Additive pores were formed after calcinations. Also, small grains were formed after sulfurization. As shown in the Table 1, BET (Micromeritics Co.,

**Table 1.** Specific surface area of CaCO<sub>3</sub> and CaO for limestone and shells

Component	Sorbent					
	Limestone	Oyster	Clam	Short-necked clam	Hard shelled mussel	
Specific surface area of CaCO <sub>3</sub> [m <sup>2</sup> /g]	0.2363	2.4465	2.1565	2.0021	1.6903	
Specific surface area of CaO [m <sup>2</sup> /g]	1.1544	2.1209	0.7647	0.5368	0.7330	

**Table 2.** TGA kinetics of sea-shells and limestone

Sorbents	Activation Energy Ea, KJ/mole	Reaction Velocity $\ln(Z)$ , sec <sup>-1</sup>	Reaction Order, n
Limestone	201.72 ± 5.17	16.47 ± 0.63	0.37 ± 0.08
Oyster	176.1 ± 8.90	15.07 ± 1.14	0.42 ± 0.10
Clam	193.68 ± 2.05	16.27 ± 0.26	0.44 ± 0.04
Short nacked clam	166.51 ± 0.24	12.97 ± 0.03	0.14 ± 0.01
Hard-shelled mussel	206.79 ± 4.11	17.59 ± 0.50	0.74 ± 0.06

**Fig. 5.** Effect of temperature on sulfidation of oyster.**Fig. 6.** Effect of particle size on sulfidation of oyster.

ASAP 2010C) surface area of limestone, oyster, clam before calcinations were 0.2363, 2.4465, 1.69 m<sup>2</sup>/g, and after calcinations were 1.1543, 2.1209, 2.17 m<sup>2</sup>/g, respectively.

TGA results showed that the activation energy of the reaction between H<sub>2</sub>S and calcined seashell was determined at 167-207 kJ/mole. This value is much higher than the value of 22 kJ/mole reported by Westmoreland *et al.* for calcined limestone.<sup>7)</sup> Short nacked shell and oyster had lower activation

energy. This means that energy requirement was low in the calcinations. And, CaCO<sub>3</sub> was converted into CaO. The reaction order in H<sub>2</sub>S was found to be 0.14-0.74 at all applied temperatures and H<sub>2</sub>S pressures. This value differs from the value of unity that was reported by Westmoreland *et al.*, who performed TGA measurements at temperatures between 300 and 800°C.<sup>7)</sup> The reaction velocity and order of hard-shelled mussel was the highest.

According to TGA results, temperature had influenced on H<sub>2</sub>S removal efficiency. As desulfurization temperature increased, desulfurization efficiency increased. Also, maximum desulfurization efficiency was observed at 800°C. Desulfurization was related to calcinations temperature. Considering temperature ranges of exhausted gas from hot gas gasification equipment were 400-800°C. Thus, desulfurization efficiency would be increased desulfurization temperature situation at highly.

Experiments by TGA showed that particle size of sorbents had influenced on desulfurization capacity. Maximum desulfurization capacity was observed at 0.631 mm for oyster and clam. Rest of sorbents showed similar capacity within 0.171-0.335 mm particle size range. So, particle size would be considered.<sup>8)</sup>

As shown in the Figs. 7 and 8, fixed bed desulfurization experiments, to obtain basic data for scale-up was indicated. Oyster was the best among the various sorbents, like the results of TGA. Especially, H<sub>2</sub>S removal efficiency of uncalcined oyster was the highest. When use oyster as desulfurization sorbents, calcinations process was not needed. Thus, desulfurization efficiency would be expected.<sup>9)</sup>

Fixed bed reactor experiments were indicated particle size of sorbents. These had influenced on desulfurization capacity. As smaller particle size was found better desulfurization capacity. Large

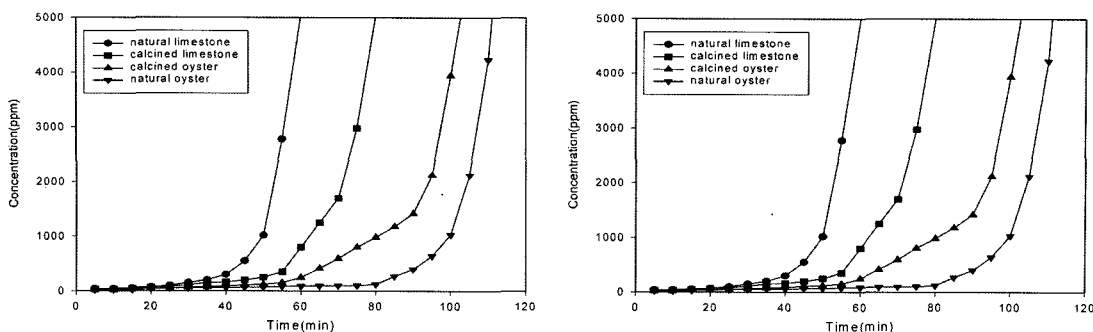


Fig. 7. H<sub>2</sub>S removal efficiency for sulfidation of sea-shells.

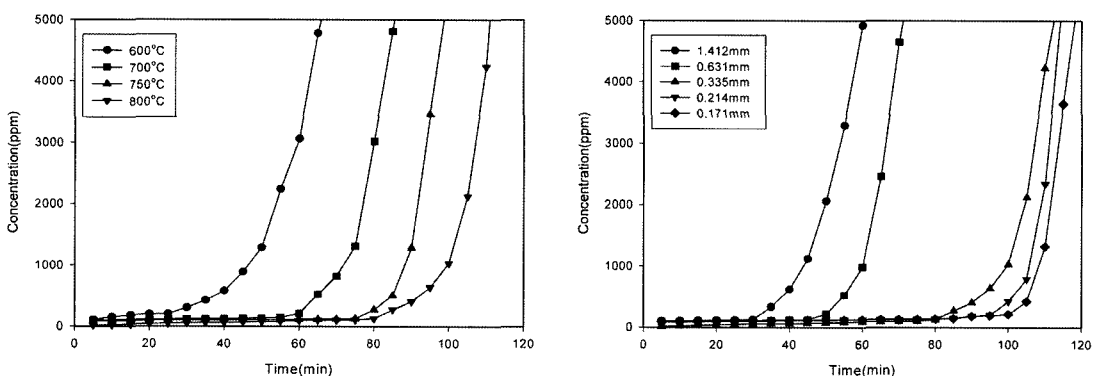


Fig. 8. Effect of temperature and particle size on H<sub>2</sub>S breakthrough for sulfidation of oyster.

capacity difference was found between 0.631 mm and 0.335 mm. But, differences between 0.335 mm and 0.24 mm was relatively small. As bed temperature increased, H<sub>2</sub>S removal capacity increased. Therefore, both particle size and bed temperature should be considered to remove H<sub>2</sub>S by sorbents.

## Conclusion

Measurements of the reaction of H<sub>2</sub>S with waste seashells show that particles smaller than 0.631 mm can achieve high conversion to CaS. According to TGA and fixed bed reactor results, temperature had influenced on H<sub>2</sub>S removal efficiency. As desulfurization temperature increased, desulfurization efficiency increased. Also, maximum desulfurization efficiency was observed at 800°C. Desulfurization was related to calcinations temperature. Considering temperature ranges of exhausted gas from hot gas gasification equipment were 400-800°C. Thus, desulfurization efficiency would be

increased desulfurization temperature situation at highly. When would be used waste seashells as IGCC (integrated gasification combined cycle) sorbent.

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