

## Reactivity of Bio-sorbent Prepared by Waste Shells of Shellfish in Acid Gas Cleaning Reaction

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**Abstract**—Acid gas cleaning activity of bio-adsorbent prepared by waste shell of different shellfish species was investigated in a fixed bed reactor to evaluate its feasibility as an acid gas cleaning agent. The physicochemical properties of prepared adsorbents were measured using ICP, BET, SEM-EDX and XRD. The results showed that active chemical species of bio-sorbent are comparable to that of commercial limestone and lime. SO<sub>2</sub>/NO<sub>x</sub> removal capacity of waste shell of shellfish was higher than that of commercial limestone due to the enhanced physical properties. In particular, the desulfurization activity of clam based adsorbent was the best among the tested waste shells because of both higher calcium content and more specific surface area. These lead to the conclusion that commercial limestone can be substituted for bio-sorbent prepared by waste shell of clam.

Key words: Waste Shell, Bio-Sorbent, DeSO<sub>x</sub>, DeNO<sub>x</sub>

### INTRODUCTION

Recently, marine pollution by waste shellfish shells has become a serious problem for the mariculture industry in Korea. Annually, hundreds of thousand tons of waste oyster-shells are dumped into public waters and reclaimed lands, which causes a foul smell as a consequence of the decomposition of fresh remnants attached to shellfish shells [Yoon et al., 2003]. As a physical recycling process, studies on the application of waste oyster-shell to construction materials had been carried out, and physical properties and processing methods were reported. However, a large scale application as construction materials was limited due to a lower mechanical strength of oyster-shell.

Another method to recycle the waste shells of shellfish can be found in acid gas cleaning processes such as flue gas desulfurization systems which can be categorized into three groups, such as dry adsorption [Yoo et al., 1994; Garea et al., 2001], wet scrubbing [Ukawa et al., 1993; Chu et al., 1997], and wet/dry system [O'Dowd et al., 1994; Karlsson et al., 1983]. In spite of the differences in the processes, calcium based alkali sorbents are widely used to remove SO<sub>2</sub>. This is because calcium based sorbents have good reactivity toward acidic gases and lower cost compared to other sodium based alkali adsorbents such as sodium bicarbonate [Keener and Davis, 1984]. However, experimental results using waste shells of different shellfish species are scarce in literature.

The objective of this study is to evaluate the feasibility of waste

shells of different shellfish species as an acid gas cleaning agent.

### MATERIALS AND METHODS

The waste shell of clams, oysters, mussels, and sea-shells from Tongyong province around the South Sea of Korea were chosen as the main materials. Limestone from Danyang province, which is commercially used in flue gas desulfurization systems, was selected for the comparison of acid gas cleaning reactivity of waste shell. These materials were crushed twice by jaw crusher and ball mill, and then sieved to prepare a sample size of 48-60 Tyler meshes (0.295-0.25 mm). Calcinations of these calcium based sorbents were carried out at 800 °C in a Lindberg furnace under N<sub>2</sub> flow and then hydrated in a hydration reactor. Physicochemical properties of waste shell of shellfish were analyzed by ICP (ICPS-7500 Shimadzu, Japan), XRD (SIMENS, Deutsche), BET (Micromeritics Co., USA), and SEM (JEOL superprobe JSM-5400, Japan). ICP was applied to analyze the atomic properties of the materials. SEM was used to observe the micro-tissue of the surface of waste shells and surface area of the adsorbent was measured by BET technique after pretreating to remove vapor in vacuum and 180 °C for 2 hours. The crystal state of shell adsorbent and the products before and after reaction was assured by X-ray diffractometer under the condition of 30 kV and 20 mA. To evaluate the acid gas cleaning reactivity of the samples (Fig. 1), a fixed bed quartz reactor (0.025 m in diameter, 0.25 m in height) was placed in a hot air bath and the temperature was controlled by PID type controller with a precision of ±1.0 °C. After the sample was put on the reactor and the temperature was stabilized in N<sub>2</sub> flow, reacting gas containing SO<sub>2</sub> and NO<sub>x</sub> was injected into

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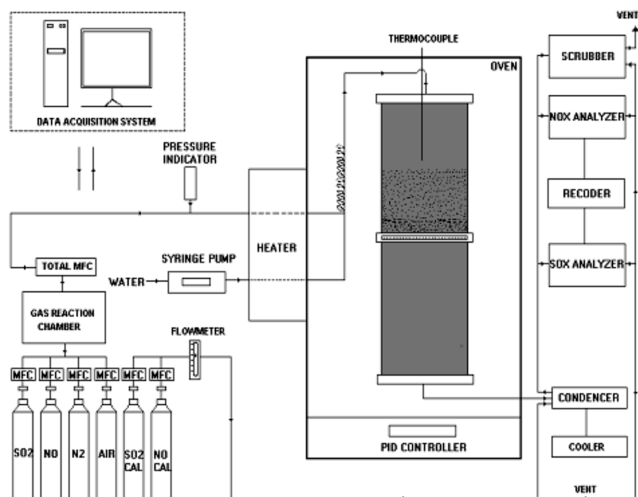
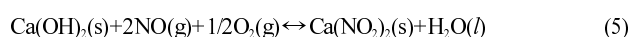
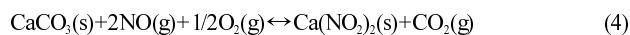


Fig. 1. Schematic diagram of packed-bed experimental apparatus.

the reactor by using mass flow controllers. The water was also injected into the reactor by Syringe pump to keep a steady  $H_2O$  concentration in the simulated gas. A hygrometer and  $SO_2/NO_x$  analyzer were used to measure the gas concentration, and signals from the measuring instrument were recorded at a personal computer with RS-232C interface.

Combining the following equation we can derive the overall reactivity of each adsorbent with  $SO_2$  and  $NO_x$  [Nakamura, 1995].



## RESULTS AND DISCUSSION

Physical properties and chemical compositions of waste shells of shellfish are summarized in Table 1 along with the data of commercial limestone. The concentration of CaO of waste shell was around 53-54 wt%, which is comparable to that of commercial Danyang limestone, and was in good agreement with the results of Yoon et al. [2003] reporting the CaO content of oyster was about 53.7 wt%. MgO content of oyster and  $SiO_2$  content of limestone are slightly higher than other samples. However, other compositions of the

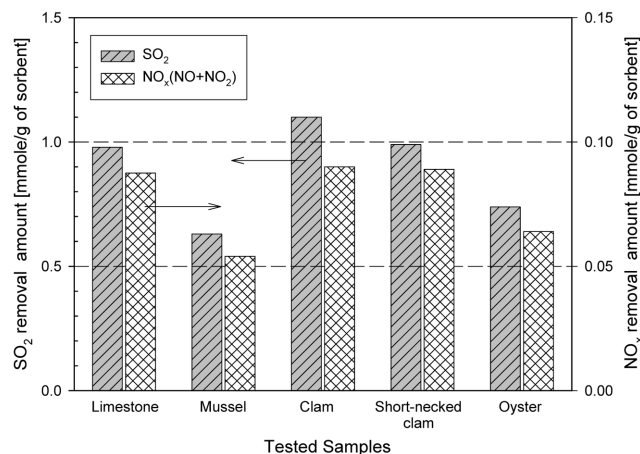


Fig. 2.  $SO_2/NO_x$  removal amount of tested adsorbents at reaction temperature of  $150^\circ C$ .

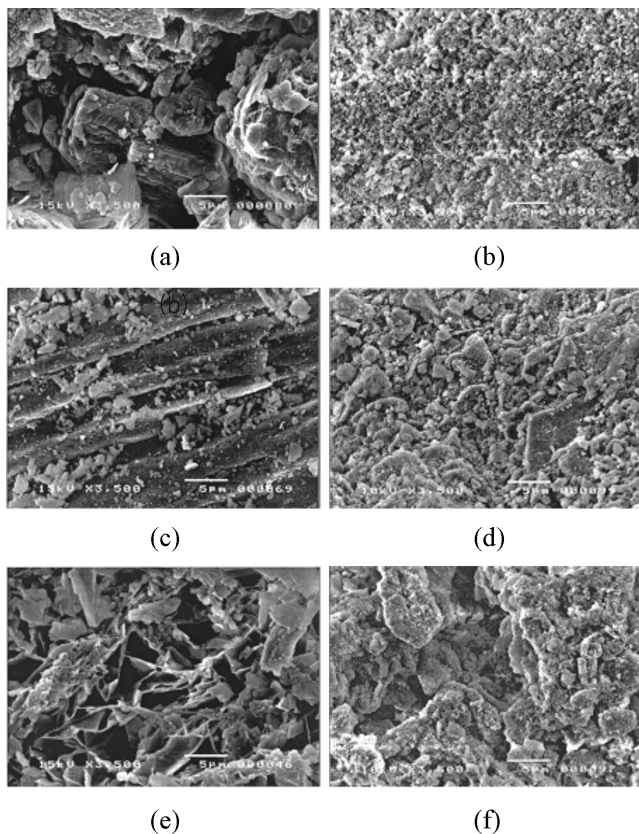
tested samples were not largely different including ignition loss by  $CO_2$  evolution. It should be also noted that the crystal phase of all the tested raw samples was identified to be calcite from the X-ray diffractometer analysis. Pore volume and specific surface area of treated samples showed similar values, except hard shelled mussel.

The reaction of samples prepared by waste shells and limestone was carried out in a fixed bed reactor;  $SO_2/NO_x$  removal capacity of the adsorbents was identified. As can be seen in Fig. 2, desulfurization capacity of the adsorbent was one order of magnitude higher than the denitrification capacity regardless of adsorbent species. This is because the Henry's Law constant and diffusion coefficient in the gas phase for  $SO_2$  is much higher than those for NO [Yuan, 1990]. Waste shells of clam showed the highest value for  $SO_2/NO_x$  removal capacity among the tested adsorbents. It can be inferred that acid gas removal capacity of adsorbents was proportional to the specific surface area which was shown in Table 1.

Acid gas removal capacity of oyster shell was slightly lower even though the specific surface area is comparable to the short-necked clam or commercial limestone. The reason can be found in Fig. 3, which shows the SEM photographs of limestone, clam, and oyster. Fig. 3(A) and (C) showed fresh limestone and clam sample condition by SEM. Fig. 3(B) and (D) showed that the particles of treated limestone and clams were more increased in specific surface area than that of the fresh particles [Jung, 2000]. In addition, it appeared that the average pore diameter and pore volume of treated waste shells were much bigger than that of raw materials. This result indicates that the treating process can enhance the removal capacity of acid gases. As can be seen in Fig. 3(E) and (F), fresh oyster shell

Table 1. Physicochemical properties of tested adsorbents

	Chemical composition [wt%]						Pore volume [cc/g]	Surface area [m <sup>2</sup> /g]
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Ignition loss		
Oyster	0.40	0.22	0.04	53.81	1.70	44.87	0.0869	12.98
Mussel	0.20	0.13	0.03	53.70	0.33	45.61	0.0129	6.51
Clam	0.46	0.20	0.04	53.92	0.22	45.16	0.1025	15.99
Short-necked clam	0.66	0.40	0.04	53.58	0.20	45.12	0.0888	12.83
Limestone	1.62	0.07	0.12	54.70	0.25	43.10	0.0697	11.98



**Fig. 3. SEM photographs of (a) fresh Danyang limestone, (b) treated Danyang limestone, (c) fresh clam, (d) treated clam, (e) fresh oyster, and (f) treated oyster.**

shows a porous structure which makes it possible for a sintering of micro grain to occur. This leads to a lower sulfating activity of oyster adsorbent. Fig. 3 also shows the fine structure is well developed in both limestone and clam samples.

In conclusion, it is clearly indicated that waste clam shells can be used as acid gas cleaning agent to reduce air pollution problems. These results can be directly applied to industries and businesses which try to reduce their emissions of  $\text{SO}_2$  and  $\text{NO}_x$ . The recycling of waste shells of shellfish helps the fishery and sea food industries worldwide that produce a large amount of waste shells.

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