

Gas Reaction Characteristics of Waste Oyster Shell Sorbent

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Abstract

The objective of this study is to develop the sorbent of oyster shell, which can remove gaseous acid pollutants emitted from the incinerator and power plants. The physicochemical properties of prepared absorbents have been measured using ICP and BET. Also, this study is to investigate the hydration/calcination reaction in the fixed bed reactor. Thus, the results could be summarized as follows. Oyster shell can be used in powder type without former processing. It should be also noted that sulfation reactivity of oyster sample increases to about 5 times by calcination/hydration reaction due to the increase of specific surface area and pore volume. From these experiments, we have found that both SO₂ and NO_x in simulated flue gas can be effectively removed by use of oyster absorbent.

Introduction

Air pollution problems due to the emission of pollutants from the various industrial facilities become serious issues and lots of air pollution control processes have been developed.¹⁻⁵⁾ It is well known that alkali sorbents such as CaO, CaCO₃, Ca(OH)₂, NaOH, Na₂CO₃, NaHCO₃, KOH, MgO, Mg(OH)₂, dolomites, dolomitic hydrates and dolomite limestones(CaCO₃/MgCO₃) are used to remove SO₂/HCl/HF and acid gas in flue gas cleaning processes.⁶⁻⁹⁾ The objective of this study is to develop a sorbent of waste oyster shell, which can remove gaseous acid pollutants emitted from the medium and small incinerators and flue gas desulfurization(FGD) system. And, the objective of this study is to investigate the waste recycling possibility, economic effect and practicable use of the oyster.

Materials and Method

The seashells of oyster from Tong-young province around the South Sea in Korea were used as

a main material. Salts and other organic substances were removed by washing and drying the waste oyster shell. To evaluate these waste oyster shells as substitute for sorbent, instead of lime, limestone from Jung-Sun(JS) province was adapted for comparison of physicochemical properties of waste seashells. The physicochemical properties of prepared oyster shell sorbent were measured using several instruments. The waste oyster shell was crushed 2 times by Jaw crusher and Ball mill after drying.

The physicochemical characteristics of the oyster shell were analyzed by ICP (ICPS-7500 Shimadzu, Japan) and BET (Micromeritics Co., USA). Surface area of the sorbent was measured by BET technique after pretreating to remove vapor at 1×10^{-3} torr of vacuum and 180°C for 2 hours. Fig. 1 shows the experimental apparatus for De-SOx/De-NOx simultaneous reactivity tests. To calculate the sorbent capacity, a fixed type reactor was installed in the air bath. It was 25mm width and 250mm-height stainless steel pan. Metal filter was on the 150mm height from its bottom and then experimental material was put on this filter under regular temperature. The temperature of air bath was the range of $0\text{-}300^\circ\text{C}$ and checked every $\pm 1^\circ\text{C}$. When the absorbents put on the reactor, simulated-gas would be injected and reacted gas is supposed to be spouted. The system was consisted of simulated-gas injection part, reactor part, reacted gas analysis and data check part.

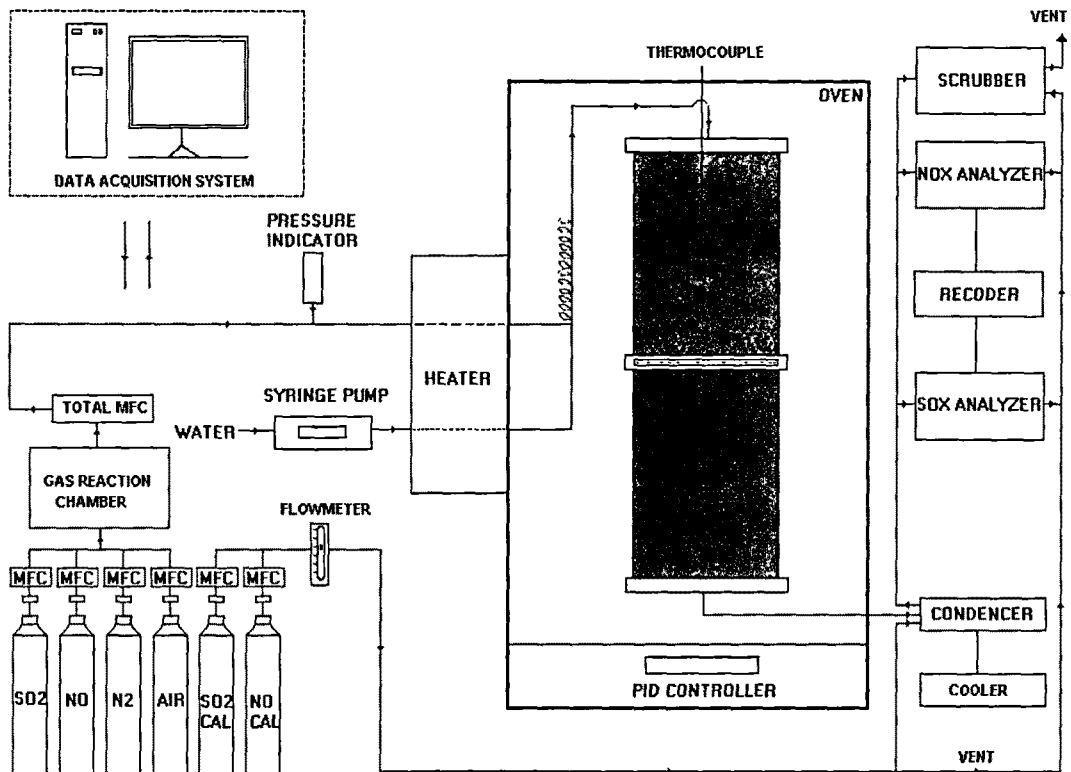


Fig. 1. Schematic diagram of experimental apparatus.

The gas injected by MFC to reactor was simulated-gas consisted of air/NO/SO₂/N₂ and total injection amount was 3.0 L/min. The water was injected by Syringe pump to keep same humidity and was supplied steam passing through the steam maker under 180 °C. For the check of water balance in reactor, Thermos Hydrometer(DAGATRON, Model : 1701) was installed in outlet and the steams went out and the area was sealed with heating tape for preventing the gas to be condensed by decreasing temperature. Since the air was eliminated hydration and dust passing through a cooling condenser and reactor filled with CaSO₄. Since hydration was eliminated two times, fixed flow was supplied through a flow meter installed in inlet. The gas injected to the reactor and NO/NO_x/SO₂ after reaction was checked continuously and analyzed by IR type NO_x and SO₂ Analyzer. Once the experimental material was put into reactor, the air oven was kept under the same temperature. Then, hydrogen and nitrogen were injected to eliminate oxygen in the oyster shell sorbents for 10 minutes and keep the simulated-gas and humidity regularly. Then valve was switched to bypass line and the volume of each gas was balanced with the injection of other gas including NO/NO_x/SO₂. When the volume of simulated gas was fixed regularly, the valve of bypass line was turned the switch to the gas and actually the experiment was commenced. It was used the real-time data system to show the reaction according to the change of temperature. RSC232 port transferred the real-time data to pentium computer, since recording continuously the electric signal generated from the measuring instrument with Hybrid Recorder.

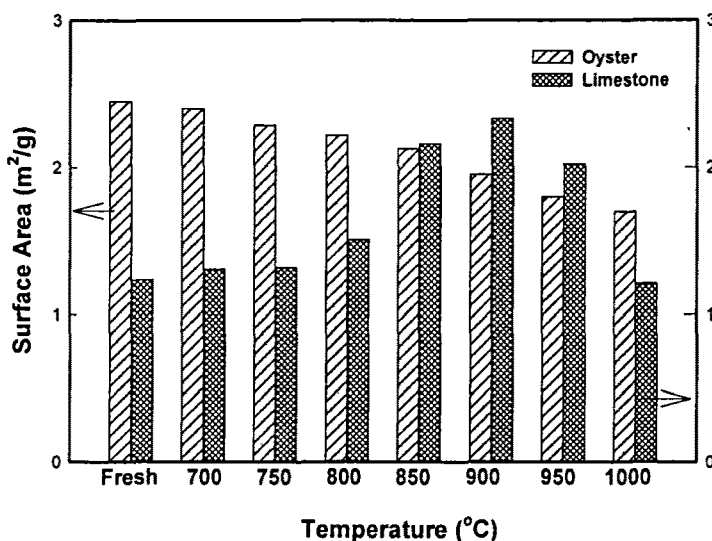


Fig. 2. Variation of surface area of oyster and JS as function of calcination temperature.

Table 1. Analysis of oyster and JS limestone (wt.%).

Components		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Igloss
Contents (%)	Oyster	0.40	0.22	0.04	53.81	0.70	44.83
	JS	2.43	0.25	0.14	53.8	0.85	42.5

Results and Discussion

The specific surface area of oyster and limestone as a function of different calcination temperatures (700, 750, 800, 850, 900, 950 and 1,000°C) was reported in Fig. 2. As shown in Fig. 2, specific surface areas of oyster's particle were changed from 2.4465 m²/g before calcination to 2.395 m²/g at 700°C, 2.281 m²/g at 750°C, 2.212 m²/g at 800°C, 2.1209 m²/g at 850°C, 1.9510 m²/g at 900°C, 1.80 m²/g at 950°C and 1.70 m²/g at 1,000°C. The specific surface area of raw oyster waste shell was larger than that of calcined oyster shell and specific surface area of oyster shell decreased with increasing calcination temperature. It was concluded that specific surface area which could react on gas decreased although the particles of calcined oyster generated pores due to the emission of CO₂.

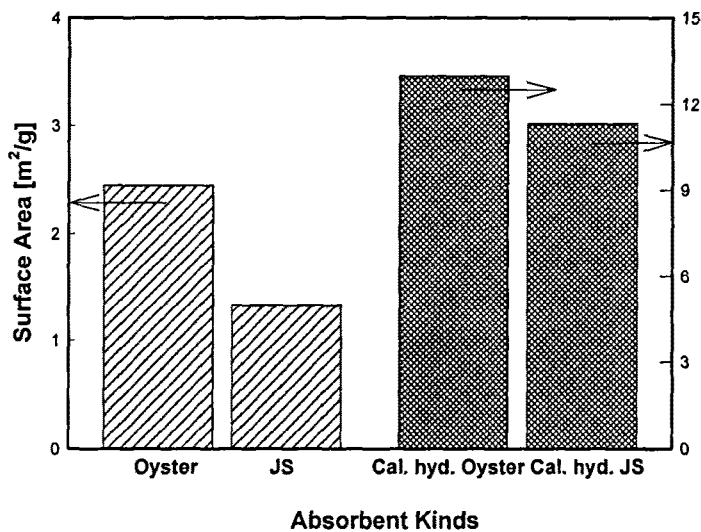


Fig. 3. Variation of surface area of oyster and limestone as function of absorbent kinds.

The specific surface area of limestone increased with increasing calcination temperature up to maximal 900°C and then a little decreased. The specific surface area value at 850°C was similar to that at 900°C. Therefore, it was concluded that calcination temperature had a positive effect on the development of the specific surface area for limestone, unlike oyster waste shell. The specific surface area of oyster and limestone as function of absorbent kinds was reported in Fig. 3. It should be also noted that sulfation reactivity of oyster sample increases to about 5 times by calcination/hydration reaction due to the increase of specific surface area and pore volume. In general, low sulfur coal of 1.5% discharged a power plant was released SO₂ of 1800-1900 ppm, O₂ of 6%, CO₂ of 13%, N₂ of 74%, water content of 10%, NO of 600 ppm and HCl of 100 ppm to the air during the combustion. In this study, experimental condition was carried out under the water content of 10%, SO₂ concentration of 1800 ppm, NO concentration of 250 ppm, reaction temperature of 150°C, gas flow of 3 L/min. Results of the research revealed that oyster shell-based sorbent can be used as the iron-manufacturing industry and chemical adsorbents for the removal of acid gases because the lime content of the waste calm was more than 53%. Total

removal quantities of SO₂ and NO according to sorbent type were reported in Fig. 4. The specific surface area, pore volume, pore size distribution greatly influenced in the SO₂ and NO_x removal reactivity. The SO₂/NO_x removal quantities and sorbent capacity were increased the oyster shell after calcinations/hydration. From physicochemical analysis and gas reaction experiments, it could be concluded that oyster shell is good sorbent for the removal of SO₂ and NO_x in waste incinerator and flue gas desulfurization processes.

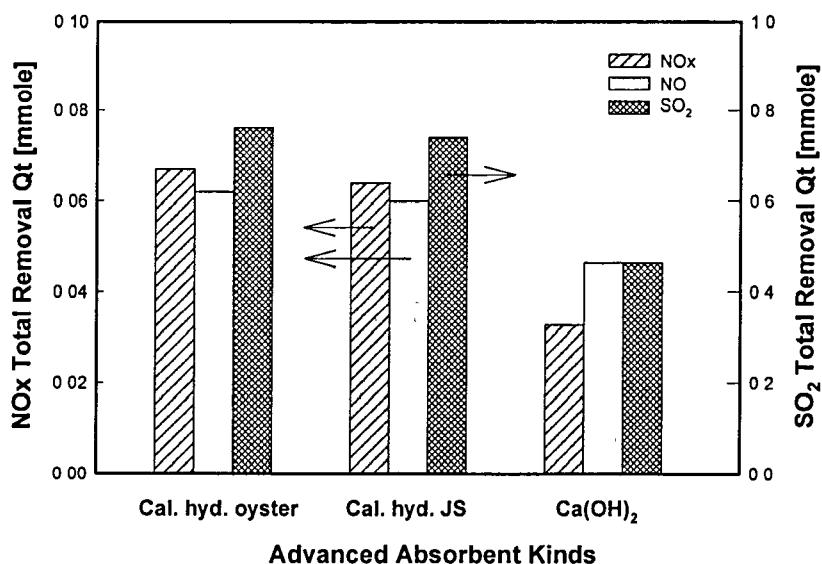


Fig. 4. Total removal quantities of SO₂ and NO_x according to calcined hydration absorbent.

Conclusion

Recently, a lot of waste seashells accumulated on the South Sea shore are focused on absorbents for the removal of acid gases. A few researches were carried out to use these oyster shells as a material for cleaning the industrial wastewater and improving skin treatment. The specific surface area, pore volume, pore size distribution greatly influenced in the SO₂ and NO_x removal reactivity. The SO₂/NO_x removal quantities and sorbent capacity were increased the oyster shell after calcinations/hydration. Oyster shell can be used in powder type without former processing. It should be also noted that sulfation reactivity of oyster sample increases to about 5 times by calcination/hydration reaction due to the increase of specific surface area and pore volume.

References

- 1) G. Krammer, Ch. Brunner, J. Khinast, G. Staudinger : Reaction of Ca(OH)₂ with SO₂ at low temperature : *Ind. Eng. Chem. Res.* 36, 1410-1418, 1997.
- 2) Chen H. Shen, Gary T. Rochelle : NO₂ absorption in limestone slurry for flue gas desulfurization : 1995 SO₂ Control symposium, 1995.
- 3) Jerry J. Kaczur : Oxidation chemistry of chloric acid in NO_x/SO_x and air toxic metal removal from gas steams : *Environmental Progress* 15(4), 1996.

- 4) Peter J. Kroll, Peter Williamson : Application of dry flue gas scrubbing to hazardous waste incineration
Journal of the Air Pollution Control Association. 36(11), 1986.
- 5) Donald E. Wolf, James P. Seaba : Opacity reduction using dry hydrated lime injection : Air & Waste
44, 1994.
- 6) Brian K., W. Jozewicz, Leonard A. Stefanski : Reaction kinetics of Ca-based sorbents with HCl : Ind.
Eng. Chem. Res. 31(11), 1992.
- 7) Kunio K. and Hidenori S. : Effective dry desulfurization by a powder-particle fluidized bed : Journal of
Chemical Engineering of Japan. 27(3), 276-278, 1994.
- 8) Jonas K., Ann-mari S., Hans T. Karlsson and Ingemar B. : Similarities between lime and limestone in
wet-dry scrubbing : Chem. Eng. Process. 18, 239-247, 1984.
- 9) Jong-Hyeon Jung, Byung-Hyun Shon, Kyung-Sun Yoo and Kwang-Joong Oh. : Physicochemical
Characteristics of Waste Sea Shell for Acid Gas Cleaning absorbent : The Korean Journal of Chemical
Engineering. 17(5), 585-592, 2000.