SO_2 and NOx Reaction Characteristics of Waste Clam Sorbent in Fixed Bed Reactor

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Abstract

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. To remove the SO_2 and NOx emitted from the solid waste incinerator and coal fired power plants, we studied the Ca-based sorbent which was prepared by waste clam and limestone. The objectives of this study were to develop a clam-based sorbent for removal of SO_2 and NOx, and to investigate the physicochemical properties of the waste clam sorbent. In order to determine acid gas removal capacity of sorbent, the batch study on SO_2 and NOx removal was performed with the Ca-based sorbent in the fixed bed reactor. Results of the research revealed that clam-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 53.92%. From physicochemical analysis and gas reaction experiments, it could be concluded that clam is good sorbent for the removal of SO_2 and NOx in waste incinerator and flue gas desulfurization processes.

Introduction

It is well known that alkali sorbents such as CaO, $CaCO_3$ and $Ca(OH)_2$ are used to remove SO_2/HCl/acid gas in flue gas cleaning processes.[1)] Dry limestone particles are used as an absorbent in a process of flue gas desulfurization(FGD) and solid waste incinerator. In this system, a product layer of $CaSO_4$ near the particle surface obstructs diffusion of gaseous reactants through the layer.[2)] Also lime is utilized as a sorbent in most commercial wet/dry scrubbing processes for SO_2 control.[3)] But, waste seashells (clam, oyster, short-necked clam, seashell, hard-shelled mussel etc.) are not considered to be absorbents from now on. 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.[4] However, the use and application of the clam in medium/small scale waste incinerator and flue gas desulfurization processes were not studied. In this study, we examined the effects of calcinations/hydration of waste clam on the physicochemical characteristics using several instrumental techniques. And, Desulfurization and denitrification capacity of clam sorbent was carried out in a fixed bed reactor.

Materials and Method

The physicochemical properties of prepared clam sorbent were measured using several instruments [ICP, BET, XRD, EDAX, SEM-EDX and pore volume, etc.]. The waste clam was crushed 2 times by Jaw crusher and Ball mill after drying. The physicochemical characteristics of the clam were analyzed by ICP (ICPS-7500 Shimadzu, Japan), XRD (SIMENS, Deutsche), and BET (Micromeritics Co., USA). Also, SEM was used to observe the microtissue of the surface of clam-based sorbent. Surface area of the sorbent was measured by BET technique after pretreating to remove vapor in vacuum 1×10^{-3} and 180℃ for 2 hours. The crystalline state of the sorbent before and after reaction was assured by X-ray diffractometer under the condition of 30kV and 20mA in the ranges of 10-70 degrees. 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 150-mm 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 0～300℃ under ±1℃. 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. The gas injected by MFC to reactor was simulated-gas consisted of air/NO/SO_2/N_2 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℃. For the check of water balance in reactor, Thermos Hygrometer was installed in outlet the steams go 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 $CaSO_4$. 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/NOx/SO_2 after reaction was checked continuously and analyzed by IR type NOx and SO_2 Analyzer. Packing a clam sorbent to the reactor, clam 1g and quartz stand 19g were mixed for preventing the experimental material to be condensed and the gas flow can be smooth when the clam sorbent was

injected to the reactor. Once the experimental material was put into reactor, the air oven was kept under same temperature. Then, hydrogen and nitrogen were injected to eliminate oxygen in the clam sorbents for 10 minutes and keep the simulated-gas and humidity regularly. Then valve was switched to bypass line and the thickness of each gas was balanced with the injection of other gas including NO/NOx/SO_2. When the thickness of simulated gas was fixed regularly, the bypass line valve was turned the switch to the reactor and actually the experiment was commenced. It is 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.[4)]

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

Components		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Igloss
Contents (%)	Clam	0.46	0.20	0.04	53.92	0.22	45.16
	JS	2.43	0.25	0.14	53.8	0.85	42.5

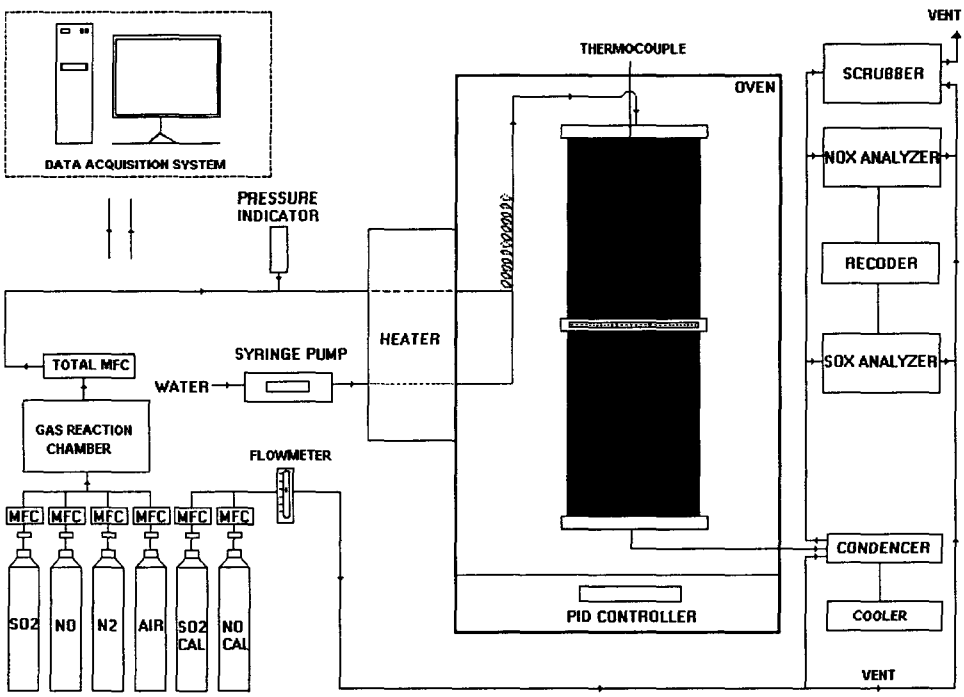

Fig. 1. Schematic diagram of experimental apparatus

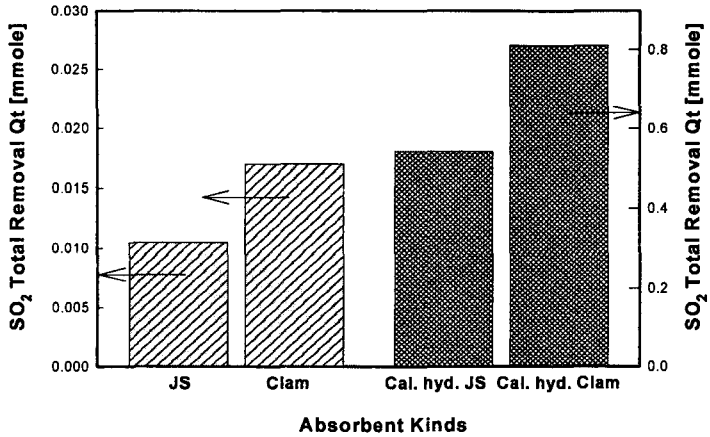

Fig. 2. Total removal quantities of SO_2 according to fresh and advanced sorbent.

Results and Discussion

The composition of the clam and JS limestone analyzed by KIRCT is shown Table 1. Clam can be used as iron-manufacture and chemical sorbents considering more than 53.92% of the clam is lime content. Comparing the results of XRD and EDAX with Table 1, the clam can be utilized as FGD process sorbent. Fig. 2 and Fig. 3 show removal quantities of SO_2 and NO according to clam making type. In general, low sulfur coal of 1.5% discharged a power plant was released SO_2 of 1800~1900 ppm, O_2 of 6%, CO_2 of 13%, N_2 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%, SO_2 concentration of 1800 ppm, NO concentration of 250 ppm, reaction temperature of 150℃, gas flow of 3 L/min. The specific surface area, pore volume, pore size distribution greatly influenced in the SO_2 and NOx removal reactivity. The SO_2/NOx removal quantities and sorbent capacity were increased the clam after calcinations/hydration.

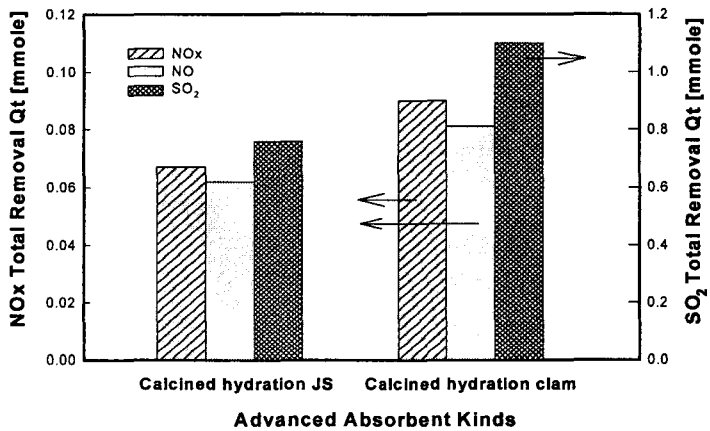

Fig. 3. Total removal quantities of SO_2 and NOx according to advanced sorbent kinds.

Conclusion

Instrumental analysis of physicochemical properties and De-SOx/De-NOx reactivity of clam have been carried out to develop the efficient clam-based sorbent for commercial flue gas treatment processes. It should be also noted that sulfation reactivity of clam-based sorbent increases by calcination/hydration reaction due to the increase of specific surface area and pore volume. From these experiments, it can be concluded that clam is good sorbent for the removal of SO_2/NOx and thus it could be used as a sorbent in waste incinerator and flue gas desulfurization processes. Therefore, the recycled clam as a substitute of limestone would be profitable. Also, we can conclude that clam can be used as a high level sorbent for the control of SO_2 and NOx gas removal.

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