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Reuse of Waste Shells as a SO₂/NO_x Removal Sorbent

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1. Introduction

Lately, many environmental pollution problems are taking place due to advancement of science and technology, enhancement of industry, rapid economic development, change of life style, and population increase. Not only in Korea but also worldwide consciousness of crisis over environmental pollution problems is spreading and especially countermeasures to solve the environmental pollution come into the limelight as concerns of the entire globe beyond any regions and nations. In the past, environmental pollutions including abnormal weather changes, global warming, El Nino, Ra Nina, ozone layer destruction, and marine pollution were issues of a limited area, but now they appear in fact as issues of the entire globe [Jung, 1999, 2008].

In the southern coast of Korea, a lot of oyster shells are dumped as a by-product of marine aquaculture industry. A large amount of oyster shells is a general waste fishermen should take care of but it seems difficult to handle it effectively due to the problems of securing of landfill sites and collection/transportation of oyster shells [Jung, 2005, 2007]. This waste piles up at coastal areas and causes many environmental problems including pollution of coastal fisheries, management problem of public water surface, damage of natural landscape, and health/sanitation problem.

In Japan, 200,000 tons of oysters were produced in 2007 [Asaoka et al., 2009]. And Table 1 shows oyster production of Korea from 1997 to 2006. On the basis of these data, generation of oyster shells is estimated on the average at 270,000 tons/year [Kim, 2007], and more than 50~70% of which was dumped into public waters and reclaimed lands, which cause an unpleasant fishy smell as a consequence of the decomposition of fresh remnant attached to oysters (Kim, 2007; Yoon et al., 2003; Shin et al., 1998). Approximately 30~50% of shells from harvested oysters was utilized and the remainder was disposed (Yoon et al., 2003; Kwon et al., 2004). Thus, recycling of waste oyster-shells has arisen as an imminent issue in the mariculture industry. As a recycling process, a lot of studies on the application of waste oyster-shells to construction materials (Yoon et al., 2003), laver farming, fertilizer (Nippon

Steel Corp., 1993), sludge conditioners (Lee et al., 2001), eutrophication control (Kwon et al., 2004), filtering medium (Park and Polprasert, 2008), catalyst (Nakatani et al., 2009), soil conditioner (Lee et al., 2008a,b), and desulphurization sorbents (Jung et al., 2000) have been reported. The desulphurization system can be divided into three groups such as dry adsorption (Garea et al., 2001), wet scrubbing (Chu et al., 1997), and wet/dry system (O’Dowd et al., 1994).

Year	Oyster Production(ton)	Estimated Generation of Oyster Shells(ton)
1997	17,210	258,150
1998	9,905	148,575
1999	11,690	175,350
2000	15,939	239,085
2001	10,056	150,840
2002	7,950	119,250
2003	20,201	303,015
2004	25,690	385,350
2005	27,320	409,800
2006	31,016	465,240

Table 1. Oyster production and estimated generation of oyster shells in Korea.

The research on application of oyster shells to a sorbent for incineration and desulfurization is judged to be very helpful in preserving marine eco-system, preventing the damage of natural landscape and solving health/sanitation problem. Therefore, new applications utilizing these wasted oyster shells are expected to contribute towards recycling consciousness within the society [Asaoka et al., 2009]. The application of many kinds of waste shells, which have been dried, crushed and calcined, to sorption of acidic gases and nitrogen oxides is not only economically valuable but also very significant in the aspect of waste recycling. In addition, considering that chlorine which has been found to be a precursor of such toxic organic substances as dioxin and furan lately creating social concerns is an acidic gas, the use of waste shells as mixed sorbents is judged to be feasible.

In this research, we are going to provide a basic data to a process for removing both sulfur oxides and nitrogen oxides at the same time from exhaust gases. For this purpose, first of all, the basic physical and chemical properties of waste oyster shells were investigated. In addition, the calcination and hydration reaction of waste oyster shells were experimented and the preparation method of sorbents was investigated. In order to investigate the feasibility of using oyster shells as a sorbent for removal of sulfur and nitrogen oxides, the performance of prepared sorbents was compared for understanding reaction characteristics using a fixed bed reactor.

2. Environmental problems of oyster shells and utilization plans for each field

2.1 Environmental problems caused by oyster shells

Environmental problems caused by waste oyster shells were as follows [Kim, 2007]; i) increase of waste, ii) pollution of marine eco-system due to illegal landfill, iii) increase of

bad smell due to negligence, iv) a huge amount of treatment expense, and v) weak demand on recycled materials (fertilizer, etc.) from oyster shells. Fig. 1 shows the generation process of waste oyster shells. Oyster meat is consumed and a significant amount of waste oyster shell is discarded.

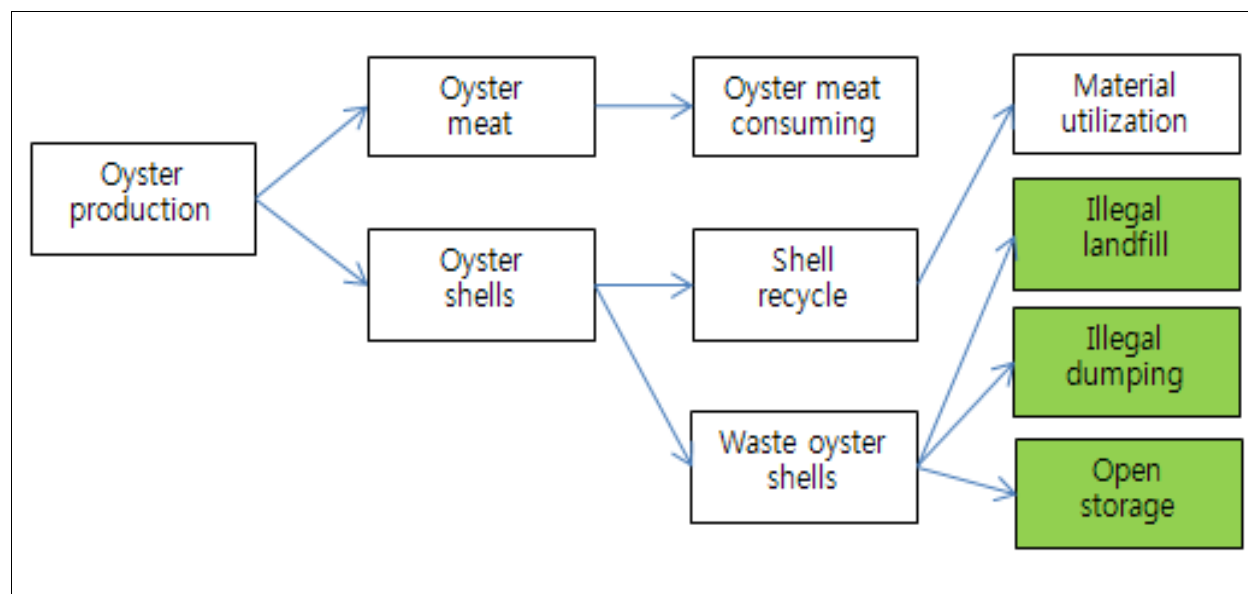


Fig. 1. Generation steps of the waste oyster shells.

2.2 Recycling plan of oyster shells on the aspect of environmental engineering

Environmental engineering research on recycling of oyster shells has been somewhat conducted in China and Japan, but most of the research has focused on the purpose of water purification in a limited scope [Kim, 2007].

2.2.1 Removal of air pollutants (SO₂, H₂S, CO₂, HCl, NO_x, etc.) from the exhaust gases

- As a desulfurization sorbents of power plants, the oyster shell is more efficient and less expensive than limestone and so its commercialization is judged to highly feasible.
- The oyster shell used in the desulfurization process exhibits a high efficiency without calcination processing.
- The treatment problem of calcium sulfate formed after the reaction should be resolved, and the cost involved in calcination should be estimated.

2.2.2 Soil improvement (acidity reduction, organics adsorption) and adsorption of heavy metals

- In case oyster shell is used as a soil conditioner, it has higher adsorption and desorption of heavy metals than general soil, and so it may bring in stable and economical effects.
- Injection of calcined and processed oyster shells would be very effective in growing plants due to increased exchange capacity of cations used by plants.
- The potential risk cannot be evaluated without long-term research and the effect on plant growth should be reviewed.

2.2.3 Application to waste water treatment (nitrogen, phosphorous, heavy metals, pH neutralization, etc.)

- The oyster shell can neutralize acidic waste water from mines very fast and remove 99% of heavy metals, and so it is judged to be a useful material to replace limestone.
- A plan for the secondary treatment after adsorption of heavy metals should be prepared.

2.2.4 Improvement of sludge dehydration capacity (digested sludge etc.)

- Dehydration capacity of the digested sludge is about the same as that of the existing limestone, which suggests that the oyster shell may be an inexpensive substitute.
- In case of dehydration of waste water sludge, injection of oyster shell/slaked lime mixture reduces the required dehydration time.

2.2.5 Others (calcination, red tide, coagulation, fertilizer, etc.)

- Oyster shell powder can coagulate and remove red tide organism.

2.3 Recycling limitation

Recycling of waste oyster shells has much limitation in environmental engineering. First, the quantity of waste oyster shells is too much to be recycled in environmental engineering. Second, a plan to retreat the waste oyster shells contaminated after adsorption of heavy metals should be prepared above all. Third, recycling of waste oyster shells would require removal of impurities through proper processing and treatment through a calcination process, which decreases the economic feasibility. Fourth, the repeated use lowers the efficiency below commercial products.

3. The kind and characteristics of sorbents

It is well known that alkali sorbents such as CaO , CaCO_3 , Ca(OH)_2 , NaOH , Na_2CO_3 , NaHCO_3 , KOH , MgO , Mg(OH)_2 , dolomites, and dolomite limestones ($\text{CaCO}_3/\text{MgCO}_3$) are used to remove SO_2 and acid gases in the flue gas cleaning processes (Kunio et al., 1994; Jonas et al., 1984; Jung et al., 2000). Under these sorbents, calcium-based alkali sorbents are the most widely used to remove SO_2 . Because calcium-based sorbents have good reactivity toward acidic gases and lower cost compared to other sodium-based alkali adsorbent.

The sorbent should be selected in consideration of the most important factors, hygroscopicity and price. Sodium-based sorbents have better removal efficiency of pollutant gases but is more expensive than calcium-based sorbents. While calcium-based sorbents exhibit hygroscopicity, but sodium-based sorbents deliquescent. In Table 2, various sorbents frequently used in flue-gas desulfurization processes are compared and the physical properties of the sorbents are also described as a part of basic research to understand whether they are utilized in flue-gas desulfurization processes. In addition, in Table 3 the molecular weight, specific gravity, density, decomposition temperature, melting point, particle size, solubility, and maleficence of the sorbents frequently used in flue-gas desulfurization processes are presented.

Sorbent	Deliquescent	Hygroscopic	Application
NaOH	Yes	Yes	Spray Drying, Wet Scrubbing, Dry Scrubbing
Na ₂ CO ₃	Yes	Yes	Spray Drying
NaHCO ₃	Yes	Yes	Dry Scrubbing
CaCO ₃	No	Yes	Spray Drying, Wet Scrubbing, Dry Scrubbing
Ca(OH) ₂	No	Yes	Wet Scrubbing, Dry Scrubbing
CaO	No	Yes	Spray Drying, Wet Scrubbing, Dry Scrubbing
Waste oyster shells (WOS)	No	Yes	FGD absorbent

Table 2. Characteristics of selected sorbents.

Sorbent Description	CaCO ₃	CaO	Ca(OH) ₂	NaHCO ₃	Na ₂ CO ₃	NaOH
Molecular Weight	100	56.08	74.09	84	106	40
Specific Gravity	2,93	3.37	2.24	-	2.53	2.13
Bulk Density(ton/m ³)	1.11	-	1.7 ~ 2.3	-	2.08	-
Decomposition Temp.(°C)	898	-	580	-	-	-
Melting Point(°C)	-	2,572	-	-	851	318.4
Size of Particle(μm)	4 ~ 44	-	4 ~ 100	-	>100	-
Solubility(g/100cc , at 20°C)	0.0014	-	0.185	7.1	6.9	-
Impact of Human	low	low	low	low	low	large

Table 3. Characteristics of sorbents in FGD process.

4. Materials and methods

4.1 Physicochemical analysis of oyster shells

The seashells of oyster, hard-shelled mussel, clam, and seashell from Tong Young province around South Sea in Korea were used as a main material. Salts and other organic substances were removed by washing and drying the waste seashells. Limestone from Danyang and Jungsun province in Korea was adapted for comparison of physicochemical properties of oyster shells. All the materials were crushed 2 times by Jaw crusher and Ball mill after drying enough. The physical and chemical characteristics of the waste oyster shells were analyzed by ICP (ICPS-7500 Shimadzu, Japan), SEM (JEOL superprobe JSM-5400, USA), XRD (SIMENS, Deutsche), and BET surface area (Micromeritics Co., USA). ICP was applied to analyze the atomic properties of the materials. SEM was used to observe the microtissue of the surface of wasted shells. Surface area of the sorbents was measured by BET technique

after pretreating to remove vapor in vacuum 1×10^{-3} and 180°C for 2 hours. The crystal state of shell sorbent and the products before and after reaction was assured by X-ray diffractometer under the condition of 30 kV and 20 mA in the ranges of 10-70 degrees.

4.2 Hydration of oyster shells

Hydration apparatus was manufactured in order to investigate the effects of properties of calcination sorbent and hydration condition on the reactivity of the hydrated lime [EPRI, 1988]. The reactivity of calcined waste shell was compared with that of imported lime samples. Also, hydration state according to initial temperature was conformed. These were conducted by measuring the reactivity of quicklime. The samples were placed in a stirred vacuum flask containing deionized water and the temperature was measured at time intervals. Rate of heat release was a measure of reactivity. The faster temperature increases the faster the slaking rate. This method can be used in flasker design, to improve slaker performance, to evaluate and compare different limes, or test incoming lime shipments for quality control purposes.

It was calculated for the hydration speed to measure the hydrated reaction using the device of Fig.2 with calcinated shell sorbents suggested by EPRI(1988), respectively. This device was designed to react under same temperature according to the change of hydration condition and was consisted of Dewar flask wrapped dual rubber plate and a mixer made with teflon. K-type thermocouple (1/8", 30 cm) and a thermoscope were installed on the upper side of flask and conformed the variation of inner temperature.

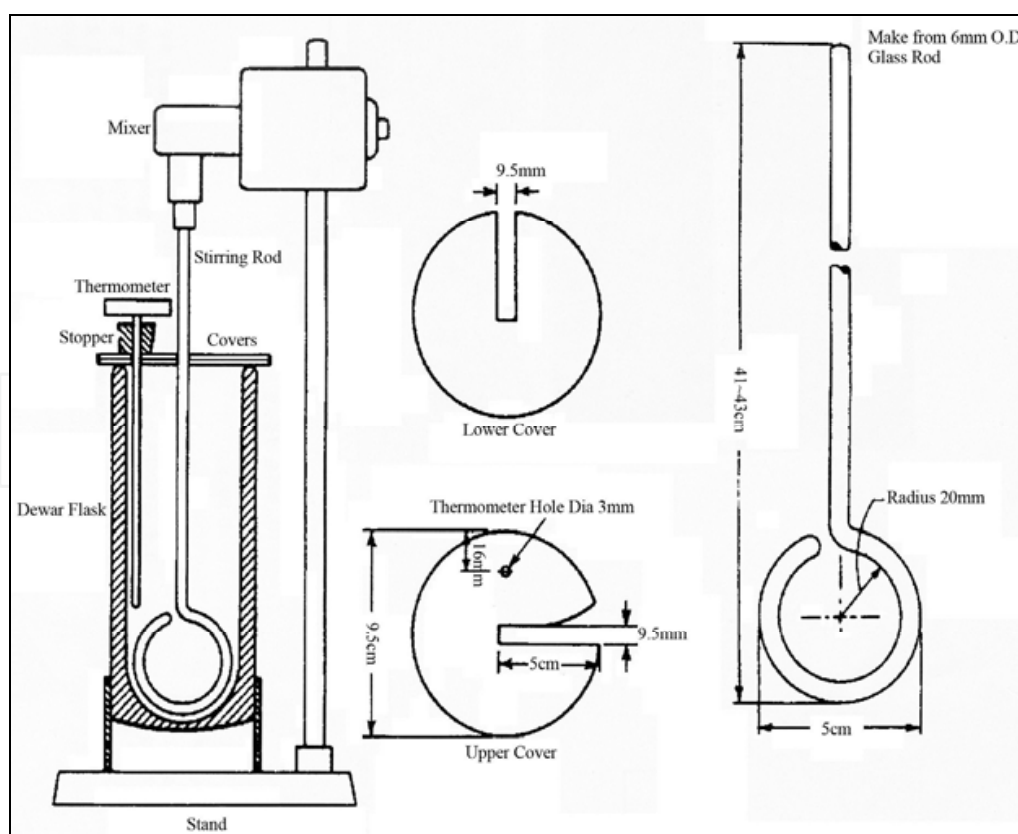


Fig. 2. Experimental apparatus for measuring the hydration rate of absorbents [EPRI, 1988].

In order to check hydration rate, the crushed seashell sieved with the degree of 6 mesh was adapted to calcination reaction. It was added 900 ml water of 25°C to Dewar flask. And a mixer was set to 400 rpm [EPRI, 1988]. After feeding of CaO (100 g), the data system was continuously operated to check the temperature variation in every 5 seconds.

As shown in Fig. 3, the reactor used to study the calcination reaction of oyster shells was made of 15 mm ID × 450 mm L quartz glass tube which is corrosion-resistant at high temperatures. The reactor was installed inside a tubular furnace insulated with ceramic wool to reduce heat loss from the inside to the outside and to maintain a constant and uniform temperature inside the electric furnace. The samples were injected where the temperature gradient of the measured reactor temperature was constant and the desired operating temperature was reached, and the flow rates were maintained constant at 2 l/min, 3 l/min, and 4 l/min (1 atm). In addition, the temperature (700 ~ 1000°C) and flow rate were varied to study the effect of calcination temperature on the BET specific surface area, and the experimental conditions are given in Table 4.

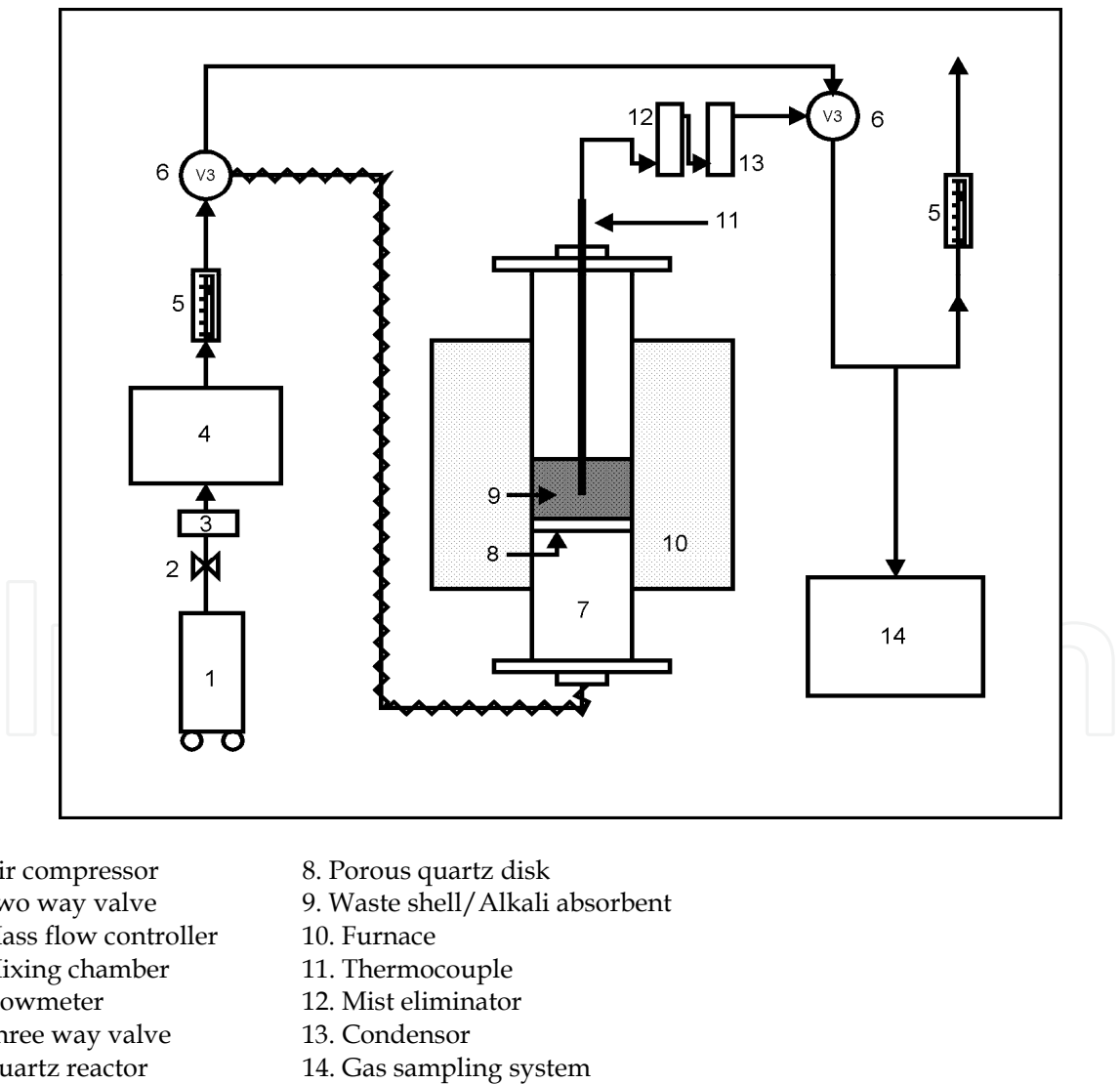


Fig. 3. Schematic diagram of the calcination apparatus.

Experimental variables		Conditions
Pretreating	Calcination temperature (°C)	700 ~ 1000
	Hydration time (hr)	24
	Hydration temperature (°C)	90
	Slurrying velocity (rpm)	200
	Absorbent drying time (hr)	24

Table 4. Pretreating and experimental conditions.

A thermo gravimetric analysis (TGA) was used to analyze the activation energy and calcination rates, and the experimental equipment was composed of a gas supply system, reactor system, and data treatment system. The specimen measurement dish of the analyzer was installed vertically inside the quartz tube reactor in the cylindrical electric furnace whose temperature can be raised up to 1,200°C. About 10 to 20 mg of 40/60 mesh crushed shells was placed on the dish and nitrogen gas was passed at a flow rate of 30 ml/min for 10 minutes through the analyzer to replace air with nitrogen in the reactor. A corrosion-resistant stainless pipe was used from the gas mixer to the entrance of the reactor, and the inside pressure of the reactor was maintained a little over the ambient pressure in the entire experiments. When the reaction conditions were stabilized, the reactor was heated to 900°C while nitrogen passed at a flow rate 30 ml/min. The reaction was judged to be completed in case of no further weight change during the heating period. The heating rate of the calcination reaction was 50°C/min over the temperature range of 100 to 600°C and 10°C/min over the range of 600 to 900°C.

4.3 Analysis of waste oyster shells as a SO₂/NO_x removal absorbent

To enhance the physicochemical properties of the waste oyster-shells, pretreating techniques were applied to the samples before SO₂/NO_x removal test. The goal of pretreating process was to convert the relatively low reactive calcium component (in the form of calcium carbonate) into a form of calcium oxide and calcium hydroxide that readily reacts with acid gases. These processing referred to calcinations and hydration, respectively.

To calculate the sorbents capacity, the SO₂/NO_x removal experiments were carried out using a fixed-bed reactor system (Jung et al., 2005) under atmospheric pressure at 150.0°C. The 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 the precision of ± 1.0°C. After the sample put on the reactor (1 g of samples) and the temperature was stabilized in N₂ flow, reacting gas containing SO₂, O₂, and NO_x was injected into the reactor using mass flow controllers (MFC, BROOKS instrument inc., Model 5850E, England). At the same time water was also injected to the reactor by syringe pump to keep a steady vapor concentration in the simulated gas. Hygrometer and SO₂/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. Table 5 shows experimental variables and experimental conditions [Jung, 1999; Jung et al, 2005, 2009].

Experimental variables		Conditions
Gas reactivity	SO ₂ concentration (ppm)	1800
	NO _x concentration (ppm)	250
	O ₂ concentration (%)	6
	Reaction temperature (°C)	150
	Water content (%)	10

Table 5. Experimental variables and conditions.

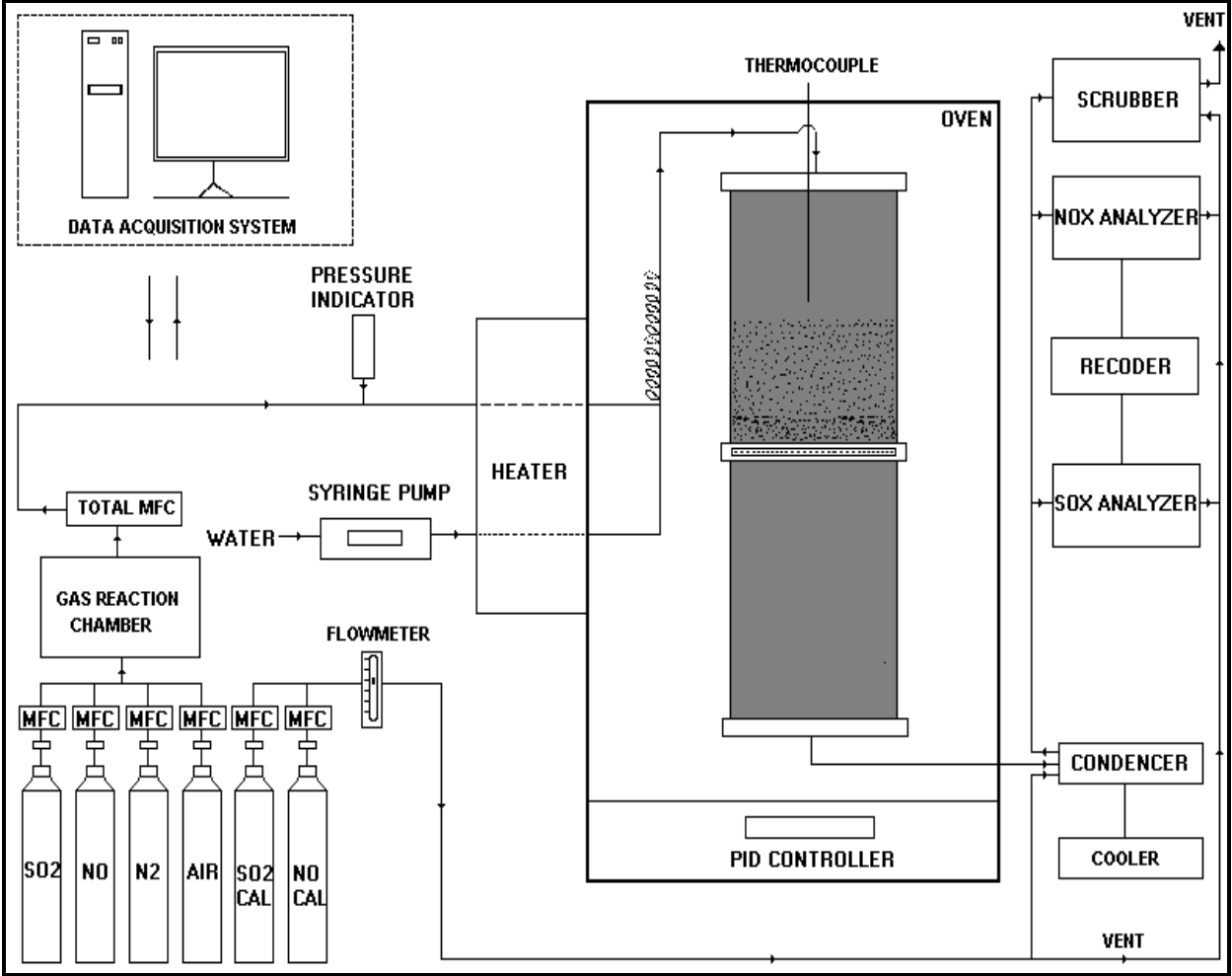


Fig. 4. Schematic diagram of packed-bed experimental apparatus.

5. Results and discussion

5.1 Physicochemical characteristics of oyster shells

The physicochemical compositions of the waste oyster shells, mussel, clam, seashell, and commercial Jungsun limestone were summarized in Table 6 [Jung et al., 2007, 2005, 2000; Kwon et al., 2003]. To perform XRF (X-ray fluorescence spectroscopic) analysis, samples were powdered after dehydrated in a drying oven at 105.0°C for 24 hours. From the composition analysis, it was found that oyster-shells consist of mostly CaO, some of SiO₂,

MgO, Al₂O₃, and Fe₂O₃. The composition of CaO in the oyster-shells was around 53.81 ~ 52.94 wt.% which is comparable to that of commercial Jungsun limestone and was in good agreement with the results of Yoon et al. (2003) reporting the CaO content of oyster-shells was about 53.7 wt.% [Jung et al., 2007, 2005, 2000].

X-ray diffraction (XRD) patterns of waste oyster shells, limestone, and calcined waste oyster shells (C-WOS) are shown in Fig. 5. Fig. 5 shows the results of XRD analyses of the waste oyster shells and limestone with and without calcination. The patterns for waste oyster-shells and limestone were nearly similar and the diffraction peaks of CaCO₃ as major phases are identified (Fig. 5a, 5b). The patterns for calcined waste oyster shells were exhibited peaks characteristics of CaO (Fig. 5c) [Jung et al, 2007]. And, the intensity of these peak increases with increasing the calcination temperature indicating CaO phase has been formed enough after calcination followed by hydration reaction. Comparing the results of Fig. 5 with Table 6, the waste oyster shells can be utilized as FGD absorbent [Jung et al, 2000].

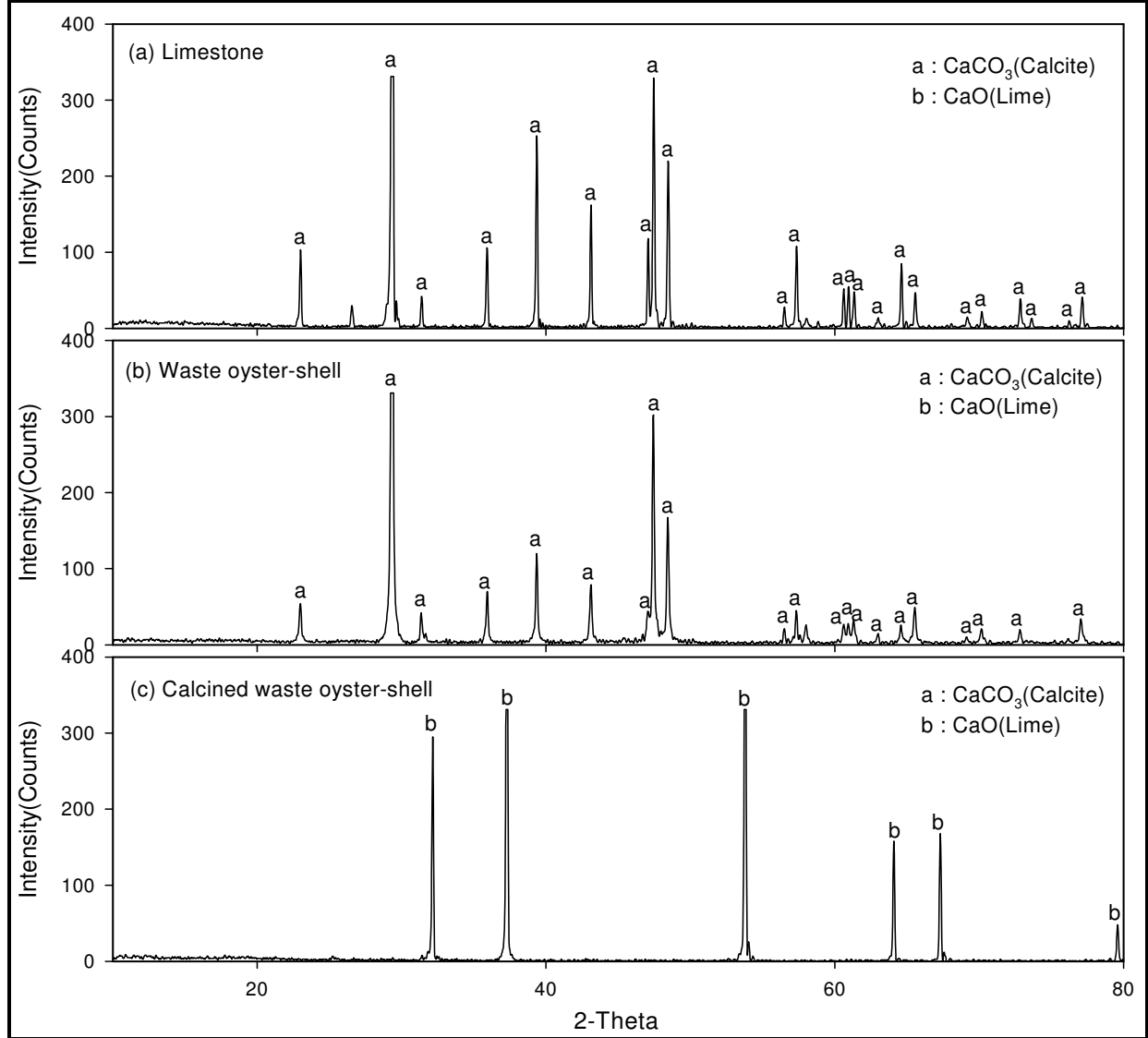


Fig. 5. XRD profiles of oyster-shells and limestone; (a) limestone, (b) oyster shells, and (c) calcined oyster shells.

Sorbents	Chemical composition [wt. %]						Pore volume [cc/g]
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Ignition Loss	
Waste oyster shells (WOS)	0.40	0.22	0.04	53.81	1.70	44.87	0.0869
	0.62	-	0.32	52.94	0.78	44.02	-
Mussel	0.20	0.13	0.03	53.70	0.33	45.61	0.0129
Clam	0.46	0.20	0.04	53.92	0.22	45.16	0.1025
Seashell	0.66	0.40	0.04	53.58	0.20	45.12	0.0888
Jungsun limestone	2.43	0.25	0.14	53.80	0.85	42.50	0.0697

Table 6. Physicochemical properties of tested absorbents and seashells [Jung et al, 2005].

5.2 Characteristics of calcination and hydration reaction with oyster shells

Fig. 6 shows the change of specific surface area of calcined hydration limestone. As shown in Fig. 6A, specific surface area of calcined hydration limestone particle increases rapidly with increasing hydration time up to 6 hours and then slowly increases to 12 m²/g. Effects of hydration temperature on the specific surface area of the calcined limestone has been shown in Fig. 6B. When the initial water temperature was in the range of 30~90°C with every 10°C, up to the 70°C BET surface area was not changed largely. However, rapid increase of BET surface area of absorbent appears above the temperature of 80°C, indicating the rapid hydration reaction occurs. We can conclude the optimum range of temperature and time for hydration reaction of absorbent is about 80~90°C and 24 hours, respectively [Jung et al, 2000].

Fig. 7A~B shows the adsorbed volume with relative pressure on the waste oyster shells and limestone. This figure shows the difference of amount of nitrogen gas according to the change of relative pressure absorbed to waste shell and limestone. We can conclude each of the sorbent shows a similar BET value in the condition of raw material.

Fig. 8 shows pore size distribution of waste oyster shells, clam, and seashell according to pore diameter. The results lead to the finding that shells have larger average pore size with the value of pore volume of 0.013~0.024 cm³/g, which is higher than that of limestone. And, other result is pore size distribution according to the change of pore diameter of oyster manufactured as an absorbent with calcination and hydration. It was appeared that the average pore diameter of oyster was much bigger than that of raw materials. This result also indicates that calcination and hydration processes can enhance the removal capacity of acid gases [Jung et al, 2005].

To clarify the effect of temperature, TGA analysis of the waste oyster shells and limestone were examined under N₂ atmosphere by Automatic Derivative Differential Thermo-balance (Fig. 9). Heating rate in the calcination, which was conversion from calcium carbonate to calcium oxide, was 10.0 °C/min in the temperature range of 600.0~ 900.0°C. As can be seen in Fig. 9, calcinations of the oyster-shells started at 645.0°C and completed at 780.0°C, whereas Jungsun limestone started over the temperature 680.0°C and completed at 845.0°C. The mass of waste oyster shells and limestone in the calcinations under N₂ atmosphere

decreased 44.8% and 44.0%, respectively. From this analysis, it could be confirmed that mass decreasing resulted from the reaction $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$. Also, in the case of Jungsun limestone, the temperature of the calcinations should be over about 850.0°C [Jung et al, 2007].

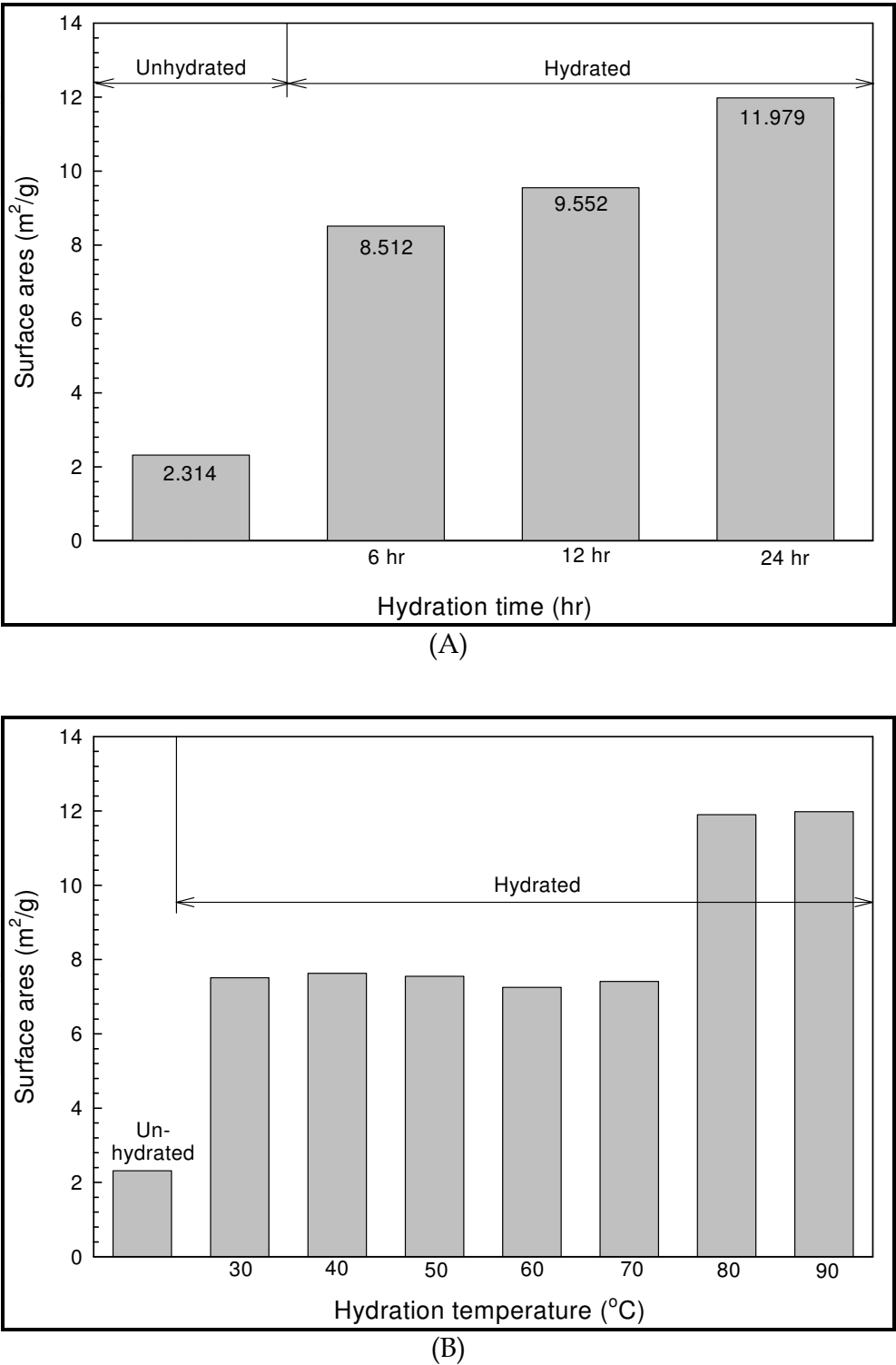
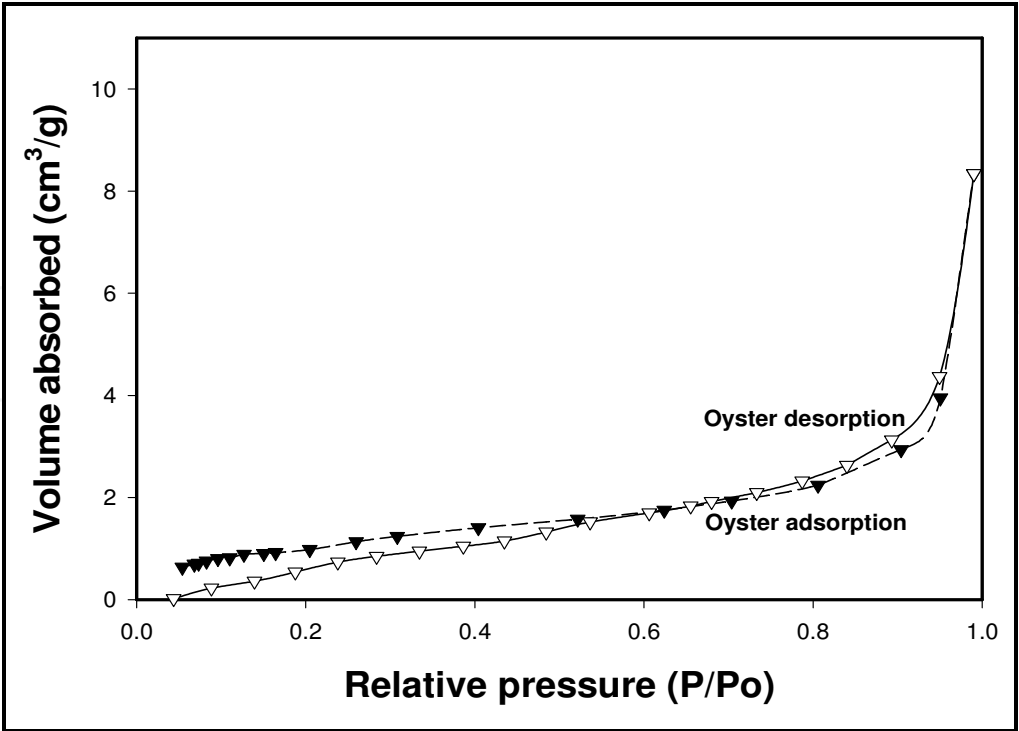
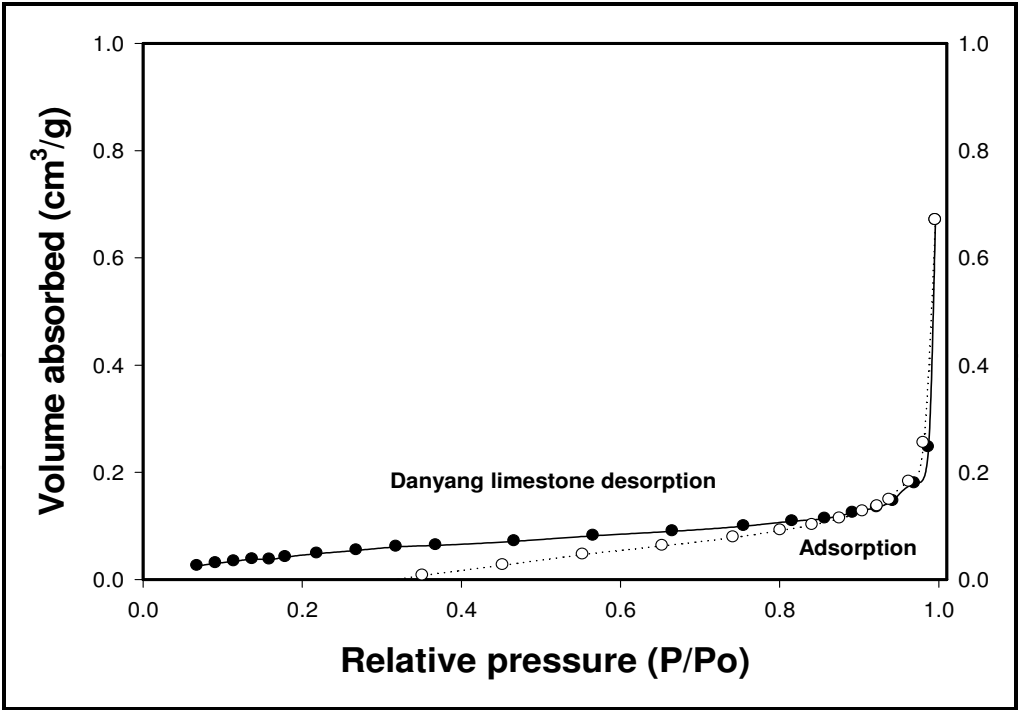


Fig. 6. (A) Variation of surface area of calcined limestone as a function of hydration time. (B) Effect of hydration temperature on the surface areas of calcined limestone.



(A)



(B)

Fig. 7. N₂ BET results of various waste oyster shells, seashell and limestone. (A) waste oyster shells, (B) limestone.

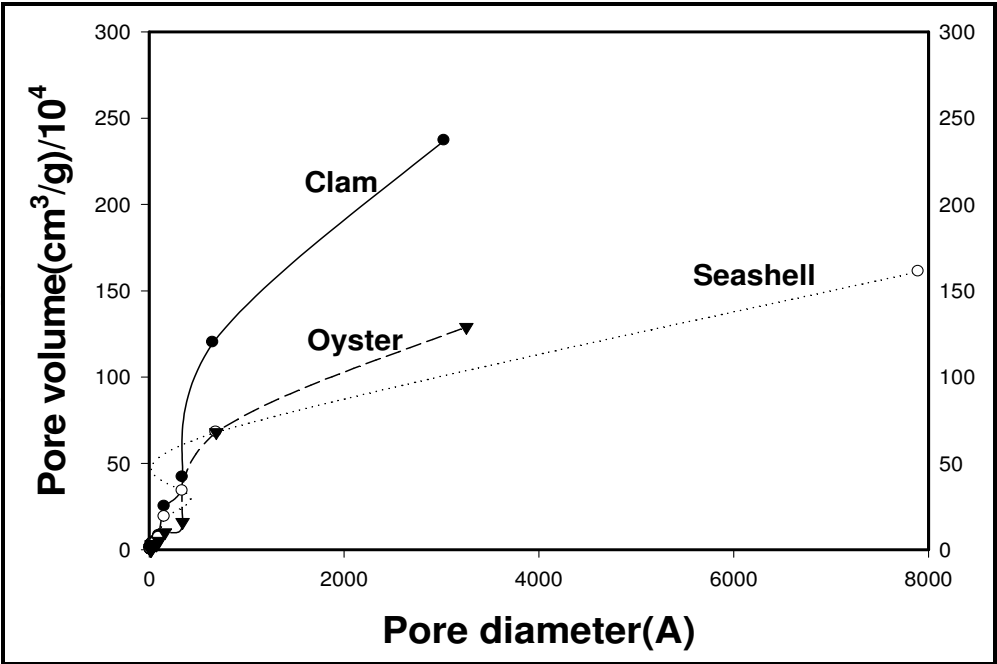


Fig. 8. Pore volume of waste oyster shells, seashell and limestone.

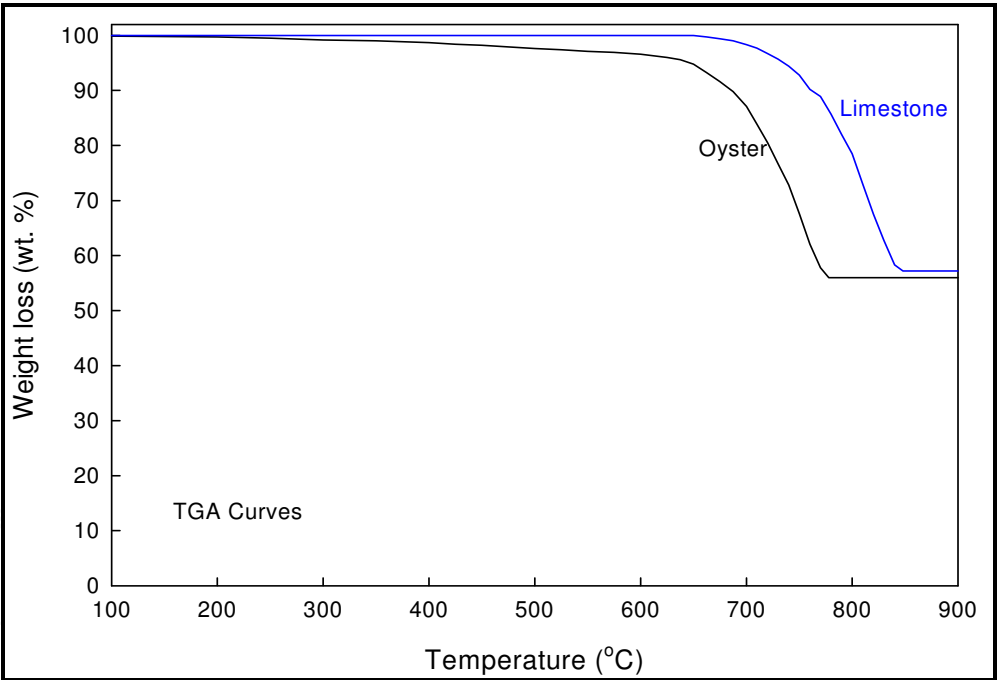


Fig. 9. TGA profiles of the waste oyster shells and limestone in the temperature range of 600 - 900°C.

The calcination reaction of waste oyster shells and limestone, main components is $\text{CaCO}_3(\text{s})$, is gas-solid reaction, in which we assumed that the calcinations reaction is n-order reaction. The activated energy and reaction order of waste oyster shells and limestone are calculated using the following equations and TGA experimental results. Where x =mass of waste oyster shells and limestone, k =reaction rate, X =conversion, n =reaction order, A =preexponential factor, E_a =activation energy, R =gas constant, T =absolute temperature.

$$\text{CaCO}_3(s) \xrightarrow{k} \text{CaO}(s) + \text{CO}_2(g)$$

(1)

$$\frac{dx}{dt} = k(1-X)^n$$

(2)

$$k = A \cdot \exp(-E_a/RT)$$

(3)

$$\frac{dx}{dt} = A \cdot \exp(-E_a/RT) (1-X)^n$$

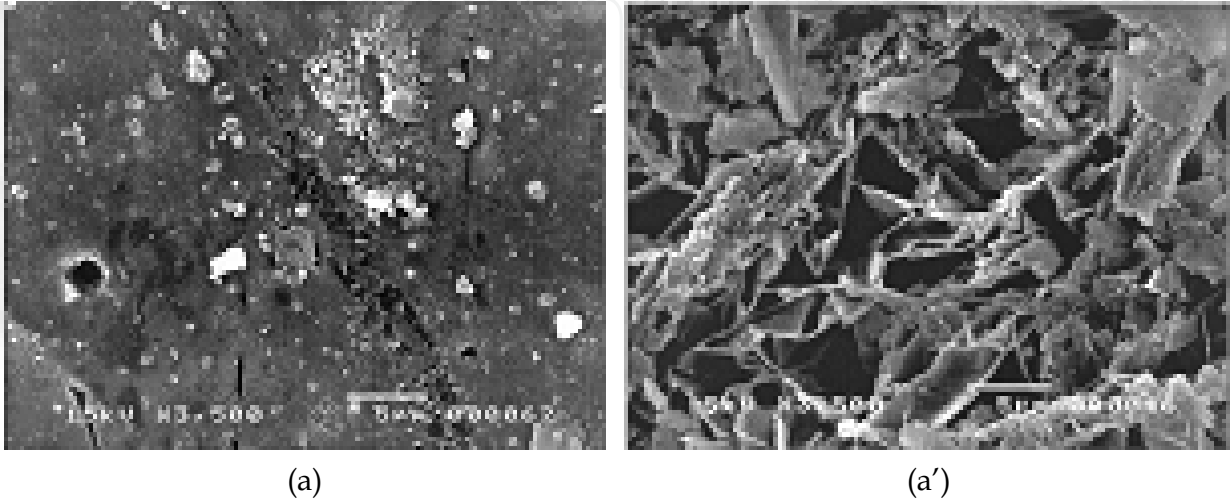
(4)

Table 7 shows kinetic data of the waste oyster shells and limestone. It was calculated from the results of calcinations experiment (Fig. 9). Activation energies, reaction constants, and reaction orders were 176±8.90 kJ/mole, 15.07±1.14 sec⁻¹, and 0.42±0.10 for oyster shells and 201.72±5.17 kJ/mole, 16.47±0.63 sec⁻¹, and 0.37±0.08 for Jungsun limestone, respectively. These values were similar to those of other calcium-based sorbents (Jung et al., 2000). The activation energy of the oyster shells was smaller than that of Jungsun limestone. As can be seen in Fig. 10, this is because structural elements of natural limestone is inorganic materials, whereas oyster shells was comprised of thin CaCO₃ layer and created by living things thus its surface was irregular and porous.

Absorbents	E _a [kJ/mole]	Order[n]	Sample wt.[mg]	Flow gas	Conditions
Waste oyster shells (WOS)	176.1±8.90	0.42±0.10	15 - 16	N ₂	Isothermal
Jungsun limestone	201.72±5.17	0.37±0.08	15 - 16	N ₂	Isothermal

Table 7. Kinetic data of tested absorbents.

Fig. 10 shows scanning electron micrographs (SEM) of the various solid Jungsun limestone and waste oyster shells. Parts (a), (a'), (b), and (b') of Fig. 10 show the scanning electron micrographs of the fresh and calcined samples, respectively. SEM pictures for the hydrated and calcined/hydrated samples are shown in Parts (c), (c'), (d), and (d') of Fig. 10, respectively. Observation of the waste oyster shells morphology indicates some agglomeration of the particle/grains in the hydrated waste oyster shells (H-WOS) as compared to the fresh oyster. However, as shown in Fig. 10(b'), in the SEM photograph of the calcined sample, enormous amount of agglomerations by sintering were observed.



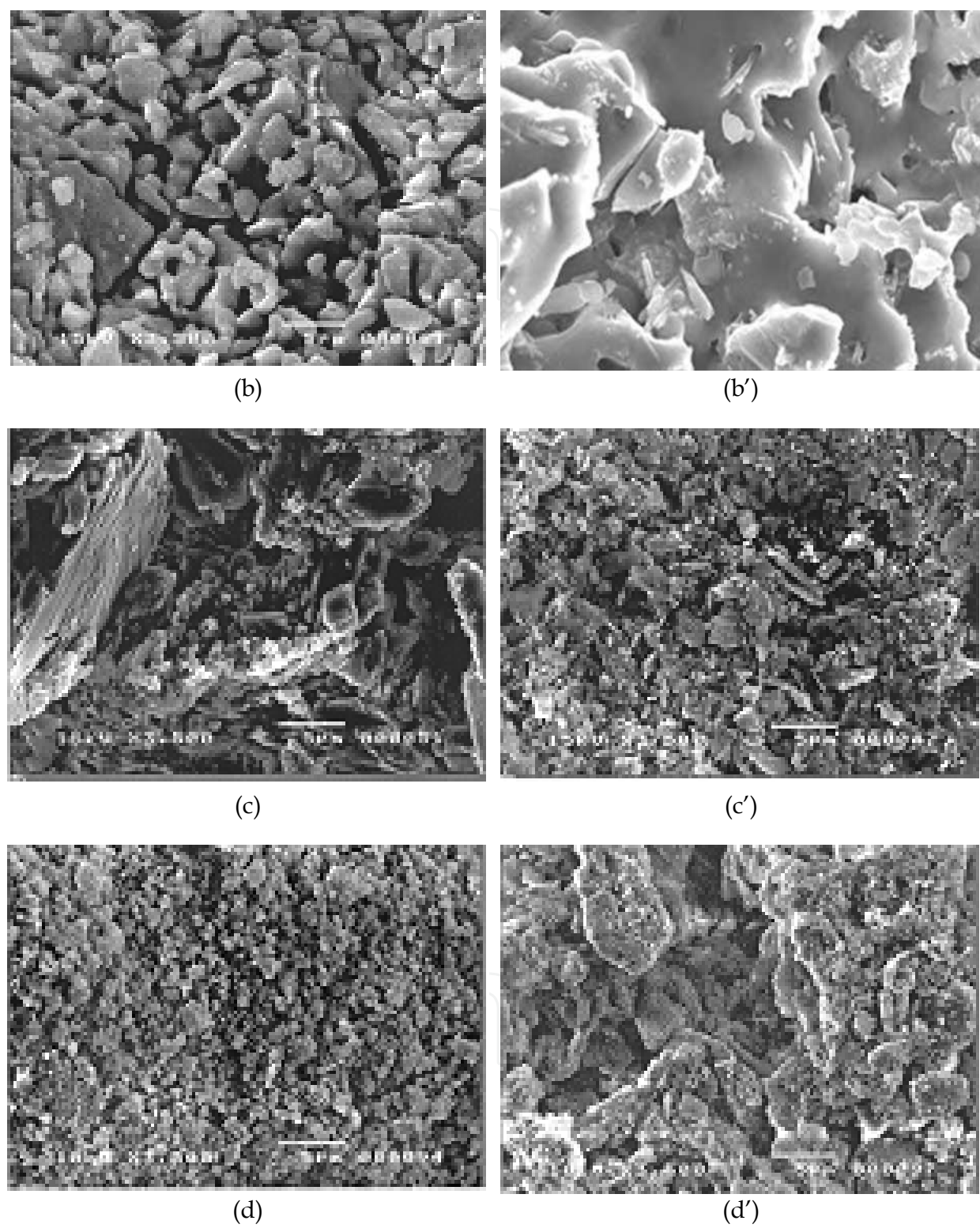


Fig. 10. SEM micrographs of limestone and oyster shells ; (a) fresh limestone, (a') fresh oyster shells, (b) calcined limestone at 850°C, (b') calcined oyster shells at 850°C, (c) hydrated limestone, (c') hydrated oyster shells, (d) hydrated limestone after calcinations, and (d') hydrated oyster shells after calcinations.

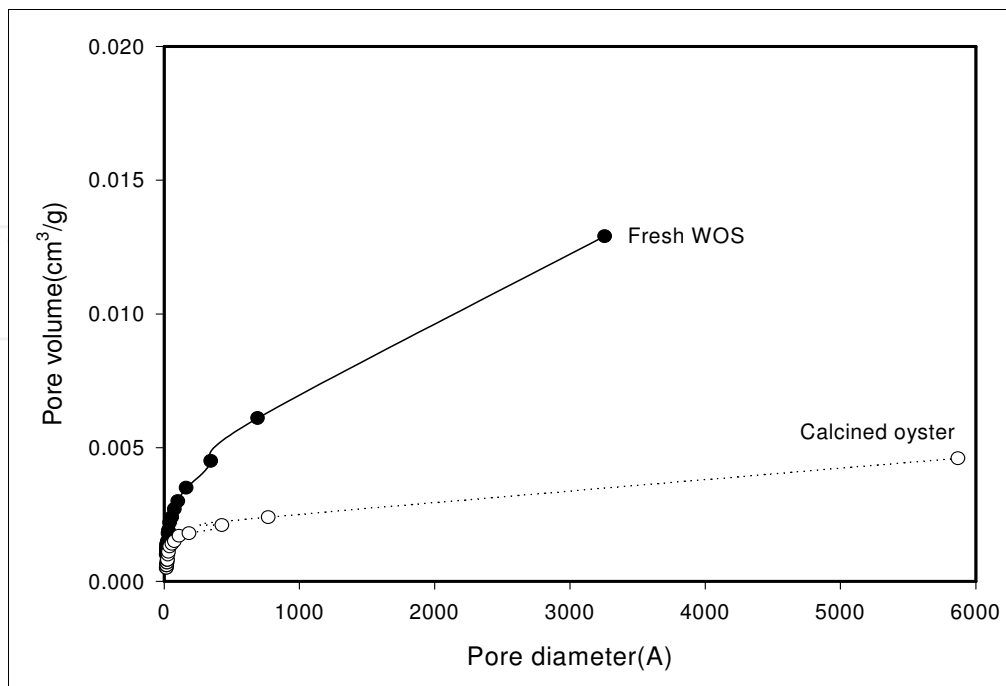


Fig. 11. Cumulative pore volume curves for two types of waste oyster shells as a function of pore diameter.

Fig. 11 shows pore volume with respect to pore diameter. The calcined oyster had a decreased pore volume relative to that of the fresh oyster. The specific surface area of oyster shells and limestone as a function of different calcination temperatures is shown in Fig. 12. The specific surface area of the oyster shell changed from 2.4465 m²/g before calcination to 2.3950 m²/g at 700.0°C, 2.2810 m²/g at 750.0°C, 2.2120 m²/g at 800.0°C, 2.1209 m²/g at 850.0°C, 1.9510 m²/g at 900.0°C, 1.8000 m²/g at 950.0°C, and 1.7000 m²/g at 1,000.0°C. The specific surface area of waste oyster shells was larger than that of calcined oyster shells and it was decreased with increasing calcination temperature. It is indicated that some agglomerations by sintering were blocking the specific surface area of calcined oyster shells. On the contrary, specific surface areas of limestone increased from 1.2368 m²/g before calcinations to 1.3100 m²/g at 700.0°C, 1.3200 m²/g at 750.0°C, 1.5100 m²/g at 800.0°C, 2.1544 m²/g at 850.0°C, 2.3205 m²/g at 900.0°C, 2.0210 m²/g at 950.0°C, and 1.2124 m²/g at 1,000.0°C. The specific surface area of limestone increased with increasing calcination temperature up to maximal 900.0°C and then a little decreased.

The specific surface area at 850.0°C was similar to that at 900.0°C. Therefore, we conclude that the calcination temperature had a positive effect on the development of the specific surface area for limestone, unlike waste oyster-shells. The change of surface area in oyster shells and limestone by processing (calcination/hydration) is shown in Fig. 13. As Fig. 13 shows, specific surface areas of oyster shells and limestone were changed from 2.4465 m²/g and 1.2368 m²/g before calcination/hydration to 12.9780 m²/g and 11.3380 m²/g by pretreating process, respectively. From this result, we could expect that the sulfating reactivity of oyster-shells sample increases to about 5 times by calcination/hydration reaction due to the increase of specific surface area and pore volume. Because of acid gas

removal capacity of absorbents was proportional to the specific surface area (Jung et al., 2005).

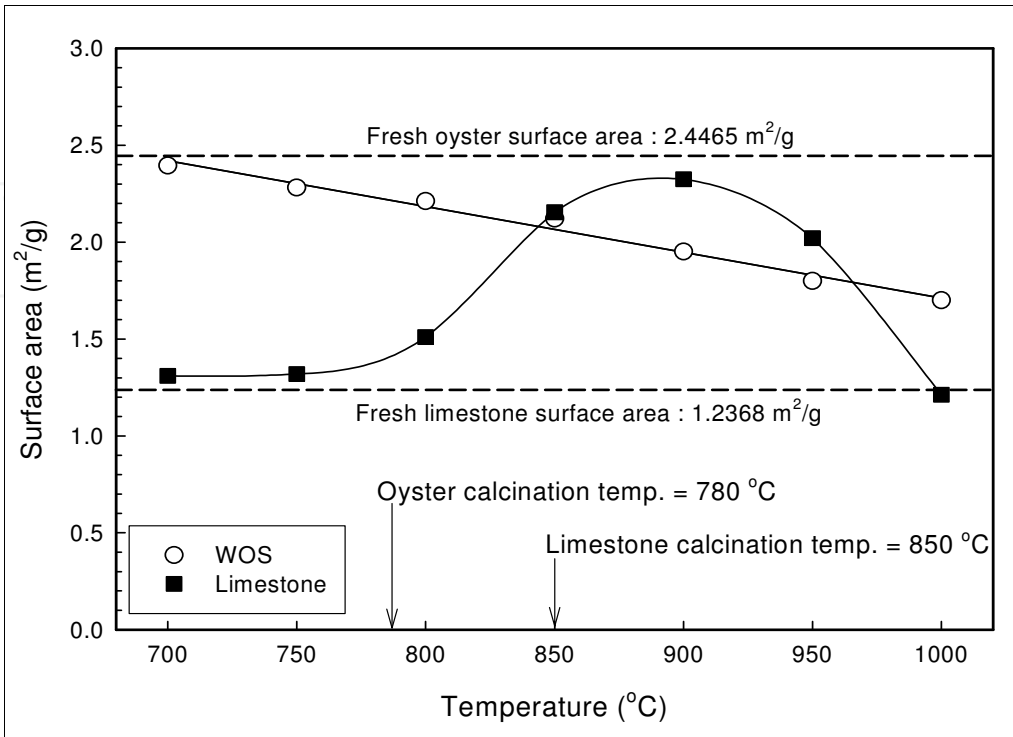


Fig. 12. Effect of calcinations temperature on the surface area.

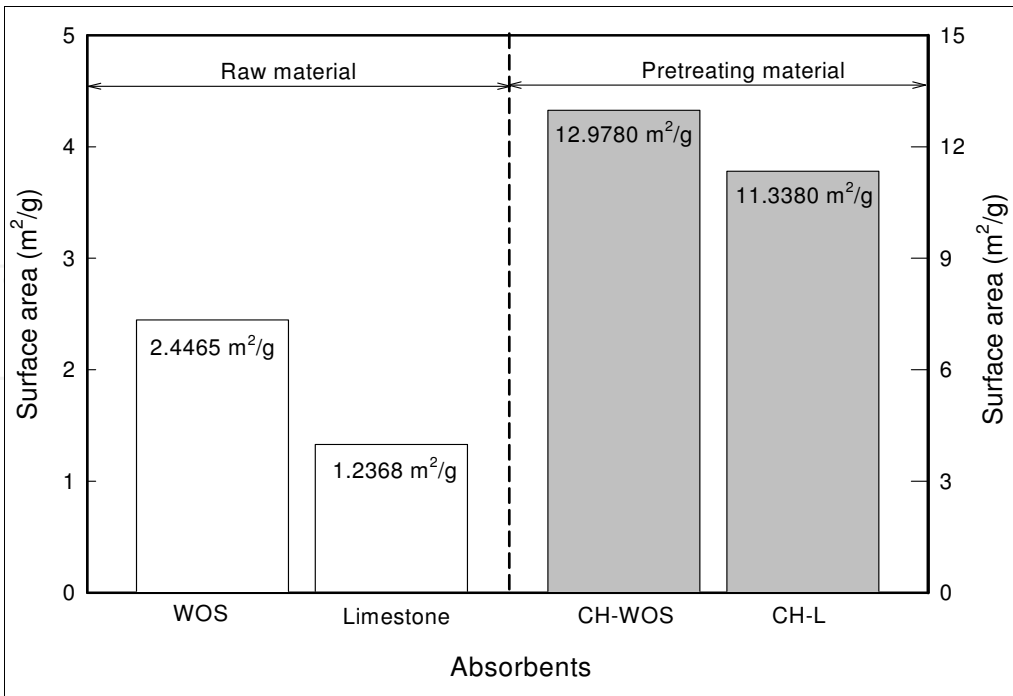


Fig. 13. Variation of surface area of oyster shells and limestone with and without pretreatment.

5.3 Characteristics of waste oyster shells as a SO₂/NO_x removal reaction

The desulfurization efficiency of the raw material was shown in Fig. 14. From a comparison of SO₂ removal quantities between waste oyster shells and limestone, the desulfurization capability of waste oyster shells was higher about 50% than that of Jungsun limestone. This means that the SO₂ removal capacity of oyster shells was superior to the limestone due to the specific surface area as can be seen in Fig. 13.

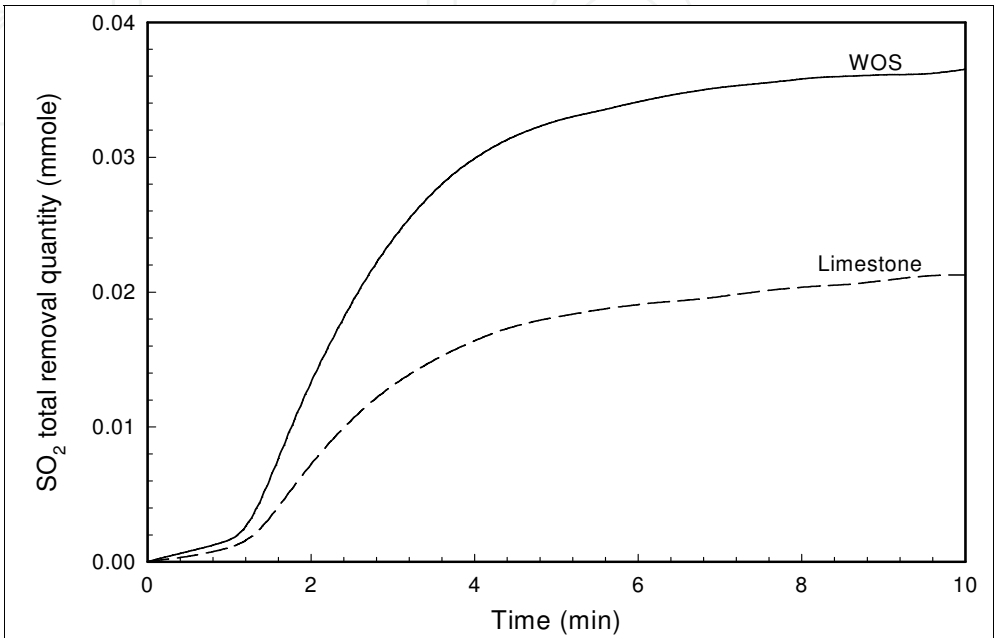


Fig. 14. Comparison of SO₂ removal quantities between waste oyster shells and limestone.

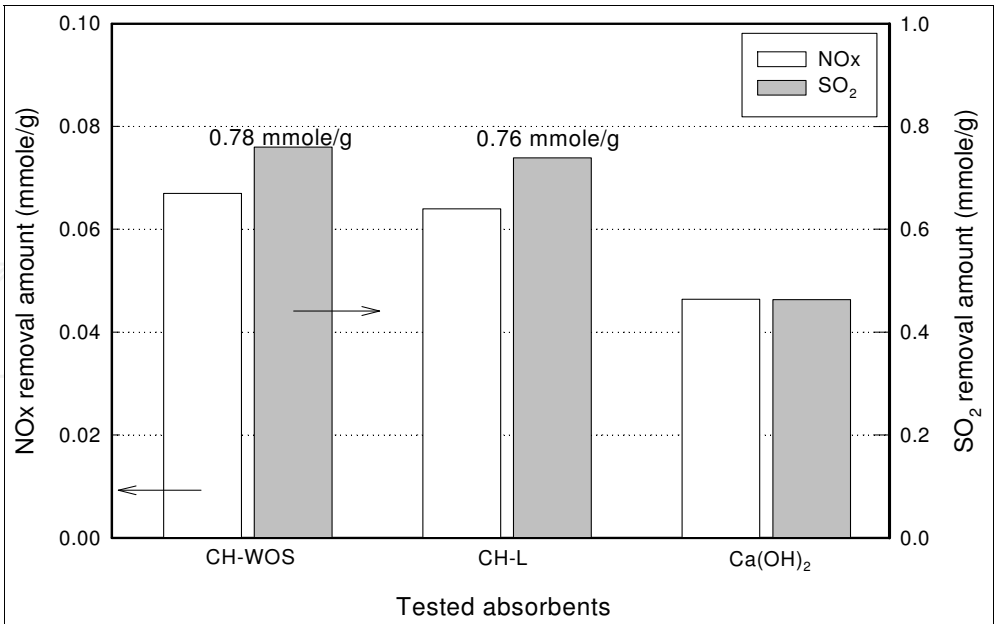
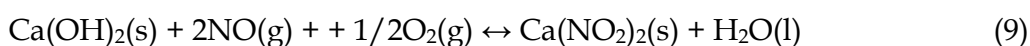
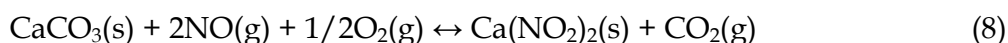
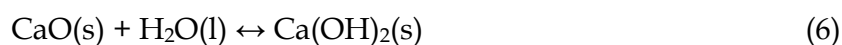


Fig. 15. SO₂/NO_x removal amounts of tested absorbents.

In general, a power plant discharges SO₂ of 1800 ~ 1900 ppm, O₂ of 6%, CO₂ of 13%, N₂ of 74%, water content of 10%, and NO of 600 ppm to the air during the combustion. The

SO₂/NO_x removal capacity of the calcined/hydrated limestone (CH-L) and calcined/hydrated waste oyster shells (CH-WOS) was carried out in a fixed bed reactor. As can be seen in Fig. 15, desulphurization capacity of the adsorbent was one order of magnitude higher than the denitrification capacity regardless of absorbent species. This is because the Henry's Law constant and diffusion coefficient in the gas phase for SO₂ is much higher than those for NO (Yuan, 1990). And, SO₂ and NO_x removal quantities of CH-WOS were higher just a little than that of CH-L. It can be inferred that waste oyster shells is a good sorbent for the removal of SO₂ and NO_x in the flue gas cleaning processes. The SO₂ and NO_x absorption mechanism on absorbent can be explained by combining equations listed below (Nakamura, 1995).



Removal of SO₂ (Ca(OH)₂ conversion ratio) in simulated flue gas by the CH-L and CH-WOS absorbents was examined under different reaction conditions to study effects of the coexistence of NO_x in a flue gas (Fig. 16). As depicted in Fig. 16, the reaction rate of desulphurization by CH-WOS increased about 30% higher than that of CH-L. In addition, SO₂ removal activity was enhanced in the presence of NO_x, which might be due to its oxidizer role of SO₂ (Tsuchiai et al., 1996).

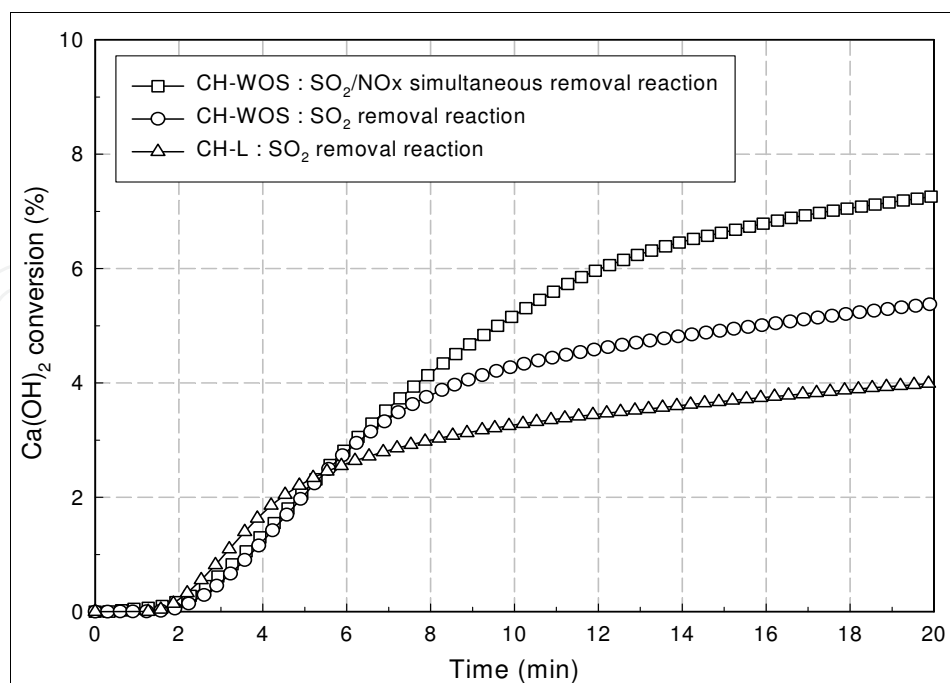


Fig. 16. Ca(OH)₂ conversions by SO₂ and SO₂/NO_x reaction for limestone and waste oyster shells.

6. Conclusions

Enormous amount of waste oyster-shells were dumped into public waters and landfills, which cause a bad smell as a consequence of the decomposition of organics attached to the shells. Also, marine pollution by waste oyster shells has become one of the serious problems in mariculture industry in Korea. The present study has conducted to develop a means of converting waste oyster shells into useful absorbent for removal SO₂/NO_x from industry. In this study, feasibility of waste seashell as absorbents for the control of air pollution has been investigated in a fixed bed reactor. To seek for a feasibility to recycle the waste oyster shells as desulfurization/denitrification sorbent, pretreating experiments and SO₂/NO_x removal activity were investigated. Physicochemical properties of waste oyster shells have been characterized using the XRD, SEM, and BET.

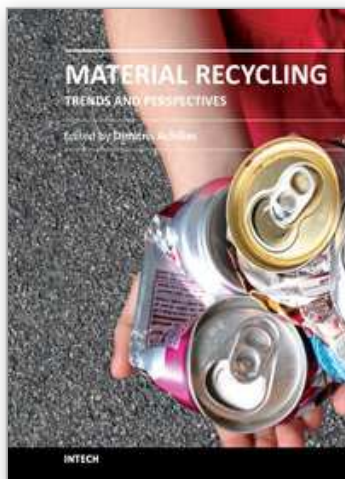
By pretreating process, such as calcinations and hydration, the specific surface area and pore volume of waste oyster-shell were increased than that of the fresh particles, which makes it possible to enhance the removal capacity in acid gases. XRD analysis of calcined waste oyster shells were exhibited peaks characteristic of calcium oxide, whereas raw waste oyster-shells showed that the main peaks were characteristic of calcium carbonate.

And it was concluded that the optimal temperatures for calcination and hydration were 800.0 ~ 850.0°C and 90.0°C respectively. Pores of absorbent are formed by the emission of CO₂ during the high temperature calcination but it was agglomerated by sintering. Therefore, the specific surface area decreased and it was completely different from limestone. SO₂/NO_x removal experiments have been carried out to test the reactivity of absorbents in a fixed bed reactor. SO₂ removal activity and reaction rate of calcined/hydrated waste oyster-shells were higher than that of calcined/hydrated limestone. It is clearly indicated that absorbent prepared by waste oyster-shells are substituted for commercial limestone and can be directly applied to industries which try to reduce their emissions of SO₂ and NO_x.

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Material Recycling - Trends and Perspectives

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The presently common practice of wastes' land-filling is undesirable due to legislation pressures, rising costs and the poor biodegradability of commonly used materials. Therefore, recycling seems to be the best solution. The purpose of this book is to present the state-of-the-art for the recycling methods of several materials, as well as to propose potential uses of the recycled products. It targets professionals, recycling companies, researchers, academics and graduate students in the fields of waste management and polymer recycling in addition to chemical engineering, mechanical engineering, chemistry and physics. This book comprises 16 chapters covering areas such as, polymer recycling using chemical, thermo-chemical (pyrolysis) or mechanical methods, recycling of waste tires, pharmaceutical packaging and hardwood kraft pulp and potential uses of recycled wastes.

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