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Oyster Shell waste is alternative sources for Calcium carbonate ($CaCO_3$) instead of Natural limestone

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Abstract

In this paper, we investigated the alternative sources of limestone. Oyster shell waste originated from aquaculture that causes a major disposal landfill problem in coastal sectors in southeast Korea. Their inadequate disposal causes a significant environmental problems araised. Bio mineralization leads to the formation of oyster shells and consists $CaCO_3$ as a major phase with a small amount of organic matter. It is a good alternative material source instead of natural lime stone. The utilization of oyster shell waste for industrial applications instead of natural limestone is major advantage for conservation of natural limestone. The present work describes the limestone and oyster shells hydraulic activity and chemical composition and characteristics are most similar for utilization of oyster shell waste instead of natural limestone

Key words : Oyster Shell Waste, Calcium Carbonate, Coffee Waste, Mineral Filler.

1. Introduction

Among the various waste shells of shellfish, oyster shells are the most predominant. Oyster waste shells are produced 275,490 tons in year 2004 [1], 70 % of which were dumped into the waters and reclaimed lands, causing a foul odor [2]. During the year 2007, in Japan, 200,000 tons of oysters were generated [3], and Korea's oyster shells production from 1997 to 2006 was shown in Table-1. The estimation of oyster shell waste were 270,000 tons/year based on these data [4- 6].

The solution of this problem is recycling of shell waste and it can be a good alternative to disposal. de Alvarenga et al. [7] conducted a Life Cycle Assessment (LCA) of oysters produced in southern Brazil. There were two scenarios were considered; one is disposal in landfills and the second one is use as raw material. In order to prevent the amount of shell waste, utilization of shell waste and developing wide applications is the great solution. However, upto now, the oyster shell waste uses have been limited and required more recycling pathways for preventing shell waste and reduce the environmental problems.

The total harvested oysters were utilized maximum 50% and remaining shell waste was disposed in nature [8]. Particularly, oyster-shells waste recycling is a significant issue in the aquaculture industry. A number of studies revealed that, the recycled waste oyster-shells were used in construction materials [2], laver farming, fertilizer [9], sludge conditioners [10], eutrophication control [8], filtering medium [11], catalyst [12], soil conditioner [13, 14], and desulphurization sorbents [15] have been reported. The desulphurization process can be consists three types i. dry

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Table 1. Oyster production and estimated generation of oyster shells in Korea [4]

Year	Oyster Production (Ton)	Estimated Generation of Oyster Shells (Ton)
1997	17210	258150
1998	9905	148575
1999	11690	175350
2000	15939	239085
2001	10056	150840
2002	7950	119250
2003	20201	303015
2004	25690	385350
2005	27320	409800
2006	31016	465240

adsorption [16], ii.wet scrubbing [17], and iii. Wet/dry system [18]. The great utilization of these oyster shell waste was neutralize the acidic ocean water, waste water from mines and also it can remove heavy metals (99%), so it is considered as alternative material to replace limestone.

In China and Japan, partial research conducted on recycling of oyster shells in environmental engineering departments, with the purpose of water purification [4]. Oyster shell has higher capacity adsorption of heavy metals than normal soil, and it used as a soil conditioner, with economy.

Lime stone with a purity of more than 90wt % $CaCO_3$ is used as adsorbent for waste water treatment, similarly Oyster shells also consists 90 to 95 wt% $CaCO_3$, in a similar way to natural lime stone and this material shows an excellent alkalinity properties for waste water treatment. In general, the oyster shell contains, approximately 90% Calcite and 10% Aragonite [19]. Limestone and oyster shells waste chemical composition almost similar and total content of calcite and aragonite was abundant.

The pure aragonite precipitated calcium carbonate (APCC) can be synthesized from oyster shell waste by carbonation process and it was used as filler for improving mechanical properties in plastics and paper industries. Li et al [20, 21] reported elongation at break point, yield strength, higher yield strain, tensile strength of polypropylene (PP) composites filled with bio-aragonite, as compared with commercial $CaCO_3$. de Melo et al [22] found that the incorporation of mollusc shell waste could enhances the degree of stiffness and crystallinity of high-density polyethylene (HDPE).

The main aim of this work is to measure the hydraulic activity of oyster shell and compared to natural limestone. It has high hydraulic activity and utilizing as an anti-microbial agent and filler for paper recycling. Therefore, oyster shell waste new applications are achieved as similar to natural lime stone.

2. EXPERIMENTAL PROCEDURE

Oyster shell waste collected from in coastal region near in Namhae, South Korea, and these shells were pretreated with alcohol and water to remove any impurities attached to the surfaces. The pretreated oyster shells and natural limestone was calcined in an electric furnace at various different temperatures from 900 to 1200 ^{o}C for 2h, which was increased to this point at a rate of 10 ^{o}C/min. The calcined raw materials were grinded for 1h until the particle size was less than 100μm. The fine powder was characterized by XRD analysis and also measured hydraulic activity of both calcinated limestone and oyster shell waste.

In hydraulic activity measuring process, 30g of quick lime sample from limestone/oyster shells was placed in the heat measuring apparatus for agitation. After 20 minutes of running the agitator, time and temperature shall be recorded to 0.01°C using the Beckmann thermometer. The change in temperature within the heat measuring apparatus during agitation shall be 25 °C. Distilled water shall be added to the reactor at a constant rate through the funnel. The amount of distilled water shall be 120 mL, and have a temperature of 25± 2 °C. The temperature inside the calorimeter shall be measured at 5-second intervals upon addition of the distilled water. Heat produced from hydration reactions of quicklime from oyster shells shall be measured for 2 h after reactions begin.

3. RESULTS AND DISCUSSION

3.1. Limestone and Oyster shell waste chemical composition

Limestone & oyster shells major composition is $CaCO_3$ are present, remaining other impurities, X-ray Fluorescence spectroscopic (XRF) results shows in Table 2, presents the chemical composition, it was found that similar composition of CaO from limestone (55.54%) and oyster shells (53-55%) was consisted and the Ignition loss nearly 44% in both limestone and oyster shells. The oysters containing $CaCO_3$ was decomposed and to release CO_2 gas by calcination.

We examine the calcination characteristics of limestone. The calcined limestone brightness gradually increase up to 1000°C and after that slightly decreased as shown in Fig.1. Natural limestone was calcinated at different temperatures (900-1200 °C).

To examine the calcination characteristics of oyster shell waste. These calcinated oyster shells brightness gradually increase up to 1200°C. Waste oyster shell calcinated at different temperatures (900-1200 °C).

X-ray diffraction (XRD) analysis of natural limestone raw material and calcined materials are shown in Fig. 2. The limestone raw material diffraction peaks showed $CaCO_3$ as major phases (99.9 %), the calcined limestone were exhibited peaks characteristics of lime (99.63%) of CaO. These results indicated that after calcination process limestone producing pure lime (CaO).

We investigated the XRD for the waste oyster shells with and without calcination. The XRD diffraction peaks of waste oyster shells raw material shows $CaCO_3$ as major phases (92.66%), the calcina-

Table. 2. Chemical composition of limestone and oyster shells waste.

Oxides	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	P_2O_5	Ig Loss
Limestone (%)	55.54	0.11	0.03	0.09	0.20	0.03	<0.02	0.01	43.79
Oyster (%)	53.66	0.45	0.12	0.06	0.26	0.06	0.55	0.16	44.56

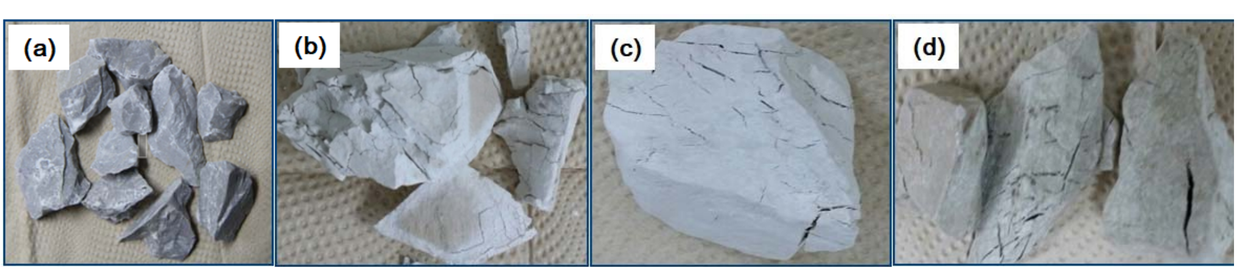

Fig. 1. Natural limestone was calcination at different temperatures (a) Before calcination, (b) Calcination at 900oC, (c) Calcination at 1000oC and (d) Calcination at 1200oC.

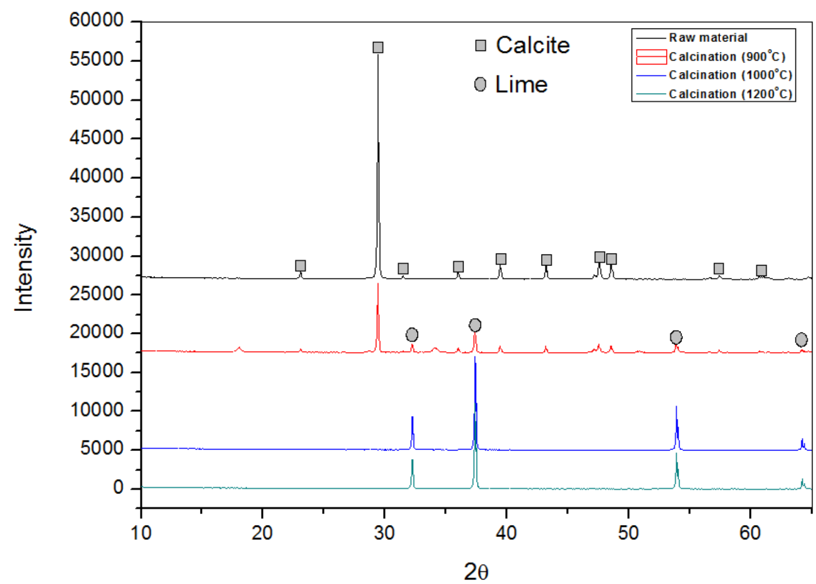

Fig. 2. XRD analyses of the natural limestone with and without calcination at different temperatures

ted oyster shell waste exhibited peaks characteristics of lime (98.3%) of CaO. These results indicated that after calcination process waste oyster shells producing pure lime (CaO).

3.2. Hydraulic activity of calinated limestone and oyster shell waste

The calcinated limestone & oyster shells from 900-1200°C/2h, were grinded for 1h until the particle size was less than 100µm. These fine powder (<100µm) of limestone and oysters shells was used to measure the hydraulic activity for heat generated by hydration reactions in relation to hydration reaction time for quicklime (CaO) from calcined limestone and oysters at different temperatures.

The calcinated at different temperatures from 900-1200°C/2h limestone fine powder was used to measure the hydraulic activity for 2 h after reactions begin as shown in Fig. 3. Hydraulic activity of calcinated limestone at different temperatures (900-1200°C). These hydraulic activity results is clearly indicated that heat generated from hydration reactions of quicklime from limestone was gradually increased up to 10min after that the temperature will gradually decreased. The calcinated lime hydraulic activity is very low at 900°C/2h, these heat generating hydration activity was drastically increase at 1000°C calcinated lime, but in the case of 1200°C calcinated lime activity was very low in initial time and when the reaction time will increase the hydraulic activity also increased due the hydration reaction of CaO.

Similarly the calcinated oyster shells at different temperatures from 900-1200°C/2h fine powder hydraulic activity also measured for 2 h after reactions begin as shown in Fig. 5. The hydraulic activity of calcinated oyster shell waste at different temperatures (900-1200 °C). These hydraulic activity results is clearly indicated that heat generated from hydration reactions of quicklime from oyster shells was gradually increased up to 40min after that the temperature will gradually decreased. The calcinated lime hydraulic activity is very low at 900°C/2h, these heat generating hydration activity was gradually increase up to 1200°C.

The limestone calcinated lime activity was increased with in 10min reaction time, but in the case oyster shells calcinated lime activity was very low in initial time and when the reaction time will increase the hydraulic activity also increased due the hydration reaction of CaO.

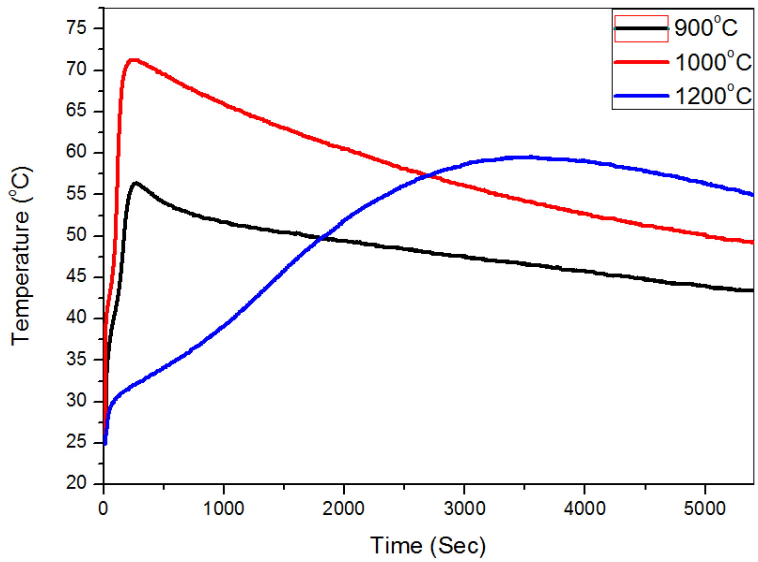

Fig. 3. Calcinated limestone powder (CaO) hydraulic activity at different temperatures (900, 1000 and 1200 oC).

4. Conclusions

The purpose of this research work was to investigate the feasibility of replacing natural limestone utilization with oyster shells waste. These experimental result of this study clearly indicated that oyster shells reused as substitute materials, containing a large content of $CaCO_3$ and less organic matter, hence it can be used as alternative material of limestone. Oyster shells have similar chemical and mechanical properties like limestone. Oyster shell waste recycling offers potential advantages and has wide application in various fields. However, Oyster shell wastes utilization are the major advantage for saving the natural limestone for future generations and avoid the oyster shells waste harmful effects in coastal areas.

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