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Using oyster-shell foamed bricks to neutralize the acidity of recycled rainwater

I.J. Chiou [a,*], C.H. Chen [b], Y.H. Li [a]

[a] *Graduate School of Materials Applied Technology, Department of Environmental Technology and Management, Taoyuan Innovation Institute of Technology, No. 414, Sec. 3, Jhongshan E. Rd., Jhongli, Taoyuan 320, Taiwan, ROC*

[b] *Department of Social and Regional Development, National Taipei University of Education, No. 134, Sec. 2, Heping E. Rd., Taipei City 106, Taiwan, ROC*

HIGHLIGHTS

- Optimum calcining condition for oyster shells was 650 °C for 1 h.
- Oyster shells gradually changed from $CaCO_3$ to CaO as temperature rising.
- The fresh oyster-shell foamed bricks offered good workability and high porosity.
- The harden oyster-shell foamed bricks performed good neutralization efficiency.

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ABSTRACT

To neutralize the acidity of recycled rainwater, oyster shells were calcined, hydrated and foamed by adding cement and foaming agent to produce oyster-shell foamed bricks (OSFBs). Experimental results demonstrate that natural oyster shells could not provide an alkali environment with sufficient metal powders for oyster-shell powder to foam, thus creating a need for additional alkali agent or calcined oyster shells. The pH of oyster shells was positively related to calcining temperature, and the optimum calcining condition was 650 °C for 1 h. The fresh OSFBs offered good workability and high porosity. Meanwhile, the 7-day and 28-day compressive strength ratios of OSFBs significantly exceeded those of normal cement paste. Through the dynamic neutralization experiments, it demonstrated that OSFB would reach the optimum condition to perform the highest neutralization efficiency when the liquid–solid ratio was 1000, the weight ratio of cement to oyster-shell was 1:5, and the foaming agent amount was 0.5% of cement.

1. Introduction

The average annual rainfall in Taiwan is 2500 mm, or 2.6 times the global average. However, Taiwan, with only a small land area, is densely populated, and hence the average per capita rainfall is only 1/7 of the world average, meaning Taiwan ranks 18th globally in terms of the severity of its water shortage issues. Lack of water resources has become an increasingly serious issue in Taiwan. While rainwater offers one potential solution to water shortage issues, rainwater with a pH value below 5.0 is defined as "acid rain". According to statistics released by the Environmental Protection Administration in Taiwan, the pH of rainfall during 2000–2012 ranged around 4.31–5.46 (average, 4.72 ± 0.31). Moreover, the occurrence of acid rain was 76.5%. Moreover, serious air pollution in coastal areas of China has further worsened the acid rain problem in Taiwan. Consequently, the Taiwan government has actively promoted water conservation and recycling. As part of these promotional efforts, the Taiwan government has incorporated rainfall recycling systems into an increasing proportion of buildings, and all public buildings require such systems. However, such systems are only useful if the recycled rainwater is purified or neutralized.

Based on statistics from the Council of Agriculture, the annual production of shucked oysters in Taiwan was 28,000 tons during 2012. If the average shucked oyster weight is assumed to be 12% of the weight including the meat and shell, then Taiwan can be assumed to have annual oyster shell production of 230,000 tons. The average annual output of oyster shells exceeded 160,000 tons in the last 10 years. Oyster shells mainly comprise calcium carbonate, followed by phosphorous, zinc, manganese, aluminosilicate, and iron oxide [1,2].

* Corresponding author. Tel.: +886 3 3791938.
E-mail address: cij@tiit.edu.tw (I.J. Chiou).

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The calcium carbonate in calcined oyster shells mostly transforms into calcium oxide, which can be used as an anti-acid agent [3]. The compressive strength of waste oyster shells is approximately 2.0 MPa [4], and oyster shell is also a highly stable biomass [3]. Oyster shell is also used as a feedstuff for chickens and ducks, for soil quality improvement and remediation [5–10], and as fertilizer. Shells can also act as a water quality buffer, water pollution indicator, and filtering material for recycling water [11,5,12–15]. As a general material, oyster shells can be used in cement, as a binder, and as an aggregate for concrete [16–19] and vermicast [20]. Additionally, shells can be used to seal leaks, for slope stabilization [3], and as a medicinal drug, in handiwork, and as a construction material coating. Recently, shells have been utilized in cosmetics as a natural antiseptic and calcareous supplement. These applications solve the odor and environmental protection issues caused by oyster shells and increase added value for the oyster industry.

While rainwater is a reliable resource in Taiwan, its acidification limits its applications. This study thus looked at oyster shells that were calcined under different temperatures to enhance their alkalinity, and then adopted to develop oyster-shell foamed bricks (OSFBs). This study then investigates the feasibility of OSFBs as a replacement for traditional alkaline chemical agents to neutralize recycled rainwater. OSFBs are low cost, generate minimal sludge, do not need cleaning, and are easily maintained. This study developed OSFBs by calcined oyster shells, a hydration reaction, and foaming at room temperature, and then used them to neutralize recycled rainwater. Finally, optimal proportions and application strategies are proposed.

2. Materials and methods

The oyster shells examined in this study were sourced from the west coast of Taiwan. The pH values and calcium oxide contents of calcined oyster shells were used to identify the specific calcining conditions required to meet the requirements of high alkalinity and energy saving. Oyster shells were washed, crushed, calcined, and then ground into powder and filtered with a #100 sieve (less 150 μm). Oyster shells were calcined for 1–3 h at temperatures of 550 °C, 650 °C, 750 °C, 950 °C, and 1050 °C, respectively. The analytical items included in the assessment of oyster-shell powder were its chemical components (measured by inductivity coupled plasma, ICP-AES), pH, foaming ratio (where the initial height (50 mm) of the fresh paste was divided by its final foaming height in the glass tube (50 mm diameter and 150 mm length)), water-soluble chloride ions, thermo-gravimetric loss (measured by DTA/TGA; heating rate of 10 °C/min under oxygen atmosphere), the total metals content (using a flame atomic absorption spectrometer, FAAS) and the leaching concentrations of heavy metals (using the toxicity characteristic leaching procedure, TCLP, as described in the Taiwan, code no. NIEA R201.14C) [21], and X-ray diffraction (XRD) crystalline species.

Oyster shells, Portland cement, and aluminum powder were used as raw materials to produce OSFBs. The hydration reaction of cement was used to achieve the required binding strength. The foaming reaction of aluminum powder in the cement paste at room temperature was used to yield porous structures [22].

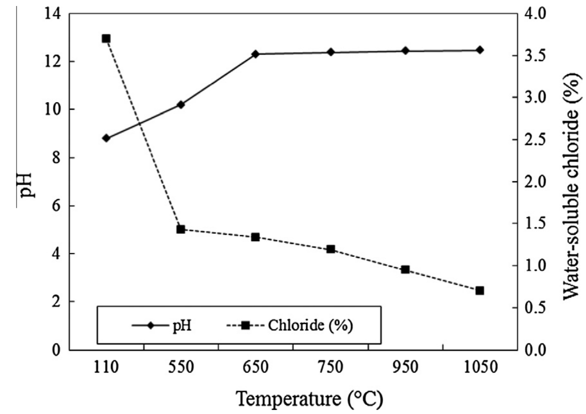

Fig. 1. pH and chloride of oyster shells at different calcining temperatures.

Meanwhile, the highly alkaline OSFBs replaced the traditional method of adding chemical agents to neutralize recycled rainwater, and further improved the applicability of recycled rainwater.

The experimental variables were weight ratio of cement and calcined oyster-shell powder, water–cement ratio, and amount of foaming agent. The weight ratios of cement and calcined oyster-shell powder were 1:3 and 1:5. Meanwhile, the amounts of foaming agent were 0.5% and 0.8% of cement. Restated, OSFBs were mixed in four proportions: $OSFB_{135}$, $OSFB_{155}$, $OSFB_{138}$, and $OSFB_{158}$ (Table 1). Additionally, flow tests were performed to test slump flow and control the flow at 100–115% to enable determination of the optimal water-to-cement and oyster shell ratios. Experimental results indicated the weight ratios water-to-cement and oyster shell for $OSFB_{135}$, $OSFB_{155}$, $OSFB_{138}$, and $OSFB_{158}$ of 1.20, 2.00, 1.30, and 2.10, respectively (Table 1). The OSFBs were analyzed to determine their unit weight (ASTM C642-13) [23], water absorption (ASTM C642-13) [23], porosity, compressive strength (ASTM C109) [24], water-soluble chloride ions (ASTM C1218/C1218M-99) [25], pH, chemical corrosive resistance, water permeability, crystalline species (by X-ray diffraction, XRD), appearance and microstructures (by scanning electronic microscopy, SEM).

This study first performed static rainwater neutralization experiments, and then identified the appropriate volume ratio of recycled rainwater (L) to OSFBs (S) (namely, L/S = 100, 300, 500, 1000, 2000, 5000). The volume ratio of recycled rainwater to OSFBs was adopted to proceed with the dynamic recycled rainwater neutralization experiment with the four types of OSFBs. A counter flow pipe column (100 mm diameter and 500 mm length), with fixed flow ratio 80 mL/min, was used to continuously neutralize recycled rainwater through OSFBs for 8 days. The pH, water-soluble chlorides ions, and weight loss of recycled rainwater were thus determined.

3. Results and discussion

3.1. Calcining condition of oyster shells

To achieve the goals of saving energy and modifying the composition of un-calcined oyster shells, natural oyster shells rich in

Table 1
Characteristics of oyster-shell foamed bricks (OSFBs).

Properties		$OSFB_{135}$	$OSFB_{155}$	$OSFB_{138}$	$OSFB_{158}$
Cement to oyster shell powder ratio (C/OS)		1:3	1:5	1:3	1:5
Foaming agent to cement ratio (F/C, wt.%)		0.50	0.50	0.80	0.80
Water to cement and oyster shell powder ratio (W/(C + OS))		1.20	2.00	1.30	2.10
Foaming ratio (%)		28.21	39.55	37.96	42.05
Unit weight (kg/m^3)	SSD	1197	1202	1224	1244
	OD	876	894	928	959
Water absorption (%)		32.30	35.11	37.23	38.81
Porosity (%)		33.33	34.12	35.04	36.36
Compressive strength (MPa)	7-day	3.48	2.65	2.76	2.36
	28-day	4.58	3.04	3.40	2.57
Water-soluble chloride ions (%)		2.63	2.10	0.35	0.56
pH		12.60	12.92	11.94	12.17
Chemical corrosion resistance (wt.%)	0.5N HNO_3	5.36	8.06	5.74	8.37
	1.0N H_2SO_4	1.24	1.83	1.39	2.05
	1.5N NaOH	0.62	1.45	1.24	1.71
Permeability ($\times 10^{-5}$cm/s)		0.534	2.77	5.14	6.44