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The Effects of Calcined Waste Oyster Shells on Physicochemical Changes in Coastal Sediments

Ilwon Jeong¹ , Tadashi Hibino¹, Seokjin Yoon²  and Kyunghoi Kim^{3,*} ¹ Graduate School of Advanced Science and Engineering, Hiroshima University, Hiroshima 739-0046, Japan; jeongiw@hiroshima-u.ac.jp (I.J.)² Fisheries Resources Management Division, National Institute of Fisheries Science, Busan 46083, Republic of Korea³ Department of Ocean Engineering, Pukyong National University, Busan 48513, Republic of Korea

* Correspondence: hoikim@pknu.ac.kr; Tel.: +82-51-629-6583

Abstract: Approximately 300,000 tons of waste oyster shells (OS) are generated annually in the Republic of Korea. Comprehensive research is required on the effects of OS on coastal environments for direct application of OS. This study aimed to investigate the physicochemical property changes in coastal sediments caused by the application of calcined OS. OS were pyrolyzed at 300 °C, 600 °C, and 800 °C, and mixed with coastal sediment at 10% (P31, P61, P81), 20% (P32, P62, P82), and 30% (P33, P63, P83). The mixed sediments' calcium content varied depending on the calcination temperature and mixing ratio of the OS, leading to accompanying physicochemical changes. OS in P31–P33 without residual organic matter could be used as a sand replacement. The calcium produced calcium silicate hydrate, densifying and increasing the sediment's shear strength by 1.4 times (P63) and 2.8 times (P81) compared to the control. The release of hydroxide ions from calcined OS alleviated acidification in P61–P63. Although P81–P83 had a high pH, they exhibited the highest PO₄-P fixation ability. OS calcined at different temperatures showed potential as a material for sand replacement, acidification mitigation, and strength improvement in coastal sediments. Therefore, the appropriate calcination temperature on OS can potentially improve the coastal sediment environment.



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Keywords: waste oyster shell; calcination; coastal sediment remediation; shear strength; cation concentration

1. Introduction

Coastal sediments play important roles in maintaining ecosystems and protecting coastal environments. Coastal sediments store and purify land-induced pollutants, provide habitats for marine organisms, and supply essential resources for primary production and the growth of various benthic organisms. They contribute to improving water quality and absorbing harmful substances and, in doing so, protect coastal environments. Therefore, efforts have been made globally to preserve and remediate coastal sediments and maintain coastal ecosystems. For example, pollutants are removed through dredging, or active capping materials are applied to efficiently improve the benthic environment of coastal areas [1,2].

Approximately 300,000 tons of oyster shells (OS) are produced annually in the Republic of Korea by the oyster farming industry [3]. Most OS are heaped in open fields, which creates environmental issues. For example, the decomposition of residual organic matter on the OS produces ammonia (NH₃-N) and hydrogen sulfide (H₂S), which can negatively

impact the coastal environment. Therefore, it is necessary for the OS to be effectively introduced into the resource circulation without abandonment.

Various positive effects have been reported in studies using calcium ions (Ca), demonstrating their potential as remediation material for contaminated coastal sediments. For example, the following results by Ca were reported: (1) neutralization of acidified sediment by the calcium oxide (CaO) hydrolysis [4], (2) fixation of excess phosphate by forming calcium phosphate [5].

Similar results can be obtained using OS. Calcium carbonate (CaCO_3), which is the main chemical component of OS, is converted into CaO by calcination through thermal decomposition at high temperatures [6]. The Ca eluted from OS has the potential for phosphorus adsorption [4], excessive nutrient removal [7], and heavy metal adsorption [8] and has been used as a filtration material in recent studies [9].

Cohesive sediments in coastal areas are characterized by low strength, high density, and slow pore water flow. Stagnant pore water inhibits oxygen diffusion and negatively affects coastal ecosystems. In addition, low-strength coastal sediments can be eroded by weak external forces, releasing pollutants into the water column through resuspension [10]. The Ca promotes the aggregation of sediment particles [11], improves pore water movement, and promotes aerobic decomposition [12]. Furthermore, the erosion threshold is increased through the pozzolanic reaction caused by Ca [13], thereby preventing resuspension and reducing secondary pollution. These results suggest that calcined OS can be used to improve coastal sediment environments.

In 2022, the government of the Republic of Korea introduced legal changes to allow the direct application of OS in coastal areas [14]. The direct disposal of OS into coastal areas became feasible. Changes in shear strength induced by the application of OS need to be evaluated, as they may have a negative impact by inhibiting the activities of benthic organisms. Several studies have measured shear strength in relation to OS. Fragmented OS were used, or the experiments were conducted in terrestrial environments [15,16]. These studies were limited in understanding the calcium-induced effects of OS.

Therefore, it is necessary to apply smaller particle-sized OS to enhance Ca leaching and to visually confirm the mechanisms by which OS interact within sediments. This study aimed to investigate the physicochemical changes in coastal sediments when OS calcinated at different temperatures were applied. This study provides insights into determining the optimal OS calcination temperatures for different types of coastal sediments.

2. Materials and Methods

2.1. Collection and Pretreatment of Coastal Sediment, Seawater, and Oyster Shells

Coastal sediment used in this study was collected from Samcheonpo harbor, Samcheonpo-Si, Republic of Korea ($34^{\circ}55'35.0''$ N $128^{\circ}04'15.7''$ E). Because of the 8–10 m water depth, the coastal sediment was collected using a dredging excavator equipped with an extension boom on a suction dredger. The collected sediment was visually identified as cohesive sediments. Impurities, such as garbage or vinyl, in the sediment were immediately removed. The collected sediments were stored in tightly sealed high-density polyethylene buckets (13 L) and transported to the laboratory. The collected coastal sediments were sieved through a 0.4 mm mesh to remove macrofauna that may activate biological decomposition. Seawater was collected from Yongho-Bay, Busan, Republic of Korea ($35^{\circ}08.282'$ N, $129^{\circ}06.842'$ E). The water depth of Yongho-Bay is less than 8 m; it is a semi-closed bay (0.5 km^2). The seawater was filtered using a $0.45 \mu\text{m}$ microfiber filter (GF/C-47, Whatman, Little Chalfont, UK) to remove plankton and debris. The sediments and seawater were kept in a refrigerator at 4°C until the experiment was conducted.

OS were provided by the oyster processing company, Geoje-Si (Republic of Korea). The OS were heaped in a designated outdoor location by the processing company after treatment. Here, they were exposed to natural environmental conditions, including rain and sunlight, for over six months. During this time, organic matter was minimized by decomposition. However, the OS were mixed with fragmented plastic-coated yarn; therefore, only the OS were collected and transported to the laboratory after the yarn was removed.

The OS were washed with tap water to remove dust from the surface and dried under natural wind and shade. Thereafter, they were pulverized and sieved through a 1 mm sieve (No. 18 sieve (ATSM), Gunpo, Republic of Korea). This was performed to prevent a temporary increase in the shear strength owing to the particle size of the OS during the shear strength test. The particle size distribution of the sieved OS was measured using a particle size analyzer (Mastersizer 3000, Malvern Panalytical, Malvern, UK) and ranged from 0.594 μm to 1260.5 μm with a D_{50} of 250 μm , as reported in previous research [9]. The powdered OS were calcinated at 300 °C, 600 °C, or 800 °C for six hours using an electronic furnace (SF-14, Wise Therm (R), Suwon, Republic of Korea). Calcination at these temperatures minimizes the water (300 °C) and organic matter contents (600 °C) and increases the ratio of calcium oxide (800 °C), respectively, in OS.

2.2. Specimen Preparation for Shear Strength Test

Coastal sediments (20 L) were homogeneously mixed with pyrolyzed OS at mixing ratios of 10% (2 kg), 20% (4 kg), and 30% (6 kg). The identification of the samples is shown in Table 1. Subsequently, 8 L of the mixed sediment was placed into cylindrical plastic buckets (diameter 23.5 cm, height: 25.5 cm, approximately 9 L). This process was used to prevent volume changes owing to mixing and compaction. The control consisted of only coastal sediment. One liter of seawater (height: 2 cm) was poured over the sediments to saturate and prevent drying. All specimens were duplicated and cured for two weeks at approximately 18 °C, which was controlled by an air-conditioner. Typically, significant strength development using seawater occurs within the first two weeks of curing [17]; therefore, this curing period was selected for the experiment. During the curing period, seawater was continuously replenished to prevent volume reduction through evaporation.

Table 1. Experimental conditions and identification of the specimen.

	Calcination Temperature	Mixing Ratio (%)	ID
Control	-	-	Control
Treatment	300 °C	10	P31
		20	P32
		30	P33
	600 °C	10	P61
		20	P62
		30	P63
	800 °C	10	P81
		20	P82
		30	P83

P31 refers to oyster shells pyrolyzed at 300 °C, which were mixed with sediment at a 10% ratio.

2.3. Shear Strength Test and Scanning Electron Microscopy

After the curing period, the overlying water was siphoned off using a syringe to prevent disturbance of the top sediment layer. The sediment temperature was measured using a thermometer and ranged from 19.2 °C to 20.6 °C. Subsequently, a shear strength test was conducted according to the KS F 2342 standard method for field vane shear in cohesive

soil [18] at a rotation speed of 0.1–0.2°/s. A vane shear apparatus (H-4227, Humboldt, Elgin, IL, USA) with an extra four-bladed vane (50.8 × 101.6 mm) was used. Shear strength was calculated by multiplying the values marked on the scale ring by 0.0625. The shear strength ranged from 0 to 8.125 kPa. A single test was performed for each specimen, and the average value is presented as the shear strength.

Scanning electron microscopy (SEM) was used to determine the property changes on the sediment surface. P33, P63, and P83 specimens were dried at 100 °C for 6 h and pulverized. The samples were analyzed using a field-emission Schottky-type scanning electron microscope (TESCAN/MIRA3 LMH, VEGA II LSU, Brno–Kohoutovice, Czech Republic).

2.4. Analysis of Sediment, Water Quality, and Oyster Shell

Sediment and overlying water quality analyses were conducted before specimen preparation and after the shear strength tests to compare changes. The pH and oxidation-reduction potential (ORP) of the coastal sediment and overlying water were measured directly using a pH/ORP meter (Horiba, LAQUA f-73, Kyoto, Japan). The pore water in the coastal sediment was extracted by centrifugation for 10 min at 3800 rpm (VARISPIN 4, CRYSTE, Bucheon, Republic of Korea). Thereafter, extracted overlying and pore water were filtered using a 0.45 µm filter for nutrient analysis. Nutrient concentration (NH₃-N, NO₂-N, NO₃-N, and PO₄-P) was measured using salicylate (Hach Method, Loveland, CO, USA: 10023), diazotization (8507), cadmium reduction (8192), and ascorbic acid (8048), respectively, using a spectrophotometer (Hach, DR-3900). The PO₄-P concentration of the overlying water was not analyzed.

Water content and loss on ignition (IL) of the sediments and OS were calculated through weight changes after calcination at 100 °C and 600 °C, respectively. IL is the representative indicator for organic matter [19]. All measurements were performed thrice. The initial sediment properties and seawater before the specimen preparation are presented in Table 2.

Table 2. Properties of the sediments, seawater, and oyster shells used in this study.

Measurements	Sediments	Seawater	Oyster Shell
pH	7.82	8.68	-
ORP (mV)	−161.7	132.6	-
PO ₄ -P (mg/L)	0.09	0.02	-
NH ₃ -N (mg/L)	6.2	0.0	-
NO ₂ -N (mg/L)	0.015	0.10	-
NO ₃ -N (mg/L)	0.0	0.0	-
Water content (%)	91.21	-	0.8
Loss on ignition (%)	9.87	-	3.4

The calcium (Ca), sodium (Na), magnesium (Mg), and potassium (K) concentrations in the pore water were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 7300DV, Perkin Elmer, Waltham, MA, USA) after the shear strength tests.

2.5. Statistical Analysis

A one-way ANOVA followed by Tukey's test was conducted with $p < 0.05$ to evaluate the significance of differences among treatments in sediments and overlying water.

Descriptive statistics (averages and standard deviations) were calculated using Microsoft Excel 365. Average values and standard deviations (standard errors) were plotted using Origin (v 2024b, OriginLab, Northampton, MA, USA).

3. Results and Discussion

3.1. Changes in Shear Strength

The shear strength was 0.069 kPa for the control, 0.063–0.069 kPa for P31–P33, 0.075–0.096 kPa for P61–P63, and 0.148–0.190 kPa for P81–P83 ($p < 0.05$ vs. Cont, except for P31–P33 and P61–P62) (Figure 1). A clear trend of increasing shear strength was observed as the calcination temperature of the OS increased. However, the shear strength of the control and P31–P33 did not differ significantly, indicating that OS pyrolyzed at 300 °C did not contribute to changes in the shear strength of the coastal sediment regardless of the mixing ratio. The previous study showed that the same OS used in this study exhibited very little change after calcination at 300 °C [20]. In addition, the low solubility of CaCO_3 in water [21] indicates that the Ca concentration in P31–P33 was relatively low compared to that in P61–P63. Therefore, calcination at 300 °C did not change the physicochemical properties of the OS, which explains the minimal change in the shear strength of P31–P33.

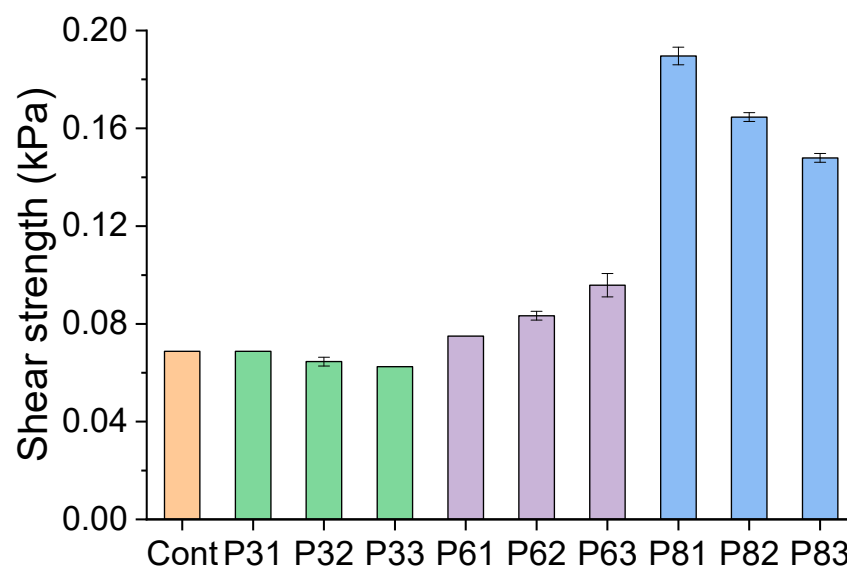
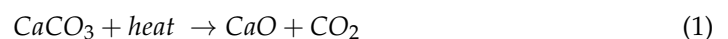
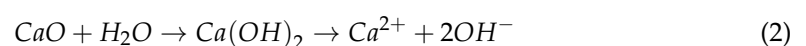


Figure 1. Shear strength of sediments in P31–P83. Cont, control.

The OS calcined at 600 °C and 800 °C significantly increased the shear strength of the sediments. The shear strengths of P61–P63 and P81–P83 were 1.1–1.4 times and 2.2–2.8 times higher, respectively, than those of the control. The chemical composition change in the OS started during calcination at 600 °C and stabilized at 800 °C [20]. The CaCO_3 in the OS was decomposed into CaO during pyrolysis (Equation (1)) [22]. The conversion of CaCO_3 to CaO at high calcination temperatures contributed to the increase in the shear strength of P61–P83.



CaO hydrolysis elutes Ca (Equation (2)), forming calcium silicate hydrate (CSH) that is incorporated with silicate ions [23]. As OS contains very little silicate [9], most of the silicate ions are considered to have originated from the coastal sediments. The CSH densifies the pores between the sediment particles, increasing sediment strength [24]. Sediment strength increased through the promotion of bonding between sediment particles facilitated by CSH [25].



In addition, the CaO hydrolysis increased the pH. To maintain electrical neutrality, it was expected that cations originally present in the sediment were released. These

released cations reduced the thickness of the electrical double layer of negatively charged clay particles. Subsequently, the attraction between clay particles was enhanced by van der Waals forces, resulting in the flocculation of clay particles [26]. This phenomenon contributed to an increase in the shear strength of the sediment.

The excessive amount of Ca negatively affected the shear strength. The shear strength in P61–P63 increased as the ratio of OS increased, whereas the opposite trend was observed for P81–P83. Calcium hydroxide ($\text{Ca}(\text{OH})_2$) is produced by CaO hydration (Equation (2)). The expansion of CaO by hydration caused opposite shear strength changes in P61–P63 and P81–P83. CaO hydration forms $\text{Ca}(\text{OH})_2$ crystals inside and outside the pores of the sediment particles [27]. $\text{Ca}(\text{OH})_2$ also expands as water infiltrates the $\text{Ca}(\text{OH})_2$ layer during carbonation [28,29]. These reactions increased the sediment density, contributing to the enhancement of shear strength.

Although this phenomenon was applicable to P61–P81, internal cracks were observed in P82–P83 because of the excessive expansion, as has been demonstrated in previous studies [30]. In addition, OS are porous [31], exhibiting a high water absorption ability. This slows the hydration process [32]. Therefore, the application of excess Ca should be limited in coastal sediments.

The effect of calcined OS on the shear strength was visualized by SEM. The platy sediment particles in the control indicated particle separation with low strength (Figure 2a) [33]. Sediment particles in P33 were covered by a small-sized CSH, which was formed by calcium ions released through Equation (2) [34] (Figure 2b). However, sediments mixed with OS calcined at high temperatures showed significant structural changes. The CSH was larger in P63 than in P33 (Figure 2c), and needle-shaped ettringites (i.e., hydrous calcium aluminum sulfate) were observed in P83 (Figure 2d). The formation of ettringite is considered to have been contributed to by sulfur, a major element in coastal sediments [35]. The growth of ettringite densified the sediments by filling the pores between the sediment particles [36,37]. In addition, the CaCO_3 crystals generated an effective bridge, bonding sediment particles at the interparticle level in P83 (Figure 2e,f) [38].

3.2. Changes in pH and Oxidation-Reduction Potential in the Sediments and Overlying Water

The pH varied depending on the calcination temperature of the OS and the mixing ratio. The initial pH in the coastal sediment was 7.82, 6.85 in the control, 7.20–7.49 in P31–P33, 7.70–8.06 in P61–P63, and 9.78–10.70 in P81–P83 (Figure 3a). No significant difference was observed between P31 and P32 and between initial and P62 in the sediments. The pH of P31–P33 was lower than that of the initial pH of sediments. This can be attributed to the production of organic acids during the decomposition of organic matter in the sediments and the little residual organic matter of OS. This implies that the limited physicochemical changes in the calcined OS led to CaO having only a minor hydrolysis effect (Equation (2)). However, the higher pH of P33 compared with that of P31 indicates that a large amount of OS calcined at low temperatures can be effective in mitigating acidification in coastal sediments.

The pH values of P62–P83 were higher than that of the control, indicating that the effect of calcium hydrolysis from OS began to surpass the influence of the organic acids produced. This phenomenon indicates that P62–P83 can effectively neutralize acidified coastal sediments. However, the pH in P81–P83 was significantly higher than that in the control and other treatments owing to the high CaO content ($p < 0.05$). CaO is more soluble than CaCO_3 , which increases the pH through hydrolysis in sediments. The sharp increase in the pH of coastal sediments could have negative environmental consequences for benthic organisms [39], implying that treating OS with high calcination temperatures should be limited.

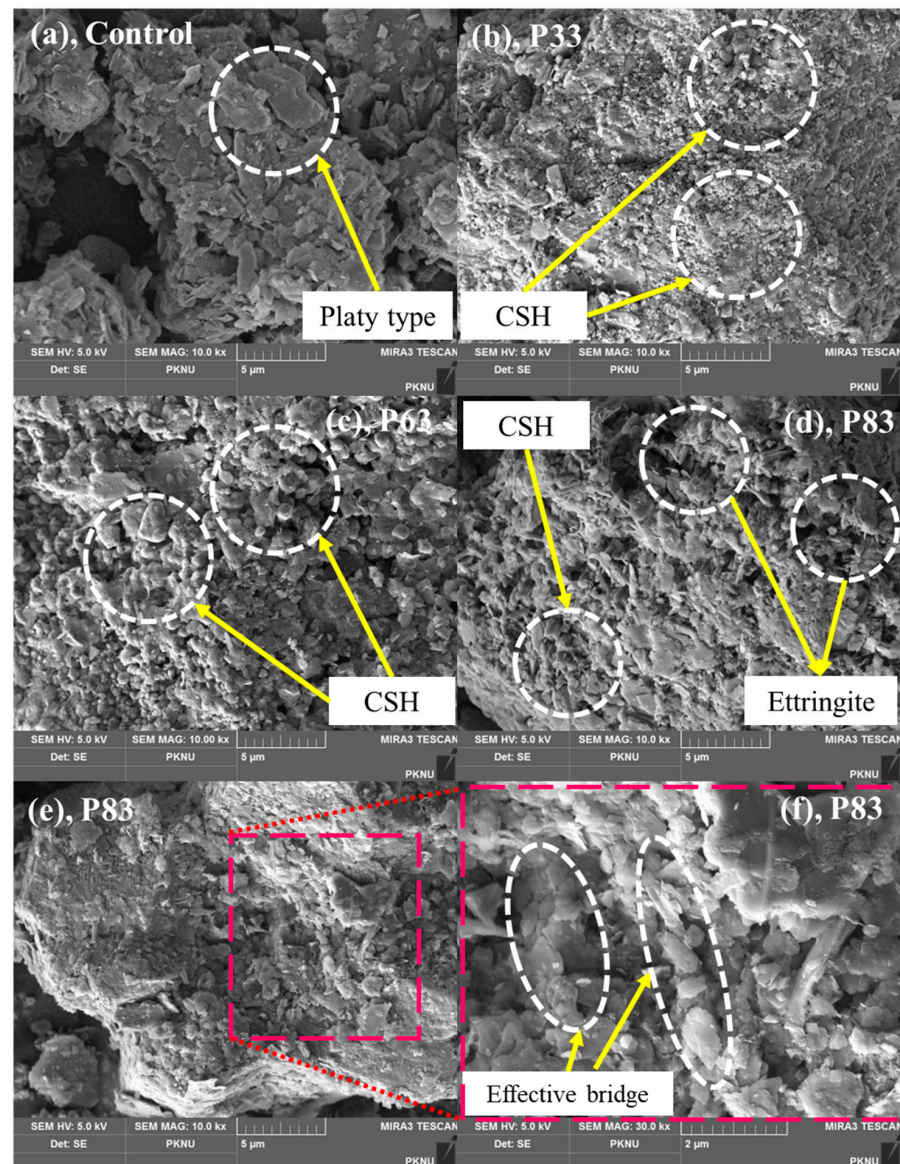


Figure 2. Scanning electron micrographs of control (a), P33 (b), P63 (c), and P83 (d–f). CSH, calcium silicate hydrate.

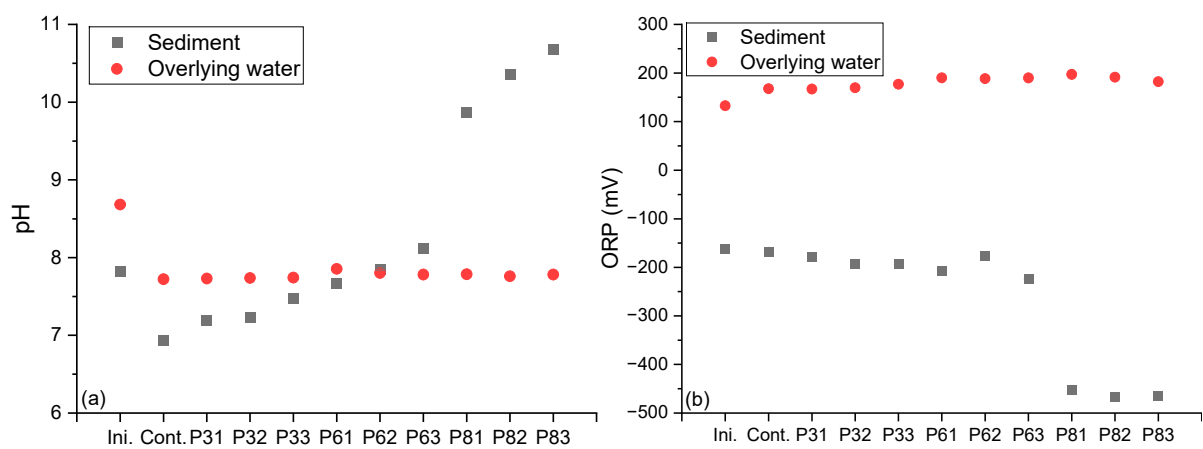


Figure 3. Changes in pH (a) and oxidation-reduction potential (b) in the sediment and overlying water of sediment. Ini, representing the initial value of the sediment before the curing period; cont, control.

The initial pH in the overlying water was 8.68, whereas, in the control, it decreased to 7.72. The pH was 7.73–7.74 in P31–P33, 7.78–7.86 in P61–P63, and 7.76–7.79 in P81–P83 (Figure 3a). The decrease in pH of the overlying water may be attributed to the influence of organic acids in the surface layer of the sediment. In particular, the pH in the overlying water of P81–P83 contrasted with the high pH in the sediments. The formation of CSH in the sediment would have suppressed the elution of OH^- ions into the overlying water.

The ORP of the coastal sediment and overlying water showed an opposite trend to that of pH (Figure 3b). The initial ORP of coastal sediments was -158.5 mV, whereas in the control, it decreased to -163.7 mV. Among the treatments, it was -195.0 – -178.9 mV in P31–P33, -195.0 – -181.8 mV in P61–P63, and -472.5 – -453.4 mV in P81–P83 ($p < 0.05$ vs. initial, except for control). The initial ORP of overlying water was 132.6 mV, and it increased to 167.9 mV in the control. In P31–P33, it was 167.0 – 169.8 mV, and it was 189.9 – 190.1 mV in P61–P63 and 182.3 – 197.3 mV in P81–P83 ($p < 0.05$ vs. initial).

The ORP in coastal sediments tends to decrease as the calcination temperature and mixing ratio increase. Ca can enhance the anaerobic decomposition efficiency by stimulating the activity of anaerobic microorganisms [40]. This is due to a shift in the composition of decomposer communities from fungi to bacteria-based communities as the pH increases with the addition of Ca [41].

However, a high pH has the potential to inhibit organic matter decomposition [42]. Coastal sediments are in an anaerobic state, where hydrogen is produced during organic matter decomposition and acts as an electron donor. This electron donor accumulation significantly decreases the ORP [43].

3.3. Changes in Dissolved Inorganic Nitrogen and $\text{PO}_4\text{-P}$ in the Sediments and Overlying Water

The initial $\text{NH}_3\text{-N}$ concentration in the coastal sediments was 6.2 mg/L, but it increased to 8.3 mg/L (control), 13.0 – 24.0 mg/L (P31–P33), 7.5 – 11.0 mg/L (P61–P63), and 13.0 – 14.0 mg/L (P81–P83) (Figure 4a). Overall, the increase in $\text{NH}_3\text{-N}$ concentration in the sediments mixed with OS was likely due to Ca elution from the OS, which enhanced microbial organic matter decomposition activity [44]. Decomposition of the organic matter remaining in the OS and sediment was stimulated by the Ca eluted from the OS, promoting microbial decomposition activities [45]. This phenomenon caused $\text{NH}_3\text{-N}$ to accumulate in the sediments of P31–P33 ($p < 0.05$). Notably, the $\text{NH}_3\text{-N}$ concentration in the calcined OS-treated sediments was 0.91 – 1.70 times higher than that in the control, with P31–P33 showing the largest increase (1.58 – 2.91 times higher than the control) ($p < 0.05$). It is considered that the excessive Ca in P61–P83 resulted in the high pH, which delayed the decomposition of organic matter [42].

The $\text{NH}_3\text{-N}$ concentration in the overlying water of the initial, control, and P61–P63 treatments was 0 mg/L. In P31–P33, it was 0.1 – 6.3 mg/L, and in P81–P83, it was 5.0 – 5.7 mg/L ($p < 0.05$ vs. initial) (Figure 4a). These concentrations were relatively low (or undetectable) compared to those in the sediments. The $\text{NH}_3\text{-N}$ in the overlying water was detected when the $\text{NH}_3\text{-N}$ concentration in the sediments exceeded 13.5 mg/L (P81). This indicates that the produced $\text{NH}_3\text{-N}$ accumulated in the coastal sediments of the control, P31, and P61–P63 without being released into the overlying water. However, $\text{NH}_3\text{-N}$ accumulation is considered to have occurred because of anaerobic conditions. Previous studies have reported that $\text{NH}_3\text{-N}$ decreases to low levels under aerobic decomposition when OS are applied [12]. Thus, the improved porosity by Ca-induced particle aggregation is expected to promote the permeability of sediments [26], decreasing the $\text{NH}_3\text{-N}$ concentrations in situ coastal sediments.

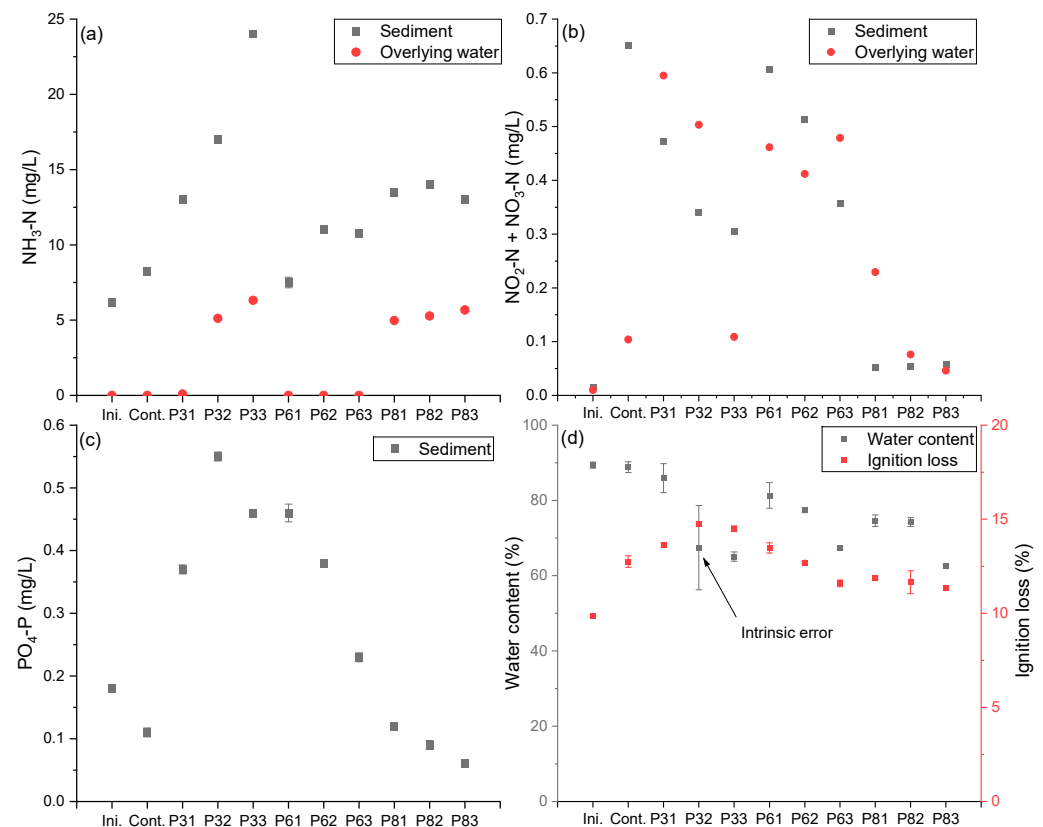


Figure 4. Concentrations in NH₃-N (a), NO₂-N + NO₃-N (b), and PO₄-P (c) and water content and ignition loss (d) of sediment before the curing period; ini, representing the initial value of the sediment during the curing period; cont, control.

The NO₂-N + NO₃-N concentration in the sediments was initially 0.015 mg/L and then increased to 0.651 mg/L (control), 0.306–0.473 mg/L (P31–P33), 0.358–0.607 mg/L (P61–P63), and 0.053–0.057 mg/L (P81–P83) ($p < 0.05$, except P81–P83) (Figure 4b). While the NO₂-N + NO₃-N concentration in the overlying water was 0.010 mg/L, it increased to 0.104 mg/L (control), 0.109–0.595 mg/L (P31–P33), 0.412–0.479 mg/L (P61–P63), and 0.046–0.230 mg/L (P81–P83) (Figure 4b). Sediment NO₂-N + NO₃-N concentrations in the control were very high. The remaining pore water in the sediment likely promoted local denitrification, which is supported by the high water content in the control compared to the other treatments (Figure 4d).

Overall, the NO₂-N + NO₃-N concentrations in the sediments and overlying water of P31–P63 decreased with an increase in the OS mixing ratio. Ca eluted from the OS facilitated denitrification, leading to the reduction of NO₂-N and NO₃-N to N₂ gas. Notably, protons are consumed during denitrification, which may be another factor contributing to the increased pH [46].

The NO₂-N + NO₃-N concentrations in the overlying water were higher in P31–P33 than in P61–P63 ($p < 0.05$), but the opposite was true in the sediments (except for P33 and P63). Surface sediments are influenced mainly by the aerobic decomposition of the overlying water. The organic matter in the less-hardened surface sediments of P31–P33 would have been more easily decomposed than those of P61–P63. The microbial decomposition activity at P61–P63 was likely promoted by Ca, resulting in the accumulation of NO₂-N + NO₃-N in the sediment. In contrast, the NO₂-N + NO₃-N concentrations in the sediments and overlying water of P81–P83 were significantly lower than those in the other treatments. This can be attributed to reduced organic matter decomposition at the interface of the sediment and overlying water and reduced microbial activity due to excess Ca.

The OS calcined at 300 °C was expected to cause a complex interaction between residual organic matter and Ca in the coastal sediment. This led to a sharp increase in the $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N} + \text{NO}_3\text{-N}$ concentrations, which may have adverse effects on the benthic environment. Although the application of Ca could improve anaerobic decomposition, high Ca application should be avoided because of sharp pH increases, as observed in P81–P83. Thus, it is necessary to select the optimal OS calcination temperature and mixing ratio.

3.4. Changes in $\text{PO}_4\text{-P}$ in the Sediments

The $\text{PO}_4\text{-P}$ concentration in the sediments was 0.18 mg/L initially, and 0.11 mg/L in the control. Treatment values were 0.37–0.46 mg/L (P31–P33), 0.23–0.46 mg/L (P61–P63), and 0.06–0.12 mg/L (P81–P83) (Figure 4c). The $\text{PO}_4\text{-P}$ concentration in P32–P33 was approximately 4–5 times higher than that in the control ($p < 0.05$). This was attributed to residual organic matter decomposition accelerated by Ca.

Although the $\text{PO}_4\text{-P}$ concentration in P61–P63 was higher than that in the control ($p < 0.05$), $\text{PO}_4\text{-P}$ concentrations decreased with increasing OS. Ca's effect on $\text{PO}_4\text{-P}$ fixation was greater than its effect on organic matter decomposition. $\text{PO}_4\text{-P}$ reacts with Ca and precipitates as calcium phosphate. The pH of P61–P83 ranged from 7.67 to 10.67, at which, phosphate species are primarily present as HPO_4^{2-} [47]. As a result, the $\text{PO}_4\text{-P}$ concentration in P61 to P83 is presumed to have decreased because of precipitation in the form of octa-calcium phosphate or brushite [48]. The fixation of $\text{PO}_4\text{-P}$ by Ca was more effective when a higher amount of CaO was present. This is because the $\text{PO}_4\text{-P}$ concentrations in P82 and P83 were 18% and 45% lower, respectively, than those in the control.

The effective use of OS as a sediment treatment relies on the concentration of $\text{PO}_4\text{-P}$ in the coastal sediment to be treated. OS calcined at 600 °C have the potential to supply $\text{PO}_4\text{-P}$ by promoting organic matter decomposition, mitigating oligotrophic coastal areas. OS calcined at 800 °C can immobilize $\text{PO}_4\text{-P}$ in eutrophicated coastal areas, preventing environmental problems, such as red tides. Therefore, the calcination temperature of OS should be determined based on the characteristics of the coastal area.

3.5. Changes in Water Content and Ignition Loss

Initially, the water content was 89.4% but changed to 88.9% in the control. In the treatments, water content was 65.1–85.9% in P31–P33, 67.3–81.3% in P61–P63, and 62.6–74.6% in P81–P83 (Figure 4d). The sediment water content generally decreases with an increasing calcination temperature and mixing ratio of OS. The microporous structure of OS is improved by calcination at high temperatures [49], leading to a corresponding increase in the water absorption capacity. However, the absorbed water was then used to generate CSH and $\text{Ca}(\text{OH})_2$ expansion, which contributed to an increase in shear strength in these sediments.

IL represents the organic matter content through combustion at 600 °C. In IL, a statistically significant difference was observed between the control and treatments compared to the initial ($p < 0.05$). The IL was initially 9.9% in the sediment. In the control, it was 12.8%, and 13.6–14.8% in P31–P33, 11.6–13.5% in P61–P63, and 11.3–11.9% in P81–P83 (Figure 4d). The IL in P31–P83 was higher than that in the control, because of residual organic matter in the OS. The IL in P31–P33 increased in proportion to the mixing ratio of OS. This was attributed to the fact that the superficial organic matter was not removed from the OS at a calcination temperature of 300 °C [50]. Meanwhile, the IL of P61–P83 decreased as both the calcination temperature of the OS and the mixing ratio increased. Ca from CaO hydrolysis promoted anaerobic decomposition, decreasing the IL in P61–P83.

3.6. Changes in Cation Concentration

The concentrations of Ca were 373 mg/L in the control, 107–220 mg/L in P31–P33, 456–749 mg/L in P61–P63, and 516–1351 mg/L in P81–P83 ($p < 0.05$) (Figure 5a). The Mg concentrations were 1099 mg/L in the control, 1100–1219 mg/L in P31–P33, 238–829 mg/L in P61–P63, and 0 mg/L in P81–P83 (Figure 5a). The Na concentrations were 5598 mg/L in the control, 6634–8166 mg/L in P31–P33, 6752–8288 mg/L in P61–P63, and 8492–10,237 mg/L in P81–P83 ($p < 0.05$) (Figure 5b). The K concentrations were 278 mg/L in the control, 305–337 mg/L in P31–P33, 267–317 mg/L in P61–P63, and 342–579 mg/L in P81–P83 ($p < 0.05$ vs. initial, except for P61 and P62) (Figure 5b). Although the Mg concentrations in the control were high, Hoskin [51] showed that the Mg concentrations can be high where carbonate sediments dominate.

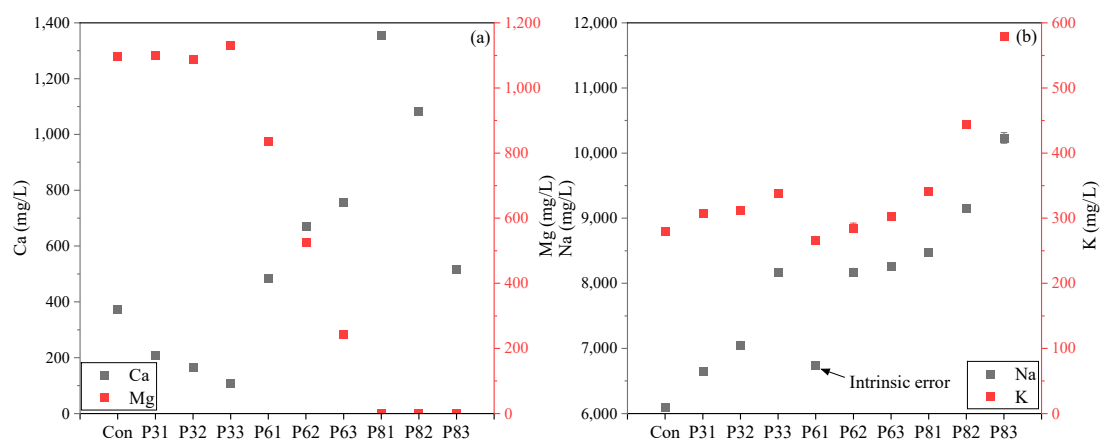


Figure 5. Cation concentrations in Ca and Mg (a), Na and K (b) of sediments. Con, control.

The OS used in P31–P33 was calcined at low temperatures and remained in the slightly soluble form of CaCO_3 . However, the relatively large amount of eluted Ca in P33 would have stimulated microbial activity, decreasing the Ca concentration in P33 compared to that in P31. The increase in Ca in P61–P83 is a typical phenomenon caused by CaO hydrolysis. However, the Ca concentration in P81–P83 was inversely proportional to the mixing ratio, which is consistent with the decreasing trend in the shear strength in P81–P83. The hydration process facilitated by the high Ca concentration likely consumed water, decreasing the release of Ca into the pore water. This assumption is supported by the fact that the water content in P81–P83 is lower than that in P61–P63 (Figure 4d).

The changes in Mg, Na, and K concentrations were related to the Ca concentration. The Mg concentration in P31–P33 increased in proportion to the OS mixing ratio, which was supported by the observations of Lee, et al. [52] of Mg accumulation derived from OS application. Although the Mg-CaCO_3 on the OS surface would have released Mg [53], the low accumulation of Mg is likely due to its release from the OS through weathering processes [54]. However, the Mg concentration decreased sharply from P61, reaching approximately 0 mg/L at P81–P83. This is because Mg was fixed as magnesium hydroxide (Mg(OH)_2) through a reaction with Ca [55].

Cation exchange by Ca led to the release of Na and K. The mechanism of this process has been thoroughly described in a previous study using calcium hydroxide [13]. Through this study, it was demonstrated that Ca derived from OS also induces the same mechanism.

On the other hand, the release of Na and K is expected to improve anaerobic microbial decomposition in sediments [56]. In addition, the release of Na and K into the overlying water stimulates primary production [57].

3.7. Selection of Optimum Tidal Flats to Apply Calcined Oyster Shells

OS can be used for sand replacement, remediation, and sediment reinforcement, depending on the calcination temperature. When the residual organic matter in the OS is properly removed, the OS calcined at 300 °C has the potential to be used as an alternative material to sand without causing negative environmental impacts [58]. The OS calcined at 600 °C and 800 °C can increase erosion resistance, promote microbial decomposition activity, and neutralize acidified and contaminated coastal areas. In addition, the OS calcined at 800 °C can be applied to tidal flats with high levels of contamination. This could facilitate the purification of tidal flats, thereby generating additional benefits, for example, by promoting fisheries resources.

The application of high amounts of Ca in coastal areas may result in sediment hardening and nutrient imbalances. The shear strength observed in Patil, et al. [59]'s study, which involved the application of oyster shells calcined at 400 °C, was found to be similar to the range of shear strength values obtained in this study. In this experiment, groundwater flow was not considered, which is believed to have resulted in higher shear strength values compared to in situ tidal flats. Therefore, when OS calcined at high temperatures are applied to in situ tidal flats, it is expected that lower shear strength values will be observed.

On the other hand, the coastal areas in the Republic of Korea are mainly located near urban areas and aquaculture farms. This indicates that the contamination levels, sediment strength, and acidity in tidal flats vary. It is necessary to select an appropriate calcination temperature according to the specific coastal sediment conditions when applying OS to coastal areas.

3.8. Potential Environmental Constraints on the Application of OS

The application of calcined OS carries several potential environmental concerns. During the calcination process, carbon is emitted, which contradicts global efforts to reduce carbon emissions. However, in South Korea, OS are calcined and processed into animal feed and fertilizer, yet annual stockpiles continue to increase. Therefore, to achieve both the goals of reducing carbon emissions and managing OS waste, an appropriate calcination temperature standard needs to be proposed to minimize carbon emissions from oyster shell calcination.

Additionally, the application of calcined OS can cause a rapid increase in pH in the coastal sediments. This may lead to a sudden shift in the ecosystem towards alkalinity, potentially causing negative ecological changes. Therefore, biological assessments should be conducted to establish site selection criteria for the application of OS.

4. Conclusions

This study aimed to investigate the effects of calcined OS on physicochemical changes in coastal sediments. Calcined OS caused significant changes to the properties of coastal sediments. CaCO_3 , the main component of OS, was converted into CaO at high calcination temperatures, releasing Ca easily. The Ca densified the sediment by forming CSH and increasing the inter-particle bonds. As a result of this reaction, P81–P83 had a more than 2.2 times higher shear strength than the control. However, the high water absorption in P83 inhibited hydration reactions and decreased the shear strength.

P33 slightly mitigated the acidified sediments, and the high $\text{NH}_3\text{-N}$ concentration was accompanied by residual organic matter on the OS surface. P62–P63 neutralized acidification in the sediment and promoted microbial decomposition, thereby increasing the $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations. P81–P83 decreased the $\text{PO}_4\text{-P}$ concentration to approximately 0 mg/L by forming calcium phosphate. The Ca concentration in the sediment increased proportionally with the calcination temperature. Subsequently, the increased Ca released

Na and K into the pore water via cation exchange. This phenomenon is expected to facilitate primary production in coastal areas.

The OS calcined at 300 °C, 600 °C, and 800 °C can be utilized in the coastal areas as materials for sand replacement, acidification mitigation, and excessive nutrient fixation, respectively. Since South Korea ranks among the top countries in oyster production, it is essential to establish large-scale disposal strategies for OS. When the application of OS in coastal areas becomes possible, new economic value can be generated by utilizing existing oyster shell processing facilities. For this purpose, further research should be conducted to apply OS calcined at various temperatures and at different ratios based on the conditions of the coastal sediments. This approach minimizes the negative effects of OS calcined at different temperatures while enhancing positive effects.

Before the large-scale application of OS, additional research is required. In this study, the estimation of long-term shear strength changes beyond 90 days and microbial analysis in sediments were limited. However, in future research, the physical and biological changes in sediments caused by calcined OS need to be investigated in depth so that the long-term environmental changes resulting from the application of OS can be evaluated more precisely.

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