

Basic Characteristics of CaO-improved Soil

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Abstract

Dredged soil is improved its physical and chemical characteristics by mixing steelmaking slag. Mixed soil is called “CaO-improved soil”. “CaO-improved soil” is improved strength and reduced H_2S -generation and P-released. Steelmaking slag has Ca, and dredged soil has SiO_2 and Al_2O_3 . They make hydration reaction, and calcify dredged soil. In this study, we examined the sulfide generation control effect and the microalgae generation control effect by phosphorus release control. Then, by the developed “biogeochemical model” based on the experiment, we predicted the improvement effect when “CaO-improved soil” are applied to a borrow pit of Osaki area in Mikawa Bay. As a result of that, “CaO-improved soil” decreased of 92% of the reduction material release such as hydrogen sulfide. And, compared with dredged soil, “CaO-improved soil” decreased of 26% of the reduction material release. The prediction shows the “CaO-improved soil” bring larger improvement effects. The restoring borrow pits process by “CaO-improved soil” is more effective for marine environmental improvement.

1. Introduction

In sand-capping/tideland construction projects, for restoration of the coastal environment and in foreshore reclamation projects, natural stone and sand (pit sand and beach sand) as well as soils, which occur as a result of shipping lane dredging, port construction work, etc., have been used as civil engineering materials. However, from the standpoint of environmental conservation, it will become increasingly difficult to secure required volumes of natural stone and sand in the future. On the other hand, soils obtained from dredging in Japan exceed 20 000 000 m³ annually. It is estimated that the volume of dredged soils will not change much in the years ahead, although those soils, which contain large proportions of silt and clay and which are difficult to handle, are buried in the ground or dumped into the ocean. From the standpoint of conserving natural resources and solving the problem of insufficient space available for disposal of dredged soil, effective utilization of dredged soil as a substitute for natural stone and sand is needed.

The CaO-improved soil described in this report is dredged soil; whose physical and chemical properties are improved by mixing a CaO improver Basic Oxygen Furnace (BOF) slag subjected to com-

position control and particle size adjustment) in the dredged soil as shown in Fig. 1.¹⁾ It can be used as a civil engineering material, specifically for refilling a deep-cut seabed in the bay, constructing a shoal/tideland, reclaiming a foreshore, etc. In fact, the scope of ap-

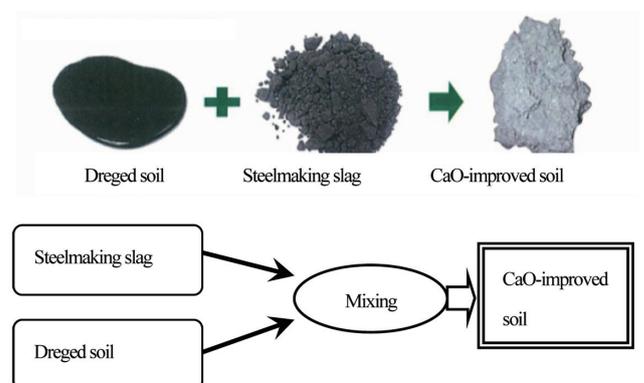


Fig. 1 Method of making CaO-improved soil¹⁾

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plication of CaO-improved soil has been ever expanding. In this report, we shall describe the basic properties of CaO-improved soil, i.e., (1) the characteristic of strength development and (2) the ability to control phosphorus and sulfides. Concerning the turbidity restraining effect and the safety of CaO-improved soil, they shall be described in a separate report.

2. Materials Used

2.1 CaO improver

BOF slag—the raw material for the CaO improver—is a granular material produced in the BOF for refining pig iron manufactured by the blast furnace process. The CaO improver is composed mainly of lime (CaO), silicon dioxide (SiO₂), and iron oxide (Fe₂O₃). Similar in chemical composition to cement, the CaO improver is an alkali having a modest hydraulic property. The role of the improver as a solidifier is played by free lime (f-CaO, CA(OH)₂) contained in lime and by calcium present in mineral layers of dicalcium silicate. The representative physical properties and chemical composition of the CaO improver are shown in **Tables 1** and **2**, respectively.

2.2 Dredged soil

Of dredged soil obtained from dredging work in sea areas, the dredged soil to be mixed with the CaO improver is mud, which can hardly be reused directly. Specifically, it is a soft dredged soil containing large proportions of fine particles of silt, clay, etc. and having considerable water content in percentage of dry weight. The representative physical properties of dredged soil are shown in **Table 3**.

Table 1 Example of chemical elements of steelmaking slag

Unit: weight%, CaO include f-CaO				
	CaO	f-CaO	SiO ₂	Al ₂ O ₃
Steelmaking slag	40.0	3.98	10.7	2.77

Table 2 Density of steelmaking slag

	Surface dry density (g/cm ³)	Dry density (g/cm ³)	Water absorption content (g/cm ³)
Steelmaking slag	3.00	2.90	2.35

Table 3 Physical and chemical characteristics of dredged soil

Dredged area	Water content	Wet density	Gravel	Sand	Silt and clay	Liquid limit	Plastic limit	Plasticity index	Dissolution of Si	Dissolution of Al	Ignition loss	TOC	pH
	(%)	(g/cm ³)											
Tokyo Bay 1	140	1.29	0.7	5.6	93.7	138.0	56.4	81.6	5.0	0.02	13.5	2.4	8.4
	200	1.24											
Tokyo Bay 2	70	1.60	0.4	53.8	45.8	58.0	30.2	27.8					
Mikawa Bay	140	1.30	0.0	4.2	95.8	124.0	42.2	81.8					
	200	1.26											
Osaka Bay 1	140	1.45	6.3	39.3	54.4	113.0	39.1	73.9	1.3	0.05	19.1	1.7	8.8
Osaka Bay 2	70	1.48	0.2	21.7	78.1	66.0	24.7	41.3	2.2	0.01	9.4	1.2	7.8

* Ignition loss was determined by JIS A 1226.

* TOC was determined by method of ministry of the environment.

* pH was determined by method of ministry of the environment of No.46.

3. Characteristic of Strength Development

As an example of improvement of the strength of soft dredged soil, **Fig. 2** shows the characteristic of strength development of CaO-improved soil prepared by mixing the CaO improver in dredged soil collected from the Bay of Osaka.

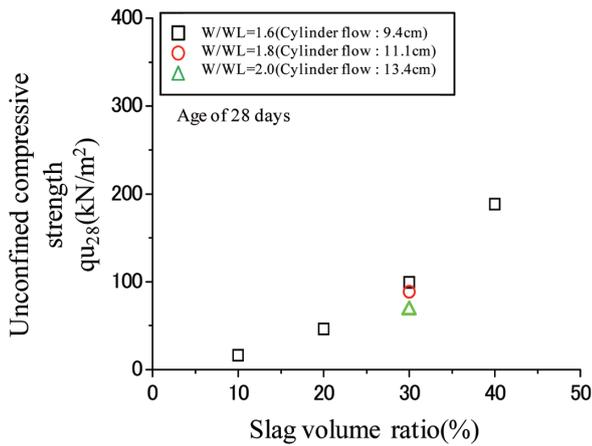
Figure 2 shows the relation between aging period and unconfined compression strength for CaO-improved soil obtained from dredged soil (liquid limit WL = 105%) added with water for adjustment and mixed with 30% CaO improver for water content in percent of dry weight W/WL = 1.6, 1.8, and 2.0, respectively. It can be seen that the unconfined compression strength of the CaO-improved soil increases with the lengthening of aging period, whereas the unconfined compression strength shows a tendency to decrease with increasing water content in percent of dry weight. Figure 2(b) shows the relation between the mixing ratio of CaO improver and the unconfined compression strength of CaO-improved soil (28 days of aging; test results obtained with soil improvers differ from those shown in Fig. 2(a)). It can be seen that the higher the mixing ratio of CaO improver, the higher becomes the unconfined compression strength of improved soil. As mechanisms for the improvement of CaO-improved soil, the following can be considered.

(1) Improvement of strength by instantaneous water absorption by CaO improver (physical improvement).

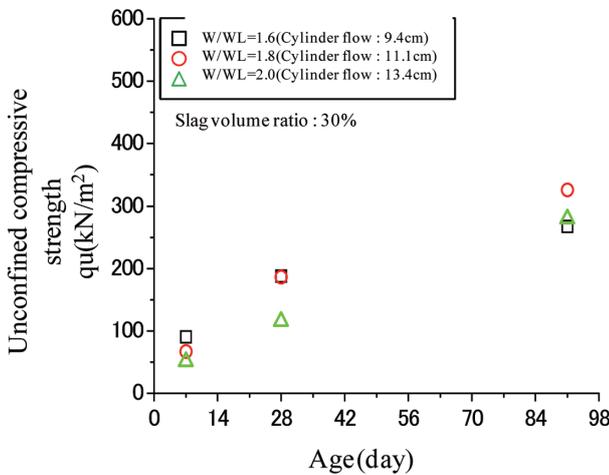
As the CaO improver mixed in the dredged soil absorbs moisture of the dredged soil, the strength of the dredged soil increases at the time of mixing. **Figure 3** shows the results of a cylinder flow test (JHS A313) of CaO-improved soil immediately after it was added with 30% CaO improver relative to the total volume (dredged soil + improver). It can be seen that the soft dredged soil increased in strength as soon as it was added with the CaO improver.

(2) Improvement of strength by continuous hydration (chemical improvement)

This is considered to occur as calcium eluted from the CaO im-



(a) Relationship between age and unconfined compressive strength



(b) Relationship between slag volume ratio and unconfined compressive strength

Fig. 2 Characteristics of strength of CaO-improved soil

prover and silica and alumina eluted from the dredged soil form calcium silicate-based hydrate (C-S-H) and calcium aluminate-based hydrate (AFm).

Figure 4²⁾ shows the results of measurement of the Ca consumption in the soil solidification process by an electron probe microanalyzer (EPM) and a scanning electron microscope (SEM), obtained with specimens prepared by mixing 30 vol% of CaO improver in dredged soil collected from the Bay of Ise. It can be seen that the concentration of Ca in the dredged soil increased because of Ca elution from the CaO improver during aging and solidification.

Figure 5²⁾ shows the results of a powder X-ray diffraction test of dredged soil samples collected from the Bay of Tokyo. Here, the results obtained with dredged soil samples added with 30 vol% CaO improver are compared with the results obtained with dredged soil samples without added improver. It can be seen that SiO₂ and Al₂O₃, which were contained in the dredged soil decreased in concentration in the solidified CaO-improved soil.

From the facts described above, it can be presumed that the CaO-improved soil solidifies as a result of the hydration of Ca eluted from the CaO improver and SiO₂ and Al₂O₃ eluted from the dredged soil.

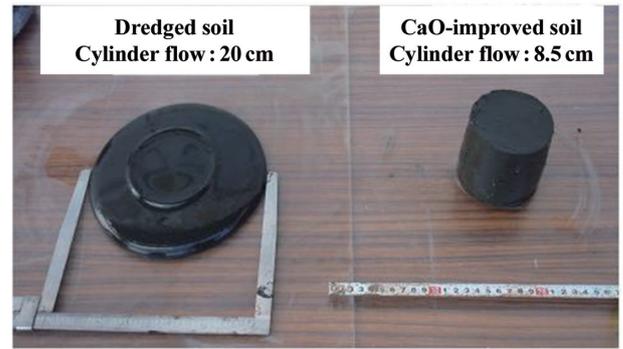


Fig. 3 Result of cylinder flow test

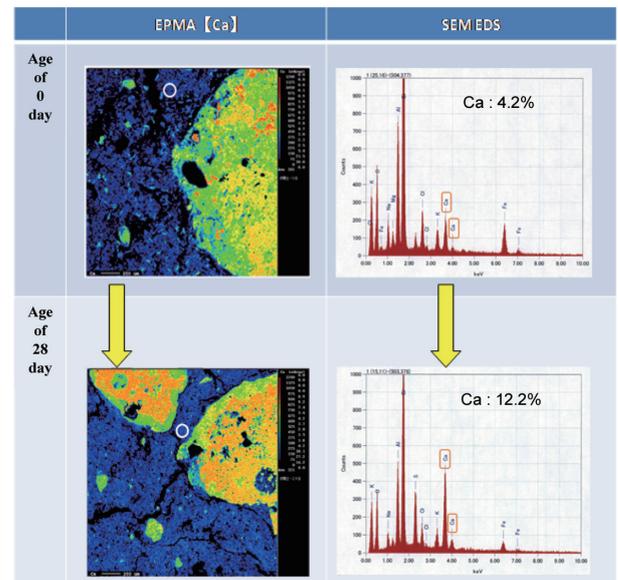


Fig. 4 Chemical mechanism of improving strength of dredged soil²⁾

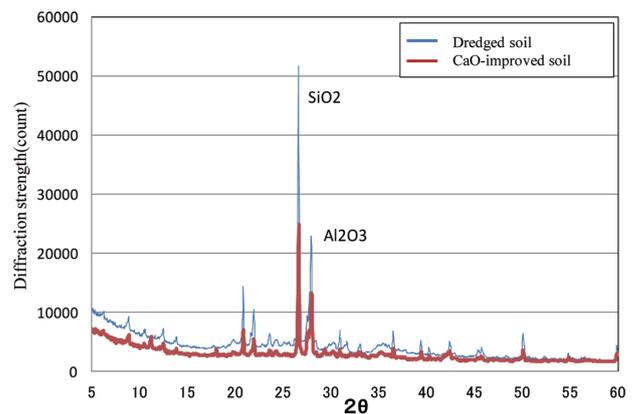


Fig. 5 X-ray diffraction²⁾

The mechanism of strength development by the hydration is considered as follows. Silica in the dredged soil and calcium in the CaO improver solidify through hydration and form a calcium silicate-based hydrate (C-S-H), causing the CaO-improved soil to solidify and increase in strength in the long run. When the aging peri-

od is within seven days, the increase in strength by the formation of calcium aluminate-based hydrate (AFm) is predominant. However, it is considered that when the aging period is three months or longer, C-S-H formed contributes to the increase in strength more than AFm.

4. Control of Elution of Phosphorus and Sulfides

4.1 Experimental procedure

Glass bottles (capacity: 1 L), each containing 100 grams of dredged soil collected from the Bay of Tokyo or 100 grams of CaO-improved soil with 30 vol% CaO improver, were prepared. For the dredged soil, glucose weighing 50 mg was thoroughly mixed in each 100 g sample in order to promote the formation of sulfides. Next, 0.9 L of artificial seawater whose dissolved oxygen (DO) was removed by aeration in nitrogen was poured into each bottle. For each series, four samples were prepared and left with the bottle caps tightly closed in a dark room at normal temperature for 60 days. Subsequently, all the samples were subjected to a water quality analysis 5, 10, 40, and 60 days.

4.2 Experimental results and discussions

4.2.1 Sulfides

In the sulfate reducing reaction, sulfate reducing bacteria (SRB) reduces sulfuric acid ions (SO₄²⁻) in seawater by organic matter and thereby produces a sulfide as shown in Equation (1). As seawater contains sufficient amounts of sulfate (2700 mg/L as SO₄²⁻), there is a tendency that the rate of sulfate reducing reaction is governed by the amount of easily decomposable organic matter in the dredged soil.

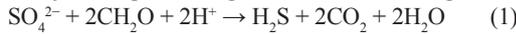


Figure 6³⁾ shows the time-serial change in dissolved sulfide concentration of seawater. The dissolved sulfide concentration of the dredged soil series gradually increased to 35 mg/L in 60 days. On the other hand, the dissolved sulfide concentration of CaO-improved soil remained almost unchanged, at 5 mg/L, though a small amount of elution of dissolved sulfide was observed in the early stage of the experiment. From the above results, it was considered that even if the dredged soil contains easily decomposable organic matter such as glucose, it would be possible to restrain the occurrence of sulfides by adding 30 vol% CaO improver to the dredged soil and accelerating the solidification thereof.

4.2.2 Phosphorus

Ordinarily, phosphorus in dredged soil exists in the form of iron oxide (FeOOH) to which PO₄-P adsorbs. It is considered that under anaerobic conditions, the PO₄-P is released when the iron oxide (FeOOH) is reduced by the organic matter and sulfide.

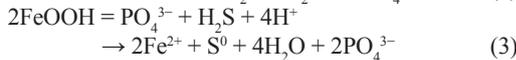
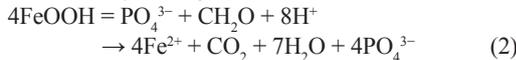
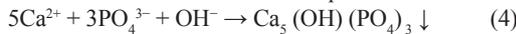


Figure 7³⁾ shows the time-serial change in PO₄-P concentration of seawater. In the dredged soil series, PO₄-P gradually increased to 0.9 mg/L in 60 days. On the other hand, the elution of PO₄-P from the CaO-improved soil was not observed at all. The CaO-improved soil shows a marked increase in the concentration of Ca. Thus, it is considered that as shown in Equation (4), PO₄-P is fixed within the CaO-improved soil in the form of calcium apatite.



4.3 Experimentation for grasping effect of CaO-improved soil in restraining multiplication of weeds

4.3.1 Experimental procedure

Five 10 L containers (each measuring 369 mm × 248 mm × 110

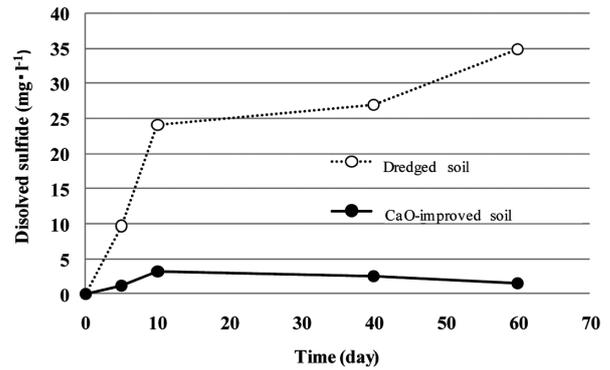


Fig. 6 Time course changes of dissolved sulfide concentration in seawater³⁾

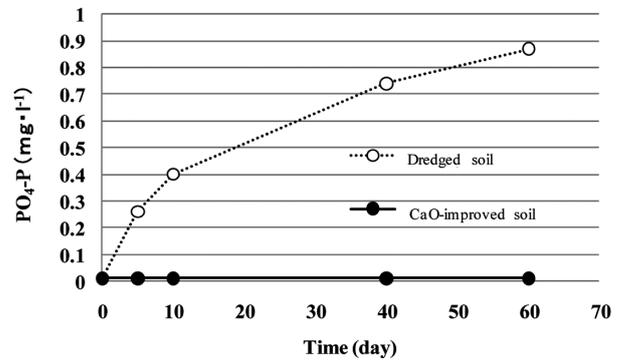


Fig. 7 Time course changes of PO₄-P concentration in seawater³⁾

mm) were filled with dredged soil or CaO-improved soil (with 30 vol% CaO improver) (total volume: 50 L, total surface area: 0.46 m²). They were then installed in two series of shallow water tank as shown in Fig. 8³⁾. Next, 600 L of artificial seawater or natural seawater collected from the Bay of Tokyo was put into the experimental apparatus (water tank capacity: 562.5 L, circulation water tank capacity: 87.5 L), and the water was circulated in such a way that it resided in the shallow water tank for one hour. The depth of water in the shallow water tank was 375 mm and the depth of water up to the container top was 150 mm.

The experiment was repeated with the type of seawater changed between 50 and 180 days. At the water tank surface, the photon flux density (μmol/m²/s) in the wavelength range 400–700 nm was measured with an apogee photon meter of SENECOM Corporation once a day at 13:00. Throughout the test period, the photon flux density was kept at a level sufficiently lower than 40–370 (μmol/m²/s), the optimum photon flux density range for the growth of seaweeds. Each series of seawater was collected two to three times a week and the quality thereof was analyzed. In addition, using a multi-wavelength excitation fluorometer (of BBE), we periodically measured the amounts of algae floating in the seawater and of algae sticking to the tank walls (chlorophyll-a).

4.3.2 Experimental results and discussions

Figure 9³⁾ compares the time-serial change in chlorophyll-a concentration between dredged soil and CaO-improved soil in artificial seawater. In the dredged soil system, the multiplication of algae (diatoms) began to be observed one week after start of the experiment. On the other hand, in the CaO-improved soil system, the mul-

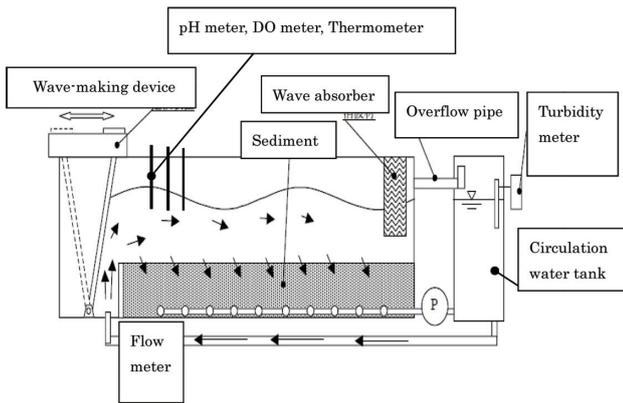


Fig. 8 Experimental apparatus for shallow seabed³⁾

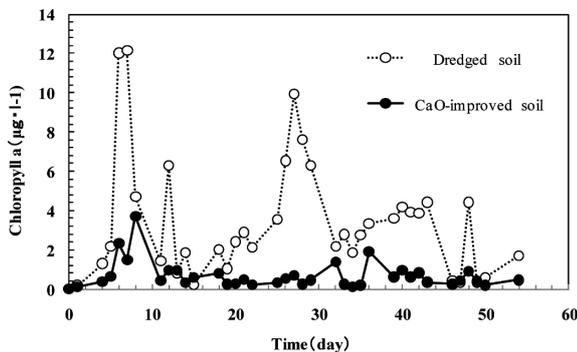


Fig. 9 Time course changes of chlorophyll-a concentration in seawater³⁾

tiplication of algae was less conspicuous than in the dredged soil system. The occurred algae mostly stuck to the water tank walls rather than floating in the seawater. When it comes to measuring the total amount of algae that occur, it was found necessary to measure the amount of sticky algae too.

In addition, a change in pH value of the seawater due to the assimilation of carbonic acid was observed as shown in Fig. 10³⁾. It was confirmed that the pH value of the CaO-improved soil system remained somewhat lower than that of the dredged soil system.

Figure 11³⁾ shows the time-serial change in PO₄-P concentration of the dredged soil system and CaO-improved soil system in seawater. In the dredged soil system, the PO₄-P concentration first increased slightly as a result of the elution of PO₄-P from the dredged soil. However, with the multiplication of algae, it started decreasing and in about one week, it dropped below the detection limit (0.005 mg/L). In the CaO-improved soil system, on the other hand, the PO₄-P concentration remained under the detection limit right from

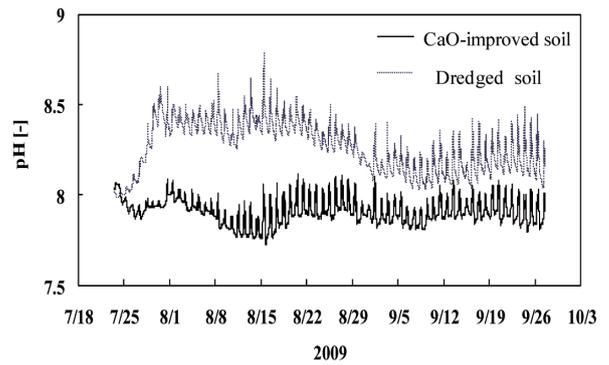


Fig. 10 Time course changes of pH in seawater³⁾

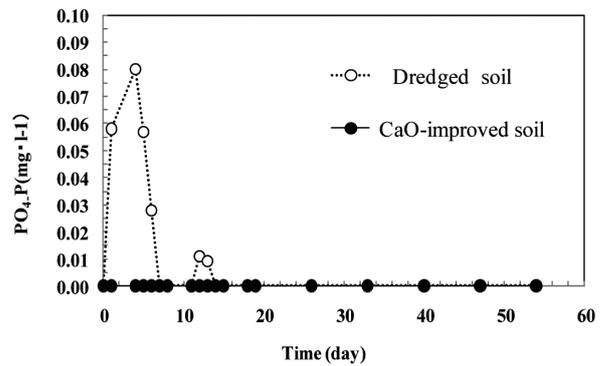


Fig. 11 Time course changes of PO₄-P concentration in seawater³⁾

the start of the experiment. This is considered due to the effect of the CaO improver in restraining the elution of PO₄-P from the CaO-improved soil.

It is said that when the seawater temperature rises above 20°C, the cysts of algae hidden in the bottom material in the sea area sprout and multiply themselves rapidly, especially when nutrient salts (nitrogen, phosphorus, and silica) abound in the seawater.³⁾ Throughout the period of the present experiment, the seawater temperature was kept at about 30°C. It is considered that in the dredged soil system, not only phosphorus but also nitrogen and silica were eluted from the soil, causing diatoms and other algae to multiply rapidly. On the other hand, when the CaO improver is mixed in dredged soil, the elution of phosphorus is restrained almost completely, though nitrogen and silica are more or less eluted. Thus, it is considered that the multiplication of algae was effectively restrained.

5. Prediction of Improvement of the Environment of Actual Sea Areas Using a “pelagic-benthic-coupled ecosystem model”

5.1 Setting conditions for prediction

As the benthic improvement effects of the CaO improver, the major phenomena that have been experimentally grasped are as follows.

- 1) The improver is effective to restrain the elution of phosphorus in the form of phosphoric acid from the bottom sediment.
- 2) The improver is not very effective to restrain the elution of nitrogen in the form of ammonia from the bottom sediment.
- 3) The improver is effective to restrain the occurrence of hydrogen sulfide from the bottom sediment.

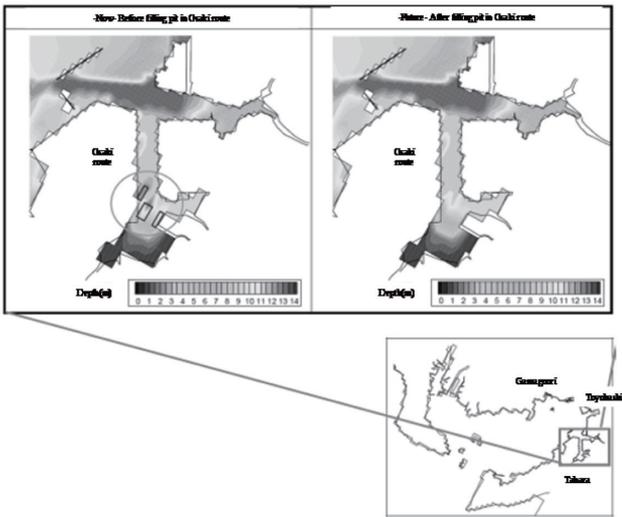


Fig. 12 Location of the borrow pit in Osaki Route and observation buoys³⁾

- 4) There is a possibility that the improver will help retard the progress of anaerobic decomposition in the bottom sediment.
- 5) The improver increases the physical strength of the bottom sediment.

Considering the above improvement effects, we predicted the effect of the CaO-improved soil in improving the ocean environment using a pelagic-benthic-coupled ecosystem model.⁴⁾ The prediction conditions that were set for the pelagic-benthic-coupled ecosystem model to express the bottom sediment improvement effects of CaO-improved soil are as follows.

- 1) The initial values for calculation of the amount of PO₄-P in the existing sediment and of the amount of PO₄-P attaching to and detaching from the bottom sediment shall be assumed to be zero.
- 2) The initial value for calculation of organic matter (detritus) in the existing sediment shall be assumed to be zero.

5.2 Predicting improvement effect of CaO-improved soil used to refill dredged pit in the Osaki District of Mikawa Bay

Taking the dredged pit within the Osaki shipping lane located at the back of the Bay of Mikawa as the subject of our case study (Fig. 7), we predicted the difference in ocean environment improvement effect between different refilling materials. The dredged pit refilled was 322500 m² in area and 1284750 m³ in volume. As the materials for refilling the dredged pit, dredged soil and CaO-improved soil were selected. In predicting the improvement effect, we focused on how the water quality and bottom sediment would change according to the difference in history of refilling and type of refilling material used under the environmental conditions (meteorology, water flow rate) prevalent in the year 2001.

First, the changes in water quality in the area (“work site”) shown in Fig. 12³⁾ are shown in Fig. 13. The predicted water qualities (average values for summer) are compared in Table 4. Although there are no marked changes in chlorophyll-a, T-N/T-P, and dissolved oxygen concentrations in the bottom layer, the concentrations of reduced substances (e.g., hydrogen sulfide) vary from one prediction case to another. It can be seen that when CaO-improved soil is used, the concentrations of reduced substances are lower than when dredged soil is used, indicating that the CaO-improved soil is effective to restrain the occurrence of hydrogen sulfide. Figure 14³⁾ com-

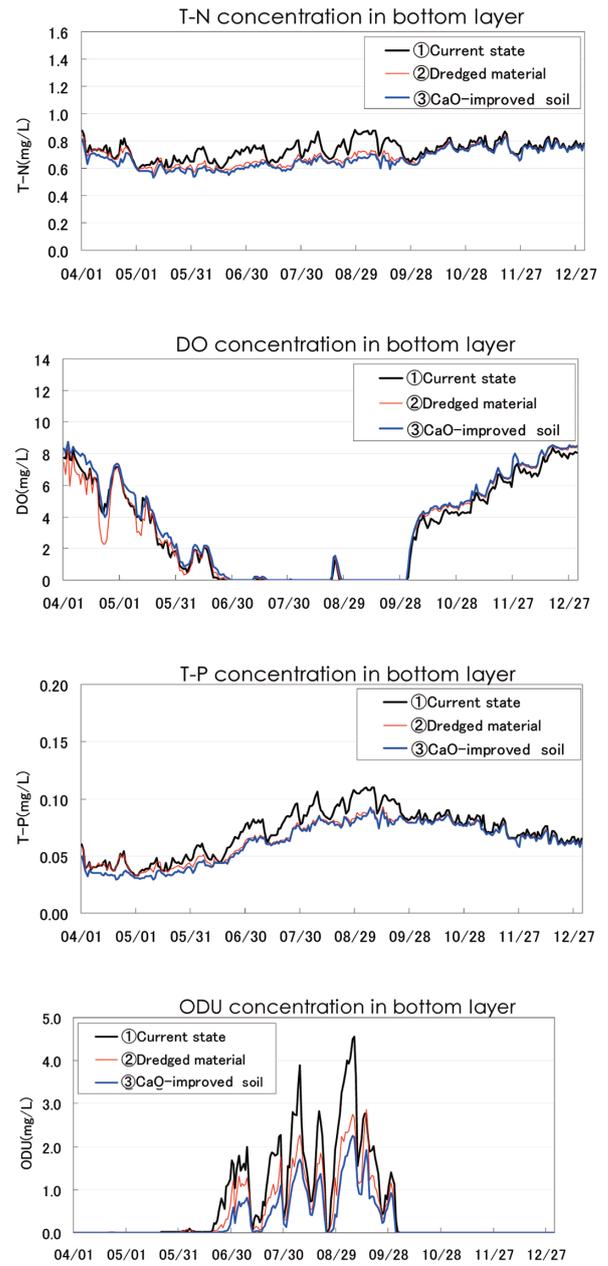


Fig. 13 Concentration in the borrow pit area³⁾
 ① Current state, ② Case buried by using dredged material and ③ Case buries by using slag added material.

Table 4 Concentration in the borrow pit area in summer season³⁾

Unit : mg/L (Chl-a : μg/L)	Surface layer			Bottom layer	
	Chl-a	T-N	T-P	DO	ODU
(1) Current state	24.6	0.95	0.117	0.05	1.49
(2) Restore by dredged material	24.5	0.94	0.116	0.07	0.96
(3) Restore by CaO-improved soil	24.5	0.94	0.116	0.10	0.62

* ODU is converted what in the oxygen demand as for the reducing substance such as Mn²⁺, Fe²⁺, HS⁻.

compares the average amounts of nutrient salts and reduced matter eluted from the bottom sediment at the work site and the oxygen consumption during the prediction period. It can be seen that the amounts of nutrient salts and reduced matter eluted from the bottom sediment and the consumption of oxygen differ according to the type of refilling material and that the CaO-improved soil is more ef-

fective to reduce the elution of nutrient salts from the bottom sediment than the dredged soil. A similar tendency was observed with respect to the consumption of oxygen and the elution of reduced matter.

6. Conclusion

Concerning the basic properties of CaO-improved soil as a civil engineering material, we obtained the following knowledge from the standpoint of the following: (1) characteristic of strength development and (2) impact on water environment.

- 1) When a mixture of CaO-improved soil and dredged soil is aged in seawater, Ca from the CaO-improved soil and SiO_2 and Al_2O_3 from the dredged soil form certain hydrates through hydration, causing the mixture to solidify.
- 2) The development of strength of CaO-improved soil becomes conspicuous with the lapse of time of aging. It was confirmed that the strength development continues up to 91 days.
- 3) The development of strength of CaO-improved soil is enhanced as the mixing ratio of CaO improver is increased. It was confirmed that the strength improving effect continues to increase till the mixing ratio of CaO improver was raised to 40%.
- 4) It was experimentally verified that by mixing the CaO improver in dredged soil, it is possible to restrain not only the elution of phosphorus and sulfides from the dredged soil but also the multiplication of algae.
- 5) The application of CaO-improved soil in an actual sea area was simulated. The simulation results showed no marked difference in water quality improvement effect between different refilling materials. However, focusing on the effect to reduce the occurrence of reducing substances, such as hydrogen oxide, which are highly poisonous to living things, CaO-improved soil was superior to dredged soil. With the reducing substance concentration of water right above the work site used as the index, the effect of CaO-improved soil was 1.4 times greater than that of dredged soil.
- 6) The above findings prove that the CaO-improved soil is a civil engineering material having strength and helping to restrain the elution of phosphorus and sulfides from dredged soil. In the future, it is expected that the CaO-improved soil will find various applications—refilling a deep-cut seabed, constructing a shoal, developing tideland.

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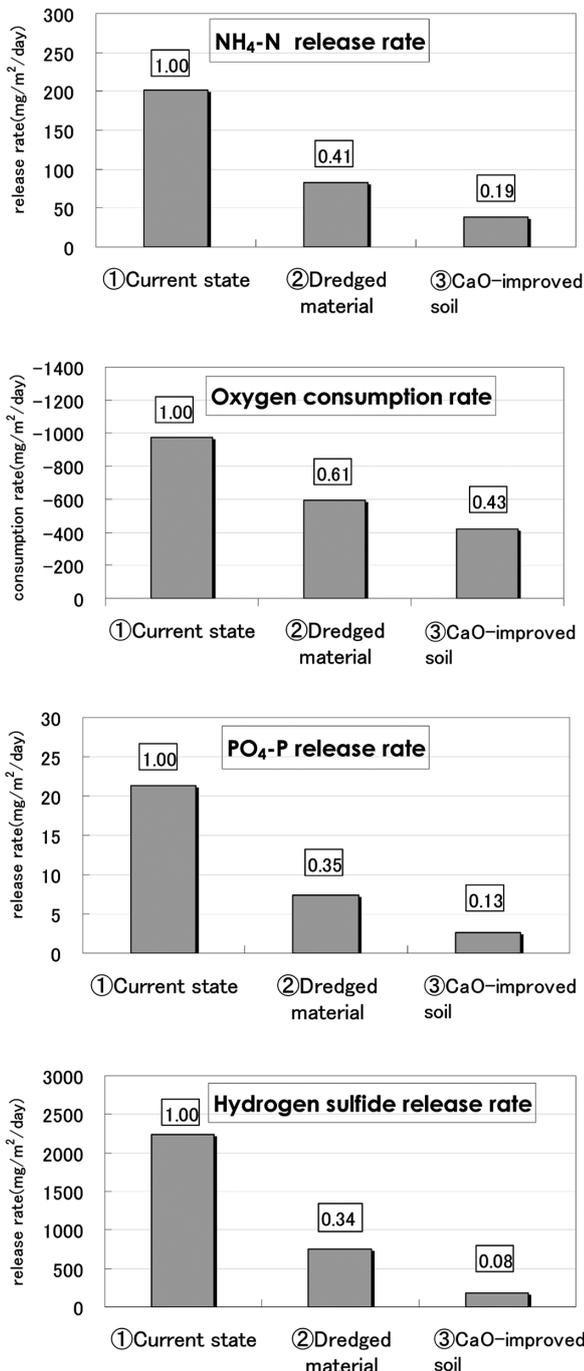


Fig. 14 Flux from sediment in the borrow pit area when current state and restored by dredged material or slag added material³⁾

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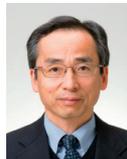
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