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Geo-Environmental Assessment on the Sludge Treated with Low Alkaline Additives

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Synopsis

Stabilized/solidified (S/S) sludge has enough strength for reusing as construction materials and the high alkalinity due to cement stabilizing can immobilize heavy metals in contaminated sludge. However, too much alkalinity affects the water quality in the geo-environment and the other ecosystem. Therefore, the alkaline migration due to the S/S treatment should be carefully considered in utilizing and reusing sludge. In this study, the suitability of the newly developed low alkalinity additives was assessed to establish the new method for the S/S treatment of sludge. Acid Neutralization Capacity test was also conducted to evaluate the effect of these additives on the immobilization of heavy metals.

Keywords: sludge; stabilization/solidification; low alkaline additives; acid neutralization capacity; heavy metal

1. Introduction

The Ordinary Portland Cement (OPC) and lime have been used to improve the properties of soft ground and dredged material. The hydration and pozzolanic reactions of these binders make the ground have high strength and reduce the high water content of sludge. However, the high alkalinity due to the hydration and pozzolanic reactions affects the water quality in the ecosystem and sometimes give bad smell during mixing with the soil, which contains organic materials. Therefore, in order to reduce and control the alkalinity of stabilized soil, many kind of research works have been carried out until now.

From the viewpoint of geotechnical waste utilization, the alkaline leaching characteristics from the stabilized soil and the buffer capacity of filter layer were studied by Kamon et al. (1996). In that research, the minimum thickness of filter layer required for the alkaline leachate control in the application of the cement stabilized soil to embankment was estimated based on the experimental results. The concept of the alkaline control is shown in Fig. 1.

Nishi et al. (2000) performed a series of laboratory experiments to evaluate the effect of carbon dioxide gas on the neutralization of cement stabilized soil, reporting that the amount of carbon dioxide in the stabilized soil significantly affects the strength and pH of stabilized soil. Moreover, several methods for muddy soil treatment for construction works with low alkalinity additives have been developed (e.g., Yamamoto et al., 1999, Nakazawa et al., 2000).

In this study, the suitability of the newly developed

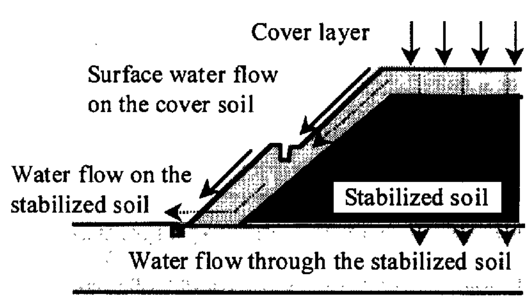


Fig. 1 Control of alkaline migration on the stabilized soil embankment (Kamon et al. 1996)

low alkalinity additives was assessed to establish the new mixing and curing method. Acid Neutralization Capacity Test (ANCT) and the Inductivity Couple Plasma (ICP) analyses on the leached water were also conducted to assess the effect of these additives on the immobilization of heavy metals.

2. Materials and samples

The additives used in this experiment are mainly composed of two types of materials (Binder A and B). Their main components are as follows:

[1] Binder A :
- Hydraulicity gypsum ($CaSO_4 \cdot 1/2H_2O$)
- pH controller (promote ion-exchange)
- Additive for hardening (include alumina)

[2] Binder B :
- Additive for flocculating water (Polymers)

Compared with OPC (Ordinary Portland Cement) and other materials for S/S, these additives exhibit low alkalinity and can make the sludge of high alkalinity stabilized in neutral state. Table 1 shows the alkaline buffer capacities of the binders.

Two types of sludge were used in the experiment. They don't have any cement component and show no self-hardening properties. Table 2 indicates the properties of raw sludge and treated sludge. According to the result of X-Ray Fluorescence Spectrometer (XRFS) analysis, sludge I and sludge II have a considerable quantity of lead (Pb). Therefore, Pb was used as a trace element to assess the immobilization capacity of heavy metals by these additives.

Table 1 Low alkalinity additives

Stabilizer	pH	Buffer capacity for alkalinity (mol/g) at pH=12 liquid
Binder A	10.2	6.14E-03
Binder B		
Self-harden sluge	9.9	2.75E-02
Non self-harden sludge	6.8	1.80E-02

Table 2 Properties of materials

		Non self-harden sludge	
		Sludge I	Sludge II
OPC Content(%)		0	0
Density of particles		2.43	2.47
Ignition Loss (%)		8.13	6.94
Liquid Limit (%)		40	38
Plastic Limit (%)		34	22
Content of Pb(mg/kg)		< 10	78
Initial Water Content(%)		94	41
pH of raw sludge		7.22	7.53
pH after solidification	Initial	8	7.87
	Stable	8.7	8.75
Solidification treatment (Binder/wet soil)		A (25%) B (0.5%)	A (10%) B (0.3%)

3. The treated sludge pH and buffer capacity

The pH related to the S/S sludge can be measured in two ways; 1) pH of the solution extracted from sludge and 2) pH of a suspension including sludge. Commonly, the pH of sludge is measured on a suspension. However, in this research, the leached solution was used for measuring the pH to assess the geo-environmental impact of leachate from S/S treated sludge. The change and buffering in the pH related to treated sludge pH is affected by the properties of sludge and the complex chemical interactions. These chemical interactions are summarized as follows.

[1] Dissolution of the calcium hydrate from hydration and pozzolanic reaction

$$Ca(OH)_2 \rightarrow Ca(OH)^{+}+OH^{-} \rightarrow Ca2^{+}+2OH^{-}$$

[2] Reaction with calcium and magnesium carbonates

$$CO_2+H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^{+}+HCO_3^{-}$$
$$CaCO_3+H^{+}+HCO_3^{-} \rightleftharpoons Ca(HCO_3)_2$$

[3] Cation exchange

$$M^{+}\,soil + H^{+} \rightleftharpoons H^{+}soil + M^{+}$$

[4] Proton adsorption by clay minerals, humus, and hydrated aluminum and iron oxides

$$\text{-COOH} \rightleftharpoons \text{-COO}^{-}+H^{+}$$
$$>CO^{-}+H^{+} \rightleftharpoons\ >COH \text{ (at a high pH)}$$

[5] Proton adsorption by aluminum ions

$$>AlO^{-}+H^{+} \rightleftharpoons\ >AlOH$$
$$>AlOH+H^{+} \rightleftharpoons\ >AlOH_2^{+}$$

[6] Solubilization of soil minerals

4. Testing procedures

To evaluate the effect of curing condition on the alkalinity of treated sludge, the treated sludge specimen were cured under open-air and sealed state. A small bottle was used to cut off air during the sealed curing. Two types of leaching test at the liquid to solid ratio (*L/S*) of 10 were carried out to assure whether low alkalinity stabilization could be achieved. The one was carried out with the 28 days aged samples to measure the pH change during soaking in distilled water for 7 days. The other was conducted for the samples aged in different period (0, 1, 3, 7, 14, and 28 days) to determine the pH of the effluents after soaking samples in distilled water for 30 minutes.

ANC test was also carried out according to the WTC standard (Wastewater Technology Center, 1991). ANC test is a kind of batch equilibrium leaching test. Testing procedure is as follows: crushed stabilized soil (≤100 μm) are conducted with nitric acid solutions of varying concentrations at the *L/S*=6 for 24hr under agitation. The leachates were filtered through 0.45μm pore size membranes. Chemical analyses were performed on the leachates. Acid reactions of stabilized sludge minerals can be described as an acid-base reaction. (Frei et al., 2000)

$$\text{Primary mineral} + nH^{+} = \text{Secondary products} + \text{cations}^{+}$$

Generally, ANC indicates the amount of the basic cation components released from stabilized sludge.

5. Results and disscussions

Photograph 1 shows the Scanning Electron Microscope (SEM) of sludge II (28 days aged) stabilized with these additives. The hydrate product, seems to be needle–shape crystals was hydrate gypsum. Fig. 2 is the result of X-Ray Diffractometer

Photo. 1 SEM photo of treated sludge

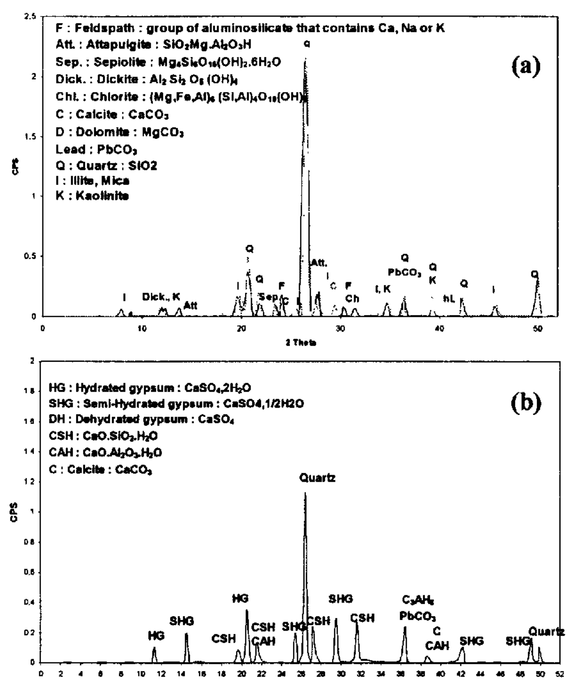


Fig. 2 XRD patterns of Sludge II; (a) raw sludge and (b) treated sludge

(XRD) analysis. Although, some hydrated cement components (e.g., CAH, CSH) were detected, the ettringite could not be investigated. After treatment of

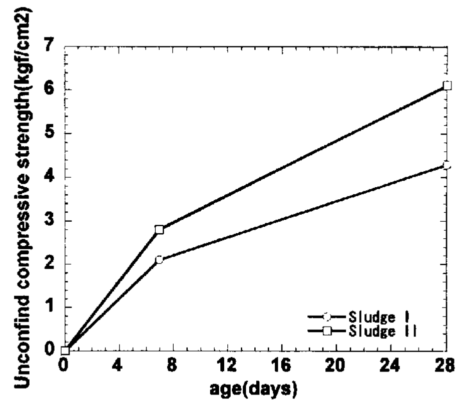


Fig. 3 Unconfined strength of treated sludge

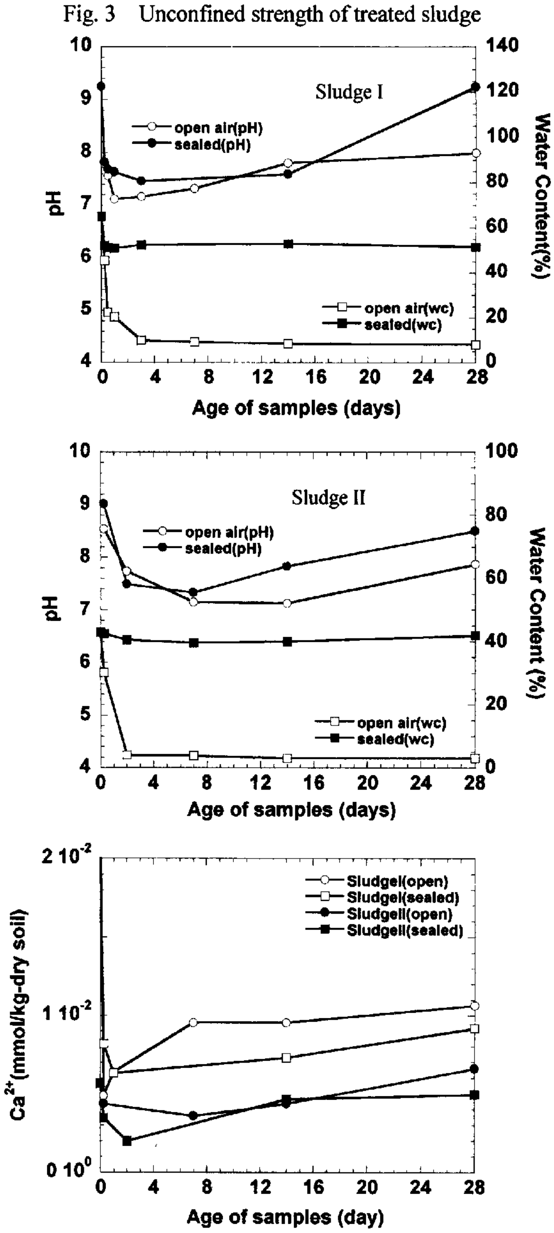


Fig. 4 pH changes of samples during curing non self-hardening sludge, the pH of treated sludge I and II was slightly increased as shown in Table 2. Originally, the raw sludge were neutral, but as the influence of binders, the treated sludge showed slightly higher pH than before S/S. However, comparing to the pH of OPC treated soil which is generally about 12, the low alkalinity stabilization could be achieved using these additives.

Fig. 3 shows the strength properties of treated sludge I and II. The treated sludge had enough strength for reusing as construction materials, according to the Japanese official manual on reusing construction surplus soils, i.e., unconfined compressive strength is more than 400 kPa (Construction High Technology Center in Japan, 1999). Despite of more additives contents, the treated sludge I had the lower strength than sludge II. It seems that the organic materials and high initial water content of sludge I affected the strength of treated sludge. Fig. 3 also shows that stabilized soil obtained larger strength according to the curing period. Because the raw sludge didn't have any cement components or hydrate material, it is due to the hydration reactions of additives.

Fig. 4 shows the pH change of effluents by soaking the treated sludge aged in different period (0, 1, 3, 7, 14, and 28 days) for 30 minutes. The pH of the samples under open-air condition was lower than sealed curing one regardless of the curing period. It is indicated that the open-air curing was effective to control the alkalinity of treated sludge. After 1 or 2days of curing, the pH decreased immediately. After the hydration with curing, the pH increased gradually. The water content of treated sludge was decreased directly after stabilization. These additives are efficient to reduce the water content of sludge. The concentration of calcium ion increases with longer curing period. And the samples in open-air curing show larger amount of leached calcium ion than sealed curing ones.

The qualities of leached water for 28 days aged samples according to the soaked period are shown in Fig.5 and Fig. 6. Fig. 5 is concerned with pH change of that soaked water. The pH of samples under open air condition is lower than ones in sealed curing. The open air curing is effective to control pH. Fig 6 shows the

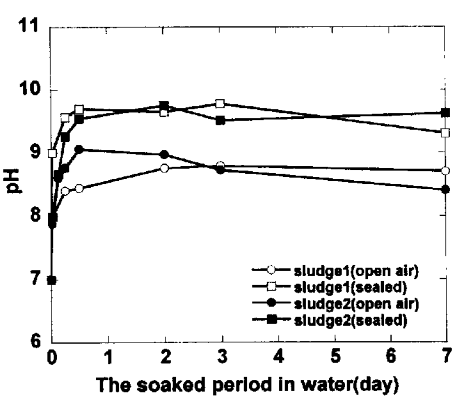


Fig. 5 pH change of leached water from 28 days age sample

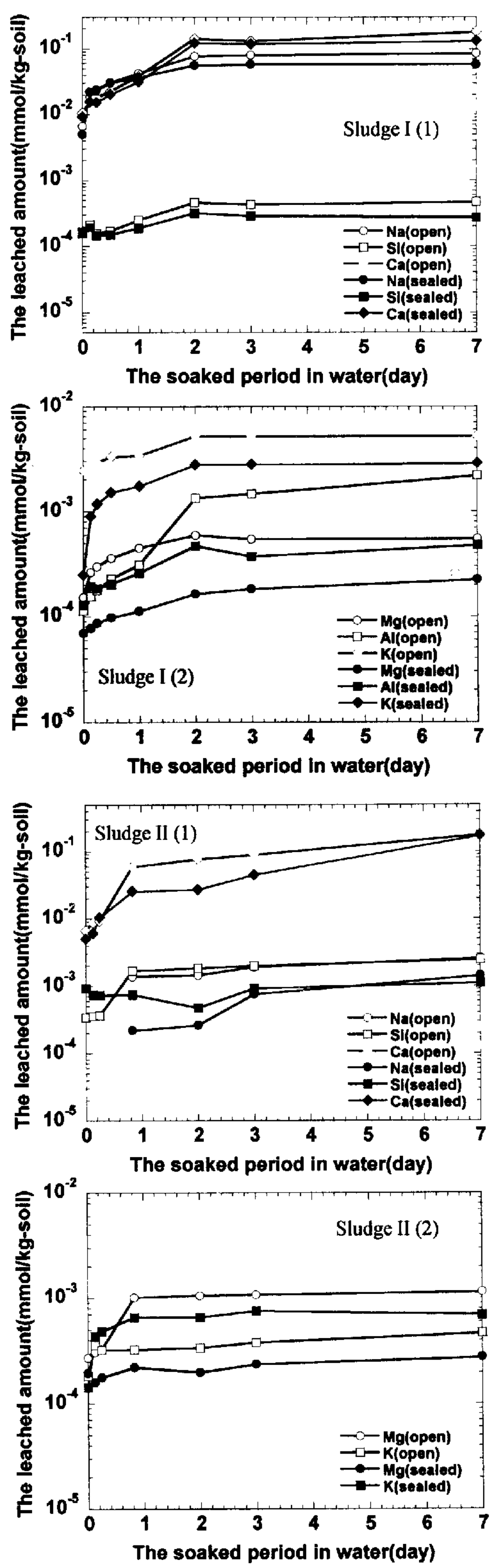
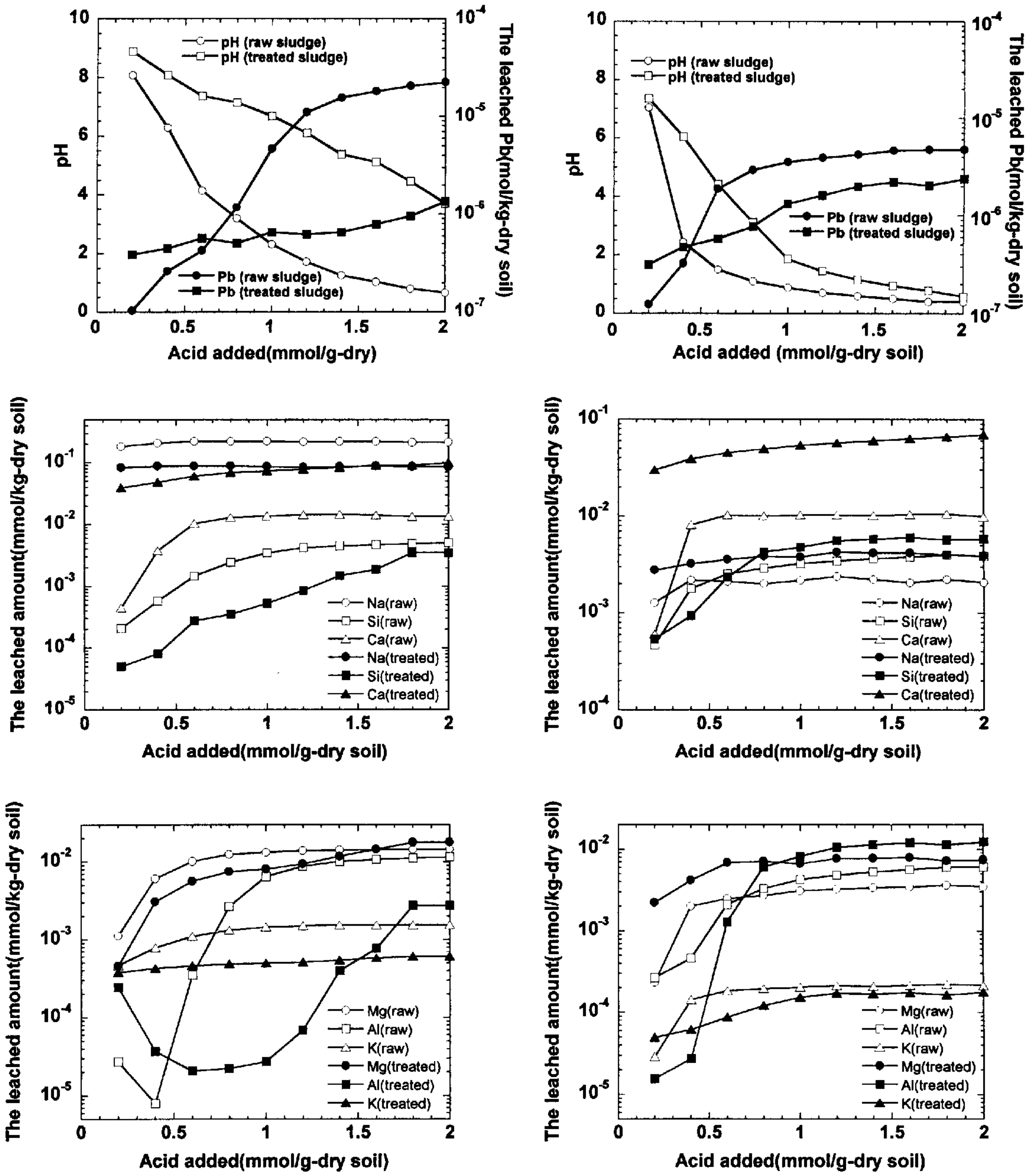


Fig. 6 Leached amount of ions from 28 days age sample



(a) Sludge I (b) Sludge II

Fig. 7 Results of acid neutralization capacity tests

leached amount of ions from 28 days age samples. These results shows that the leached amount of ions in open-air samples is slightly larger than sealed curing samples. In open-air treated sludge, sodium, silicate, calcium, magnesium, and aluminum except potassium were more leached than sealed curing one. The Acid Neutralization Capacity Test results are shown in Fig. 7. When adding an acid into soil, secondary products were created by reaction between soil mineral and hydrogen ion. The acid neutralization capacity was result of this reactions and some cation dissolved in liquid. The raw sludge I has larger acid neutralization capacity than sludge II. It indicates that the raw sludge I originally had more exchangeable cations on its particle surface. Fig. 7 also indicates the relationship between the amount of leached Pb and the added acid. After treatment, the amount of leached Pb from sludge I is less than sludge II. Sludge I and Sludge II get higher capacity for acid and less leached lead by stabilization with this additives. The leached calcium ion of sludge I and II became larger than before treated.

The magnesium quantity of sludge II increase after S/S. Because the solubility of cations is different in conditions of liquid (e.g. pH, redox and temperature etc), to understand these phenomena, more detail study is required.

6. Conclusions

The strength test, leaching test and ANC test evaluated the low alkalinity additives composed with gypsum, some slag and polymer. These additions have the effect of controlling the pH due to stabilization procedure and could be substitute for cement and lime, to stabilize and treat dredge material and high water content sludge. The polymer material was also effective to treat high water content sludge. In case of open-air curing samples, the pH of treated sludge was less than sealed curing ones. It seems to the effect of CO_2. Although, the added amount of binder in sludge I was larger than sludge II, the pH of treated samples were similar in same curing condition. And a larger ANC, generally reflects the chemical stability or weathering, was achieved by stabilization with these low alkalinity additions.

The low alkalinity additions obtained a high applicability to stabilized dredged sludge with the stable pH variation.

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要　旨

浚渫に伴い発生する高含水比汚泥の処理方法としては、普通ポルトランドセメントもしくは石灰による固化処理が一般的である。セメントもしくは石灰による固化処理は強度と耐久性の面で優れており、さらに浚渫土に含まれうる重金属に関しても、封じ込め効果による溶出の低減が期待できる。しかし、固化処理に起因するアルカリ分の溶出が木質、植生等へ影響を与えることが指摘されており、従来から、その制御に関する研究が進められている。本研究では、石膏を主体とした固化材を用して、固化処理土からアルカリ分の溶出を低減する配合、養生方法について検討を行った。さらに、各種溶出試験を行い、重金属の封じ込め効果についても評価を行った。

キーワード：浚渫土、固化処理、低アルカリ性固化材、酸緩衝容量、重金属