Effectiveness of immobilizing agent used as a sorption layer against natural contamination

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ABSTRACT

Excavated soils and rocks generated from construction works sometimes contain heavy metals derived from nature. Without proper treatment, these soils will generate hazardous leachate and cause environmental contamination. Sorption layer method is a newly developed technology which has a potential to be an economical countermeasure. It utilizes a permeable soil layer with sorption capacity lying beneath piled soil and rock in embankments to retain the chemicals of concern dissolved in the leachate, thus making the effluent meeting the environmental standard. In this study, the performance of sorption layer by mixing decomposed granite soil with Ca/Mg composite immobilizing agent is discussed. The mechanical, hydraulic and sorption performances of soil-immobilizing agent mixture affected by different mixing ratio and curing period is evaluated. Experimental results showed that curing increase the unconfined compressive strength of the mixture. Higher immobilizing agent content exhibited higher sorption capacity.

Keywords: natural contamination, sorption layer, immobilizing agent, unconfined compressive strength, hydraulic conductivity, sorption

1 INTRODUCTION

Excavated soils and rocks generated from construction works sometimes contain heavy metals (e.g. lead, cadmium) and/or metalloids (e.g. arsenic, selenium). Once excavated in construction works, leaching of these metals may be triggered due to the oxidization and decomposition of sulfide minerals contained in the soils and rocks. Without proper managements and/or treatments, acid leachate containing unacceptable concentrations of heavy metals and/or metalloids might be generated (Mo et al. 2014).

For the remediation of soils containing heavy metals derived from nature, several countermeasures including containment method, insolubilization method and sorption layer method have been proposed by the Amending Soil Contamination Countermeasures Act issued by the Japan Ministry of the Environment in 2010. Containment method uses seepage control works to reduce generation of leachate, and low-permeable compacted soil layers or geomembrane sheets to prevent migration of the leachate. The potential slope failure due to low interface friction between piled soils/rocks and geomembrane sheet is a concern of this method. In addition, its execution cost is hard to afford when treating a huge amount of soils and rocks. Insolubilization method mixes contaminated soils with solidification and/or stabilization agents to fix the heavy metal and reduce the leaching potential. Its long-term performance under field conditions is not fully verified and has been a major concern. Sorption layer method (Technical Committee of Environmental Conservation Technology Association, Hokkaido 2012) utilizes a permeable soil layer lying beneath the piled soils and rocks to retain the leachable amount of contaminants to an acceptable level. To strengthen the sorption capacity as well as the bearing capacity of the sorption layer, immobilizing or stabilizing agent is often employed by mixing with a clean host soil.

This study was conducted to evaluate the performance of the sorption layer, which was prepared by mixing a typical soil, decomposed granite soil, with the Ca/Mg composite immobilizing agent (The Society of Material Science, Japan 2014). The specific objective of this paper is to obtain mechanical, hydraulic and equilibrium sorption performances of the soil-immobilizing agent mixture, influenced by mixing ratio of the agent and curing period after mixing. The effectiveness of immobilizing agent addition on improving the geotechnical properties and against natural contamination was evaluated.

2 BACKGROUND

Active volcanic activity and diastrophism due to the circum-Pacific earthquake belt result in higher
concentration of heavy metals and metalloids in soils and rocks. Different from man-made contaminated soils, natural soils and rocks often contain sulfide minerals such as iron pyrites, which will be oxidized and decomposed when exposed to air and rain, thus stimulating the leaching of metals since these process produce sulfide acid, and the leachate pH is decreased accordingly. Excavated amounts of soils containing natural derived heavy metals and metalloids in selected tunnel construction projects executed in Japan are listed in Table 1.

Table 1. Construction projects generating soils containing heavy metals derived from nature

| Project                    | Heavy metals | Soil volume | Reference       |
|----------------------------|--------------|-------------|-----------------|
| Nakagoshi Tunnel, Hokkaido | As           | 800,000 m³  | Fuji et al. (2005) |
| Hakkoda Tunnel, Aomori     | As, Pb, Cd, Se | 540,000 m³ | Sasaki et al. (2005) |
| Subway Tozai line, Sendai  | As, Cd, F, Pb, Se | 400,000 m³ | MLIT, Japan (2010) |
| (Odatekita-Kosaka, Akita)  | Se, As, F    | 900,000 m³  | Igarashi (2007)  |

Because of the huge generation amount of soils and rocks, containment in situ is a reasonable solution. Thus, sorption layer method was developed for in situ containment of excavated soils and rocks. This method utilizes a permeable soil layer with sorption capacity for contaminants of concern underlying the piled soils and rocks in embankment. The concentrations of contaminant in the leachate should be lowered, and the time when the contaminants reach the surrounding environment should also be retarded. The effluent flowing out of the sorption layer is expected to meet the environmental standard (Fig. 1). This method can achieve two targets at the same time, first is to prevent underground water from being contaminated and second is to remove the contaminant from soil.

Rainfall infiltration is limited by soil cover to avoid generating more leachate. The composition of this layer can be natural material (soil, minerals), artificial material (immobilizing agents) or the mixture of them. The process is similar to that of a horizontally placed permeable reactive barrier, where the leachate can pass the sorption layer under a certain velocity and contaminants of concern is decomposed or sorbed by the composition material of the layer during permeation. The definitive aim of this method is not to completely block the contaminants, but to lower their concentrations to an acceptable level.

Construction of the sorption layer is relatively easy, which usually consists of mixing and laying the layers with proper compaction. The contact between piled soils/rocks with soil layer is more stable compared to geomembrane sheet. There is no need for additional drainage equipment/work, which enables it low cost and easy management. However this method also has its limitations. It is not applicable when the groundwater level is high, because the groundwater may pass the sorption layer and enter the embankment. Thus, when certain working conditions for the sorption layer method can be met, its advantage of easy construction, low cost and good stability make this method act as an economical countermeasure for huge amount of excavated soils and rocks, although some technical issues should be addressed.

Immobilizing or stabilizing agent is often employed to strengthen the sorption capacity as well as the bearing capacity of the sorption layer. The process is quite different from the conventional immobilization or stabilization practices. The clean host soil-immobilizing agent mixture contact the contaminants dissolved in the leachate instead of mixing agent directly with contaminated soil. Thus, how this difference affects the sorption performance is needed to be studied. Particularly, the hydraulic performance should be preliminarily evaluated to ensure whether the leachate flows through the sorption layer continuously as expected, since flow conditions (flow rate, retention time, etc.) are key issues for the sorption performance. In addition, the effect of adding immobilizing agent on mechanical properties of the sorption layer, including the strength and deformation properties, should be taken in consideration in designing the sorption layer.

The authors verified that Ca/Mg composite immobilizing agent was able to immobilize both metal cations and anions in water-soluble forms (Bobea et al. 2012). Thus, the agent is expected to effectively immobilize arsenic, which is most frequently contained in naturally contaminated soils and rocks found in Japan. This study was conducted to evaluate the geotechnical properties and performances of the sorption layer using Ca/Mg composite immobilizing agent under different conditions, by conducting a series of laboratory experiments. The main focus was placed on effects of the stabilizer content and curing time on the mechanical, hydraulic, and sorption performances of the mixtures.

3 MATERIALS AND METHODS
3.1 Materials
Commercially available decomposed granite soil
(particle density, $\rho_s = 2.70 \text{g/cm}^3$) was used as a host soil. Soil particles which passed a 2 mm-opening sieve were used. The particle size distribution curve of decomposed granite soil after sieving is shown in Fig. 2. pH of the suspended soils in the liquid to solid ratio ($L/S = 5$) was used as a host soil. Soil particles which passed a 2 mm-opening sieve were used. The particle size distribution curve of decomposed granite soil after sieving is shown in Fig. 2. pH of the suspended soils in the liquid to solid ratio ($L/S = 5$) was determined.

Ca/Mg composite immobilizing agent, which was manufactured through calcination of selected natural minerals by Sumitomo Osaka Cement Co., Ltd., was used. Properties of the material are shown in Table 2 (The Society of Materials Science, Japan, 2014).

![Fig. 2. Particle-size distribution curve of decomposed granite soil under 2mm](image)

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| Items                        | Standard/Method | Value          |
|------------------------------|-----------------|----------------|
| Bulk density                 | JIS R 9301      | 0.90 g/cm$^3$ |
| pH (25 °C)                   | 1 g in 100 mL water Mixing 1 hour | 10.3            |
| Blaine’s specific surface area | JIS R 5201     | 4200 cm$^2$/g |
| Water content                | 5g, Dried under 110 °C | 0.21 wt%       |
| Main component               | JIS R 9011      |                |
| CaO                          |                 | 35.6 %         |
| MgO                          |                 | 19.4 %         |
| SO$_3$                       |                 | 3.98 %         |
| Fe$_2$O$_3$                  |                 | 3.73 %         |
| SiO$_2$                      |                 | 1.52 %         |
| Ignition loss                |                 | 33.5 %         |

To prepare the soil-immobilizing agent mixture, Ca/Mg composite immobilizing agent was mixed with the air-dried decomposed granite soil by 0%, 3% and 5% of its dry weight. Distilled water was then added to adjust the water content of the mixture to its optimum water content (10.1 to 11.3%), which was determined by the A-a method of JIS A 1210 (2009).

3.2 Unconfined compression test

Unconfined compression test were conducted according to JIS A 1216 “Method for unconfined compression test of soils”. The soil-immobilizing agent mixture was compacted in a cylindrical mold in three layers immediately after being prepared. The dimension of the mold is 5 cm in diameter and 10 cm in height. The compaction degree was set to 95%. After compaction, specimen was taken out of the mold, warped by cling film and put in a fully-sealed plastic box to be cured for 0 or 7 days.

3.3 Hydraulic conductivity test

Hydraulic conductivity tests were conducted according to ASTM D 5084 “Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter” (Fig. 3). The hydraulic gradient is set to 5 and cell pressure of 30 kPa was applied. Distilled water was used as permeant solution.

![Fig. 3. Schematic view of a flexible-wall permeameter](image)

The compaction condition was similar with unconfined compression test, except that the specimen dimension was 6 cm in diameter and 7 cm in height. After compaction, cling film was used to wrap the mold, and the specimen was cured for 0 or 7 days with the mold together. After curing, the specimen was submerged in distilled water and saturated by vacuum deaeration for at least 24 hours. Then, the specimen was set on the flexible-wall permeameter. It was sandwiched with filter papers, filter clothes, porous caps and pedestals, confined by a latex membrane on the sides. Permeation was conducted until hydraulic conductivity value was stable and 5 or more pore volumes of flow are permeated.

3.4 Batch sorption test

The preparation of specimens was same with that for the unconfined compression test. After curing, specimens were crushed ($\leq 2$mm) and mixed with the NaAsO$_2$ solution in $L/S = 20$. The concentration of the solution is 0.1, 0.5, 1, 5 and 10 mg/L. The samples were subjected to 24 hours horizontal shaking at 150 rpm, then left for 15 minutes. Solid-liquid separation was done by centrifugation under 3,000 rpm for 20 minutes and filtering using a 0.45μm-opening membrane filter. Arsenic concentrations before and after the sorption test were analyzed by an atomic absorption spectrometry (AAS) method (SHIMAZU, AA-6800).

4 RESULTS AND DISCUSSION

4.1 Unconfined compressive strength

For each mixing ratio (0, 3, and 5%) and curing period (0 and 7 days), unconfined compression tests
were conducted in triplicate. The stress-strain curves were shown in Fig. 4.

(a) Stress-strain curves of samples with mixing ratio of 0% (decomposed granite soil after compaction)

(b) Stress-strain curves of samples with mixing ratio of 3%

(c) Stress-strain curves of samples with mixing ratio of 5%

Fig. 4. Stress-strain curves variation with different cases

After 7-day curing, the unconfined compressive strength \(q_u\) of soil-immobilizing agent mixture were greatly improved compared to that of 0-day-curing specimens. Hydration reactions which occurred during curing are considered as the main reason for improving unconfined compressive strength, which can be expressed as follows:

\[
x_{\text{Ca} (OH)_{2}} + \text{SiO}_2 + n\text{H}_2\text{O} \rightarrow x\text{CaO} \cdot \text{SiO}_2(n+1)\text{H}_2\text{O} \quad (1) \\
x_{\text{Mg(OH)}_2} + x\text{SiO}_2 + n\text{H}_2\text{O} \rightarrow x\text{MgO} \cdot \text{SiO}_2(n+1)\text{H}_2\text{O} \quad (2)
\]

The calcium/magnesium silicate hydrates and sequent crystallization resulted in the cohesion of soil particles and thus increased the strength of soil-immobilizing agent mixture.

However, mixing ratio has no obvious on improving the unconfined compressive strength since the \(q_u\) value between mixing ratio of 3% and 5% after curing is both approximately 100 kN/m². Kamon et al. (1996) also revealed same limited improving effect of additional immobilizing agent content after curing. The similar improving effect indicates that the extent of hydration reactions of two cases is similar, which is due to the insufficient water amount in the curing period. Generation of calcium and magnesium hydroxide was limited because water was supplied according to the optimum water content and only part of the calcium/magnesium oxide offered by the immobilizing agent can react with water. Thus, the limited and similar generation of calcium/magnesium hydroxide resulted in the similar extent of hydration reactions and accordingly the same improving effect. The \(q_u\) value at 0-day curing of mixing ratio of 5% is higher than that of 3%, which reflects that additional immobilizing agent can slightly increase the unconfined compressive strength without curing, which is probably caused by the reaction happens immediately after addition. But the improving effect is not as obvious as curing.

4.2 Hydraulic conductivity

For each mixing ratio (0, 3, and 5%) and curing period (0 and 7 days), the tests were conducted in duplicate. The results of hydraulic conductivity test were shown in Fig. 5. The representative hydraulic conductivity is determined after the value was stable over time.

There is no obvious change in hydraulic conductivity and all representative value is within one order between 1×10⁻⁶ m/s to 1×10⁻⁷ m/s. Thus, hydraulic conductivity of the soil-immobilizing agent mixture is not greatly affected either by mixing ratio or by curing periods. Since the leachate needs to flow through the sorption layer in long term to ensure that heavy metal can be sorbed, it is preferable that hydraulic conductivity is not too low and can keep almost constant throughout the application period.

Curing increases unconfined compressive strength however has no obvious effect on hydraulic conductivity. This is probably because the hydration reactions, which are considered as the main reason for improving unconfined compressive strength during curing period, could also happen during permeation in 0-day curing specimens considering that the tests lasted for several days. Thus, the microstructure of the specimens with or without curing, and accordingly the hydraulic conductivity values became similar.

Decomposed granite soil has relatively lower hydraulic conductivity than soil-immobilizing agent mixture. This is probably due to aggregation after addition of the immobilizing agent. However, mixing ratio has no obvious effect on the hydraulic conductivity.
conductivity, which is probably caused by the similar extent of hydration reactions. The total amount of silicon dioxide offered by the decomposed granite soil in both 3% and 5% case was almost same and the hydration reactions were limited to similar extent.

Japanese environmental standard of arsenic for soil and ground water quality, which is 0.01 mg/L was applied as a reference value for equilibrium concentration. Following relation was applied to calculate the sorption amount:

$$ S = (C_0 - C_{eq}) \times \frac{V}{m} $$

where $V$ is the volume of the solution (L), $m$ is the mass of the sorbent (g), $C_0$ is the initial concentration of the solution (mg/L). The results are shown in Table 2.

### 4.3 Sorption performance

For each mixing ratio (0, 3, and 5%) and curing period (0 and 7 days), batch sorption tests were conducted in triplicate. Initial pH of each arsenic solution without adjustment ranges from 6 to 10.

Sorption isotherms in linear scales with the equilibrium concentrations ranging from 0 to 1.5 mg/L are shown in Fig. 6.

Sorption isotherms were determined by an empirical relation between the equilibrium concentration of the solute and the sorbed amount based on Freundlich equation expressed as follows:

$$ S = kC_{eq}^n $$

where $S$ is the sorption amount (mg/g), $C_{eq}$ is the equilibrium concentration of the solute (mg/L), $k$ and $n$ are constants.

The sorption amount on soil-immobilizing agent mixture with different mixing ratio and curing periods were calculated under a same hypothetic equilibrium concentration to compare the sorption capacity. The sorption capacity of soil-immobilizing agent mixture increases with increasing mixing ratio. However, it is not affected by curing periods.
Table 2. Sorption amount for the equilibrium concentration of 0.01 mg/L

| Mixing ratio | Curing periods | Sorption amount (mg/g) |
|--------------|----------------|-----------------------|
| 0%           | 0 day          | 0.0013                |
| 3%           | 0 day          | 0.014                 |
| 3%           | 7 days         | 0.012                 |
| 5%           | 0 day          | 0.021                 |
| 5%           | 7 days         | 0.023                 |

Three different sorption mechanisms for arsenic may exist when using Ca/Mg composite immobilizing agent as the sorbent. First is the generation of low solubility substance such as CaHAsO₃ by calcium and arsenic. Second is the surface attraction by magnesium hydroxide, which has a high positive charge and strong electrostatic affinity for the negatively charged arsenate. Third is the surface attraction by hydration products such as calcium/magnesium silicate hydrate, which has very high specific surface area. The negative charged SiO₂⁻ surface can be reversed by accumulated Ca²⁺ or by chemical reaction with calcium (Phenrat et al. 2005).

Since curing has no obvious effect on sorption capacity, thus hydration products which are the main outcome of curing are not responsible for the sorption of arsenic. There are two possible explanations for the inconspicuous effect of curing. First explanation is that effect of hydration reactions were eliminated in batch sorption test by crushing and shaking. The cohesive soil structure was broken and the advantage of high specific surface area and positive surface charge no longer existed during the test. Second reason is that most Ca²⁺ precipitated with arsenic oxyanion directly instead of overcompensation of the hydrate surface or participated in the chemical reaction to reverse the surface change. The negative charge of the hydrate surface is not able to attract arsenic oxyanion onto its surface.

Thus, the other two mechanisms, which is the precipitation by calcium with arsenic and the surface attraction by magnesium hydroxide should have the major effect. This is corresponding with the increasing sorption capacity with adding immobilizing agent. Because higher immobilizing agent content provides more available calcium and magnesium which promotes the sorption of arsenic.

5 CONCLUSIONS

This research was conducted to evaluate the unconfined compression, permeability and equilibrium sorption characteristics of the soil improved by the Ca/Mg composite immobilizing agent as a sorption layer against natural contamination.

Curing increases the unconfined compressive strength and mixing ratio has no obvious effect. After curing, additional immobilizing agent after 3% did not increase the unconfined compressive strength.

Hydraulic conductivity keeps almost constant and not affected by curing periods and mixing ratio under

the addition of the agent with 5% in dry weight basis in maximum. Due to time constraints, only 7-day curing was conducted, longer curing period is necessary in future research to verify the results.

Sorption capacity increases with the increasing immobilizing agent. However, curing periods has a minor effect on the sorption capacity in batch test. Major mechanism for sorption of arsenic is formation of precipitation between arsenic with calcium and surface attraction on magnesium hydroxide.

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