

Chemical compatibility of fine and coarse Ca/Mg composite to mitigate natural contamination

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ABSTRACT

Utilization of excavated surplus soil, in which arsenic (As) and lead (Pb) occur naturally, as a geomaterial is of increasing significance over the past decades in Japan because of limited remaining landfill space. For minimizing the release of hazardous heavy metals and metalloids to the surrounding environment from such naturally contaminated geomaterials in an embankment, installing a permeable soil layer with sorption capacity beneath the embankment should be an effective and sustainable way without excessive investments. The containment function of the soil layer can be enhanced when the sorption capacity of the clean parent soil for targeted contaminants is increased. In this regard, the applicability of calcium/magnesium (Ca/Mg) composite, as an immobilizing agent, to enhance the sorption capacity for As was evaluated via batch equilibrium and saturated column sorption testing. Non-linear sorption of As onto soil amended with agent was observed over the concentration ranges of interest. Adding Ca/Mg composite to clean parent soil can enhance the containment of As via an increase in sorption capacity, but the enhanced sorption capacity will be a function of both the amount of agent added and agent particle size. Addition of 5% agent increased the sorption capacity relative to that of soil amended with 3% agent by 50%, whereas the amount of As sorbed by soil amended with fine (under 2-mm) agent was higher relative to that amended with coarse (above 2-mm) agent by a factor of 2. Ca-As compounds which are less mobile and toxic, and stable in the alkaline condition, are likely to be precipitated from the soil-agent sorption layer.

Keywords: arsenic; Ca/Mg composite; particle size; naturally contaminated soils; sorption layer

1 INTRODUCTION

Utilization of surplus soil generated from many large-scale construction projects, such as excavation in mountainous terrains for the shinkansen lines, is of increasing significance over the past decades in Japan because of limited remaining landfill space. However, heavy metals are naturally present in the geological strata in many parts of Japan. As a result, surplus soil which are naturally contaminated are frequently encountered in many construction projects nationwide (Ministry of Land, Infrastructure, and Transport, 2014). Since such excavated surplus soil often contain non-anthropogenic heavy metals at relatively low levels, we must properly manage them not to pollute the surrounding environment when utilized as geomaterial. Notably, metals present in such soils can have a wide range of debilitating effects on the human body if subjected to prolonged exposure as some, such as arsenic (As) and lead (Pb), are carcinogenic or toxic (Matta and Gjyli, 2016). Therefore, by considering the characteristics of heavy metals and environmental risks, we need to reasonably utilize the naturally contaminated soils by controlling the environmental

risks within acceptable levels.

In some construction works, such contaminated soils have been utilized as subgrade or fill-material of embankment, with hydraulic barriers to isolate them from the surrounding environment. However, it has been pointed out that containment of the contaminated soils with the barriers is not cost-effective. In addition, boundaries between the barrier materials and soil layers can be geotechnically weak and may behave as a slip surface (Koerner and Daniel, 1997). An alternative way (sorption layer method) which can be effective and sustainable, without excessive investments is been promoted (Tabelin et al., 2018). In this approach, the contaminated soils are placed on top of a permeable clean soil layer with sorption capacity (sorption layer), and then covered with low-permeable soils, in a structural configuration as illustrated in Fig. 1.

The release of hazardous metals to the surrounding environment from such contaminated geomaterials in an embankment, can be minimized by the sorption layer. Immobilizing agent is often employed to enhance the sorption capacity as well as the bearing capacity of the soil layer. It is mixed with the clean parent soil, and

its sorption capacity is expected to be enough as a sorption layer. In this regard, several authors have looked into the sorption of As with natural materials such as volcanic ash soil (Tangviroon et al., 2017), and synthetic materials which mainly contain Mg, Si/Ce, and Fe (Tabelin et al., 2013). The authors indicated that optimal performance depends on the pH and metal speciation at various magnitudes for the different materials studied. In laboratory studies it is possible to control such parameters, but it would be difficult to do so in natural environments.



Fig. 1. Schematic of the sorption layer installed beneath the naturally contaminated soils in an embankment.

Calcium/magnesium (Ca/Mg) composite, which is manufactured from thermal treatment of dolomite-like natural minerals, was verified to immobilize both metal cations and anions in water-soluble forms (Bobeia et al., 2012). In addition, Seo et al. (2015) pointed out that the material can strongly enhance the As sorption capacity of soil in a wide range of pH (4-12) and has a high pH buffering effect. However, handling of the powder type agent can be difficult, and it cannot be homogeneously distributed in the parent geomaterial, which can affect performance of the sorption layer. Therefore, we proposed the use of coarser type agent to solve this issue. However, since the sorption layer method has a limited fail-safe option, we must assert that the coarser material is still effective as an immobilizing agent, and this was done via sorption testing with As solution.

To investigate the factors which can influence the extent of enhanced sorption, batch equilibrium testing, was carried out. Specifically, we examined the effects of different particle sizes of agent, amount of agent added, and curing period. Although the results of these tests can provide proof of enhanced sorption, the extension of the results to practical application is limited, in part, by the conditions inherent in the testing method, such as static (no-flow) conditions. For this reason, we also carried out saturated column testing whereby the material is permeated with solution of targeted contaminant, which is more representative of practical application. The findings can help clarify the mechanism and factors affecting the enhanced sorption of clean parent soil. This is our most important research objective, which is to assess the reliability and risk associated when using a clean parent soil amended with the coarser type agent, as a sorption layer.

2 EXPERIMENT DETAILS

2.1 Materials and reagents

Commercially available, clean decomposed granite soil with particle density of 2.70 g/cm^3 , was oven-dried and used after sieving with a 2-mm opening screen, as a parent geomaterial. This soil was selected because of its wide distribution in Japan and low chemical activity which helps to evaluate exclusively the performance of the Ca/Mg composite.

Ca/Mg composite, which is mainly composed of CaCO_3 , MgCO_3 , MgO , and FeSO_4 , was obtained from Sumitomo Osaka Cement, and used as an immobilizing agent. Two types of the agent with distinct particle size i.e., fine (under 2-mm) and coarse (above 2-mm) were used for the experiments. The specific surface area of both the fine and coarse type agent was estimated via the Brunauer-Emmett-Teller (BET) method. The surface area values are almost same, which indicates that the pores and voids in both materials are identical. The physicochemical properties of the material are summarized in Table 1.

Table 1. Physicochemical properties of Ca/Mg composite.

Property		Value	
Specific surface area ¹		3.7 m ² /g (fine)	
		3.6 m ² /g (coarse)	
Main component ²			
CaO	35.6%	Fe ₂ O ₃	3.73%
MgO	19.4%	SiO ₂	1.52%
SO ₃	3.98%	Al ₂ O ₃	0.07%
		P ₂ O ₅	0.04%

¹Brunauer-Emmett-Teller (BET) NO_2 method

²JIS R 9011. The Society of Material Science, Japan (2014)

Clean parent soil was amended by adding the agent in different proportions on dry mass (wt.) basis i.e., 3% wt. agent with 97% wt. soil and 5% wt. agent with 95% wt. soil. The water content of the mixture was adjusted to its optimum value (10-11%) by adding distilled water and then thoroughly mixed again.

Arsenic solutions used in the sorption experiments were prepared by dissolving accurate amount of reagent grade NaAsO_2 powder (Wako, Japan) in distilled water to produce stock solution of 1000 mg/L. Appropriate dilutions were then made to give a range of As concentrations.

2.2 Batch equilibrium test

The mixture was compacted in three equal layers (= 2.3 cm each) in a mold 6 cm in inner diameter and 7 cm in height. The amount of sample mass for each layer was standardized based on standard Proctor compaction test (JIS A 1204) results and with a compaction degree of 95%. The compacted sample was extruded and cured for 7 days or 28 days, by wrapping it with a cling film and storing in a humid, sealable plastic bag.

In this experiment, the cured sample was gently etwujgf" *x" 607" o o+" cpf" rwv" kpq" eqpvcev" ykvj" Cu" solution with concentrations varying in the range of

0.1-10 mg/L, to achieve a liquid/solid ratio (L/S) of 10, in a capped plastic bottle and shaken at 20°C room temperature with a mechanical shaker (TAITEC TS-10) for 24 hours at 150 revolutions per minute (rpm) in the horizontal direction. Solid-liquid separation was achieved via centrifugation under 3,000 rpm for 1 hour and filtering with c"2067 o-opening membrane filter.

Following the sorption experiment, the residual As concentration in solution, C (mg/L), of each of the sample effluents was determined. The sorbed amount, S (mg/g), accomplished by the agent was calculated by subtracting the residual As concentration from initial As concentration. Sorption isotherms were determined by an empirical relation between residual concentration and sorbed amount, based on the Freundlich equation.

2.3 Saturated column test

Saturated column percolation tests were conducted using rigid-wall columns. The samples were prepared in a similar manner to that of the batch test, but curing was not done. Samples were compacted in three equal layers (= 1 cm each) with a 95% compaction degree into the acrylic cylinder 10 cm in inner diameter and 3 cm in height, to achieve a void ratio of 0.40 and saturated density of 2.20 g/cm³. The inner cylinder surface was smeared with silicone grease (HIVAC-G) to prevent wall-edge flow. Filter paper and porous plate were placed at each end of the soil column to contain the soil and prevent any blockages in the tubes by small particles. After filling, distilled water was first supplied into the column to saturate the samples. Arsenic solution with a concentration of 0.1 mg/L was then continuously supplied from the lower end of column at a constant flowrate of 15 cm³/hour by a peristaltic pump. Effluent was collected at various cumulative flow volumes (L/kg). Collected effluent was filtered using a 0.45 µm-opening filter, and the pH, EC, Eh, and concentrations of water-soluble constituents measured.

3 RESULTS AND DISCUSSION

3.1 Factors affecting enhanced As sorption of soil

Non-linear sorption of As onto the samples was observed over the concentration ranges of interest, as illustrated in Fig. 2. Sorption data was best described by the Freundlich isotherm, which indicates sorption is not limited to monolayer and the As molecules migrate to the heterogenous surfaces (Adamson and Gast, 1997). All samples were capable of As sorption, but the amount sorbed by fine agent amended soil was higher relative to soil amended with coarse agent by a factor of 2. Since BET surface area values were almost same, as indicated in Table 1, the higher sorption capacity was due to an increase in the outer contact surface area provided by fine agent particles, which increased the active-sorption sites. Furthermore, addition of 5% agent in soil increased its sorption capacity relative to that amended with 3% agent by 50%. The increase in agent

content provides more available Ca and Mg that enhances the sorption of As.

Since the ability of the agent to immobilize dissolved As is predominantly due to the presence of Ca- and Mg- hydroxide phases formed via hydration, we examined the effect of curing time on the sorption of As. Fig. 2 clearly shows that the sorption isotherms for the samples cured for 7 days and 28 days were similar, which indicates that curing period had no effect on the sorption of As. Results suggest that hydration of Ca- and Mg- compounds occurred at an early stage (within 7 days), and no further hydration occurred with prolonged curing time, which may have increased the availability of Ca and Mg ions.

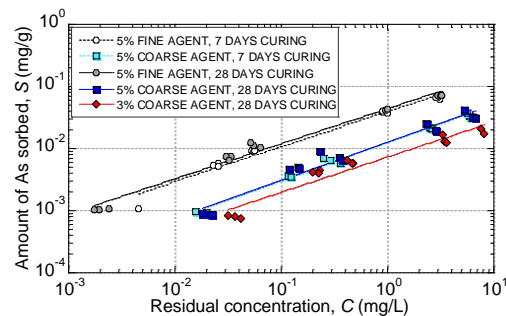


Fig. 2. Linearized plot of Freundlich isotherms.

The As sorption capacity increased with rise in the initial As concentrations. However, at concentrations above 0.5 mg/L, the residual As concentration exceeded the environmental leachate standard in Japan (10µg/L). This suggests that use of the soil-agent sorption layer should be limited to As concentrations below 0.5 mg/L, which is the typical concentration of As leached from naturally contaminated soils.

3.2 Enhanced As sorption based on column testing

The As sorption capacity of the samples in column test (at 10 L/kg) was found to vary from that of batch test by ±20%. Fig. 3 shows that soil amended with fine agent offered better sorption performance and the dissolved As was lowered to below 32" i1N."wpvkn"72 L/kg. The difference in residual As concentration between soil amended with fine agent and that amended with coarse agent was observed until 100 L/kg, after which about 50% As was sorbed.

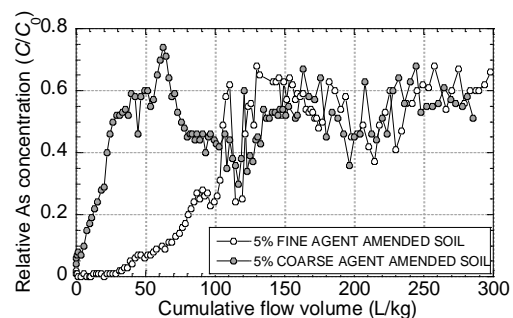


Fig. 3. Arsenic breakthrough curve.

Effluent pH was increased from slightly alkaline (pH 7) to strongly alkaline condition (pH 9-10), but the effluent pH reduced with time, which indicates that the pH buffering property of the agent is not consistently high. Based on the Eh-pH characteristics (i.e., pH 9-10, Eh 300-400 mV) under equilibrium conditions, As(V) in the protonated anion state, HAsO_4^- , was speculated to be dominant in the effluent.

During sorption of As, cations particularly Ca and Mg ions were leached, as shown in Fig. 4, but the Ca^{++} concentration (at any given time) was higher than Mg^{++} . One of the reasons for this is that the agent contains more Ca- than Mg- compounds, as indicated in Table 1. Correlation was observed between the leaching of Ca ions and the sorption of As.

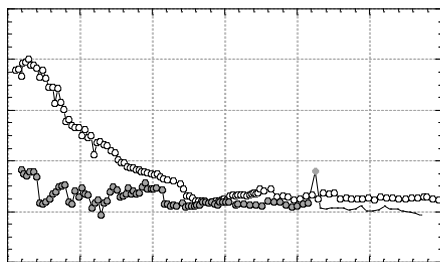


Fig. 4. Leaching trend of Ca and Mg ions during sorption of As.

The results suggest that the main As sorption mechanism is controlled by the dissolution and precipitation of Ca-As compound [$\text{CaHAsO}_4(\text{H}_2\text{O})$], which is less mobile and toxic, and stable over a wide pH range of about 3-12.5 (Bothe and Brown, 1999).

4 CONCLUSIONS

The applicability of fine and coarse type Ca/Mg composite, as an immobilizing agent, to enhance the As sorption capacity of clean parent soil was evaluated via batch equilibrium and saturated column testing. From this research, we reached the following conclusions:

- (i) Adding 5% agent to soil increased the As sorption capacity relative to that of soil amended with 3% agent by 50%, whereas the amount of As sorbed by soil amended with fine type agent was higher relative to that amended with coarse type agent by a factor of 2.

- (ii) Effluent pH was increased from slightly alkaline (pH 7) to strongly alkaline condition (pH 9-10), but the pH buffering effect of agent reduces with time.
- (iii) Ca-As compounds which are less mobile and toxic, and stable in the alkaline condition, are likely to be precipitated from the soil-agent sorption layer.

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