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# Enhanced sorption of attenuation layer underlying excavated soils with natural contamination

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**ABSTRACT:** Naturally-contaminated soils are frequently generated in surplus amounts through construction activities in Japan. To minimize impact of the contaminants on the surrounding environment when such soils are reused in geotechnical structures, installing a permeable soil layer with sorption capacity beneath the contaminated soils should be an effective way without excessive investments. Mineral-based immobilizing agent is added to the natural soil to improve its sorption capacity against heavy metals and metalloids. In this study, the effect of agent particle size on the arsenic (As) sorption performance of soil amended with calcium/magnesium (Ca/Mg) composite was investigated in batch and saturated column tests, in order to evaluate whether 2-9.5 mm (coarse) agent is feasible in the attenuation layer. When agent was employed, concentrations of As at the column outlet did not exceed 5% that at inlet where it was 0.1 mg/L, and they were under the allowable limit of 0.01 mg/L, regardless of agent size used. Precipitates released are less toxic and mobile, and stable in a wide pH range.

## 1 INTRODUCTION

In recent years, many stakeholders have become aware of the fact that surplus soils and rocks generated by mining and/or construction activities in many countries around the world often contain naturally-derived toxic heavy metals and/or metalloids due to past geological phenomena (Tabelin et al. 2018). In Japan, based on the results of batch leaching tests (Japanese Notification No. 46) such soils, although containing relatively low-level of contaminants, have frequently been reported to exceed the limits of leaching values regulated under the Soil Contamination Countermeasures Law (SCCL) amended in 2010, particularly for arsenic (As), boron (B), fluorine (F), and lead (Pb) (Inui et al. 2010, Tabelin et al. 2018).

Excavated soils and rocks that contain naturally-derived contaminants will continue to increase in quantity due to the many relatively large construction works that are and/or will be conducted, such as the Maglev lines. Promoting their reuse in earthworks can reduce costs and environmental impact since landfilling and usage of quarry materials is reduced (Magnusson et al. 2015). However, presence of toxic constituents in the soils might have discouraged their reuse as some construction works follow too conservative manners towards natural contamination (Katsumi et al. 2019). As a result, each year many tons of soil end up in the limited landfills, while some are illegally dumped (Katsumi et al. 2004, Ministry of Land Infrastructure and Transport 2014).

Naturally-contaminated soils can only be reused for earthworks when technical safeguards are considered in design (Katsumi et al. 2004, Birlle et al. 2010). Technical safeguards are necessary to restrict their adverse effects on the environment to an acceptable level. Containment (using geomembranes) and insolubilisation method have been widely applied when such soils are reused in geotechnical structures (Hosokawa et al. 2007), but such countermeasures are considered excessive for natural contamination. Even if the regulatory limits of leaching values are exceeded, in most cases it is so by just a small margin (Katsumi et al. 2019). The cost of executing such countermeasures is very high when treating the huge amounts of excavated soils. It is also quite challenging to ensure adequate shear strength to prevent failures by slippage at the geomembrane-soil interface (Fleming et al. 2006). Sorption layer method illustrated in Figure 1 offers better mechanical stability and constructability with sufficient compaction unlike layered system using geomembranes (Tatsuhara et al. 2012).

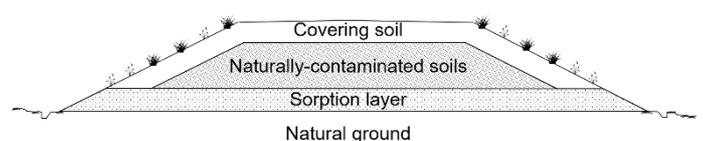


Figure 1. Schematic of the sorption layer method

Contamination of the surrounding environment can be prevented by the attenuation capacity of the

permeable soil layer installed beneath the embankment even when the soils with natural contamination are used in embankment without any barrier system (Tangviroon et al. 2017). Since the sorption layer is constructed beneath the embankment, differential settlement, hydraulic performance, and the attenuation capacity are important technical issues to consider, although the public is just likely to focus on the latter when contaminants are involved.

Utilisation of natural geological materials for construction of the sorption layer is preferred due to its abundance and low-cost, which are fundamental to an economical countermeasure. Past studies have shown that natural soil can have a certain level of sorption performance and attenuate metal concentrations particularly at the circumneutral pH range (Tabelin et al. 2014, Mo et al. 2015). However, due to the heterogeneous leachate characteristics found in the surface environment (Inui et al. 2013), immobilizing agent should be added to the natural soil to enhance its attenuation function against heavy metals and metalloids.

Calcium/magnesium (Ca/Mg) composite is a low-cost material with a simple production process from abundant natural minerals. In recent years, several studies have investigated the effectiveness of Ca/Mg composite in powder form (which is one of the three available particle sizes of the material) as an immobilizing agent (Bobea et al. 2012, Mo et al. 2015, 2018). The material was found to enhance the sorption capacity of a host soil (Mo et al. 2015) and immobilize both metal cations (e.g. Pb) and anions (e.g. As) in water-soluble phases (Bobea et al. 2012). In practical application, coarse agent is preferred because it offers better handling and can be homogeneously distributed in the host soil. Also, less, but long-term reactivity is expected for the coarse agent. Since sorption layer is not accessible after construction, the long-term sorption performance of soil amended with coarse agent needs to be assured.

In this study, two particle sizes of Ca/Mg composite i.e. under 2 mm (fine) and 2-9.5 mm (coarse) were separately added to a host soil. Preliminary evaluation of the As sorption performance of the amended soils was done in batch tests. Saturated column tests were employed for better representation of practical condition. The objective was to understand the effect of agent particle size on the sorption performance of amended soil, in order to evaluate whether coarse agent is feasible in the attenuation layer.

## 2 EXPERIMENTAL DETAILS

### 2.1 Materials

Clean decomposed granite soil, which is widespread in Japan, was oven-dried and used after sieving with a 2-mm opening, as host soil. The sieved soil has a particle density of 2.69 g/cm<sup>3</sup>. Particle size

distribution of the soil is shown in Figure 2 and was determined according to the Japanese Geotechnical Society Standards (JGS 0131). It can be classified as S-F (sand with fine fraction) according to JGS 0051.

Ca/Mg composite obtained from Sumitomo Osaka Cement was produced from mixing calcined natural minerals with special additives. Main constituent of the material is calcium (as CaCO<sub>3</sub>) and its content is about 35.6 %. Magnesium (as MgCO<sub>3</sub> and MgO) content is only about 19.4 %. It also contains trace amounts of iron (as FeSO<sub>4</sub>). In this study, two particle sizes of Ca/Mg composite that ranged from under 2 mm (fine) and 2-9.5 mm (coarse) were employed as immobilizing agent. Particle size distributions of the fine and coarse agent are shown in Figure 2. Specific surface area (SSA) value of the agents was estimated via the Brunauer-Emmet-Teller (BET) method. Table 1 summarizes the chemical composition and physical properties of the material.

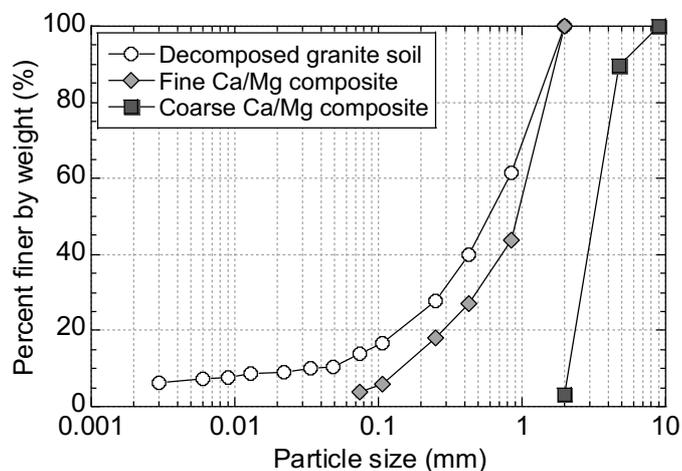


Figure 2. Particle size distribution of soil after passing a 2-mm opening, and agent of under 2 mm (fine) and 2-9.5 mm (coarse)

Table 1. Physicochemical properties of Ca/Mg composite

Chemical composition or property	Value
Chemical composition*	(wt. %)
CaO	35.6
MgO	19.4
SO <sub>3</sub>	3.98
Fe <sub>2</sub> O <sub>3</sub>	3.73
SiO <sub>2</sub>	1.52
Al <sub>2</sub> O <sub>3</sub>	0.07
P <sub>2</sub> O <sub>5</sub>	0.04
Loss on ignition	33.5
Physical property	
BET specific surface area (m <sup>2</sup> /g)	3.7 (Fine) 3.6 (Coarse)

\* Source: Data from The Society of Materials Science (2014). Analysis was conducted according to JIS R 9011 "Chemical Analysis of Lime".

### 2.2 Preparation of samples

The agent was added to host soil at 0 or 5 % by dry weight of mixture and mixed together in the dry state first. The dry soil or soil-agent mixture was then admixed with the required amount of distilled water that

depends on their optimum moisture content (10–11%). All mixing was done with a mechanical mixer, and proper care was taken to prepare a homogeneous mixture at each stage of mixing.

Afterwards, mixture was compacted in three equal layers ( $\approx 2.3$  cm each) in a cylindrical mould of 6 cm in inner diameter and 7 cm in height. The inner wall of mould was smeared with silica gel and a laboratory film applied to inhibit sample damage during the extrusion process. The amount of mass for each layer was standardised based on the results of standard Proctor compaction test (JGS 0711) and considering a compaction degree of 95%. After compaction, the samples had a void ratio and dry density of 0.40 and  $1.90 \text{ g/cm}^3$  respectively.

### 2.3 Preliminary sorption performance evaluation using batch test

Batch tests were performed to investigate the sorption capacity of the amended soils. The test method has been described in detail by Mo et al. (2015). In brief, 7-day cured samples were agitated in As solutions at 150 rpm for 24 h, for a single solution/soil ratio of 20 L/kg. Supernatant was extracted after the shaking step and the equilibrium As concentration in solution,  $C$  (mg/L), for each of the sample effluents was analysed. The sorbed amount,  $S$  (mg/g), accomplished by the sample was then calculated. Sorption isotherms were determined by an empirical relation between  $S$  and  $C$ , based on the Freundlich equation 1.

$$S = K C^n \quad (1)$$

where  $K$  and  $n$  are Freundlich parameters.

### 2.4 Sorption performance evaluation using flexible-wall permeameter

Sorption 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” as shown in Figure 3. Samples were saturated beforehand for at least 48 h in a vacuum deaerator. The upper and lower surface of sample were confined with acrylic pedestal of 6 cm in diameter. A sheet of filter paper and geotextile separated the surface of the sample from the acrylic pedestals to prevent clogging of the channels by fine soil particles. To prevent air from intruding into the samples during test, filter papers and geotextiles were deaerated in a container filled with distilled water beforehand.

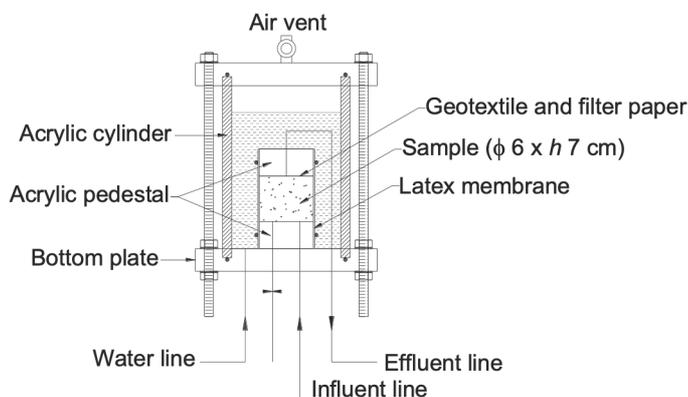


Figure 3. Schematic details of the flexible wall permeameter and experimental column setup

A latex membrane smeared with silicone grease on the lateral face was used to confine the sides of sample along with the top and base pedestal, to prevent side-wall leakage. Two O-rings were employed at the top and bottom pedestal to seal the sample. After assembling the apparatus and saturating all channels with distilled water, a confining pressure of 50 kPa was applied during permeation.

A peristaltic pump was employed to maintain a constant flow (bottom to top) at a rate of 4.5 mL/h, to simulate a 12 h contact time of solution with sample during permeation. A 12 h contact time can provide a better evaluation of the long-term sorption performance (Gathuka et al. 2018).

Arsenic solution with a concentration of 0.1 mg/L was used as permeant, after deaerating with a vacuum deaerator for at least 24 h. The solution was prepared by dissolving accurate amounts of  $\text{NaAsO}_2$  powder in distilled water to produce stock solution of 1000 mg/L, and appropriate dilutions were then made. Since most soils with natural contamination exhibit arsenic leaching values of 0.02–0.03 mg/L (Katsumi et al. 2019), the influent concentration employed represents an extreme case. Effluent was collected at regular time intervals and filtered with a  $0.45 \mu\text{m}$ -opening membrane filter. Afterwards, physico-chemical parameters, particularly pH, electric conductivity (EC), and redox condition (Eh), and concentrations of As and other water-soluble elements were analysed.

## 3 RESULTS AND DISCUSSION

### 3.1 Attenuation of arsenic and pH changes

Arsenic sorption, based on batch test results, follows a non-linear behaviour and was fitted by the Freundlich isotherm. Which means that sorption is not limited to monolayer and As molecules will migrate to heterogenous surfaces (Adamson & Gast 1997).

Figure 4 shows that when employing coarser ( $> 0.075$  mm) agent, sorption performance of amended soil reduced. Lowest As sorption amount was reached when coarse agent was employed, where

$S$  was 0.02 mg/g for an initial concentration of 10 mg/L. Freundlich parameter,  $K$ , which is a good index for quantifying the sorption performance of solid materials, was determined to be 0.36, 0.04, and 0.01 m<sup>3</sup>/g for powder, fine, and coarse agent amendment respectively. Highest  $K$  value of 0.36 m<sup>3</sup>/g, obtained when employing powder agent, is due to its high SSA of 9.85 m<sup>2</sup>/g (Itaya et al. 2013) that increased the number of active-sorption sites. A logarithmic fit was used to describe the correlation between SSA and  $K$ , as shown in Figure 5.

When agent was employed, concentrations of As at column outlet did not exceed 5% that at inlet where it was 0.1 mg/L, and they were under the allowable limit of 0.01 mg/L, as shown in Figure 6. Also, in the short-term, sorption performance was similar for soil only and that amended with coarse agent.

While batch tests indicated that sorption amount will be lowest when employing coarse agent, it was found out, from column tests, that there is no significant difference in sorption performance when either fine or coarse agent is used, as the variation in As concentrations at outlet was only 1-2 µg/L.

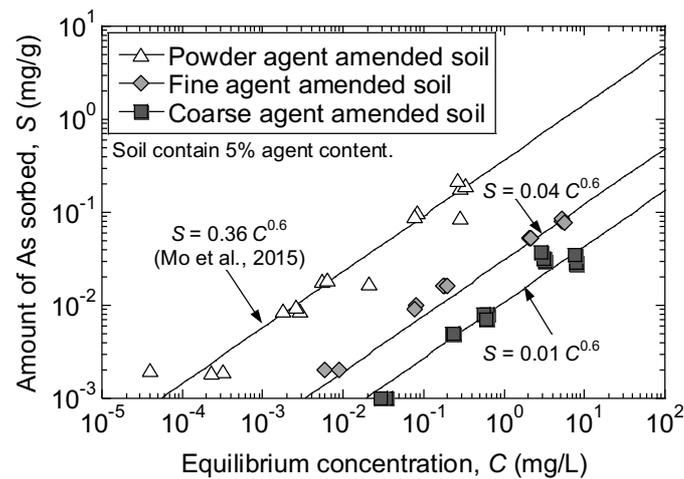


Figure 4. Linearized Freundlich isotherm

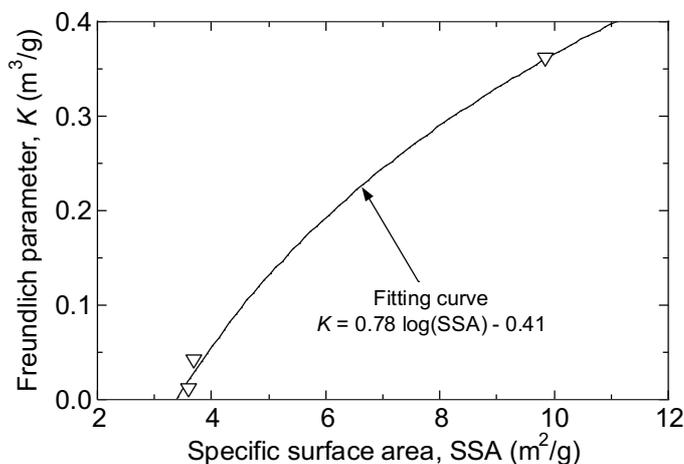


Figure 5. Correlation between  $K$  and SSA

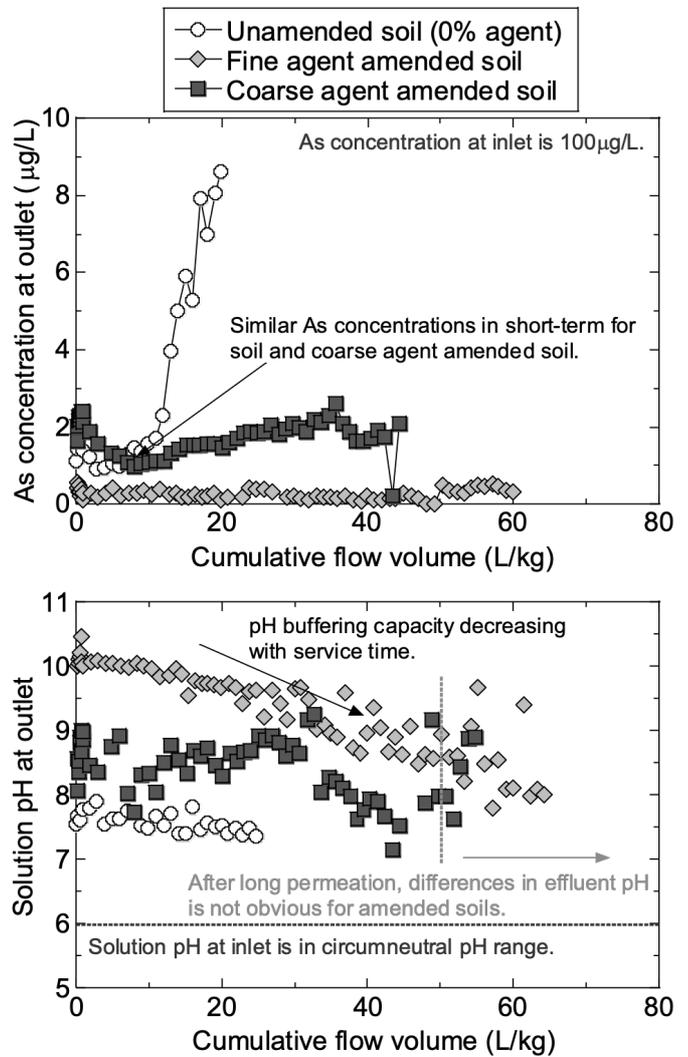


Figure 6. Effect of employing agent of different particle size on the sorption of arsenic and pH buffering capacity of soil

When agent was employed, the pH buffering capacity of the host soil was also improved, but to what extent seems to depend on the agent size used. When coarse agent was employed, permeant pH was raised to pH 9, and to pH 10 when fine agent was used, at the beginning of permeation. However, the pH buffering effect gradually reduced with further permeation, but pH at outlet was still much higher than that at inlet. The pH buffering effect can be expected for a much longer period when employing agent.

Carbonate mineral and/or exchangeable base cations buffering are speculated to be the governing pH buffering mechanisms. Since natural soil does not contain any carbonate minerals, it will buffer pH due to the presence of exchangeable base cations. But, when agent is employed, carbonate dissolution and precipitation will occur and the presence of free carbonates will buffer pH (McBride 1994). However, leaching of carbonates from the amended soil will slowly deplete the carbonate buffer capacity, and ultimately the pH buffering effect is reduced, which can explain why effluent pH reduced after longer period.

Chemical forms of many dissolved compounds are influenced by the pH of the water. Additionally, for redox sensitive elements like As, the Eh condition of

the water should also be considered, and it was found to be in the range of 200–400 mV. Eh-pH characteristics of effluents were found to favour the occurrence of As as  $\text{HAsO}_4^{2-}$ , that has low mobility and toxicity.

### 3.2 Mechanisms involved in the attenuation of arsenic

Presence of free metal ions was indicated by the EC values that were relatively higher at column outlet than at the inlet, where it was 0.1 mS/m, as shown in Figure 7. Cations, particularly  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , leached from soil and agent during permeation, but presence of agent in soil was found to suppress the release of  $\text{Ca}^{2+}$ , while promoting the leaching of  $\text{Mg}^{2+}$ . Due to their positive charge, they may promote the sorption of negatively charged ions like arsenate ( $\text{HAsO}_4^{2-}$ ).

Arsenic sorption by soil only is speculated to be mainly governed by sorption reactions but when agent is employed, the presence of Ca and Mg carbonates (which is the main constituent of agent) in soil increases the extent of precipitation mechanism. Precipitates in the form of oxides, hydroxides and/or carbonates are likely to be formed (Salameh et al. 2015). Precipitates formed are less mobile and toxic, and stable over a wide pH range of about 3–12.5 (Bothe & Brown 1999).

When agent is employed, dissolution of carbonate minerals will occur during permeation, to form free  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . While  $\text{Ca}^{2+}$  at outlet was in abundance and same amount was leached regardless of agent size used, the concentrations of As at outlet was relatively lower when employing the fine agent, which implies that agent size has a greater effect in the sorption of As by amended soils.

### 3.3 Practical implications

Attenuation function of host soil can be enhanced by employing agent. When coarse agent is used, the As concentration in leachate, after passing through the sorption layer, can be expected to be below the acceptable levels of 0.01 mg/L, for a much longer period. Also, the pH buffering effect can be expected for a much longer period. Precipitates that are less toxic and mobile, and stable in a wide pH range will be released from the sorption layer. Therefore, employing coarse agent should be a reasonable and practical way to improve the attenuation function of sorption layer.

## 4 CONCLUSIONS

Addition of Ca/Mg composite can be employed to enhance the attenuation function of sorption layer. To evaluate whether employing coarse agent is feasible, the effect of agent size on As sorption performance of soil amended with agent was investigated using batch and saturated column tests.

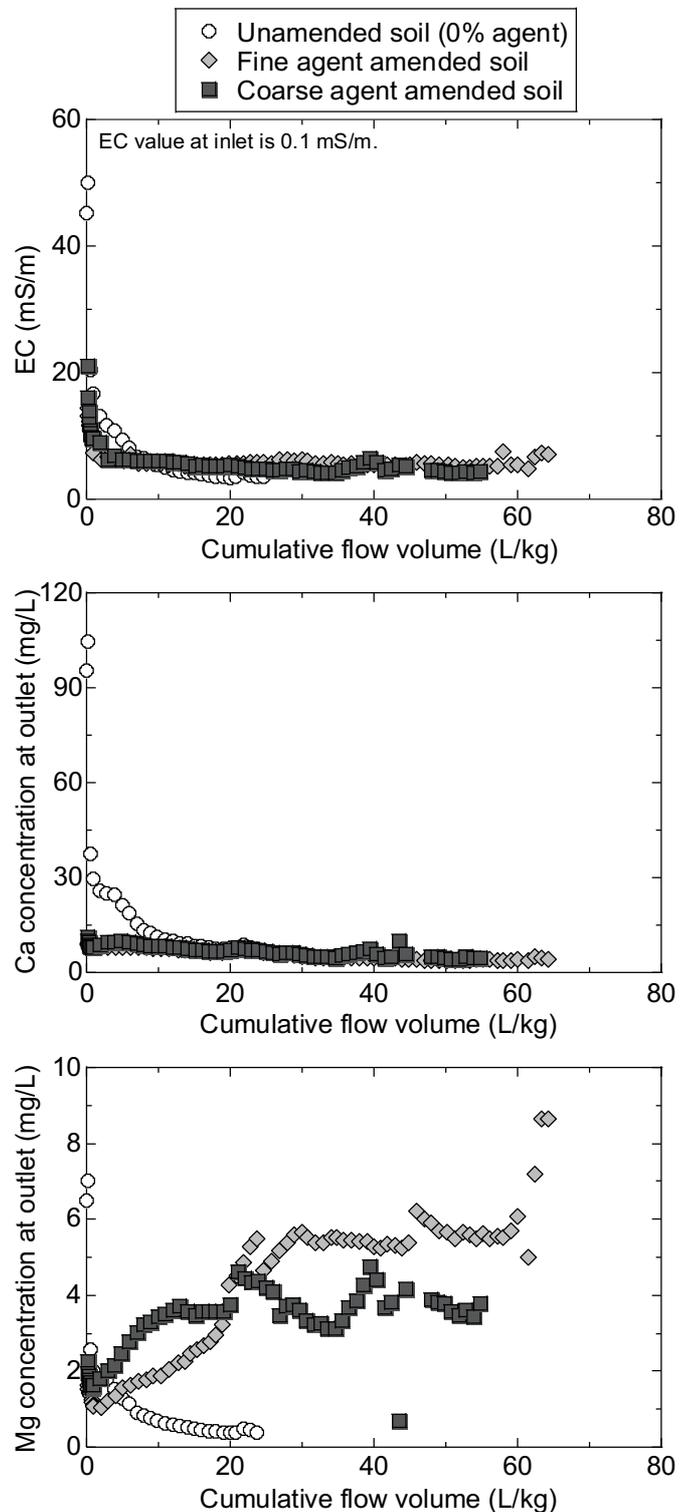


Figure 7. Profiles of EC and cations leached during As sorption

From batch tests, the sorption performance of amended soil was found to reduce when employing coarser ( $> 0.075$  mm) agent. Lowest sorption amount was obtained when using coarse agent, where  $S$  was 0.02 mg/g for an initial concentration of 10 mg/L.

While coarse agent provides the lowest sorption performance among the three available agent sizes, the As concentrations at the column outlet did not exceed 5% that at inlet where it was 0.1 mg/L, and they were under the allowable limit of 0.01 mg/L. Also, from column test, no significant variation in As concentration at outlet was found when employing either

coarse or fine agent. Therefore, employing coarse agent should be a reasonable and practical way to enhance the attenuation function of the sorption layer.

Employing agent also improves the pH buffering capacity of soil but it is expected decrease with service-time. Also, the extent to which the capacity to buffer pH is improved will depend on the agent size, with fine agent offering the highest increase.

Presence of Ca and Mg carbonates (from agent) in the soil increases the extent of precipitation mechanism. The precipitates formed are less mobile and toxic, and stable over a wide pH range.

## 5 ACKNOWLEDGMENTS

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