Technical Paper

Evaluating the arsenic attenuation of soil amended with calcium–magnesium composites of different particle sizes

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Abstract

An attenuation layer composed of ground mixed with stabilising agents can prevent the contamination of the surrounding area when using soils and rocks with geogenic contaminants in embankments. The optimum particle size of the stabilising agent must be selected based on the requirements of the construction site because the mechanical and chemical properties of the attenuation layer are site-specific. However, the relationship between the particle size of the stabilising agent and the attenuation performance of soil–agent mixtures has yet to be fully clarified. This study employs batch sorption tests to evaluate the attenuation of arsenic by a soil mixed with a calcium–magnesium composite with different particle sizes, ranging from powder particles (<0.075 mm in size) to granular particles with diameters between 2.0 and 9.5 mm. Amended soil more effectively attenuates the contaminant than the original soil. In one experiment, a stabilising agent of granular particles (between 2.0 and 9.5 mm) for the amendment increased the soil's partition coefficient K_d from 14.5 to 22.2 cm^3/g, which is more than a 50% improvement in the attenuation. Using a stabilising agent with a smaller particle size for the amendment has a greater impact. K_d increases linearly as the particle size of the stabilising agent decreases down to 0.075 mm. Using the K_d from laboratory tests, simulations with a one-dimensional advection–dispersion equation demonstrate the durability of the attenuation layer. Both the powder and the granular particles show promise as attenuation layer materials.
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Keywords: Attenuation layer method; Arsenic; Batch sorption test; Partition coefficient; Specific surface area; Geogenic contamination; Excavated soils; Sustainable soil management

1. Introduction

Subterranean construction generates large volumes of soils and rocks. When excavated soils and rocks are not used at the site, they are usually taken to soil fills (or dumped illegally) instead of being redirected for use elsewhere (Katsumi, 2015; Magnusson et al., 2015; Kataguiri et al., 2019). Soil fills are designated landfill sites for surplus soils. The use of such soils and rocks has been encouraged in embankments and other geotechnical applications as part of ongoing efforts to achieve sustainable soil management (SSM). SSM has been widely discussed in the fields of agricultural soil and plant science (e.g., FAO, 2017; Rodrigo-Comino et al., 2020). However, the concept can also be extended to geotechnical and geoenvironmental

fields by using excavated soils and rocks in construction works.

There is a certain amount of reluctance to use excavated soils or rocks at construction sites when they are contaminated with geogenic contaminants (Katsumi et al., 2019). Geogenic toxic metals and metalloids are widely distributed. They occur in different types of natural rocks and sediments, ranging from marine clays to igneous and hydrothermally altered rocks. Moreover, the excavation of these soils and rocks can alter them physically and chemically. For example, when soils or rocks are exposed to air and water, toxic elements can be released to the surrounding ground, sometimes at levels that are unacceptable (e.g., Inui et al., 2014; Tabelin et al., 2014; Li et al., 2017a; Ito and Katsumi, 2020). Consequently, environmental regulatory agencies, researchers, and authorities, which handle the construction and development of infrastructures, have debated how to properly manage excavated soils and rocks with geogenic contaminants.

One alternative to directly disposing them is to use these soils and rocks while taking economical and effective countermeasures against the risks due to geogenic contamination. Firstly, the leaching concentrations are relatively low. In most cases, the concentrations only slightly exceed the environmental standards (e.g., Tabelin et al., 2014, 2018; Li et al., 2017a, 2017b; Cui et al., 2018; Ito and Katsumi, 2020). Secondly, only a certain percentage of the soils and rocks is contaminated, although significantly large volumes of excavated soils and rocks are generated (e.g., MLIT, 2010). Another crucial reason for the use of these materials in Japan is that landfills have a limited capacity (Katsumi et al., 2021). The Soil Contamination Countermeasures Law (SCCL), which is the national law dealing with soil contamination, was extensively revised in 2017 to comply with the technical guidelines of the Ministry of Land, Infrastructure, Transport and Tourism (MLIT) and to permit the use of excavated soils and rocks with geogenic contaminants under proper contaminant control.

Fig. 1 presents a schematic diagram of the attenuation layer method, which has recently been developed to meet the aforementioned goal. This method has a unique approach. Toxic elements are sorbed by the constituent materials of the attenuation layer during the flow of leachates through the attenuation layer. An attenuation layer is typically a mixture of soil, a stabilising agent, and water, spread on the ground (Nozaki et al., 2013; Mo et al., 2020). A significant advantage of the attenuation layer method over the common method of encapsulation using geomembrane sheets is that stable earthen structures can be constructed using simple and traditional methods for earthen works. However, several issues must be addressed to enhance the reliability of the attenuation layer method.

Since the stabilising agent affects the mechanical and chemical properties of the attenuation layer, the particle size of the stabilising agent needs to be optimised according to the requirements of the construction site. However, the relationship between the particle size of the stabilising agent and the attenuation performance of the soil–agent mixture has yet to be clarified because previous studies only used one or two particle sizes (e.g., Mo et al., 2020; Gathuka et al., 2021; Kato et al., 2021a).

This study examines eight different particle sizes of stabilising agents with the same chemical composition to elucidate the influence of particle size on the attenuation layer performance. The stabilising agent is composed mainly of calcia and magnesia. Previous studies have demonstrated that this material has a high capacity to attenuate contaminants (Bobea et al., 2012; Mo et al., 2020; Gathuka et al., 2021), making it a promising candidate for use in the attenuation layer. Batch sorption tests are conducted on soil–agent mixtures to assess their ability to attenuate arsenic (As), which is an important contaminant in geogenic contamination in Japan (e.g., Tabelin and Igarashi, 2009; Takahashi et al., 2011; Tabelin et al., 2012, 2018; Inui et al., 2013, 2014, 2019; Yokobori et al., 2015; Ho et al., 2021). Using the partition coefficient K_d, obtained from laboratory experiments, simulations are performed with a one-dimensional advection–dispersion equation to demonstrate the durability of the attenuation layer, which contains powder and granular particles of the stabilising agent.

2. Materials and methods

2.1. Materials

The clean parent material was decomposed granite soil purchased from a local market in Kyoto. The soil was selected due to its wide availability in Japan. It was sieved through a screen with 2-mm openings to obtain soil
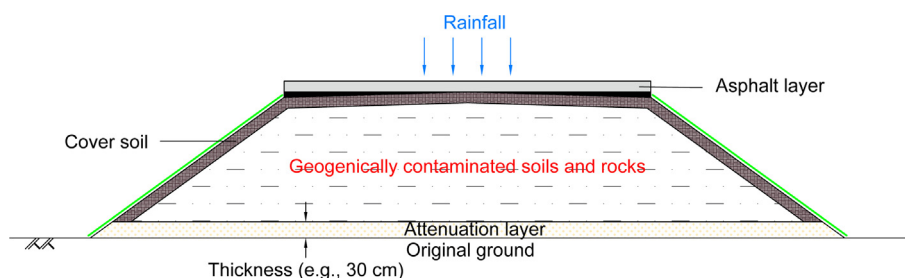

Fig. 1. Schematic diagram of attenuation layer under geogenically contaminated soils and rocks in embankment (edited from Gathuka et al., 2021).

particles less than 2 mm, which were required for the tests. Table 1 summarises the basic properties of the sieved soil.

The stabilising agents were calcium–magnesium composites manufactured by Sumitomo Osaka Cement. The main components were calcia and magnesia, which are essentially calcinations of minerals with some similarity to dolomite (Table 2). One notable difference between the basic and the modified agents was that the latter contained additives such as ferrous sulphate ($FeSO_4$). This difference should have a minimal impact on the attenuation capacity of the materials, especially against As. According to gas pycnometry using nitrogen gas, the basic and the modified agents have particle densities of 2.90 and 2.86 g/cm^3, respectively, demonstrating a negligible difference between the materials.

This study employed eight different particle sizes of the stabilising agents: seven basic and one modified. Six size fractions of the basic agent were obtained by sieving through screens with different openings. Five of the fractions were 9.5 to 2.0 mm, 2.0 to 0.425 mm, 0.425 to 0.25 mm, 0.25 to 0.106 mm, and 0.106 to 0.075 mm. As the sixth fraction, the material was also sieved through a 2-mm sieve to obtain particles <2.0 mm. Additionally, the material was crushed to yield powder particles (~90% were less than 0.075 mm in size). Due to the crushed nature of the modified agent, only powder particles were obtained from the material. Fig. 2 shows the particle size distributions of the stabilising agents. For granular particles (larger than 0.075 mm), the sieving method specified in JIS A 1204 (2009) was used. In the case of the powder particles, a laser diffraction method was employed.

The specimens were prepared as follows. Dry soil was poured into a steel bowl. Next, the stabilising agent was
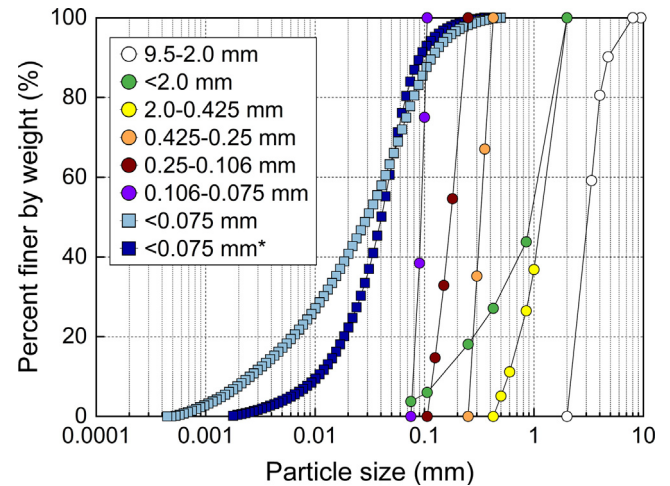

Fig. 2. Particle size distributions of eight particle size fractions of Ca–Mg agents used in this study. The modified agent is denoted by <0.075 mm*.

added to prepare the amended soil samples. Each amended soil contained one of the eight particle sizes of the stabilising agent. The agent content was equal to 5% (or 50 g of stabilising agent per kg of soil by dry weight). Then distilled water was added to the dry materials to reach the optimum water content, w_{opt}, which was about 10% for the original soil and between 10 and 11% for the amended soil. The w_{opt} values were determined as per the A-a method of JIS A 1210 (2009). The soil, stabilising agent, and water were mixed together using a soil mixer. While mixing, the machine was temporarily stopped from time to time to scrape the sides and bottom of the bowl.

2.2. Experiments

2.2.1. Estimation of specific surface area of the Ca–Mg composites

An important parameter when evaluating the attenuation performance of a stabilising agent is its specific surface area (SSA). Analytical measures of the surface area and the pore size distribution of microporous and mesoporous materials are often obtained using the Brunauer-Emmett-Teller (BET) nitrogen gas adsorption technique (e.g., Sinha et al., 2019). Here, the BET technique was used to measure the SSAs of the stabilising agents with a Belsorp 18 Plus-HT automatic vapour adsorption apparatus. Before the measurements, the materials were dried at 110 °C for about 5 h in a vacuum. The BET theory was applied to determine the SSAs.

Table 1
Basic properties of the soil particles less than 2 mm in diameter.

Parameter	Value	Method of measurement
Particle density	2.69 g/cm^3	JIS A 1202 (2009)
Particle size distribution		JIS A 1204 (2009)
Sand fraction [0.075–2 mm]	85.9%	
Silt fraction [0.005–0.075 mm]	7.7%	
Clay fraction [<0.005 mm]	6.4%	
Chemical composition		X-ray fluorescence
SiO_2	45.5%	analysis—XRF
Fe_2O_3	20.6%	(EDX-720, Shimadzu)
CaO	6.6%	
Al_2O_3	16.9%	
Others	10.4%	

Table 2
Chemical composition of the basic and modified Ca–Mg agents as per JIS M 8851 (2006) (unit: wt%).

Agent type	Ig. loss*	CaO	MgO	Fe_2O_3	SiO_2	Al_2O_3	P_2O_5	Total S
Basic	31.18	44.29	22.02	0.06	0.07	0.09	0.07	0.01
Modified with additives such as $FeSO_4$	31.54	36.05	19.99	4.26	0.13	0.06	0.03	4.34

*Loss on ignition at 1050 ± 50 °C in air.

2.2.2. Batch sorption tests

Batch tests evaluated the attenuation performance of the specimens against As. The tests were performed on the specimens as prepared (i.e., not dried) to reflect their actual state in the field since water plays a role in the reaction and sorption behaviour of the materials. Testing was conducted in sets of three. Four As concentrations were prepared using sodium arsenite (NaAsO$_2$) salts: 0.1, 0.2, 0.3, and 0.4 mg/L. In the case of geogenic contamination, the leaching concentrations are generally up to ten-fold higher than the regulatory limit in Japan (Ito and Katsumi, 2020). Thus, relatively low concentrations were used for the tests. The specimens were mixed with the As solutions in 500-mL capped plastic bottles with a liquid-to-solid (L/S) ratio of ~10. The mixtures were subjected to horizontal shaking at 150 rpm for 24 h using a mechanical shaker (TS-10, TAI-TEC) at room temperature (~20 °C). After shaking, the bottles were left standing for 15 min. The solid particles were then separated from the liquid through centrifugation at 3,000 rpm for 10 min and filtered using a membrane filter with a 0.45-μm pore diameter. Table 3 summarises the test conditions.

The water chemistry of the solutions was analysed. The pH and electrical conductivity (EC) were measured using a Horiba F-54 pH/EC meter. The oxidation–reduction potential (ORP) was measured using a Horiba F-73 pH/ORP meter and converted to E_h. The As concentrations were measured using a Shimadzu AA-7000 atomic absorption spectrophotometer. The concentrations of several co-existing ions (Al, Ca, Fe, K, Mg, and Na) were measured using an Agilent Technologies ICP-OES 710 inductively coupled plasma optical emission spectrometer.

3. Results and discussion

3.1. SSAs of the Ca–Mg composites

Table 4 summarises the SSAs measured by the BET technique (S_{BET}). The S_{BET} is between 3.60 and 3.98 m^2/g for the granular particles. The values are similar because the materials are aggregates of the same parent material. For the powder particles, however, the S_{BET}'s of the basic and modified agents are 9.40 and 7.72 m^2/g, respectively. Powder particles have a higher SSA than granular particles. This difference in the SSA values may be due to crushing.

Table 3
Conditions in the batch sorption tests.

Solvent	NaAsO$_2$ solution (conc.: 0.1, 0.2, 0.3, and 0.4 mg/L)
Agent content	0, 5% (=50 g/kg-soil by dry weight)
Specimen mass	>50 g
Liquid-to-solid ratio	10 L/kg
Mixing	Horizontal shaking at 150 rpm
Shaking time	24 h

The SSA was also calculated according to the particle size of the materials (hereafter, this is referred to as S_w). The S_w of a particle of size x was calculated as

$$S_w = \frac{\varphi}{\rho \cdot x} \tag{1}$$

where ρ (g/cm^3) is the particle density of the material and φ is the SSA shape factor. The φ value was set to 6 because the particles were assumed to be perfectly spherical without pores. The mean particle size of each pair of consecutive plots in the distribution data (Fig. 2) was inputted as x in the above equation, and the S_w for each mean size was calculated. The results were summed to give the S_w corresponding to the particle size.

Fig. 3 shows the relationship between the S_{BET} and the S_w. The S_{BET} is over 20 times higher than the S_w. It should be noted that these materials have mesopores with an average pore size between 2.2 and 2.4 nm. Mesopores are pores with a diameter of 2 to 50 nm. In addition, the materials have a rough surface morphology, as reported in an article by The Society of Material Science, Japan (JSMS, 2014). The fact that the BET method considers these features, but the S_w calculation does not, explains the large difference between the S_{BET} and the S_w.

3.2. Batch sorption tests

3.2.1. Sorption isotherms

The amount of As retained, S (mg/g), and the concentrations of As remaining in the solutions, C (mg/L), exhibit a linear relationship (Fig. 4) when fitted with the empirical Henry isotherm, which is given as

$$S = K_d C \tag{2}$$

where K_d (cm^3/g) is the partition coefficient. Table 5 summarises the K_d values of the soils. It should be noted that K_d describes only the sorption data within the range of the concentrations investigated herein. It cannot describe the sorption outside of this range.

Amending the soil with a 5% stabilising agent improves its attenuation performance. A larger inclination of the sorption isotherm indicates a higher attenuation performance. The changes in attenuation performance were quantified using K_d as an index. In one experiment, employing a stabilising agent with granular particles (between 2.0 and 9.5 mm) for the amendment increased the soil's partition coefficient K_d from 14.5 to 22.2 cm^3/g. This is an improvement of over 50%. The impact of the stabilising agent was larger when the amendment had smaller particles. The highest K_d value recorded was 3,010 cm^3/g, which was for soil amended with a basic agent of powder particles. This is more than a 200-fold increase compared to the K_d of the basic soil.

Fig. 5 plots the normalised K_d of the amended soil against the S_w of the stabilising agent. The normalised K_d is the K_d of the amended soil versus that of the basic soil (herein referred to as $K_{d0\%}$), (i.e., $K_d/K_{d0\%}$). The normalised

Table 4
Specific surface areas of different particle size fractions of the Ca–Mg agents used in this study. The nitrogen adsorption method, based on the BET (Brunauer-Emmett-Teller) theory, was used to measure the specific surface area.

Agent size (mm)	S_{BET} (m^2/g)
9.5–2.0	3.60
<2.0	3.70
2.0–0.425	3.85
0.425–0.25	3.97
0.25–0.106	3.98
0.106–0.075	3.92
<0.075	9.40
<0.075*	7.72

* Modified agent.

Fig. 4. Henry sorption isotherms for basic and amended soils. The amended soils are denoted by the particle size fractions of the employed agent. Furthermore, the soil amended with the modified agent is denoted by <0.075 mm*.

Table 5
Henry sorption isotherm parameters for basic and amended soils.

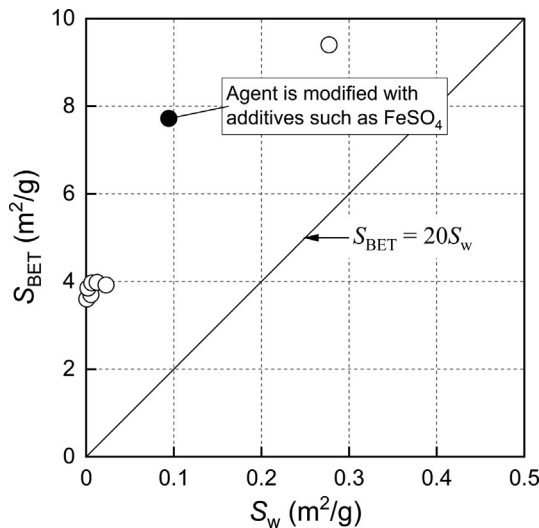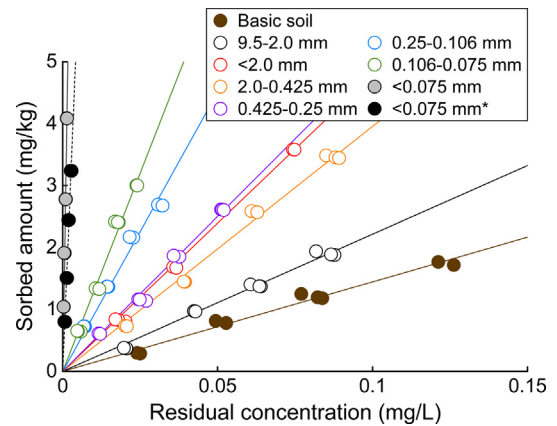| Agent size (mm)	K_d (cm^3/g)	R^2
Basic soil (no agent)	14.5	0.996
9.5–2.0	22.2	0.998
<2.0	47.9	0.999
2.0–0.425	39.6	0.998
0.425–0.25	50.1	0.998
0.25–0.106	90.3	0.995
0.106–0.075	128.1	0.997
<0.075	3,009.5	0.993
<0.075*	1,237.4	0.995

* Modified agent.

Fig. 3. Comparison between measured and calculated SSAs of the Ca–Mg agents.

K_d increased linearly as the S_w increased when the size of the amendment materials was larger than 0.075 mm. Since the S_{BET} was similar for granular agents (between 3.60 and 3.98 m^2/g), the ability of the soil–agent mixtures to attenuate As may be a function of the particle size of the amendment materials and not a function of the S_{BET}. However, the relationship between the normalised K_d and S_w might be nonlinear when powder agents are used.

3.2.2. Changes in pH and co-existing ions in solutions

The addition of a stabilising agent resulted in higher pH levels than those in the soil itself (Fig. 6), which may be due to the hydration reaction of the magnesium oxide (MgO) as well as the Ca and Mg dissolved from the calcium carbonate ($CaCO_3$) and calcium magnesium carbonate [$CaMg(CO_3)_2$]. The change in pH was more dramatic as the particle size of the amendment decreased. The ability of the soil–agent mixtures to increase the pH to high levels (e.g., pH > 10) may be beneficial at an actual site, especially in situations where the leachates are acidic. By buffering the

acid and releasing leachates with a pH > 6, the attenuation layer can ensure that the attenuation capacity of the original ground is used (Gathuka et al., 2021).

The amounts of dissolved Ca and Mg for the soil–agent mixtures were much higher than those for the soil itself (Fig. 7). This may be due to the hydration of MgO as well as the Ca and Mg dissolved from the $CaCO_3$ and $CaMg(CO_3)_2$. In addition, the leaching of Ca follows the pH profile depicted in Fig. 6. Thus, the dissolved Ca may directly affect the pH levels. On the other hand, the addition of a stabilising agent probably hindered the leaching of Al and Fe from the soil. Thus, these elements may not significantly influence the chemical reactions and sorption behaviour of the materials. For example, the co-precipitation of As with Al or Fe oxides/hydroxides may be limited.

3.2.3. Expected As attenuation mechanism by amended soil

The data obtained from the atomic absorption spectrophotometer did not provide details on the oxidation state of the dissolved As. Consistent with the stability relations of the As compounds in the E_h–pH diagrams by Lu and Zhu (2011), it was assumed that the dissolved As was the negatively charged $HAsO_4^{2-}$. The assumptions suggested that the As applied as $NaAsO_2$ [or As(III)] was
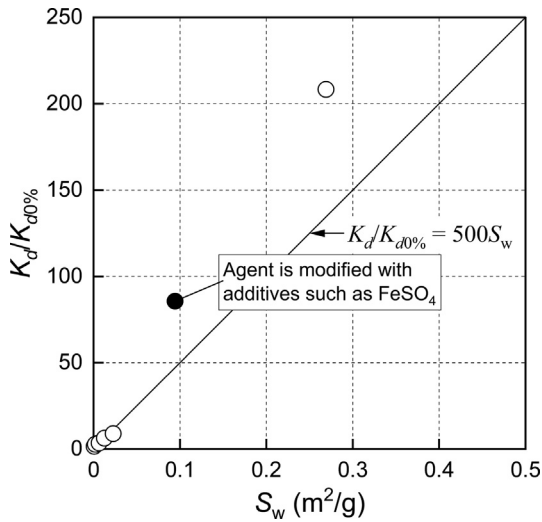
Fig. 5. Relationship between normalised K_d of amended soil and calculated SSA of corresponding amendment material.
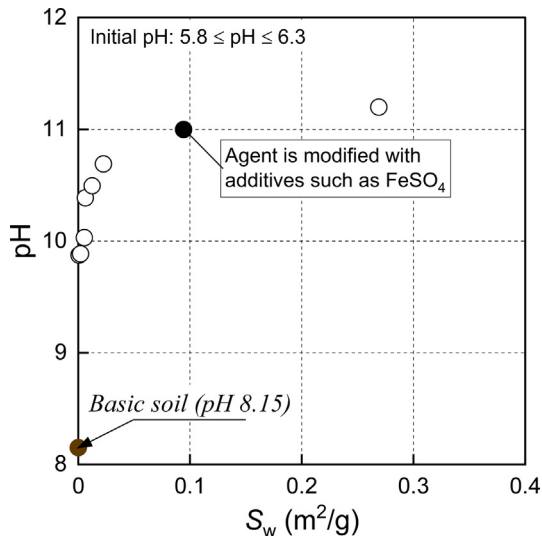

Fig. 6. Changes in pH levels by basic and amended soils. The average pH value for each case is plotted, and the SSAs are calculated for the amendment materials.

oxidised to As(V). However, this could not be clarified with the available data. The As species and its associated compounds has less mobility and toxicity. Additionally, it is stable over a wide pH range (Bothe and Brown, 1999).

The surface charge of the pure decomposed granite soil may vary. It is likely that the charge is negative at or above a pH of 8, suggesting that the retention of the As species is unfavourable. However, with the relatively high concentration of Ca in the leachate of the soil, the co-precipitation between Ca and As might be the primary As attenuation mechanism. It should be noted that the precipitation of Ca–As will not occur after the Ca is depleted. On the other hand, there are two mechanisms by which the stabilising agents can remove the As. The first mechanism involves

the removal of As using MgO. Considering the conditions used in the tests, it is reasonable to assume that the MgO is completely hydrated. However, further investigation is needed. Once hydrated, it can still remove contaminants, but its performance deteriorates. The second mechanism involves the co-precipitation between the As and the Ca and Mg dissolved from the $CaCO_3$ and $CaMg(CO_3)_2$. In a previous study (Itaya et al. 2013), it was reported that Ca–As, which has low solubility, is formed during the interaction of the calcined material with dissolved As. In practice, the soil, stabilising agent, and water are mixed. The mixture is then spread on the ground to construct the attenuation layer. Hence, MgO may be hydrated before it comes into contact with the contaminants in the infiltrating water since the attenuation layer should be moist after construction. In this case, the constituent materials remove the contaminants primarily through precipitation reactions.

4. Advection-dispersion analysis for As transport through attenuation layer

The transport of As through the layer was simulated to better understand the impact of using powder or granular stabilising agents. The simulation used the following one-dimensional advection–dispersion equation, which considered seepage, dispersion, and sorption simultaneously

$$R_d \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{3}$$

where R_d is the retardation factor, D (m^2/s) is the dispersion coefficient, and v (m/s) is the seepage velocity.

R_d represents the sorption effect of the materials without considering or clarifying the individual chemical reactions. In this analysis, the sorption behaviour was assumed to be modelled as linear behaviour. Therefore, R_d was calculated as

$$R_d = 1 + \frac{\rho_d}{n} K_d \tag{4}$$

where ρ_d (g/cm^3) is the dry density and n is the porosity of the materials.

Assuming that the initial and 'constant concentration' boundary conditions are expressed as

$$C|_{x \geqslant 0, t=0} = 0, \, C|_{x=0, t \geqslant 0} = C_0, \, C|_{x=L, t \geqslant 0} = 0 \tag{5}$$

the solution to Eq. (3) for these conditions is given by Ogata and Banks (1961) as

$$C_e = C_0/2 \left\{ \mathrm{erfc}\left[(R_d L - vt)/(4R_d Dt)^{1/2}\right] \\ + \exp(vL/D)\mathrm{erfc}\left[(R_d L + vt)/(4R_d Dt)^{1/2}\right] \right\} \tag{6}$$

where C_0 (mg/L) is the initial concentration, C_e (mg/L) is the concentration at distance x from the source at time t, L (cm) is the attenuation layer thickness, and erfc is the complementary error function. The analysis assumed that the solute transport parameters, C_0, R_d, D, and v, are constant.
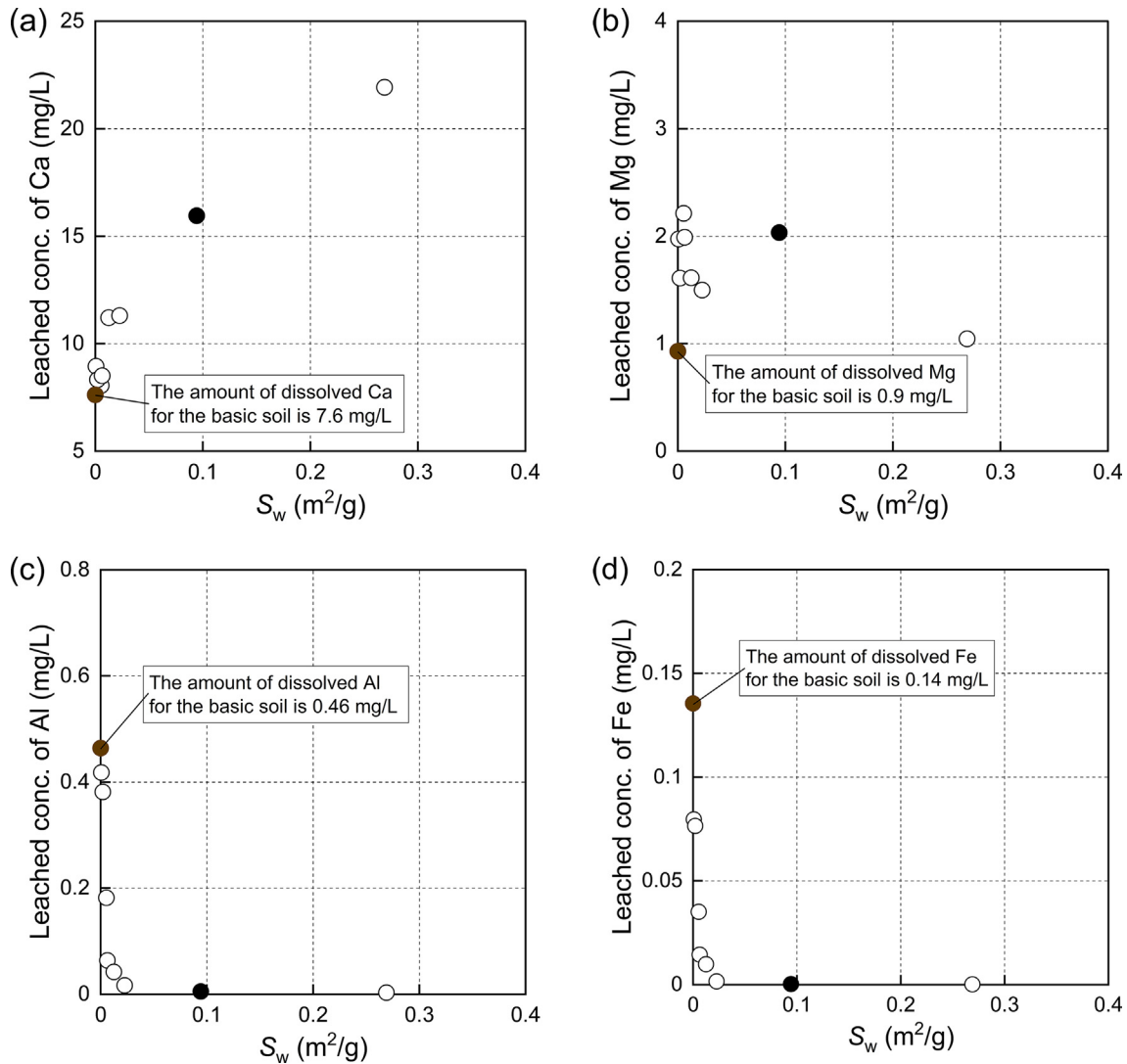
Fig. 7. Concentrations of elements released from basic and amended soils. The average concentrations for each case are plotted, and the SSAs are calculated for the amendment materials.

Table 6 summarises the parameters used in this simulation. The layer thickness was assumed to be between 20 and 50 cm. The ρ_d and n of the layer were 1.9 g/cm^3 and 0.28, respectively. The sorption parameter K_d of the materials was determined from the batch tests. D was calculated as $D_m + \lambda|v|$, where λ (cm) is the longitudinal dispersivity, which is roughly approximated as $0.1L$ (Gelhar et al., 1992). D_m (cm^2/s) is the effective diffusion coefficient, which is estimated as 0.905×10^{-5} cm^2/s for As (Lide, 2001). The precipitation was taken for Kyoto City, which is roughly 1,500 mm each year (Gulsen et al., 2019). The analysis assumed that 30% (450 mm) of the annual precipitation infiltrated into the embankment. Based on the assumptions that the attenuation layer was saturated and that infiltration occurred immediately after precipitation, the number of years to reach a certain C_e/C_0 was calculated as

$$t = (PVFs \times L \times n)/I_{rate} \qquad (7)$$

where $PVFs$ are the pore volumes of flow and I_{rate} (cm/y) is the infiltration rate.

Fig. 8 plots the calculated breakthrough times against the thickness of the layer for $C_e/C_0 = 2$, 10, 20, and 50%. Using only the decomposed granite soil to create a 30-cm-thick layer, it should take about 8 years for C_e/C_0 to reach 10% (or C_e equals 0.01 mg/L, which is the regulatory limit in Japan). The breakthrough time for $C_e/C_0 = 10\%$ should increase to 13 years if the soil is amended with the stabilising agent containing granular particles with diameters between 2.0 and 9.5 mm. It should increase to 28 years if the amendment materials are <2.0 mm in size, and to 1,740 years if they are powder particles.

It should be noted that there are some issues involved with this evaluation. Firstly, the actual attenuation layer is generally unsaturated. The water retention capacity of the attenuation layer should retain leachates (Kato et al., 2020). Consequently, the retention period of the leachates should increase, enhancing the attenuation of As. Sec-

Table 6
Parameters considered to simulate As transport through attenuation layer.

Attenuation layer thickness	20–50 cm
Dry density	1.9 g/cm^3
Porosity	0.28
Precipitation	1,500 mm/y
Infiltration rate	45 cm/y
Darcian velocity	0.123 cm/d
As concentration in leachates entering the layer	0.1 mg/L
Partition coefficient	14.5, 22.2, 47.9, and 3,009.5 cm^3/g

ondly, it will take many more years than predicted because water does not continuously infiltrate into the embankment. Thirdly, leachate concentrations fluctuate and decrease to almost zero over time (e.g., Inui et al., 2014; Kato et al., 2021b). The attenuation performance of the materials will improve as the concentration decreases. These effects, which should occur at an actual site, were not considered. Hence, this study applied relatively conservative assumptions in the calculations. Based on the above

points, stabilising agents comprising not only powder particles, but also granular ones, hold promise as attenuation layer materials. Due to safety concerns and uncertainty considerations, constructing a 50-cm-thick attenuation layer is realistic for an actual site.

5. Conclusions

Batch sorption tests and modelling were used to evaluate the impact of the particle sizes of stabilising agents on the attenuation layer performance. Specifically, eight different particle sizes of stabilising agents, composed primarily of calcia and magnesia, were investigated. The results support the following conclusions:

- Amending the soil with a stabilising agent improved the As attenuating performance, even when only 5% of the agent was added. In one experiment, a stabilising agent with granular particles (between 2.0 and 9.5 mm) for the amendment increased the soil's partition coefficient K_d from 14.5 to 22.2 cm^3/g. This is more than a 50% improvement in attenuation.
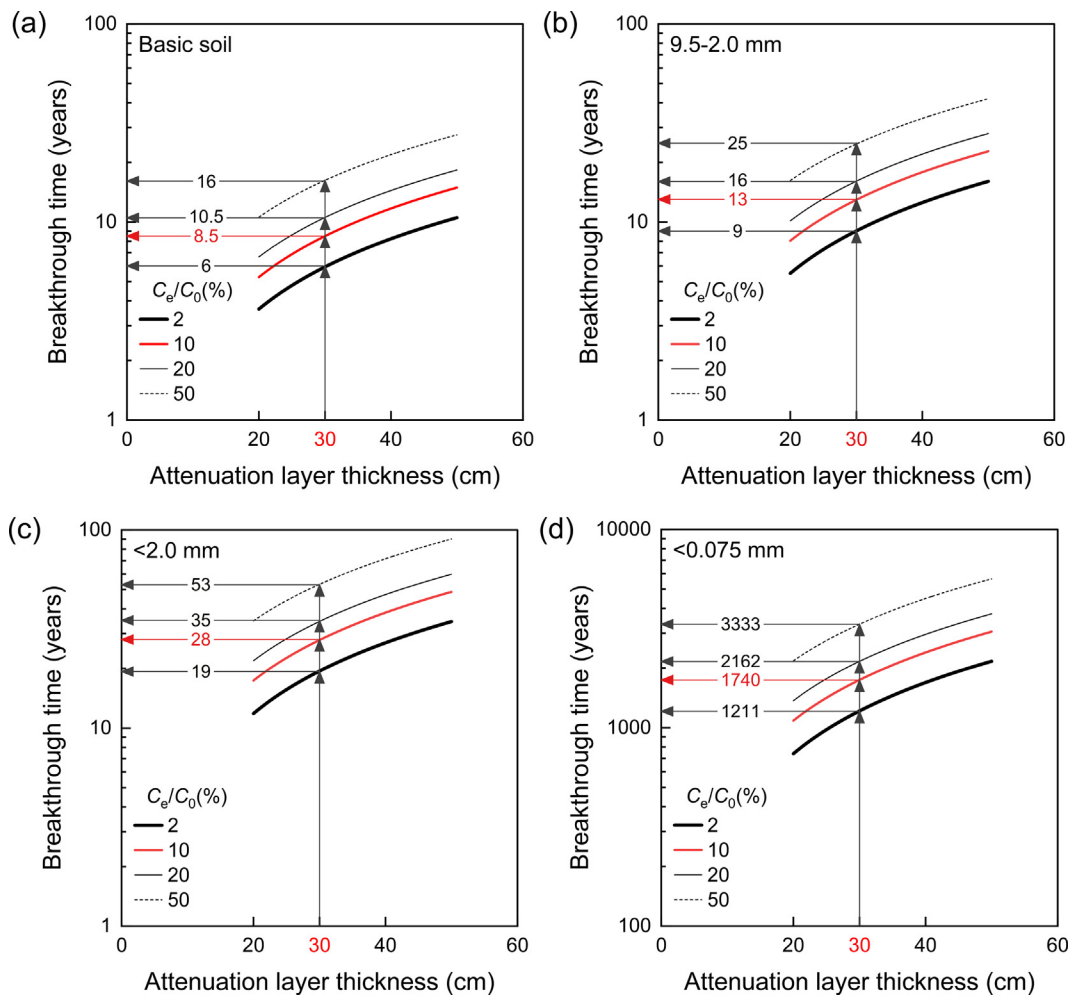

Fig. 8. Breakthrough times when employing basic or amended soil as attenuation layer. The amended soils are denoted by the particle size fractions of the amendment material.

- The impact of the stabilising agent increased when smaller particles were used as the amendments. K_d increased linearly as the particle size of the stabilising agent decreased when the amendment materials were larger than 0.075 mm in size. The ability of the soil–agent mixtures to attenuate As may be a function of the particle size of the amendment material and not S_{BET}.

- Adding a stabilising agent increased the pH to a higher level than the pH of the soil itself. High pH levels of 10 and above were noted for the soil–agent mixtures. The change in pH was more pronounced as the particle size of the amendment material decreased. The ability to increase the pH to such high levels may be beneficial at actual sites, especially in situations where leachates are acidic. The leaching of Ca followed the pH profile. Thus, dissolved Ca may directly affect the pH levels.

- Simulations using a one-dimensional advection–dispersion equation revealed that a 30-cm-thick saturated attenuation layer reduced the As concentrations from 0.1 mg/L to below 0.01 mg/L (which is the regulatory limit in Japan) for periods of 13, 28, and 1,740 years when using stabilising agents with sizes of 9.5 to 2.0 mm, <2.0 mm, and <0.075 mm, respectively. However, considering the drawbacks of the simulations, not only stabilising agents comprising powder particles, but also granular ones, hold promise as attenuation layer materials.

Acknowledgements

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