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研究課題名（和文）Hydraulic and chemical performance of a sandy soil mixed with calcium-magnesium composite as the attenuation layer for geogenic heavy metals

研究課題名（英文）Hydraulic and chemical performance of a sandy soil mixed with calcium-magnesium composite as the attenuation layer for geogenic heavy metals

研究代表者

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研究成果の概要（和文）：本研究では、粉末状から粒状のカルシウム・マグネシウム複合材を混合した真砂土の吸着性能と透水係数を評価した。透水係数試験では、原地盤と改良地盤の透水係数に有意差はなかった。バッチ収着試験では、改良地盤が原地盤よりも効果的に汚染物質を減衰させることが示された。ある実験では、粒状粒子（2.0～9.5mm）の安定化剤を用いた改良の結果、土壌の分配係数Kdが14.5から22.2cm3/gに増加し、吸着性能が50%以上改善された。Kdは、安定化剤の粒径が0.075mmまで小さくなると、直線的に増加した。実験で得られたKdを用いた、一次元移流分散方程式によるシミュレーション結果、吸着層の耐久性が実証された。

研究成果の学術的意義や社会的意義
Since stabilising agent affects the mechanical and chemical properties of the attenuation layer, particle size of agent needs to be optimised as per the site requirements. Soil mixed with agent of different sizes were examined, and powder and granular particles were confirmed as suitable materials.

研究成果の概要（英文）：This work was carried out to evaluate the attenuation performance and hydraulic conductivity of a soil mixed with calcium-magnesium composite with different particle sizes, ranging from powder particles to granular ones. According to the hydraulic conductivity tests, the original soil and the amended soil were not significantly different in hydraulic conductivity. Batch sorption tests demonstrated that amended soil more effectively attenuates contaminants 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 Kd from 14.5 to 22.2 cm3/g, which is more than a 50% improvement in the attenuation. Kd increased linearly as the particle size of the stabilising agent decreased down to 0.075 mm. Using the Kd from laboratory tests, simulations with a one-dimensional advection-dispersion equation demonstrated the durability of the attenuation layer.

研究分野：Geoenvironmental Engineering

キーワード：Attenuation layer　Geogenic contamination　Stabilising agent　Hydraulic conductivity　Sorption　Arsenic　Soil management　Excavated soils

１．研究開始当初の背景

Many cases have been reported in which substantially large volumes of excavated soils and rocks generated during mining and subterranean construction contain toxic elements of geological origins. **There is some reluctance about using these materials on construction sites because they could leach toxic elements in unacceptable concentrations**. Consequently, environmental regulatory agencies, researchers, and authorities, which handle the construction and development of infrastructure, have debated how to properly manage these materials.

One alternative to directly disposing them is to use these soils and rocks while taking economical and effective countermeasures against the risk due to geogenic contamination (Katsumi 2015). Thus, in 2017, the Soil Contamination Countermeasures Law, which is the national law dealing with soil contamination, was extensively revised to comply with the technical guidelines of the Ministry of Land, Infrastructure, Transport and Tourism and to permit their use under proper contaminant control. Figure 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. A significant benefit of the attenuation layer method over the common method of encapsulation using geomembrane sheets is that stable earthen structures can be constructed using simple traditional methods for earthen works. However, several issues must be considered to create a successful attenuation layer method.

The selection and design of appropriate constituent materials for attenuation layer is a fundamental step to creating a successful attenuation layer method. Working toward this goal, the attenuation performance of soil and stabilising agent has been individually evaluated (e.g., Tatsuhara et al. 2012, Tabelin et al. 2013), while the soil–agent mixture has not been fully evaluated. The attenuation performance of the mixture needs to be evaluated since the interactions of different properties of materials and the sorption mechanisms are not clear. In recognition of this, several researchers, including myself, have been assessing soil–agent mixtures for their attenuation capabilities.

２．研究の目的

Since the stabilising agent affects the mechanical, hydraulic, 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 stabilising agent and the attenuation or hydraulic 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. 2021).

This study examined different particle sizes of a stabilising agent with the same chemical composition to clarify the effects of particle size on the attenuation layer's attenuation performance and hydraulic conductivity. The stabilising agent used in this study is composed mainly of calcia and magnesia. Previous studies have demonstrated this material has a high capacity to attenuate contaminants (e.g., Mo et al. 2020, Gathuka et al. 2021), making it a promising candidate for use in the attenuation layer. Batch sorption tests were conducted on soil–agent mixtures to assess their ability to attenuate arsenic (As), which is an important contaminant in geogenic contamination in Japan. Hydraulic conductivity *k* of the mixtures was evaluated using flexible-wall permeameters with a constant head system and As solution as permeant.

３．研究の方法

3.1.　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 particles less than 2 mm, which were required for the tests.

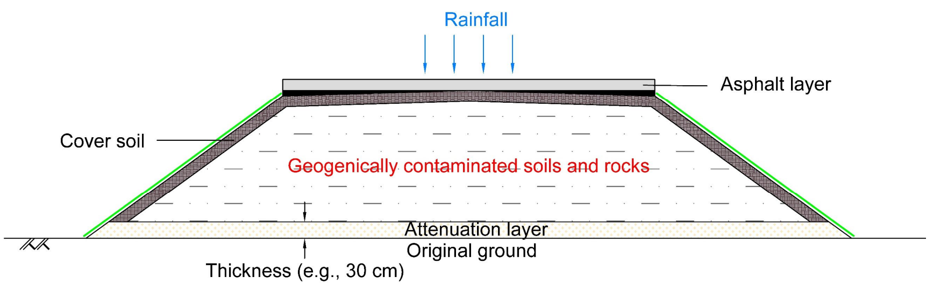

Figure 1 Schematic diagram of an embankment installed with an attenuation layer underlying geogenically contaminated soils and rocks.

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. One notable difference between the basic and the modified agents was that the latter contained additives such as ferrous sulphate. 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 these materials.

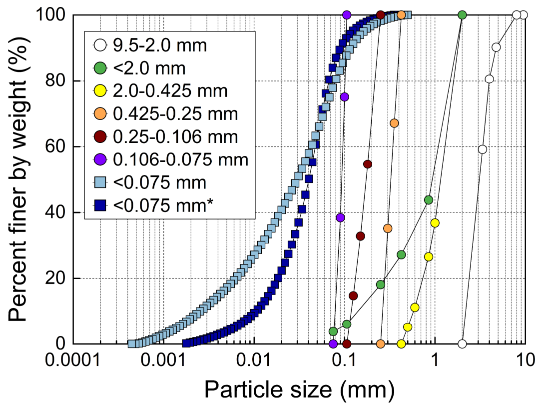

Figure 2 Particle size distributions of eight particle size fractions of Ca–Mg agents used in this study. The modified agent is denoted by <0.075 mm*.

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. Figure 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.

3.2. Experiments

3.2.1. 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 porous materials are often obtained using the Brunauer-Emmett-Teller (BET) nitrogen gas adsorption technique (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.

3.2.2. Batch sorption tests

Batch tests evaluated the attenuation performance of the soil–agent mixtures against As. The tests were performed on the mixtures 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 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. 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, TAITEC) 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 coexisting ions (Al, Ca, Fe, K, Mg, and Na) were measured using an Agilent Technologies ICP-OES 710 inductively coupled plasma optical emission spectrometer.

3.2.3. Hydraulic conductivity tests

Flexible-permeameters with a constant head system were employed to evaluate the hydraulic conductivity of the mixtures. A schematic diagram of the flexible-wall permeameter is shown in Fig. 3.

Table 1
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 agent per kg of soil by dry weight)
Specimen mass	>50 g
Liquid-to-solid ratio	10 L/kg
Mixing	Horizontal shaking at 150 rpm

Mariotte's bottle was filled with a solution containing 0.1 mg/L As ($5.8 \leq pH \leq 6.3$). The solution was prepared using sodium arsenite salts. The solution was permeated at a constant head level continuously through the influent line into the specimen. The hydraulic gradient i was set to 2. Effluents were periodically collected in glass bottles connected to Smart Bag PA (GL Sciences Inc.) to avoid any contact with the environment.

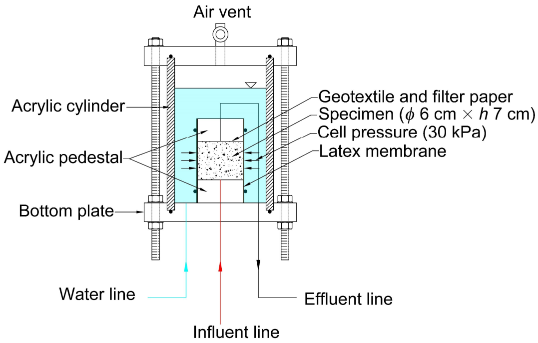

Figure 3 Schematic diagram of the flexible-wall permeameter.

4．研究成果

Table 2 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.

Amending the soil with a 5% stabilising agent improves its attenuation performance. A larger inclination of the sorption isotherm in Fig. 4 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. Figure 5 plots the normalised K_d of the amended soil against the calculated SSA of the stabilising agent (hereafter, this is referred to as S_w). The S_w was calculated according to the particle size of the materials

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., $K_d/K_{d\ 0\%}$). **The normalised 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.

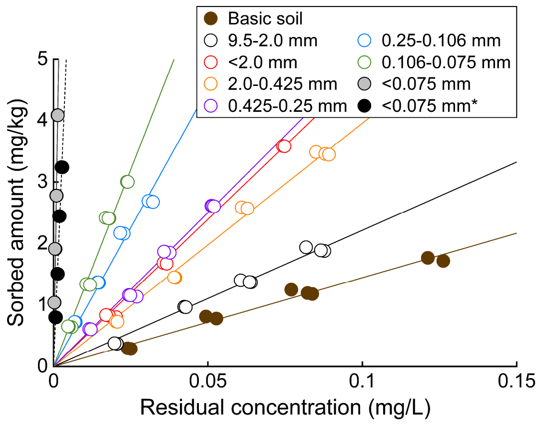

Figure 4 Henry sorption isotherms for basic and amended soils. The figures in the legend denote the particle size fraction of the stabilising agent used for the amendment. Furthermore, the soil amended with the modified agent is denoted by <0.075 mm*.

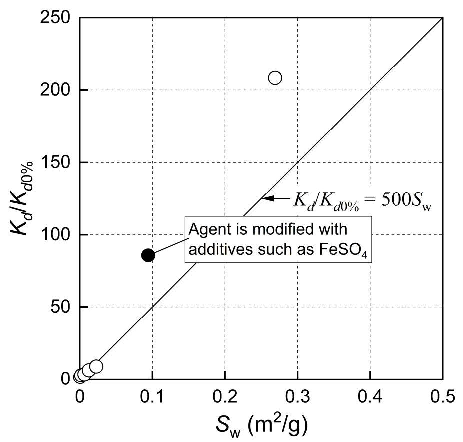

Figure 5 Relationship between normalised K_d of amended soil and calculated SSA of corresponding amendment material.

Table 2
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.

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).

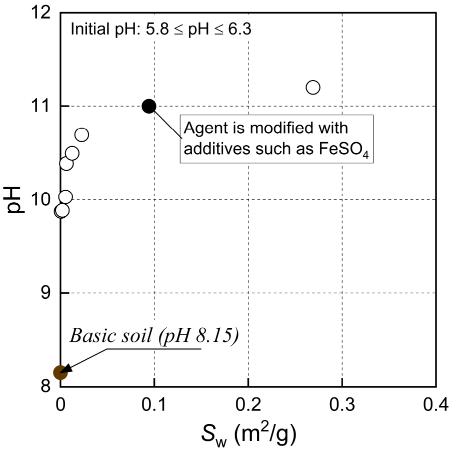

Figure 6 Changes in pH by basic and amended soils.

Hydraulic conductivity was found not to differ significantly between the original soil and the amended soil, as shown in Fig. 7. The initial *k* value of the soils was between 2×10^{-7} and 5×10^{-7} m/s. As continuous permeation progressed, *k* of the soil–agent mixtures tended to decrease but remained over 1×10^{-8} m/s. **According to the available data, the particle size of the stabilising agent does not seem to significantly impact the hydraulic conductivity of the soil–agent mixtures**. This suggests that the attenuation layer's hydraulic performance will not be significantly impacted by using either powdery or granular particles of a stabilising agent. Thus, various particle sizes of a stabilising agent can be used to create the attenuation layer.

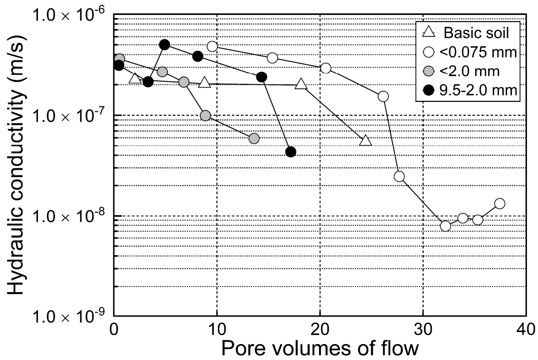

Figure 7 Variations in hydraulic conductivity with continuous permeation. The figures in the legend denote the particle size fraction of the stabilising agent used for the amendment.

Data on hydraulic conductivity and attenuation performance of the soil–agent mixtures will continue to be accumulated. In addition, **the effect of particle size of a stabilising agent will be further investigated to establish a more rational method for designing the attenuation layer**.

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5．主な発表論文等

〔雑誌論文〕　計7件（うち査読付論文　5件／うち国際共著　3件／うちオープンアクセス　2件）

1．著者名 Gathuka, L.W., Kasai, H., Kato, T., Takai, A., Inui, T., and Katsumi, T.	4．巻 N/A
2．論文標題 Effect of particle size of stabilising agent on hydraulic conductivity of soil-agent mixtures	5．発行年 2022年
3．雑誌名 Proceedings of the 20th Global Joint Seminar on Geoenvironmental Engineering	6．最初と最後の頁 GEE11
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 ―

1．著者名 Gathuka, L.W., Kasai, H., Kato, T., Takai, A., Inui, T., and Katsumi, T.	4．巻 62
2．論文標題 Evaluating the arsenic attenuation of soil amended with calcium-magnesium composites of different particle sizes	5．発行年 2022年
3．雑誌名 Soils and Foundations	6．最初と最後の頁 101130
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.sandf.2022.101130	査読の有無 有
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1．著者名 Gathuka, L.W., Kato, T., Takai, A., and Katsumi, T. N	4．巻 N/A
2．論文標題 Column test for arsenic attenuation by sandy soil amended with calcium-magnesium composite of different particle sizes	5．発行年 2022年
3．雑誌名 Proceedings of the 20th International Conference on Soil Mechanics and Geotechnical Engineering	6．最初と最後の頁 775-3780
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1．著者名 Kasai, H., Gathuka, L.W., Kato, T., Takai, A., and Katsumi, T.	4．巻 N?A
2．論文標題 Compaction characteristics and attenuation performances of soil amended with Ca-Mg stabilising agent of different particle sizes	5．発行年 2021年
3．雑誌名 Proceedings of the 14th Japanese Geotechnical Society Symposium on Environmental Geotechnics	6．最初と最後の頁 61-64
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1．著者名 Gathuka, L.W., Kato, T., Takai, A., Flores, G., Inui, T., and Katsumi, T.	4．巻 61
2．論文標題 Effect of acidity on attenuation performance of sandy soil amended with granular calciummagnesium composite.	5．発行年 2021年
3．雑誌名 Soils and Foundations	6．最初と最後の頁 1099-1111
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.sandf.2021.05.007	査読の有無 有
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1．著者名 加藤智大，Lincoln W. Gathuka，岡田雄臣，高井敦史，保高徹生，勝見武	4．巻 -
2．論文標題 カラム吸着・脱着試験による酸化マグネシウム系材料を添加した吸着層におけるフッ素移行特性評価	5．発行年 2020年
3．雑誌名 関西geoシンポジウム	6．最初と最後の頁 181-186
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1．著者名 加藤智大，正木佑典，Lincoln W. Gathuka，高井敦史，勝見 武	4．巻 -
2．論文標題 脱気水を用いた嫌気条件下でのバッチ溶出試験方法の検討	5．発行年 2021年
3．雑誌名 26回 地下水・土壌汚染とその防止対策に関する研究集会	6．最初と最後の頁 -
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〔学会発表〕　計0件

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関