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Evaluation of sorptive materials for attenuation layer: Opportunities for batch sorption tests

T. Kato[1], L. W. Gathuka[2], A. Takai[3], and T. Katsumi[4]

[1]Assistant Professor, Kyoto University, Kyoto, Japan, email: kato.tomohiro.6u@kyoto-u.ac.jp

[2]Researcher, Kyoto University, Kyoto, Japan, email: gathuka.lincolnwaweru.4a@kyoto-u.ac.jp

[3]Associate Professor, Kyoto University, Kyoto, Japan, email: takai.atsushi.2s@kyoto-u.ac.jp

[4]Professor, Kyoto University, Kyoto, Japan, email: katsumi.takeshi.6v@kyoto-u.ac.jp

ABSTRACT

Installing an attenuation layer is a promising engineering measure for reducing contamination risk associated with soils and rocks containing geogenic contaminants in embankments. Sorptive materials must be evaluated for their attenuation performance in order to ensure environmental safety when they are used as attenuation layers. This work discusses the fluorine attenuation of magnesium oxide as a stabilizing agent using batch sorption tests. During the 3 to 168 hours tests, three liquid-to-solid ratios (L/S), namely, 250, 500, and 1000 mL/g, were applied. With the partition coefficient data from the batch tests, column test results were fitted using a one-dimensional advection—dispersion equation. Longer contact times resulted in more fluoride sorption in the amended soil. While the sorption behavior was affected by the contact period, most of the reaction might have been completed within 48 hours. This is because, within 48 hours, approximately 80% of the fluoride was sorbed. A partition coefficient (K_d) of 1740 mL/g for the L/S 1000 case run for 168 hours was determined, which may be an overestimate of the attenuation layer's performance at the site. For a safe evaluation of the attenuation layer's performance, the partition coefficient obtained from batch tests run for shorter periods is recommended.

Keywords: Geogenic contamination, Partition coefficient, Fluoride, Solute transport analysis

1   INTRODUCTION

The amount of excavated soils and rocks increases as development continues. Increasing the utilization of soils and rocks, and consequently decreasing the amount of disposed materials, will help expand sustainable soil management into the geotechnical and geoenvironmental engineering fields (e.g., Magnusson et al., 2019). However, geogenic contamination in the soils and rocks may bring a conservative influence on the utilization of such materials at construction sites (e.g., Tabelin et al., 2018; Kato et al., 2023). If the soils and rocks fail to meet the set environmental standards, actions for contaminant control or disposal of such soils and rocks are usually implemented. However, considering the leaching load and the nature of these materials, actions such as disposal or strict measures, might not be appropriate for two main reasons. First, in many cases, toxic chemicals are leached in low concentrations that slightly exceed the mandated limits (e.g., Ito & Katsumi, 2020). Second, significantly large volumes of excavated soils and rocks are generated, although only a certain percentage contains the toxic elements. Thus, utilizing the soils and rocks under proper contaminant control conditions are highly recommended, rather than the simple disposal of them. The countermeasures should be established based on the scientific and technical considerations of the nature of geogenic contamination.

Toward the aforementioned goal, countermeasures such as containment in an embankment, immobilization treatment, and installation of attenuation layer have been considered (Tatsuhara et al., 2012). The attenuation layer method has attracted attention as a unique concept from other methods (Tamoto et al., 2015; Mo et al., 2020; Gathuka et al., 2022). The attenuation layer is a soil layer with attenuation/sorption capacity The principle of the underlain attenuation layer method is that stable earthen structures can be constructed using simple and traditional methods for earth work, as shown in Fig. 1. A typical attenuation layer material is clean soil mixed with a stabilizing agent to stabilize the

contaminants and enhances the sorption capacity of the host soil. The sorptive materials must be clarified in terms of their attenuation performance to assure environmental safety.
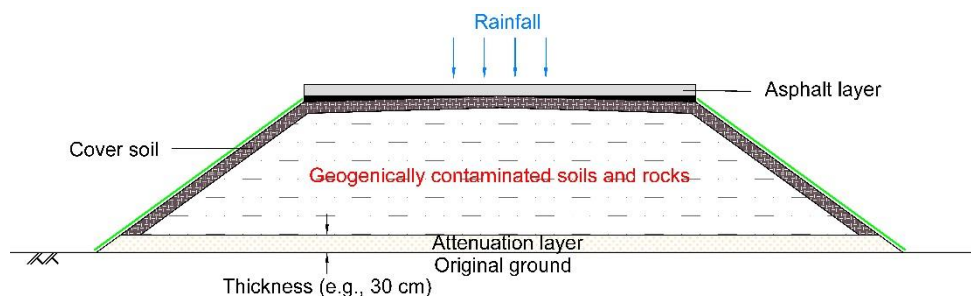

Figure 1. *Schematic of the attenuation layer method (edited from Gathuka et al., 2021)*

The partition coefficient, K_d, is a general index for evaluating the attenuation performance of the layer materials. This sorption parameter can be determined through various laboratory experiments, including batch tests, column tests, and other experimental methods. It is noted that batch sorption tests are more prevalent because they can be conducted with a simple experimental protocol and short testing time. On the other hand, column sorption tests can well simulate on-site conditions, but they have more complex testing protocols than the batch tests. The K_d can also be used in a one-dimensional advection-dispersion equation (ADE) to predict the attenuation performance of the sorptive materials (e.g., Mo et al., 2020; Kato et al., 2021; Gathuka et al., 2022). However, limitations exist in this conservative analysis. For instance, Kato et al. (2021) noted that the sorption behavior of a soil amended with magnesium oxide (MgO) might be difficult to be predicted using K_d because the transformation of MgO to magnesium hydroxide [$Mg(OH)_2$] is not considered. This means that predictions using K_d may have limitations, especially for the attenuation layer method. Since the chemical reaction cannot be described entirely as adsorption, incorporating the sink-source terms and the time-dependent sorption behavior into the ADE should be considered to address these limitations. However, such a complex analytical method is challenging to apply in practice. It is therefore important to apply a rational way to assess the attenuation performance of the layer from a safe standpoint, especially when using sorption parameters, such as K_d obtained from batch tests.

The attenuation performance of a stabilizing agent is evaluated in this work through batch tests. MgO was used as the stabilizing agent because it is a promising agent for the attenuation layer (Wada & Morishita, 2013; Kato et al., 2021; Nishikata et al., 2022). The K_d values for different liquid-to-solid ratios (L/S), contact times, and initial contaminant concentrations (C_0) were determined from the tests. Fluoride (F^-) was used as the contaminant in this work. This is because it is one of the geogenic contaminants likely to be leached from the soils and rocks at concentrations exceeding the mandated limits (e.g., Tamoto et al., 2015; Naka et al., 2016; Ito & Katsumi, 2020). With the K_d from the batch tests, the analytical solution for the ADE was fitted to the breakthrough curves obtained from column experiments in our previous study (Kato et al., 2021).

2   MATERIALS AND METHODS

2.1   Materials

The stabilizing agent mainly constituted MgO, and its content was ~91%. It also contained a certain amount of CaO (~6.7%). The chemical composition was evaluated by X-ray fluorescence using a Shimazu EDX-720 apparatus. The powder was manufactured by Taiheiyo Cement; the residue on a 90-μm sieve was 21.2 wt.%. It had a Blaine-specific surface area of 5970 cm^2/g, which was determined as per JIS R 5201 (2015). It had a particle density of 3.21 g/cm^3, which was determined as per JIS R 5201 (2015).

2.2   Batch sorption tests

Batch tests were used to discuss the fluoride attenuation of the agent. The tests were conducted at a room temperature of ~20 ºC. Three initial concentrations, C_0, namely, 40, 80, and 160 mg/L, were used for the tests. They were prepared using sodium fluoride (NaF). For the tests, 30 mL of the F$^-$ solution

and 120, 60, and 30 mg stabilizing agent were put into plastic centrifuge tubes, to achieve an L/S of 250, 500, and 1000 mg/L, respectively. The mixtures were agitated at 60 rpm using a rotary shaker (MX-RL-Pro, AS ONE). The turning radius was set to 8 cm. The sorption kinetics of the agent were investigated by running the tests for 3 to 168 hours. After the agitation step, centrifugation at 3000 rpm for 10 minutes and filtration using a 0.45-μm membrane filter was done to separate the agent from the solution. Then, the pH and fluoride concentration of the filtrates were immediately measured using a pH meter (LAQUAtwin-pH-33B, Horiba) and a selective ion electrode (6561S-10C, Horiba), respectively.

The sorption parameters, S and K_d, were calculated as follows:

$$S = (C_0 - C_r)V/m \tag{1}$$

$$K_d = S/C_r \tag{2}$$

where S (mg/kg) refers to the sorption mass, C_r (mg/L) refers to the residual concentration measured in the filtrate, V (L) refers to the volume of solution used for the tests, and m refers to the mass of agent used for the tests.

2.3   Solute transport analysis

With the K_d data from the batch tests, analytical solution of ADE was used to fit the breakthrough curve obtained from column tests in our previous study (Kato et al., 2021). The following conservative solution is given under the assumption of a "constant flux" boundary condition (van Genuchten & Parker,1984):

$$\frac{C_r}{C_0} = \frac{1}{2}\mathrm{erfc}\left[\frac{R_d L - vt}{\left(4R_d Dt\right)^{1/2}}\right] + \left(\frac{v^2 t}{\pi R_d D}\right)^{1/2}\exp\left[-\frac{\left(R_d L - vt\right)^2}{4R_d Dt}\right] - \frac{1}{2}\left(1 + \frac{vL}{D} + \frac{v^2 t}{R_d D}\right)\exp\left(\frac{vL}{D}\right)\mathrm{erfc}\left[\frac{R_d L + vt}{\left(4R_d Dt\right)^{1/2}}\right] \tag{3}$$

where R_d (= 1 + $\rho_d K_d/n$, in which ρ_d (g/cm^3) and n are the dry density and porosity of the specimen, respectively) is the retardation factor, D (cm^2/s) is the longitudinal dispersion coefficient, v (cm/s) is the average pore water velocity, C_r (mg/L) is the solute concentration at distance x from the source at time t, C_0 (mg/L) is the initial solute concentration, and L (cm) is the column length. For this evaluation, R_d, D, v, and C_0, were assumed to be constant.

The longitudinal dispersion coefficient, D was determined by a tracer test from our previous study (Kato et al., 2021). The test was conducted after the column sorption test on the same specimen. The experiment used chloride (Cl$^-$) as the non-sorbed chemical. A 1000 mg/L Cl$^-$ solution was prepared from sodium chloride (NaCl). The value for D was determined as 2.5 × 10^{-4} cm^2/s, which equals to the dispersion length, λ, of 0.28 cm.

3   RESULTS AND DISCUSSION

3.1   Batch sorption tests

Figure 2(a) shows the results of batch sorption tests. The amount of F$^-$ sorbed was seen to increase with prolonged contact period. The fact that F$^-$ concentration decreased even after 168 hours, shows that this agent has relatively slow sorption kinetics. Slow reactions, such as precipitation, instead of immediate reactions, such as electrostatic attraction, may play a major role in sorption. Considering that most of this agent is MgO, F$^-$ should be sorbed in the form of Mg(OH)$_x$F$_{2-x}$ (Sasaki et al., 2011; Wada & Morishita, 2013). As MgO hydrates to Mg(OH)$_2$, some hydroxide ions (OH$^-$) will be replaced with F$^-$. In the first 48 hours, there was a dramatic decline in the relative concentration, C_r/C_0. However, the changes in C_r/C_0 were insignificant after 48 hours. The fact that 80% of fluoride was sorbed by the agent within 48 hours, it can be assumed that most of the sorption reactions were completed within 48 hours. It should be noted that the sorption reactions may not yet have reached equilibrium. The results of this study suggest that to guarantee optimum attenuation of contaminants in the attenuation layer, they should be kept in the attenuation layer for a long time. Construction of a thick attenuation layer (e.g., 50 cm) or selection of materials with low hydraulic conductivity can be employed to achieve this goal. Additionally, lower C_0 led to smaller C_r/C_0. Geogenic contamination levels are typically low, for instance

3 mg/L for F[-] (Ito & Katsumi, 2020). Since the higher sorption performance is performed under lower concentrations, stabilizing agents, such as MgO, are especially beneficial for the attenuation layer.

Figure 2(b) shows the sorption isotherms obtained using Eq. (2). Within the concentration ranges used in this study, the sorption behavior seems to be linear. However, it is noted that outside of this concentration range nonlinear sorption behavior might be observed. Table 1 summarizes the values of K_d. Higher K_d values were associated with longer contact times. Additionally, as L/S decreased, K_d values increased, though the effect was not as significant as contact time.

The filtrates were noted to be strongly alkaline (10.9 < pH < 11.7), as shown in Table 1. The high pH levels are associated with magnesia and calcia in the agent (e.g., Sasaki et al., 2011).

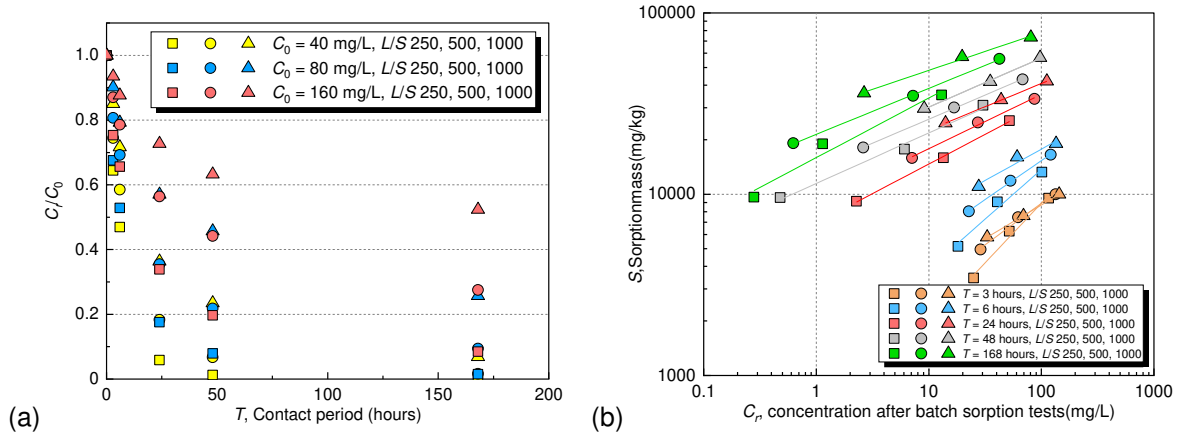**Figure 2.** Results of batch tests for (a) sorption kinetics and (b) sorption isotherms

Table 1. Results of K_d and pH levels

Case	Time (hours)	L/S (L/kg)	K_d (L/kg)	pH	R^2
1		250	64	11.2	0.965
2	3	500	46	11.0	0.959
3		1000	37	10.9	0.987
4		250	92	11.3	0.944
5	6	500	83	11.1	0.976
6		1000	69	11.0	0.876
7		250	306	11.7	0.957
8	24	500	205	11.4	0.920
9		1000	169	11.3	0.958
10		250	665	11.6	0.956
11	48	500	345	11.6	0.915
12		1000	293	11.4	0.970
13		250	1740	11.6	0.908
14	168	500	785	11.6	0.916
15		1000	422	11.4	0.857

3.2   Solute transport analysis

The authors conducted column tests in a previous study (Kato et al., 2021). The tests were conducted using acrylic columns (ϕ 5 cm $\times$ h 10 cm) with the room temperature set to ~20 ºC. The test specimen was a dry soil mixed with MgO as an agent. The agent content was 10% or 100-g agent per kilogram dry soil. The specimen's ρ_d and n were 1.43 g/cm^3 and 0.47, respectively. Fluoride solution was prepared using NaF with a concentration of 80 mg/L. The solution was continuously permeated to the specimens after saturating them with distilled water. Up-flow permeation was applied via a peristaltic pump at 36 mL/h. The column sorption test was terminated when the concentration in the effluent exceeded 76 mg/L F[-]. Effluents were collected periodically in plastic bottles and filtered using a 0.45-µm membrane filter. The fluoride concentration and pH of the filtrate were measured in the same way as in the batch test. As the attenuation of soil is supposed to be lower than the stabilizing agent, the sorption mass is calculated using only the mass of the stabilizing agent in the specimen.

Figure 3 shows the breakthrough curve from the column test. The blue line represents the result of the fitting curve in our previous study, which was obtained though minimizing the error between the predicted and experimental data (Kato et al., 2021). The prediction overestimated the breakthrough point of the column test data, which is $C_r/C_0 = 0.05$, as shown in Fig.3. Among the cases studied here, case 3 significantly underestimated the results while case 13 significantly overestimated them. This shows that the sorption behavior of soils amended with MgO is difficult to be predicted using the conservative ADE analysis because the transformation of MgO to $Mg(OH)_2$ is not considered (Sasaki et al., 2011; Kato et al., 2021). Based on the fitting curve from our previous study, we calculated a K_d of 561 mL/g. Comparing the K_d from the previous study with that from prolonged batch tests (e.g., over 48 hours), the K_d from the previous study was relatively lower. Therefore, the K_d obtained from batch tests with shorter run times could be an appropriate way to evaluate the attenuation performance of the layer materials.
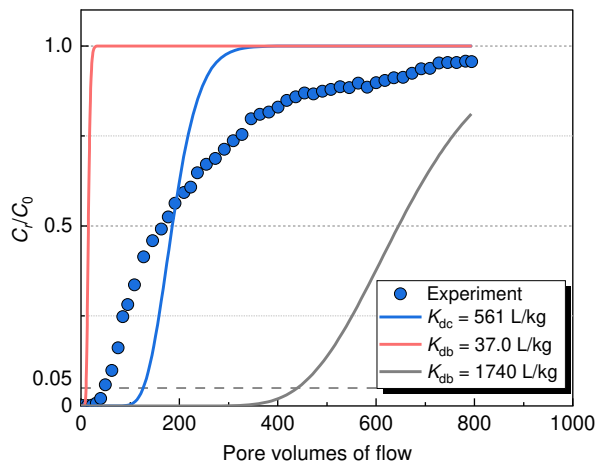

Figure 3. *Result of column tests and fitting curves from cases 3 and 13*
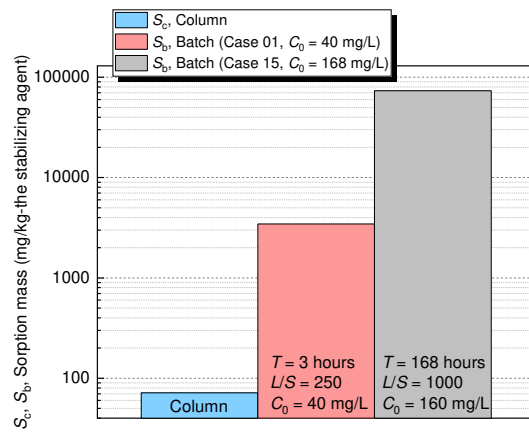

Figure 4. *Calculated sorption mass based on column tests and cases 1 and 15 of batch tests*

3.3   Column vs. batch sorption tests

Figure 4 illustrates the sorption mass determined from batch and column tests. The minimum sorption mass according to the batch tests was 3450 mg/kg (i.e., for case 01), whereas the maximum sorption mass according to batch tests was 73400 mg/kg (i.e., for case 15). An increase in sorption mass was observed as the contact time increased. Furthermore, with larger L/S, greater sorption mass was obtained. There was a significant difference between the sorption mass of the column test and the sorption mass of the batch test. It is reasonable to assume that batch sorption tests with longer contact times and larger L/S will overestimate the sorption mass because column tests should simulate in-field conditions better than batch tests. Taking this perspective into consideration, column tests should be used to evaluate the attenuation performance of the attenuation layer. However, if column tests cannot be conducted because of time or cost constraints, ADE analysis should be done using K_d obtained from batch tests run for a short time.

4   CONCLUSIONS

This work discusses the fluorine attenuation of magnesium oxide as a stabilizing agent using batch sorption tests. During the 3 to 168-hours tests, three L/S, namely, 250, 500, and 1000 mL/g, were applied. With the sorption data from the batch tests, column test results were fitted using ADE. The results support the following conclusions:

- The amount of F⁻ sorbed was seen to increase with prolonged contact time. The fact that 80% of fluoride was sorbed by the agent within 48 hours, it can be assumed that most of the sorption reactions were completed within 48 hours. However, it should be noted that the sorption reactions may not yet have reached equilibrium.

- Among the cases studied here, case 3 significantly underestimated the column test results while case 13 significantly overestimated them. This shows that the sorption behavior of an attenuation layer with MgO is difficult to predict using the conservative ADE analysis.
- For the L/S 1000 case run for 168 hours, the partition coefficient (K_d) of 1740 mL/g was determined, which may be an overestimate of the attenuation layer's performance at the site. For a safe evaluation of the attenuation layer's performance, the K_d obtained from batch tests run for shorter periods is recommended.
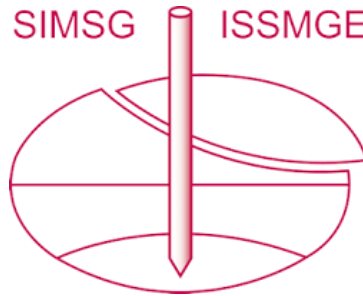
5   ACKNOWLEDGEMENTS

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