

Technical Paper

Evaluating temperature effects on leaching behavior of geogenic arsenic and boron from crushed excavated rocks using shaking and nonshaking batch tests

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Received 22 March 2022; received in revised form 13 December 2022; accepted 27 December 2022

Abstract

The leaching behavior of arsenic and boron is evaluated in this work through two types of excavated rocks with geogenic contaminants under different temperatures. Excavated rocks with geogenic contaminants are expected to be used in embankments with appropriate countermeasures being taken against the risks brought about by geogenic contamination. The leaching behavior might change because of changes in the ground temperature. However, the effects of temperature on the leaching behavior of such rocks have not been well examined. Herein, batch leaching tests at temperatures between 5 and 60 °C were performed under shaking and nonshaking conditions. Mudstone and shale rock were crushed into particles smaller than 2 mm, which were required for the tests. The tests were carried out for durations ranging from 6 h to 15 days because changes in leaching kinetics also require careful evaluation. After conducting the nonshaking tests for 15 days at 40 °C, the mudstone sample leached arsenic and boron at concentrations of approximately 0.7 and 1.0 mg/L, respectively. The arsenic and boron concentrations were about 20 and 40% higher than those of the sample leached at a temperature of 20 °C. Elevated temperatures were seen to increase the leaching kinetics of the toxic elements. For the shale rock sample, the leaching rate for arsenic was 7.7×10^{-2} /h at 40 °C, which was about 2.5 times greater than the value at 30 °C. The nonshaking tests showed higher leaching amounts of arsenic and boron than the shaking tests, especially at elevated temperatures. As unrealistic estimations should be avoided, nonshaking tests are suggested. Moreover, nonshaking tests lasting longer than 6 h are necessary due to the relatively slow dissolution of minerals.

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Keywords: Soil contamination; Excavated rocks; Ground temperature; Batch leaching test; Leaching kinetics

1. Introduction

Many construction projects generate substantial amounts of excavated soils and rocks. A certain percentage of these soils and rocks contain toxic metals and metalloids that are derived from geological processes. Geogenic toxic

metals and metalloids, such as arsenic (As) and boron (B), are widely distributed. They are found in different types of natural rocks and sediments, including marine clays, igneous rocks, and hydrothermally altered rocks. Such soils and rocks are expected to be used in embankments as a part of the ongoing efforts to achieve sustainable soil management. However, their proper use is sometimes a concern, especially because toxic elements can be released from the soils and rocks (Katsumi, 2015). Given the importance of developing economical and effective utilization methods for geogenically contaminated soils and rocks, evaluating the leaching behavior of these materials is important.

Peer review under responsibility of The Japanese Geotechnical Society.

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<https://doi.org/10.1016/j.sandf.2023.101274>

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Working toward the aforementioned goal, researchers have used various batch tests to evaluate the leaching behavior of different geogenically contaminated soils and rocks (e.g., Tabelin and Igarashi, 2009; Li et al., 2018; Tabelin et al., 2018; Kamata and Katoh, 2019; Ito and Katsumi, 2020). When the soils and rocks are used in embankments or other shallow geostructures, the effects of the ground temperature on the leaching behavior of toxic elements are of technical concern because the daily and seasonal changes in temperature in shallow grounds can be much larger than those in deep grounds (Menberg et al., 2013; Alam et al., 2015; Saito et al., 2016). According to Menberg et al. (2013), the ground temperature can sometimes reach 60 °C. In addition, various thermally active geosystems, introduced recently (e.g., thermal energy storage and ground-source heat pumps), involve changes in ground temperature (Wang et al., 2015; Başer et al., 2018), which might influence the leaching potential of the toxic elements in soils and rocks. Given these points, the effects of temperature on the behavior of geostructures need to also be clarified from a geoenvironmental perspective because the leaching behavior of such materials can change as a result of thermo-mechanical-chemical interactions. However, when the leaching concentrations of toxic elements are measured in laboratory tests, the tests are typically conducted at room temperature (approximately 15 to 20 °C) because of the nearly constant ground temperature at depths greater than 10 to 15 m below the surface.

In addition, the leaching behavior of soils and rocks differs depending on how long the water has been in contact with them. Japanese Leaching Test Method No. 46 (JLT46) is a standard leaching method used in Japan (MOE, 1995). For this test, the liquid obtained after shaking for six hours at a liquid-to-solid ratio (L/S) of 10 and separation with a 0.45- μm opening filter is analyzed to determine the concentration of the chemicals of concern. It should be noted that this leaching test was developed to test for artificial contamination. There is no certainty that it can be applied to geogenic contamination. The chemical forms and leaching processes differ between geogenically and artificially contaminated soils and rocks (Li et al., 2018). Thus, the standard leaching test may underestimate the risks of contamination if the leaching kinetics of the geogenic contamination is relatively slow. In order to assess the risks of geogenic contaminants with a higher level of safety, it is necessary to investigate their leaching kinetics. Moreover, any method employed to evaluate geogenic contamination must take into consideration the time needed for soil reactions to reach equilibrium.

The leaching behavior of As and B is evaluated in this work through two types of excavated rocks with geogenic contaminants under different temperatures. The tests were performed under both shaking and nonshaking conditions to elucidate how shaking, which is applied in the standard leaching tests, affects the leaching behavior of the materials. Temperatures between 5 and 60 °C were applied to

account for the possible changes in temperature due to solar radiation and thermally active geosystems. The tests were conducted for 6 h to 15 days because changes in the leaching kinetics also require careful evaluation. A first-order kinetic model was used to fit the experimental results to investigate the leaching kinetics.

2. Materials and methodologies

2.1. Materials

The shale rock and mudstone used in this work were excavated from tunnel construction sites. The rock samples were crushed into particles smaller than 2 mm for the batch leaching tests. Fig. 1 shows the appearance of the rock samples after they were crushed and sieved through a 2-mm screen. The rock samples were then stored in sealed plastic bags to prevent their oxidation by air.

Table 1 highlights the fundamental physicochemical properties of the rock samples. The chemical composition and the total content of As were evaluated by X-ray fluorescence (XRF) analysis using a Shimadzu EDX 720 energy-dispersive X-ray spectrometer. The total content of B was determined by the acid digestion method.

Fig. 2 shows the X-ray diffraction (XRD) patterns of the samples (PANalytical X'Pert PRO MPD, Cu $K\alpha$, 45 kV, 40 mA). Peaks of calcite were identified. The calcite in the rocks contributes to the sorption of toxic elements and neutralizes acidic solutions (Barton and Vatanatham, 1976; Niu and Lin, 2021). Toxic metals and metalloids can be leached via desorption from soil particles (e.g., Tabelin et al., 2018). As the pH level affects desorption reactions, the trends in pH should be carefully examined.

The zeta potential of the rock samples was measured to better understand how their surface charge changes with the pH level. A 0.1-g rock sample and 100 mL of water were poured into a beaker. A 100-W ultrasonic wave irradiated the beaker for 3 min. Next, the pH values of the solution were adjusted to pH levels of 2, 4, 6, 8, and 10 using hydrochloric acid or sodium hydroxide. Then, the solution was poured into a capillary cell, and the zeta potential was measured using the electrophoresis method (Malvern Zetasizer Nano ZS). The refractive index, dielectric constant, and viscosity of the solution were assumed to be the same as those of water. Fig. 3 plots the zeta potential of the rock samples against the pH. The results show that the soil particles became more negatively charged as the pH increased. The isoelectric point of the shale rock sample was at pH 3.12. No isoelectric point was detected for the mudstone sample.

2.2. Batch leaching tests

2.2.1. Shaking conditions

Batch leaching tests were conducted under shaking conditions and at an L/S of 10. Fig. 4 shows the test setup. Rubber heaters connected to a temperature control system

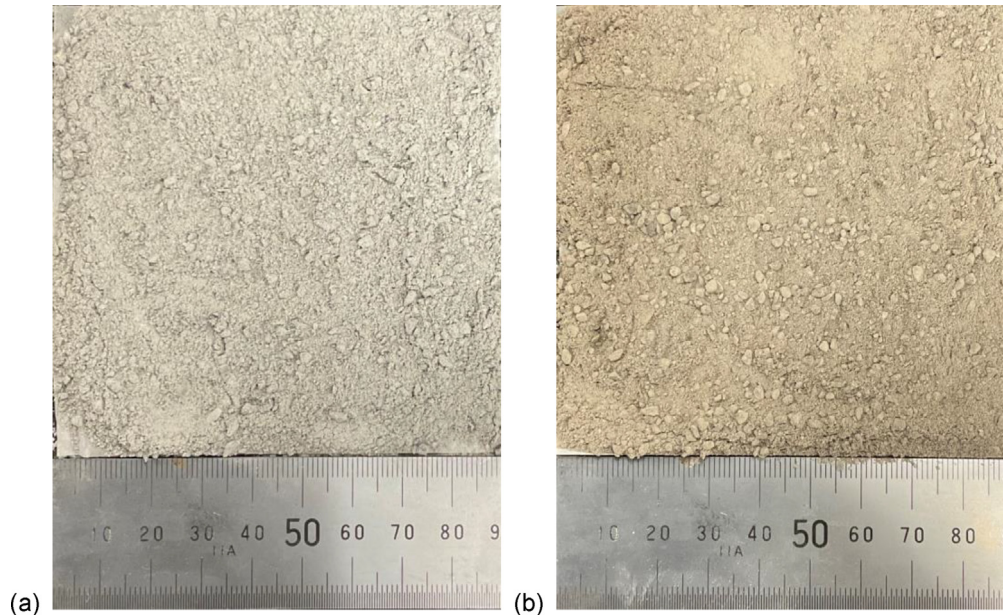


Fig. 1. Appearance of the (a) shale rock sample and (b) mudstone sample after crushing and sieving through a 2-mm screen.

Table 1

Properties of the rock samples used in this study.

Parameter	Shale rock	Mudstone	Method of measurement
Particle density	2.73 g/cm ³	2.64 g/cm ³	JIS A 1202 (2009)
Particle size distribution			JIS A 1204 (2009)
Sand fraction [0.075–2 mm]	85.5%	94.5%	
Fines fraction [<0.075 mm]	14.5%	5.5%	
Average particle size	0.50 mm	0.52 mm	
Chemical composition			XRF analysis
SiO ₂	24.7%	54.5%	
CaO	41.1%	7.2%	
Fe ₂ O ₃	20.4%	17.3%	
Al ₂ O ₃	7.1%	12.9%	
K ₂ O	2.5%	3.2%	
SO ₃	0.9%	1.4%	
MgO	–	1.4%	
Others	3.3%	2.1%	
As content	20 mg/kg	27 mg/kg	XRF analysis
B content	29 mg/kg	150 mg/kg	Acid digestion method

were wrapped around plastic bottles. The rubber heaters heated the bottles during the tests. Distilled water was used as the solvent. After the water temperature was adjusted to the required temperature, the water was poured into the bottles. Temperatures between 20 and 60 °C were used for the tests. The appropriate amount of each rock sample was then poured into the bottles to achieve an L/S of 10. Afterwards, the bottles were horizontally shaken for 6 h to 15 days at 200 rpm using a mechanical shaker (TAITEC NR-30) to evaluate the leaching kinetics. The test conditions are briefly summarized in Table 2.

2.2.2. Nonshaking conditions

Batch leaching tests were also conducted under nonshaking conditions. Shaking conditions are typically used to promote chemical reactions and to ensure homogeneous

contact between soil and water. However, shaking conditions can lead to an inaccurate assessment of how the materials will leach. Thus, nonshaking conditions were also considered herein. Nonshaking tests can provide important information for properly evaluating the leaching behavior in practical situations because geomaterials in the ground or geostructures should make contact with rainwater and/or groundwater without disturbance or agitation. The nonshaking tests also used an L/S of 10. Temperatures between 5 and 60 °C were used for the tests. Temperatures greater than 20 °C were controlled via the rubber heaters wrapped around the bottles during the tests. The tests performed at 5 °C were conducted in a refrigerator. The bottles containing the rock samples and distilled water were placed on a table or in a refrigerator and allowed to stand for 6 h to 15 days.

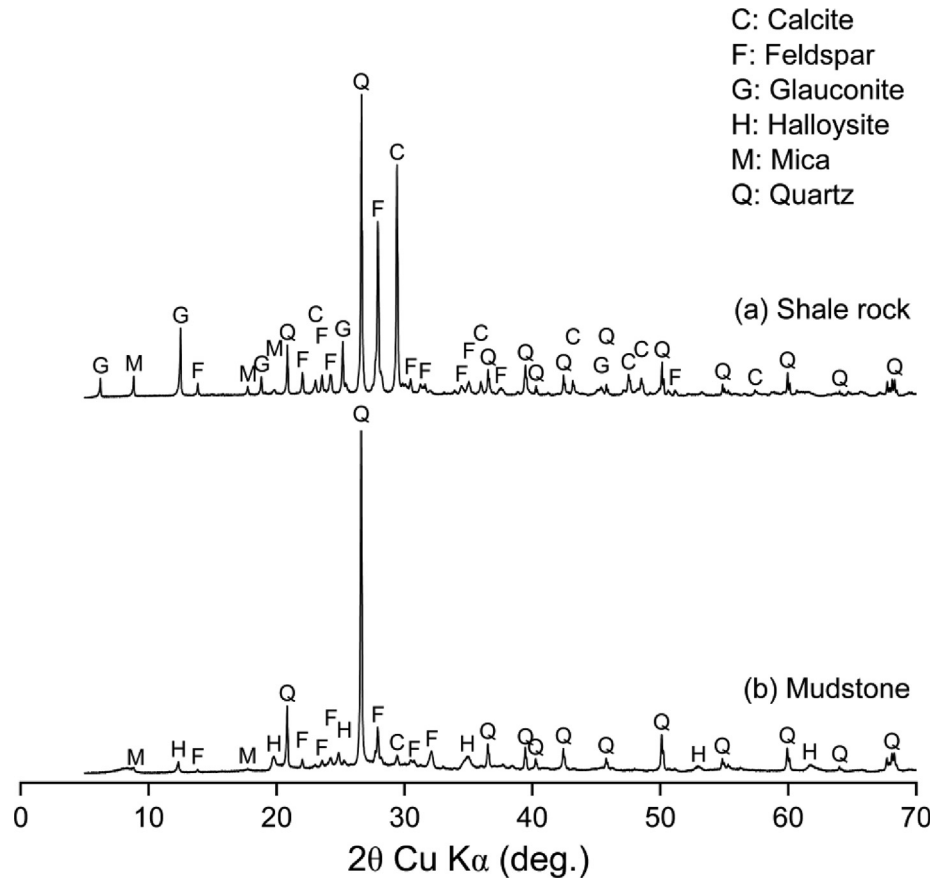


Fig. 2. X-ray diffraction patterns of the rock samples.

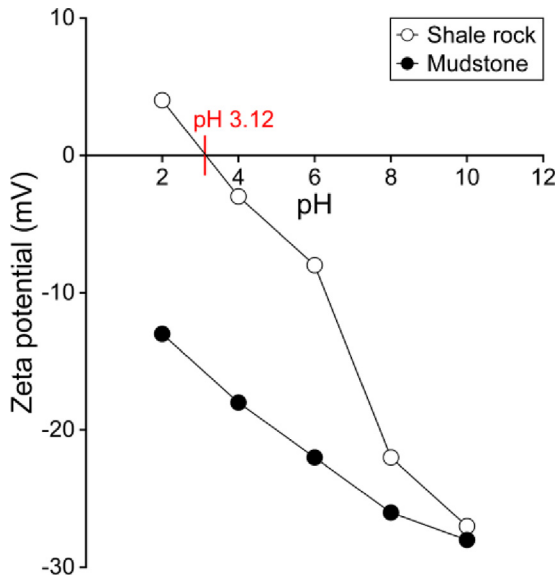


Fig. 3. Zeta potential of the rock samples.



Fig. 4. Batch leaching tests under the shaking conditions using a temperature control system.

Table 2
Conditions of the batch leaching tests.

Sample form	Particles smaller than 2 mm
Solvent	Distilled water ($5.8 \leq \text{pH} \leq 6.3$)
Solvent temperature	5–60 °C (5 °C for nonshaking condition only)
Test duration	6–360 h
Liquid-to-solid ratio	10 L/kg
Filter type	0.45- μm membrane filter

2.2.3. Chemical analyses

After the aforementioned tests, centrifugation at 3000 rpm for 10 min and filtration with a 0.45- μm membrane filter were carried out to separate the liquid from the solids. The pH of the filtrate was measured using a pH/EC meter (Horiba F-54). The As concentrations were

measured using an atomic absorption spectrophotometer (Shimadzu AA-6800). The concentrations of cations (B, Ca, and Fe) were measured using an inductively coupled plasma optical emission spectrometer (Agilent Technologies ICP-OES 710). The concentrations of Ca and Fe were measured because they are key indices for evaluating the leaching behavior of As and B (Tabelin et al., 2018).

2.3. Modeling the leaching behavior

2.3.1. Theory

The changes in the leaching kinetics of As and B, due to an increase in temperature, were evaluated. A first-order model was fitted to the experimental results to obtain the parameters of the leaching kinetics, according to the method used in a previous study (Igarashi et al., 2002). The following equation was used:

$$\frac{\partial Q_s}{\partial t} = -kQ_s \quad (1)$$

Eq. (2) was obtained by integrating Eq. (1).

$$Q_s = Q_{so} \exp(-kt) \quad (2)$$

The leached mass during the batch leaching tests was conserved as

$$Q_{so} = Q_s + CV \quad (3)$$

The leaching model was obtained by combining Eqs. (2) and (3) as

$$C = Q_{so}[1 - \exp(-kt)]/V \quad (4)$$

where t (h) is the solid–liquid interaction time, Q_s (mg/kg) is the concentration of toxic elements in the solid phase at time t , k (1/h) is the rate constant for leaching, Q_{so} (mg/kg) is the initial concentration of toxic elements in the solid phase with the potential to leach out, C (mg/L) is the concentration of toxic elements in the liquid phase at time t , and V (L/kg) is the volume of water per kilogram of sample.

2.3.2. Estimation of leaching kinetics

To model the experimental results of the batch leaching tests, the experimental data were fitted using Eq. (4). The values for k and Q_{so} were obtained by minimizing the residual sum of the squared estimate of errors (SSE) between the model and the experimental data as

$$SSE = \sum_{i=1}^n (C_i - C'_i)^2 \quad (5)$$

where C_i represents the experiment data and C'_i represents the predicted data.

3. Results

3.1. Shaking conditions

Fig. 5(a) shows the chemistry of the leachate from the shale rock sample. Arsenic was leached in greater amounts

at temperatures of 30 and 40 °C than at a temperature of 20 °C. These results suggest that the leaching concentrations might increase when the rocks are exposed to elevated temperatures. Furthermore, the concentrations at temperatures of 30 and 40 °C were higher than the regulatory limit of As in Japan (0.01 mg/L). The leaching of Ca increased with the increasing temperature. This result suggests that the dissolution of Ca minerals in the rock sample increased because of the increase in temperature. The shale rock sample did not leach B or Fe. The pH values decreased as the temperature increased, although the leachates were still alkaline. The alkaline conditions are attributed to the dissolution of the carbonate minerals in the rock sample. The pH values at 20 °C were one pH unit higher than those at 40 °C. The sulfide minerals in the rock (refer to Table 1) may dissolve under high temperatures and reduce the pH values (Sasaki, 1998; Tabelin and Igarashi, 2009).

Arsenic is leached because of the dissolution of minerals or because of the desorption from soil particles (Tabelin et al., 2018). The clay minerals in the rock sample are generally negatively charged, which will promote the desorption of As (Masscheleyn et al., 1991; Carrilo and Drever, 1998). Moreover, the surface charge of the soil particles became more negatively charged as the pH decreased (Fig. 3). Given these points, As should have desorbed during the tests because of the high pH values. However, the As concentrations were lower under the high pH conditions. Therefore, the leaching of As might be mainly attributable to the dissolution of the minerals in the rock, suggesting that the leaching mechanism due to dissolution is affected by temperature.

Fig. 5(b) shows the chemistry of the leachate from the mudstone sample. The leaching concentrations of As were generally lower at higher temperatures, and the concentrations generally exceeded the regulatory limit in Japan (0.01 mg/L). In contrast, the leaching concentrations of B were similar at both 20 and 40 °C. More importantly, the concentrations were acceptable values in Japan (<1.0 mg/L). The Ca concentrations increased as the temperature was raised. The dissolution of the Ca minerals in the rock may have increased under the higher temperatures. Leaching greater amounts of Ca can improve the sorption of As by rendering the surface of the Fe-oxyhydroxides/oxides more positive (Wilkie and Hering, 1996). Therefore, the decrease in the As concentration observed in the present study might be attributed to coexisting Ca. Increasing the shaking time reduced the amount of released Fe. It is possible that Fe was released and precipitated, but this process could not be verified with the available data. Additional studies will be necessary to fully understand the effects of the shaking time. The pH values decreased because of the elevated temperatures; however, the leachates were still alkaline. The alkaline conditions are attributed to the dissolution of the carbonate minerals in the rock sample. The pH values at 20 °C were one pH unit higher than those at 60 °C, similar to the case of the shale rock sample.

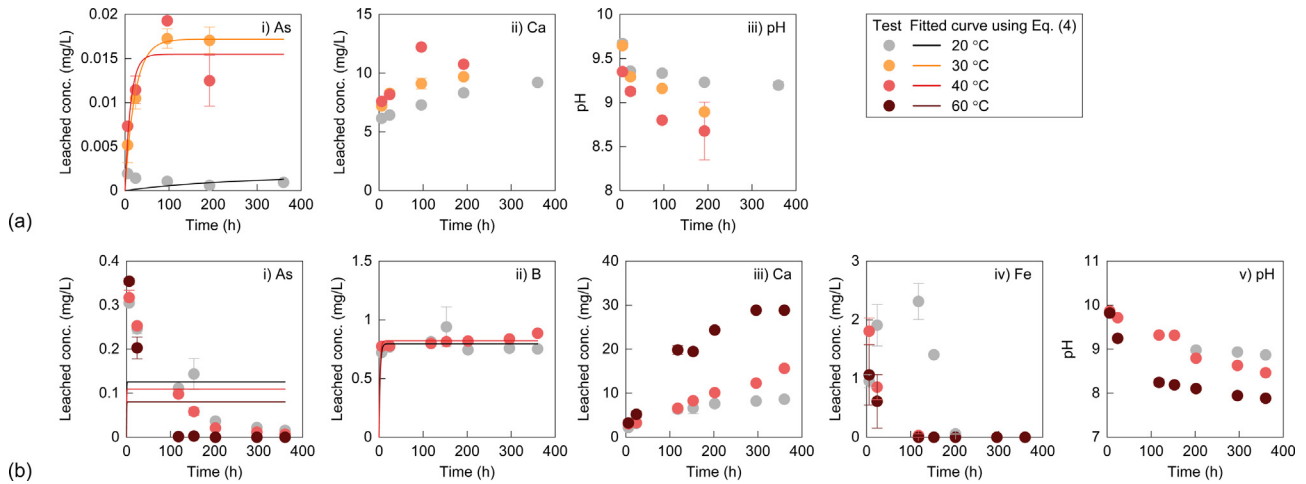


Fig. 5. Leachate chemistry after the shaking tests for the (a) shale rock sample and (b) mudstone sample. These data are the average values. The error bars are the standard deviations.

Boron is leached because of the dissolution of the carbonate minerals, such as calcite or aragonite (Tabelin et al., 2018), and the desorption from soil particles. As the chemical form of B in the solutions is a negatively charged oxyanion [i.e., $\text{B}(\text{OH})_4^{2-}$] or charge-neutral H_3BO_3 (Magara et al., 1998), B is easily desorbed from the soil particles as the pH level increases. When only desorption is considered, differences in the leaching amount should be observed because the pH values differ between the temperatures of 20 and 40 °C. However, the leaching amounts are similar, which suggests that desorption mechanisms are not critical to the leaching of B under these pH conditions. Thus, the dissolution of B, which is strongly temperature-dependent, might be the primary mechanism.

3.2. Nonshaking conditions

Fig. 6(a) shows the chemistry of the leachate from the shale rock sample. Arsenic was leached in greater amounts at 40 °C than at temperatures <30 °C. The results also suggest that leaching concentrations can increase when the temperatures are greater than room temperature. The concentrations at 40 °C were higher than the regulatory limit in Japan. The leaching concentrations of Ca increased with the increasing temperature, and a similar trend was observed in the shaking tests. An increase in the Ca concentration with an increase in temperature suggests that the dissolution of the Ca minerals in the shale rock was promoted under elevated temperatures. The shale rock sample did not leach B or Fe even under nonshaking conditions. Due to the elevated temperatures, the pH values decreased, but the leachates remained alkaline.

Fig. 6(b) shows the chemistry of the leachate from the mudstone sample. As and B were leached in greater amounts when the temperature was increased from 20 to 40 and 60 °C. Notably, the nonshaking tests resulted in higher concentrations of As than the shaking tests when the tests were run for more than 24 h. The leaching concentrations of Ca and Fe did not seem to change in response to

an increase in temperature. The nonshaking tests resulted in smaller amounts of Ca and Fe than the shaking tests, suggesting that the dissolution of these minerals was less promoted under the nonshaking conditions. Due to the elevated temperatures, the pH values decreased; however, the leachates were still alkaline.

3.3. Changes in leaching kinetics of As and B

The rate constant k was used as an index to characterize the changes in the leaching kinetics of As and B. Tables 3–6 summarize the k values obtained using the steps described in Section 2.3. For the shale rock sample, the k value increased as the temperature was raised in the shaking test, as shown in Table 3. At 40 °C, the k value was $7.7 \times 10^{-2}/\text{h}$, which is approximately 2.5 times greater than the k value at 30 °C. Thus, the leaching kinetics of As increased with the increasing temperature. The shaking test results were well fitted using the first-order kinetics model, except for the case of 20 °C. The reason for the disagreement in the results obtained at 20 °C is unclear. When the sample was subjected to nonshaking tests, no noticeable change in k in response to an increase in temperature was observed (Table 5).

For the mudstone sample, the shaking test results for As could not be fitted using the aforementioned model [Fig. 5 (b)]. Thus, the trends in the leaching kinetics of As could not be evaluated. Further study will be required to evaluate the leaching kinetics for the cases in which the leaching concentrations decrease with time. For the nonshaking tests, the k values increased with the increasing temperature (Table 6). At 40 °C, the k value was $5.7 \times 10^{-2}/\text{h}$, which is approximately six times greater than that at 20 °C.

The results for B from the shaking and nonshaking tests on the mudstone sample were well fitted using the model, as shown in Fig. 5(b) and 6(b). Tables 4 and 6 show that the leaching kinetics of B increased with the increasing temperature in both the shaking and nonshaking tests. Table 4 shows that, during the shaking tests at 40 °C, the k value was $4.7 \times 10^{-1}/\text{h}$, which is approximately 1.2 times greater

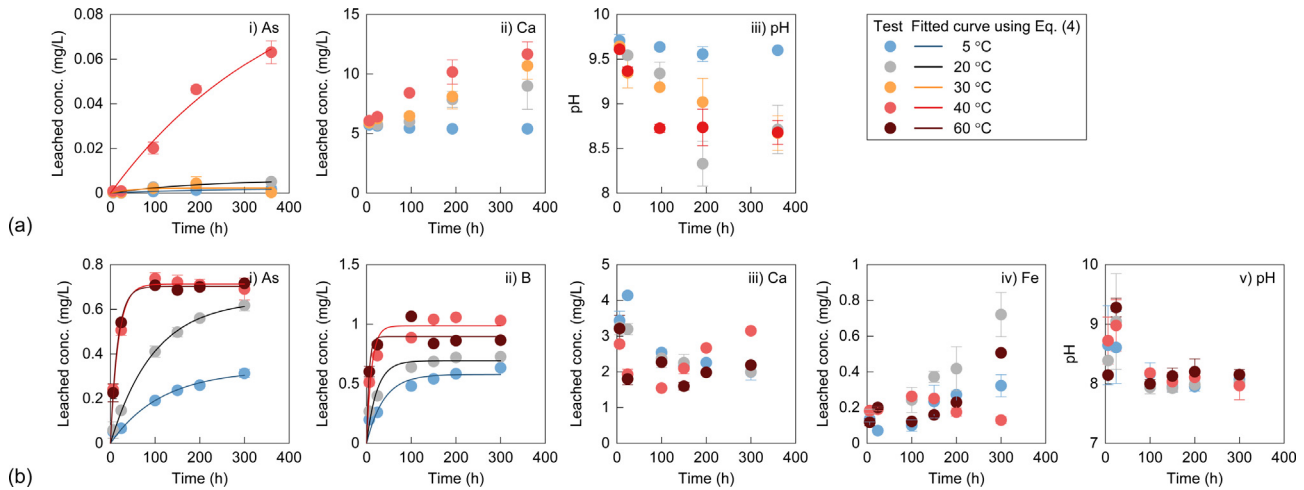


Fig. 6. Leachate chemistry after the nonshaking tests for the (a) shale rock sample and (b) mudstone sample. These data are the average values. The error bars are the standard deviations.

Table 3
Fitting parameters for the results of the shaking tests on the shale rock sample.

	Temperature (°C)	Q_{so} (mg/kg)	k (1/h)	R^2
Arsenic	20	1.6×10^{-2}	4.6×10^{-3}	0.03
	30	1.7×10^{-1}	4.6×10^{-2}	0.99
	40	1.6×10^{-1}	7.7×10^{-2}	0.86

Table 4
Fitting parameters for the results of the shaking tests on the mudstone sample.

	Temperature (°C)	Q_{so} (mg/kg)	k (1/h)	R^2
Arsenic	20	1.3	3.0	0.15
	40	1.1	2.8	0.10
	60	8.0×10^{-1}	3.2	0.04
Boron	20	8.0	4.0×10^{-1}	0.95
	40	8.2	4.7×10^{-1}	0.99

Table 5
Fitting parameters for the results of the nonshaking tests on the shale rock sample.

	Temperature (°C)	Q_{so} (mg/kg)	k (1/h)	R^2
Arsenic	5	2.1×10^{-2}	5.1×10^{-3}	0.99
	20	6.0×10^{-2}	5.1×10^{-3}	0.98
	30	2.3×10^{-1}	2.1×10^{-2}	0.40
	40	1.1	2.6×10^{-3}	0.99

than that at 20 °C. Table 6 shows that, during the nonshaking tests at 40 °C, the k value was 8.8×10^{-2} /h, which is approximately two times greater than that at 20 °C.

4. Discussion

4.1. Temperature effects on leaching behavior

The leaching concentrations of toxic metals and metalloids might increase as a result of the increasing ground temperature. In some cases, the concentrations can exceed

Table 6
Fitting parameters for the results of the nonshaking tests on the mudstone sample.

	Temperature (°C)	Q_{so} (mg/kg)	k (1/h)	R^2
Arsenic	5	3.3	8.8×10^{-3}	0.99
	20	6.4	1.0×10^{-2}	1.00
	40	7.1	5.7×10^{-2}	0.99
	60	7.0	6.3×10^{-2}	1.00
Boron	5	5.8	2.6×10^{-2}	0.95
	20	6.9	4.4×10^{-2}	0.97
	40	9.9	8.8×10^{-2}	0.95
	60	9.0	1.8×10^{-1}	0.95

the regulatory limits, necessitating an evaluation of the effects of temperature. The leaching of toxic metals and metalloids occurs mainly via the dissolution of the minerals in the rocks or the desorption from the soil particles (Tabelin et al., 2018). The results herein indicate that the leaching concentrations due to dissolution changed drastically as the temperature increased. Since the rock samples contained certain amounts of sulfide minerals, it is reasonable to assume that the dissolution of sulfide minerals is one of the leaching mechanisms of As. Moreover, at high temperatures, the As derived from sulfide minerals is more likely to leach. However, not only sulfide minerals, but also other minerals (e.g., calcite) are present in the rock samples. Thus, the amount of As leaching cannot be attributed to sulfide mineral dissolution alone. It has been shown that calcite will have a significant impact on As adsorption (Tabelin et al., 2012). However, these processes could not be verified with the available data. The fact that the results of the nonshaking tests fit the first-order rate law well suggests that surface reactions may be driving the dissolution process, as noted by Igarashi et al. (2002). When leaching concentrations decrease with time, it is difficult to understand the leaching behavior based on the first-order rate law.

Implications of this research are discussed herein. When excavated materials containing geogenic contaminants are utilized in embankments, a solute transport analysis is usually conducted to predict the risks of geogenic contamination to the surrounding ground and to design appropriate countermeasures against these risks (e.g., [Tabelin et al., 2014](#)). Since the initial concentrations of leachates applied in the analysis drastically affect the predictions, the appropriate leachate concentrations expected in practice must be carefully determined. This study indicates that leaching concentrations of As could be up to five times higher than the regulatory limit under elevated temperatures. For this reason, leachate concentrations several times the regulatory limit should be accounted for in the analysis.

4.2. Soil–water interaction time for evaluation of geogenic contamination

Leaching concentrations were found to change because of increases in the soil–water interaction time. These results indicate that the dissolution of minerals is an important factor that should be further evaluated. Generally, the dissolution process requires a longer time to complete ([Tabelin et al., 2017](#)). Therefore, to obtain equilibrium concentrations from the batch tests, the tests need to be conducted for a relatively long period of time. Short test times (e.g., 6 h, as specified in the standard leaching test in Japan) may not be suitable because they might lead to underestimations of the leaching concentrations. When rocks are used in an embankment, the materials will make contact with water for a relatively long time during the infiltration of water into the embankment. The leaching concentrations are expected to increase before chemical equilibrium is achieved. The leaching of geogenic contaminants may continue for a long time because of dissolution.

The attenuation layer method is a recently proposed countermeasure for geogenically contaminated soils and rocks ([Tatsuhara et al., 2012](#); [Gathuka et al., 2021](#); [Kato et al., 2021](#)). The attenuation layer is a soil layer with attenuation capacity, underlying the geogenically contaminated soils and rocks. Typically, the attenuation layer is constructed of soils mixed with a stabilizing agent ([Gathuka et al., 2021](#); [Kato et al., 2021](#)). The stabilizing agent for the attenuation layer method should be carefully selected because the dissolution of minerals might occur slowly, as shown in this study. Stabilizing agents that quickly hydrate and lose their attenuation capacity after a short period should be avoided because leaching is expected to continue for a relatively long time.

4.3. Shaking versus nonshaking conditions

Batch tests were conducted under shaking and nonshaking conditions. Although shaking conditions are commonly used in standard leaching tests in Japan, nonshaking conditions might better represent the in situ conditions. Differences in the shaking and nonshaking conditions were

noticeable for the mudstone sample. For example, the shaking tests resulted in higher leaching concentrations of As than the nonshaking tests during the first hours of the tests. In contrast, the concentrations increased with the increasing test duration in the nonshaking tests.

Such differences in the leaching behavior might be attributable to the mudstone being friable. Crushing during the shaking tests might have promoted the release of Ca. A higher Ca concentration is known to promote the sorption of As onto soil particles (e.g., [Tabelin et al., 2012](#)). Crushing could also have contributed to the release and precipitation of Fe during the shaking tests. Accordingly, the dissolved As can be immobilized via precipitation reactions to form less-soluble compounds (e.g., [Tabelin et al., 2018](#)). Furthermore, the surface area increases as a result of the soil particles being crushed during the shaking tests; the greater surface area might promote the sorption of As. Further study will be required to elucidate the effects of shaking tests on such friable rocks. When the leaching behavior of excavated rocks is investigated, nonshaking tests might be more suitable, especially for friable samples. Nonshaking conditions might be closer to the in situ conditions. Water flowing through the rocks might prevent the substantial crushing of the rocks that would induce greater amounts of released As.

5. Conclusions

Batch leaching tests were performed under shaking and nonshaking conditions at temperatures of 5 to 60 °C to investigate the leaching behavior of As and B from two crushed excavated rock samples with geogenic contamination. In addition, a first-order kinetic model was used to fit the experimental results to investigate the leaching kinetics. The results support the following conclusions:

1. Elevated temperatures often led to the release of greater amounts of As and B. After conducting the nonshaking tests for 15 days at 40 °C, the mudstone sample leached arsenic and boron at concentrations of approximately 0.7 and 1.0 mg/L, respectively. The arsenic and boron concentrations were about 20 and 40% higher than those of the sample leached at a temperature of 20 °C.
2. The first-order kinetic model fitted the experimental data when the leaching concentrations increased or remained stable over time, but it was not applicable when the concentrations decreased. The rate constant k obtained from the fitting line was used as an index to characterize the changes in the leaching kinetics of As and B. Elevated temperatures increased the leaching kinetics of the toxic elements. For the shale rock sample, the k value for As was $7.7 \times 10^{-2}/\text{h}$ at 40 °C, which was about 2.5 times greater than the value at 30 °C.
3. Leaching concentrations of As and B did not reach equilibrium within 6 h. To better assess the risk of geogenic contamination, it is important to run batch tests for a

relatively longer period of time than the 6 h indicated in the Japanese standard leaching test.

- Nonshaking tests are recommended for friable rocks because possible crushing may lead to unrealistic estimations of the leaching amounts.

Acknowledgments

The authors acknowledge and appreciate the support provided by the JSPS KAKENHI (Grant numbers: 20J23160, 18K13828, 21H01426, and 18H03797). This appreciation extends to Aoi Seo (former Kyoto University student) for his assistance with the experiments.

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