Anaerobic batch leaching tests of shale rock grains

Tomohiro Kato \textsuperscript{i)}, Yusuke Masaki \textsuperscript{ii)}, Lincoln W. Gathuka \textsuperscript{iii)}, Atsushi Takai \textsuperscript{iv)} and Takeshi Katsumi \textsuperscript{v)}

\textsuperscript{i)} PhD Student, Graduate School of Global Environmental Studies (GSGES), Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan.
\textsuperscript{ii)} Master Student, GSGES, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan.
\textsuperscript{iii)} Postdoctoral Researcher, GSGES, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan.
\textsuperscript{iv)} Associate Professor, GSGES, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan.
\textsuperscript{v)} Professor, GSGES, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan.

ABSTRACT

Arsenic leaching from shale rock grains was evaluated by the regulatory and modified batch leaching tests. The regulatory test was in accordance with the Japanese Leaching Test No. 46. The modified batch leaching tests were carried out using de-aired distilled water and eliminating headspace to simulate anaerobic conditions. The results show that dissolved oxygen (DO) in normal batch leaching tests is \(~6.0\, \text{mg/L}\). DO can be reduced to \(~2.0\, \text{mg/L}\) by using de-aired water and eliminating the headspace and shaking step. The results suggest that a pseudo anaerobic condition can be achieved by eliminating the headspace and shaking step and conducting the tests in the vacuum deaerator since the DO was very low (\(~1.1\, \text{mg/L}\)). Under the pseudo anaerobic conditions, the arsenic leaching concentrations are lowest (\(~0.001\, \text{mg/L}\)), implying that arsenic leaching might be suppressed under anaerobic conditions. Furthermore, these arsenic concentrations are below the regulatory standard (As < 0.01 mg/L), suggesting that the shale rock grains are environmentally safe for utilisation in geotechnical applications.

Keywords: arsenic, dissolved oxygen, headspace, shale rock, geogenic contamination

1 INTRODUCTION

Proper management and effective utilisation of soils and rocks with geogenic (natural) contamination are essential in Japan. For decades, the utilisation of the soils and rocks of concern has been promoted with proper contamination control since large volumes of soils and rocks are usually excavated (e.g. Haid and Hammer, 2009; Katsumi, 2015; Kataguiri et al., 2019; Magnusson et al., 2019; Walsh et al., 2019). For proper utilisation, the leaching characteristics and behaviour of the soils and rocks should be evaluated.

Evaluating the leaching behaviour of soils or rocks of concern is often carried out using batch leaching tests. In Japan, the Soil Contamination Countermeasures Law (SCCL) prescribes the Japanese Leaching Test Notification No. 46 (JLT46) as the regulatory test for determining the leaching values. Environmental suitability of the soils and rocks and proper contaminant control methods can be decided or established based on their leaching values. In this test, soils with a particle size of \(<2\, \text{mm}\) are contacted with water for 6 hours at a liquid-to-solid ratio (\(L/S\)) of 10. The hazardousness of the soils is determined based on whether the concentrations of the target chemicals exceed the regulatory limit or not. JLT46 can be conducted quickly. However, JLT46 does not fully simulate the field condition; therefore, the applicability of the findings remains an issue. One crucial issue is that the soils would exist under the anaerobic condition when utilised in an embankment, as shown in Fig. 1. Tamoto et al. (2008) observed that the oxygen levels inside the embankment are lower than outside the embankment.

Leaching behaviour can be changed dramatically over time and under different leaching conditions (Tamoto and Kurahashi., 2017; Tabelin et al., 2018). However, leaching behaviour under anaerobic conditions cannot be clarified using JLT46. Therefore, leaching tests that more closely represents the actual site are required. Because of this, several studies have been carried out to evaluate the leaching behaviour under anaerobic conditions.

Fig. 1. Oxygen levels in the embankment (Tamoto et al., 2008).
conducted focusing on anaerobic batch leaching tests using nitrogen gas (e.g. Kamon et al., 2002; Tamoto and Kurahashi, 2017).

This study aims to establish batch leaching tests for evaluating the leaching behaviour of soils under anaerobic conditions. Here, normal batch leaching tests regulated by JLT46 and modified batch leaching tests were conducted on the excavated shale rock after crushing it to <2 mm. Several parameters of JLT46 were changed in the modified batch leaching tests, including using de-aired distilled water, elimination of headspace, no shaking condition, etc. Arsenic (As) was selected as the target contaminant because it is a geogenic contaminant whose concentration exceeds the acceptable limit regulated in Japan (e.g. Ito and Katsumi, 2020; Naka et al., 2016).

2 MATERIALS AND METHODS

2.1 Materials

The shale rock excavated from a tunnel construction site was used after crushing the rock and sieving it to <2 mm. Figure 2 shows the appearance and particle distribution of the shale rock grains. The test for the particle size distribution corresponds to JIS A 1204 (2009). The soil particle density of 2.73 g/cm\(^3\) was determined per JIS A 1202 (2009).

For the chemical analysis, the sample was manually ground to <75 μm using an agate mortar and pestle and then analysed by X-ray fluorescence (XRF) (EDX-720, Shimadzu). Table 1 shows its chemical composition in terms of chemical oxides. It has an As content of 20 mg/kg, which is well within the 1–20 mg/kg values reported for soils formed from igneous and sedimentary rocks (Panagiotaras and Nikolopoulos, 2015).

The acidification potential test determined the acidification potential of the shale rock grains. The test corresponds to JGS 0271 (2016). In this test, the soils and rock samples will be forcibly oxidised using a certain concentration of H\(_2\)O\(_2\) solutions (e.g., 30%), and the pH of the solution was measured. The pH values for H\(_2\)O\(_2\) solutions can be used as an index to assess the possible pH change of geomaterials when they are oxidised under weathering conditions.

Here, 2 g shale rock grains and 20 mL of 3% or 30% H\(_2\)O\(_2\) solution were mixed in a tall beaker because effervescence might occur. The reaction continued for 30 minutes, and then the pH of the solution was measured.

Table 2 summarises the acidification potential test results. Since the pH values were higher than pH 3.5, it was concluded that the shale rock grains are not easily oxidised.

2.2 Batch leaching test

Normal batch leaching tests regulated by JLT46 and modified batch leaching tests were conducted in triplicate to evaluate the As leaching behaviour of the shale rock grains under anaerobic conditions. The conditions of the tests are shown in Table 3.

In normal batch leaching tests regulated by JLT46, distilled water was poured into a 1-L polypropylene bottle (see ‘Type-1 test’ in Table 3). Shale rock grains were gently poured into the water, and mixing was done by horizontal shaking at 200 rpm for 6 hours.

Table 2. Results of the acidification test.

| Case | Solution | pH   |
|------|----------|------|
| 1    | H\(_2\)O  | 9.29 |
| 2    | 3% H\(_2\)O\(_2\) | 8.18 |
| 3    | 30% H\(_2\)O\(_2\) | 11.0 |

Table 3. Test conditions of the batch leaching test.

| Type | Solution | Method | Headspace | Remarks       |
|------|----------|--------|-----------|---------------|
| 1    | Distilled water | Shaking | 500 mL | JLT46         |
| 2    | De-aired water | Non-shaking | 0 mL | In the deaerator |
| 3    |                   |        |           |                |

Fig. 2. Photo and particle size distribution curve of the shale rock grains.
Shaking tests using de-aired water were conducted. This test differs from the normal batch leaching test because the distilled water was used after de-airing it (see ‘Type-2 test’ in Table 3). De-aired water was prepared in a vacuum deaerator for more than 24 hours.

The shaking test with de-aired water was modified to eliminate headspace (see ‘Type-3 test’ in Table 3). The influence of the headspace was investigated because the headspace may influence the dissolved oxygen (DO) concentration. Hereafter, this test is referred to as shaking tests without headspace (or Type-3 test). The amount of de-aired water and shale rock grains were appropriately adjusted to eliminate the headspace.

The non-shaking tests without headspace were also conducted (see ‘Type-4 test’ in Table 3). The influence of the shaking was evaluated because the shaking may influence the leaching behaviour (Takai et al., 2020). The non-shaking test provides essential findings for leaching in practical situations because it should contact rainwater without disturbance and agitation on site.

Non-shaking tests without headspace were also conducted in a vacuum desiccator (see ‘Type-5 test’ in Table 3). In these tests, deaeration was carried out because there is a possibility that oxygen in the air may flow through slight gaps in the lid during the leaching tests.

Using a DO meter (Hanna, HI2004-01), the initial DO of 6.3 and 0.9 mg/L were measured for distilled water and de-aired water, respectively. Using an oxidation-reduction potential meter (HORIBA, F-73), the initial $E_h$ value of 483.5 and 435.7 mV were measured for distilled water and de-aired water, respectively.

After the completion of the shaking step, the solution’s DO was measured immediately. $E_h$ and As concentrations were not measured immediately after the test. Instead, they were measured after solid-liquid separation because they may not be stable if the turbidity of the solution is high (Someya et al., 2021). Also, if colloidal particles remain in the solution, in that case, As may be resorbed, and its concentration may not be accurately measured (Shimada, 2009).

The solid-liquid separation was completed using centrifugation at 3000 rpm for 10 minutes under 3000 rpm and filtration using a 0.45 µm membrane filter. The filtrate was measured for $E_h$, electric conductivity (EC) and pH using $E_h$, EC and pH/EC meter (HORIBA, F-54). Concentrations of As were measured using an Atomic Absorption Spectrophotometer (AAS) (AA-6800, Shimadzu). Concentrations of cations (Fe, Ca, Mg, Al, Na, etc.) were measured using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (ICP-OES 710, Agilent Technologies).

3 RESULTS

3.1 Influence of leaching test conditions on the DO

Figure 3(a) shows the concentrations of DO in solutions after the tests. Although the initial DO in the normal batch leaching test (Type-1 test) and shaking tests using de-aired water (Type-2 test) were different, final DO values were similar for the two tests (i.e., ~6 mg/L). It was concluded that anaerobic conditions might be challenging to achieve just by de-airing the distilled water. Further comparative analysis of DO between Type-2 test and shaking test without headspace (Type-3 test) showed that the final DO was lower in Type-3 tests even though the initial DO was the same. The results show that DO can be reduced by eliminating headspace, but the system remains partially anaerobic. In addition, the DO can be further reduced because of the elimination of the shaking steps (Type-4 test). By eliminating the headspace and shaking step and conducting the tests in the vacuum deaerator, the anaerobic condition was achieved since the DO of the Type-5 test was very low. Comparing Type-4 and Type-5 tests, oxygen from outside the system might leak through the cap and bottle interface.

3.2 Chemistry of solution of the leaching test

Figures 3(b)–(e) show the arsenic concentrations and selected cations after the different batch leaching tests. Figure 3(b) shows that the As concentrations were ~1 µg/L in Type-4 and Type-5 tests, the lowest leaching value among the five tests. The environmental safety of the shale rock grains were confirmed because arsenic leaching concentrations were lower than the acceptable concentrations (i.e., As < 10 µg/L). Considering the DO determined from Type-4 and Type-5 tests, it was concluded that anaerobic conditions might suppress As leaching from shale rock grains.

Figure 3(c) shows EC values which indicate cations were leached from the shale rock grains. Figure 3(d) shows that very low Fe concentrations (10 µg/L) were leached regardless of the type of tests. There was no apparent relation between DO and Fe concentrations.

Figure 3(e) shows that Ca$^{2+}$ was leached in high concentrations (~9 mg/L). The concentrations did not significantly change with the type of tests. Contrast to Ca$^{2+}$, the Mg$^{2+}$ concentrations were relatively low (0.4–0.6 mg/L), as shown in Fig. 3(f). The high concentrations of Ca$^{2+}$ were considered the reason for the high pH of 9–10 [Fig. 3(g)] and low As leaching values due to the sorption effect. Arsenic leached is expected to have low solubility and mobility, considering the pH and $E_h$ values (Bothe and Brown, 1999).

3.3 Comparison of $E_h$ and DO

Arsenic leaching characteristic and behaviour is affected by several factors including $E_h$ (e.g. Shimada, 2009; Tabelin et al., 2013). Since $E_h$ is affected by various chemical indices such as the DO, $E_h$-DO relation should be investigated.
Fig. 3. Chemistry of solutions after the batch leaching tests.
Figures 3(a) and (h) show the DO and $E_h$ after the batch leaching tests. While different DO concentrations were obtained from the different leaching tests, the $E_h$ values were between 300 mV and 340 mV. The results suggest that although the anaerobic conditions are achieved, the $E_h$ is not usually in the reducing state.

Anaerobic conditions are assumed in the embankment. Therefore, evaluating the leaching behaviour of soils and rocks should be carefully discussed, considering the on-site situation. In this study, the low oxidising potential of the shale rock grains might also affect the oxidation-reduction states.

4 DISCUSSION

Anaerobic condition is expected in the practical situation. However, the anaerobic condition is relatively difficult to achieve during the batch leaching tests, as shown in this study. For maintaining the solution in anaerobic conditions, three factors should be carefully considered. Firstly, the air in the headspace must be eliminated. Secondly, carrying out the leaching tests without the shaking step is more desirable because low DO can be obtained. Thirdly, the batch test should be conducted in the deaerator to make as little oxygen as possible dissolve in the solution. Comparative analysis of the leaching behaviour under aerobic and anaerobic conditions should be carried out to evaluate the potential of increasing the contaminant leaching under anaerobic conditions.

Since relatively low leaching concentrations are obtained under anaerobic conditions (as shown in this study), several ways can be considered to mitigate geogenic contamination. First of all, the embankment should be well compacted to reduce the voids to achieve the anaerobic condition during the foundation. Second of all, a cover soil should be installed on the layer of the excavated materials. The oxygen penetration can be prevented to install the cover soil (Pawit et al., 2017).

5 CONCLUSIONS

Normal batch leaching tests regulated by JLT46 and modified batch leaching tests were conducted on the excavated shale rock after crushing it to <2 mm to evaluate the leaching behaviour of the shale rock grains under anaerobic conditions. From this study, the results support the following conclusions:

1. DO in normal batch leaching tests is ~6.0 mg/L. DO can be reduced to ~2.0 mg/L because of using de-aired water and eliminating the headspace and shaking step. The results suggest that pseudo anaerobic conditions can be achieved by eliminating the headspace and shaking step and conducting the tests in the vacuum deaerator since the DO was very low (~1.1 mg/L).

2. Leaching concentrations of As were smaller as the concentrations of DO decreased. Under the pseudo anaerobic conditions, the As leaching concentrations were lowest (~1.0 µg/L), implying that As leaching might be suppressed under anaerobic conditions. Furthermore, these arsenic concentrations are below the regulatory standard (As < 0.01 mg/L), suggesting that the shale rock grains are environmentally safe for utilisation in geotechnical applications.

3. DO decrease from approximately 6 to 1 mg/L, while similar $E_h$ values were obtained between 300 and 340 mV, implying the system is under an oxidised state. Further investigation is required to examine the environment in the embankment is in the reducing or oxidising state.

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