Contribution of immobilization material for arsenic immobilization in excavated rock with different particle size

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ABSTRACT

Excavated rock and sediment in which arsenic release naturally occurs is necessary to be treated with an appropriate technique such as chemical immobilization. The physical condition such as particle size ratio of rock to the immobilization material possibly enhancessuppresses the effects of arsenic immobilization because arsenic should be contacted and reacted with the immobilization material in the rock pores for the immobilization. This study prepared the up-flow column percolation test using the excavated rocks with the different particle sizes and immobilization material with constant particle size to determine a suitable ratio of the diameter of the average particle size in the rock samples to that in the immobilization material. The column percolation test showed that the contribution of arsenic immobilization by the immobilization material was higher in the larger particle size of excavated rock while the arsenic retention capacity of excavated rock was high in the smaller particle size. The arsenic concentrations in the leaching water were the lowest and the percentage of arsenic retained during the column percolation test was the highest in the particle size of 1.0–2.0 mm of excavated rock. Based on these results, this study suggests that the suitable particle size ratio of excavated rock to the immobilization material was 2 to 10.

Keywords: arsenic, column percolation test, excavated rock, immobilization, particle size

1 INTRODUCTION

A huge amount of massive rocks is excavated for the effective need of underground space and construction of modern and high-speed railways and roads. The excavated rock often contains arsenic at the same level as or just a slightly higher level than the background. Arsenic phases in the excavated rock and/or sediment are often altered to be more soluble with the excavation process such as increase of specific surface area, exposure of water and air, and drying. The excavated rock/sediment becomes an environmental concern if the level of arsenic release exceeds the environmental standard (0.01 mg/L). Due to limited disposal sites, such naturally contaminated excavated rock is expected to be treated appropriately and reused without posing an environmental risk.

The chemical immobilization technique can alter toxic metal(loid)s to a more insoluble phase by applying immobilization material, and can suppress their mobility and bioavailability (Suzuki et al., 2015). The effects of immobilization are influenced by various factors such as types of immobilization material and toxic metal(loid), toxic metal(loid) content and phases, pH, oxic-redox condition (Tsunematsu et al., 2012). In addition, the toxic metal(loid) immobilized has the potential to be re-released depending on the physicochemical environment in which the excavated rock is reused (Ogawa et al., 2020). Toxic metal(loid)s are immobilized by the immobilization material during their migration after the release from the excavated rock; i.e., toxic metal(loid)s should be contacted and reacted with the immobilization material in the rock pores before the immobilization (Ogawa et al., 2018). This strongly implies that the physical condition such as particle size ratio of rock and the immobilization material enhancessuppresses the effects of arsenic immobilization. However, the effects of physical condition on the arsenic immobilization in the excavated rock have not been focused on although the chemical condition has been investigated (Kamata and Katoh, 2019). This study focused on the ratio of the diameter of the average particle size in the rock samples to that in the immobilization material (hereafter referred as to “particle size ratio”). The difference between the excavated rock size and soil on the immobilization is the particle size ratio. The particle size of excavated rock is large compared with the soil, and thus, the particle size ratio of the excavated rock to the immobilization material is larger than that of soil. In the case of excavated rock, arsenic may not be contacted and reacted with the immobilization material during the migration, and not be immobilized.

This study prepared the up-flow column percolation test using the excavated rocks with the different particle sizes and the immobilization material with constant par-
Table 1. Chemical properties of rock samples (under 0.5 mm)

| Property                  | Value   |
|---------------------------|---------|
| pH                        | 8.9     |
| EC (mS/m)                 | 6.3     |
| Water-soluble As (mg/kg)  | 17.7    |
| Amorphous Fe (Am-Fe) (mg/g)| 56.1    |
| As retained on rock samples (mg/kg) | 34.6 |
| Total amounts of As (mg/kg) | 16.8 |

Table 2. The grain size distribution of FeSO₄ · 7H₂O.

| Grain size (μm) | (%) |
|-----------------|-----|
| ~425           | 7.9 |
| 425~250        | 41.6|
| 250~106        | 41.3|
| 106~75         | 7.0 |
| 75~            | 2.2 |

ticle size. The arsenic solution was inflowed. The amounts of arsenic retained in the column with and without the immobilization material were evaluated to determine the suitable particle size ratio of excavated rock to the immobilization material.

2 MATERIALS AND METHODS

2.1 Preparation of excavated rock and immobilization material

Excavated shale of 50–70 cm in diameter was collected from tunnel construction sites in Japan and used as the excavated rock. Rock samples were crushed to obtain particle sizes of < 0.5, 1.0–2.0, and 2.0–5.0 mm using a chisel, hammer, and an agate mortar. Table 1 shows the chemical properties of rock samples with a particle size of < 0.5 mm. In order to determine the level of arsenic retention on the rock samples, arsenic sorption was conducted. The rock samples were mixed with 1.0 mg/L of arsenic solution at a liquid/solids ratio of 10. Water extraction was carried out with a liquid/solids ratio of 10 and determined pH, EC, and water-soluble arsenic. The amorphous iron was extracted by H₂C₂O₄ buffer. The amorphous iron content was relatively high, resulting in a high arsenic sorption capacity. Iron sulfate heptahydrate (FeSO₄ · 7H₂O) as a reagent was used as the immobilization material in this study. The immobilization material was passed through a 0.5-mm sieve prior to use. Table 2 shows the grain size distribution of the immobilization material.

2.2 Up-flow-saturated column percolation test

0.1 g of absorbent cotton and 3.57 g of silica sand was added to the glass column with an inner diameter of 2 cm and height of 12 cm for obtaining a smoother bottom of the column. 46.00 g of excavated rock with and without the immobilization material at 5 wt% was packed with 10 cm height on the silica sand. The bulk density was 1.46 g/cm³ (without the immobilization material) and 1.53 g/cm³ (with the immobilization material); the void volume (Vᵥ) of sample packed was calculated to be 14 cm³ (without the immobilization material) and 13.2 cm³ (with the immobilization material). Three columns were prepared for each particle size of excavated rock. An arsenic solution as Na₃H₂AsO₄ · 7H₂O at 1.0 mg/L was prepared without the pH adjustment. The arsenic concentration in the solution was 10 times higher than that observed in the excavated rock by the column percolation test (Suzuki et al., 2013). The arsenic solution was flowed from the bottom of a column using a constant flow rate pump at 0.30 mL/min, which was corresponded to 57.3 mm/hr precipitation. The column leaching test continued for 10 days (total 4320 mL), and the leaching water was collected 5 times every 48 hrs.

2.3 Analysis of leaching water

After measurement of leaching water volume, the leaching water sample was passed through a 0.45 μm filter. The pH and EC values were measured, and the arsenic and iron concentrations were determined using inductively coupled plasma optical emission spectrometry (ICP-OES: Optima 8300, PerkinElmer Co., Ltd., USA). In addition, the arsenic concentration in the arsenic solution was also determined.

2.4 Analysis of excavated rock after column percolation test

After the column percolation test, the excavated rock was collected to evaluate the amount of water-soluble arsenic in the excavated rock. The top 2 mm of the excavated rock sample were removed, and the remaining sample was collected evenly in five layers, air-dried, and the rock samples of < 0.5 mm passed through a 0.5-mm sieve (1.0–2.0 mm and 2.0–5.0 mm were used without sieving). Water-soluble arsenic was extracted from the samples using ultra-pure water at a liquid/solid ratio of 10 and analyzed using ICP-OES. The amount of water-soluble arsenic in the excavated rock was calculated based on L/S ratios.

3 RESULTS AND DISCUSSION

3.1 Arsenic concentrations in the leaching water

The arsenic concentrations in the leaching water from the excavated rock with the particle size of < 0.5 mm and 1.0–2.0 mm without the immobilization material were 0.418 and 0.512 mg/L at the first sampling, respectively (Fig. 1a). This suggests that 50% of arsenic inflowed was not retained on the excavated rock during the percolation. In contrast, in the excavated rock with the particle size of 2.0–5.0 mm without the immobilization material, most of the arsenic inflowed was not retained until the first sampling. In the excavated rock with the particle size of 1.0–2.0 mm with the immobilization material, the arsenic concentrations in the leaching water were the lowest at < 0.03 mg/L during the column percolation te-
Fig. 1. As concentration in the leaching water (a) without the immobilization material, (b) with the immobilization material.

Table 3. The percentage of arsenic retained to inflowed during the column percolation test.

| Particle size (mm) | Without the immobilization material | With the immobilization material |
|-------------------|-------------------------------------|---------------------------------|
|                   | 0.5       | 1.0-2.0 | 2.0-5.0 | 0.5       | 1.0-2.0 | 2.0-5.0 |
| Total As inflowed (mg/column) (a) | 4.29 ± 0.17 | 4.26 ± 0.05 | 4.29 ± 0.09 | 4.30 ± 0.05 | 4.17 ± 0.02 | 4.29 ± 0.02 |
| Total As leached (mg/column) (b) | 0.456 ± 0.15 | 0.688 ± 0.05 | 2.94 ± 0.07 | 0.262 ± 0.05 | 0.072 ± 0.06 | 0.725 ± 0.02 |
| Total As retained (mg/column) (c) = (a-b) | 3.84 ± 0.11 | 3.57 ± 0.02 | 1.35 ± 0.09 | 4.04 ± 0.05 | 4.10 ± 0.06 | 3.56 ± 0.02 |
| % of As retained (%) (c)/(a) × 100 | 89.4 | 83.8 | 31.4 | 93.9 | 98.3 | 83.1 |

Table 4. The amounts of As retained on the immobilization material.

| Particle size (mm) | 0.5       | 1.0-2.0 | 2.0-5.0 |
|-------------------|-----------|---------|---------|
| As retained with the immobilization material (mg/column) "1 (a) | 4.04 ± 0.05 | 4.10 ± 0.06 | 3.56 ± 0.02 |
| As retained on the excavated rock (mg/column) "2 (b) | 3.84 ± 0.11 | 3.57 ± 0.02 | 1.35 ± 0.09 |
| As retained on the immobilization material (mg/column) (a) - (b) | 0.20 | 0.53 | 2.21 |

*1 the amounts of As retained on the excavated rock were taken as the value from total As retained with the immobilization material in Table 3.
*2 the amounts of As retained on the excavated rock were taken as the value from total As retained without the immobilization material in Table 3.

Table 5. The percentage of iron leached to added as the immobilization material.

| Particle size (mm) | The first sampling (%) | End of test (%) |
|-------------------|------------------------|-----------------|
| 0.5               | 89.5                   | 91.4            |
| 1.0-2.0           | 92.8                   | 94.5            |
| 2.0-5.0           | 95.4                   | 97.2            |

Fig. 2. Fe concentration in the leaching water with the immobilization material.
The amounts of water-soluble (WS) As in the excavated rock (a) without the immobilization material, (b) with the immobilization material.

Table 5. The amounts of WS-As in the excavated rock after column percolation test.

| Particle size (mm) | Without the immobilization material | With the immobilization material |
|-------------------|-------------------------------------|----------------------------------|
|                   | 0.5  | 1.0-2.0 | 2.0-5.0 | 0.5  | 1.0-2.0 | 2.0-5.0 |
| WS-As (mg/column) (a) | 0.012 | 0.0021 | 0.0011 | 0.0054 | 0.0020 | 0.0022 |
| % of WS-As (%)* | 0.312 | 0.059 | 0.081 | 0.134 | 0.048 | 0.062 |

* (a) / total As retained in Table 2 x 1

In the excavated rock without the immobilization material, the arsenic concentrations in the leaching water increased from the sampling number 3 or 5 depending on the particle sizes of excavated rock. This would be explained by the re-release of arsenic retained on the excavated rock or the immobilization material. In particular, the increase of the arsenic concentration in the excavated rock with the particle size of 2.0–5.0 mm with the immobilization material would result from the low capacity of arsenic immobilization in the immobilization material compared with the other particle size of excavated rock.

Table 3 shows the percentage of arsenic retained to inflowed during the column percolation test. In the rock samples without the immobilization material, the percentages of arsenic retained were higher in the smaller particle size of excavated rock. The higher specific surface area of the excavated rock with the small particle size would result in a high level of arsenic retention on the excavated rock. More than 80% of arsenic inflowed was retained on the excavated rock with particle sizes of < 0.5 mm and 1.0–2.0 mm. In the rock samples with the immobilization material, more than 80% of arsenic inflowed was retained on the excavated rock or the immobilization material despite the particle size of excavated rock. In particular, the highest percentage of arsenic retained was observed in the particle size of 1.0–2.0 mm of excavated rock at 98.3%. The amounts of arsenic retained on the immobilization material were high in the following order: the particle size of 2.0–5.0 mm > 1.0–2.0 mm > < 0.5 mm (Table 4). The amount of arsenic retained on the immobilization material was 4.2 and 11 times higher in the excavated rock with the particle size of 2.0–5.0 mm than 1.0–2.0 mm and < 0.5 mm, respectively. The amounts of arsenic retained on the immobilization material were 1/20, 3/20 times lower, and 1.6 times higher than those retained on the excavated rock with the particle size of < 0.5 mm, 1.0–2.0 mm, and 2.0–5.0 mm, respectively. These results indicate that the contribution of arsenic immobilization by the immobilization material was higher in the larger particle size of excavated rock. This may be because arsenic was easily percolated through the large pore space in which a large amount of immobilization material existed, and arsenic could be easily contacted and reacted with the immobilization material.

3.2 Iron concentrations in the leaching water

In the rock samples without the immobilization material, iron was not detected from the leaching water during the column percolation test (data not shown). In the rock samples with the immobilization material, the iron concentrations in the leaching water were 500 mg/L at the first sampling despite the particle size (Fig. 2). Those greatly decreased at the second sampling, and then ranged from 0.1–0.01 mg/L. Table 5 shows the percentage of iron leached to added as the
immobilization material. The percentages of iron leached were not different between the particle size of the excavated rock, ranging from 89.5%–95.4% and 91.4%–97.2% at the first sampling and end of the test, respectively. This result suggests that 90% of immobilization material was leached by the first sampling. However, the arsenic was not leached even after the leaching of the immobilization material (Fig. 1b). This suggests that the amount of immobilization material required for arsenic immobilization is not large. In this study, the column percolation test was conducted under water-saturated conditions, which can easily contact and react with arsenic and the immobilization material compared with the water unsaturated condition. Thus, in the case of immobilization material application on-site, the required amount of immobilization material may be large compared with this study.

3.3 Water-soluble arsenic in the excavated rock after column percolation test

In the rock samples without the immobilization material, the amounts of water-soluble arsenic were constant despite the distance from the inflow in the excavated rock with the particle size of 1.0–2.0 mm and 2.0–5.0 mm while those decreased at the longer distance from the inflow in the excavated rock with the particle size of < 0.5 mm (Fig. 3a). The amounts of arsenic retained on the excavated rocks were not greatly different between the excavated rock with the particle size of < 0.5 mm and 1.0–2.0 mm (Table 3). These results suggest that the arsenic was strongly retained on the excavated rock with a particle size of 1.0–2.0 mm compared with the particle size of < 0.5 mm. The amounts of water-soluble arsenic in the excavated rock with the immobilization material were lower than those without the immobilization material with some exceptions. The application of immobilization material could alter arsenic phases to be more insoluble.

Table 5 shows the percentage of the amount of water-soluble arsenic to that retained during the column percolation test (Table 3). The percentages of water-soluble arsenic were greatly low despite the treatments. This indicates that more than 99% of arsenic retained was existed as non-water-soluble. The percentage of water-soluble arsenic was the lowest in the particle size of 1.0–2.0 mm of excavated rock with the immobilization material at 0.048%. Moreover, the percentage of arsenic retained during the column percolation test was the highest in the particle size of 1.0–2.0 mm of excavated rock with the immobilization material at 98.3% (Table 2). These results suggest that the application of immobilization material with the particle size of 0.5 mm to the excavated rock with the particle size of 1.0–2.0 mm could effectively immobilize arsenic, and arsenic immobilized could not be easily re-released.

4 CONCLUSION

The column percolation test showed that the contribution of arsenic immobilization by the immobilization material was higher in the larger particle size of excavated rock while the arsenic retention capacity of excavated rock was high in the smaller particle size. The percentages of the immobilization material leached were not different between the particle sizes of excavated rock. The percentage of water-soluble arsenic in the excavated rock after the test to the arsenic retained during the column percolation test was the lowest in the particle size of 1.0–2.0 mm. The arsenic concentrations in the leaching water were the lowest and the percentage of arsenic retained during the column percolation test was the highest in the particle size of 1.0–2.0 mm of excavated rock. Based on these results, this study suggests that the suitable particle size ratio of excavated rock to the immobilization material was 2 to 10. However, the rock samples used in this study had Am-Fe rich (Table 1), which would result in high arsenic retention on the rock sample regardless of the particle size of the rock samples. In the case of the rock with lower Am-Fe, the particle size of the rock samples would affect the arsenic immobilization. Thus, the suitable particle size ratio of the excavated rock to the immobilization material should be investigated using some rock samples with different chemical properties such as Am-Fe content.

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