Evaluation of Long-Term Leaching of Arsenic from Arsenic Contaminated and Stabilized Soil Using the Percolation Column Test

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Abstract: Arsenic in the soil can leach into groundwater and contaminate drinking water, posing a serious risk to human health. The stabilization of arsenic in contaminated soil is one of the immobilization technologies used to remediate contaminated lands. However, few studies have evaluated the long-term release of As and pH changes in stabilized soils. We compared different stabilization techniques in the field by mixing contaminated soil with 5% of either acid mine drainage sludge (AMDS), coal mine drainage sludge (CMDS), steel slag, or cement. We evaluated the results using an up-flow percolation column test to observe any pH changes and As releases from the stabilized soils up to a liquid–solid (L/S) ratio of 50 (approximately representing a 50 year period). At the initial stage of percolation (at an L/S ratio of 0.2 or 0.2 of a year of exposure), some alkaline components and any incompletely bound As in the soils washed out with the eluent. The pH of the cement-stabilized soil was approximately 12 throughout the experiment (up to 50 L/S). Adding stabilizers to the soil reduced As leaching by 54–81% (overall efficiency) compared to the control (contaminated soil only). The order of stabilization efficiency was: steel slag (55.0%) < AMDS (74.3%) < cement (78.1%) < CMDS (81.5%). This study suggests that the groundwater of the stabilized soil should be carefully monitored for the initial five years because the soluble ionic species can leach over this period.

Keywords: As-contaminated soil; stabilization; percolation test; L/S ratio; TCLP; leaching

1. Introduction

Soils can become contaminated with heavy metal(loid) emissions from anthropogenic and natural sources [1–3]. Although there are several heavy metal(loid)s, arsenic (As) is a carcinogenic metalloid, and is known to be one of the world’s most hazardous chemicals, causing several health-related complications in humans [4–6]. Arsenic in the soil can leach into groundwater and contaminate drinking water, posing a serious risk to human health. Various methods have been employed to remediate heavy metals in soil, such as soil washing, in situ flushing, adsorption, phytoremediation, immobilization techniques (e.g., solidification/stabilization or encapsulation), and electrokinetic extraction [7–11]. In recent years, solidification/stabilization (S/S) of arsenic in contaminated soil has emerged as a promising immobilization technology to remediate contaminated lands [8,11–14]. In this technique, the constituent contaminants are bound to the contaminated soil using simple stabilizing agents (or stabilizers), hindering the release of heavy metal(loid)s from the soil [8,13,15,16]. This method has various advantages; for example, it is cost-effective, the raw materials are easily available, and it does not produce harmful byproducts during application [15]. The stabilized land can be used for several purposes, such as plantings, gardens, or industry buildings. The stabilized soils can be used as secondary construction material for roads, buildings, and parking lots.
Studies have shown that stabilization helps to reduce heavy metal(loid) leaching [8,15,16]. Evaluating heavy metal(loid) leaching from stabilized contaminated soil after long-term exposure is important for assessing effective remediation (stabilization) and environmental impacts, because the stabilization bonding has the potential to weaken with long-term weathering. Furthermore, aggregates of stabilized soil may disintegrate into smaller particles with external stresses, such as parking lots or roads. The fractures may be exposed to rainwater infiltration, allowing metal leaching in the water-soluble constituents. Thus, the long-term release of As and any severe release from the stabilized soils requires assessment if we are to protect human health in stabilization-remediated sites.

The constituent chemicals leached from contaminated soil and/or other solid materials can be evaluated using different leaching tests [17]. Tests include the batch leaching test, toxicity characteristics leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP), and single and sequential chemical extractions [8,18–20]. These leaching tests have been widely used due to their simple design, low cost, and short duration. However, these methods cannot represent the release of constituents over different time intervals, and the information is limited to a single liquid-to-solid (L/S) ratio time period [18,19]. Furthermore, all leaching tests use acidic solutions, making it impossible to evaluate any pH changes with leaching.

Recently, studies have tested the release of chemicals using various percolation column tests, such as Nordest (1995), CEN (2004), NEN (2004), OECD (2004), ISO (2007), DIN (2009), and USEPA (2013) [17–19]. These experiments replicate long-term leaching conditions. To the best of our knowledge, only one study has evaluated the release of constituents from stabilized soil using column tests [21]. However, this study used acid rain as a percolating fluid, it did not assess any long-term releases beyond 15 days, and samples were not examined for any cumulative releases as a function of the cumulative L/S ratio. In the current study, we conducted up-flow percolation column tests, representing the actual field leaching conditions, to evaluate chemical leaching and pH changes in the stabilized soil materials for long-term exposure to precipitation. This study performed up-flow column percolation tests with As-contaminated stabilized soils following the United States Environmental Protection Agency (USEPA) Method 1314. This method comprises a column filled with granular materials with moderate compaction to evaluate the release of constituents from the material as a function of the cumulative L/S ratio [22,23].

The main objective of this study was to assess pH changes and long-term release (over approximately 50 years) of As from stabilized As-contaminated soils and to evaluate the effectiveness of different stabilizers in reducing the release of As from the soil. An up-flow column percolation test was used to compare the release of As in stabilized soils with long-term exposure. This study also evaluated the leaching of As from As-contaminated or stabilized soil in the worst-case scenario conditions using the TCLP test, and compared the results with the percolation test.

2. Materials and Methods

2.1. Soil Used in This Study

Arsenic-contaminated soil was collected from a mine site located in Hongcheon-ri, Cheonan-si, Chungcheongnam-do Province, Korea. Soil samples (500 g) of the topsoil layer (15–30 cm from the soil surface) and the subsoil layer (80–100 cm from the soil surface) were collected at 3 m intervals from each side of the site. Soils collected from different sampling points were mixed in the laboratory and naturally dried at room temperature. The soil was compacted and passed through a #10 sieve (2 mm opening), before use as experimental soil. The physicochemical properties of the contaminated soils are presented in Table 1. The arsenic concentration of the soil was $82.5 \pm 7.1$ mg/kg. Supplementary Text S1 briefly describes the methods used to analyze the soil properties. The concentrations of the major heavy metal(loid)s in the soil samples are presented in Table S1; only arsenic exceeded the Korean soil standard limit (zone 1: residential areas) by more than three-fold. We selected
arsenic (As) to further investigate due to its mobility/leachability in a percolation column. No other heavy metals were investigated in this study.

**Table 1. Major physicochemical properties of the As-contaminated soil.**

| Parameter                                | Unit   | Value   |
|-------------------------------------------|--------|---------|
| Soil texture: Loamy sand                  |        |         |
| Sand (0.020–2.000 mm)                     | %      | 80.0    |
| Silt (0.002–0.020 mm)                     | %      | 14.0    |
| Clay (<0.002 mm)                         | %      | 6.0     |
| pH (H$_2$O, 1:5)                          |        | 7.6     |
| Soil-moisture content                     | %      | 8.5     |
| Electric conductivity (EC)                | mS/cm  | 0.034   |
| Oxidation-reduction potential (ORP)       | mV     | 80.5    |
| Redox potential (Eh)                      | mV     | 280.5   |
| Organic matter (OM), loss on ignition (LOI) | % | 4.07 ± 0.07 |
| Arsenic                                   | mg/kg  | 82.5 ± 7.1 |

**2.2. Reagent and Materials**

All reagents used were of analytical grade. Calcium chloride (Daejung, Korea), glacial acetic acid (Daejung, Korea), NaOH (Samchun, Korea), HCl (35–37%, Samchun, Korea), HNO$_3$ (68–70%, Samchun, Korea), ascorbic acid (Samchun, Korea), and KI (Samchun, Korea) were used in this study. Deionized water (Human Corporation, Korea) was used to prepare each reagent. White Portland cement (WPC) was obtained from Union Corporation (Korea). Acid mine drainage sludge (AMDS) was obtained from the Mine Reclamation Corporation (Korea) and the coal mine drain sludge (CMDS) was provided by Sanha E & C, Korea. The steel slag was collected from a coastal site in Korea that had been landfilled (since the 1980s) as industrial waste [8]. The mineralogical composition of the stabilizers was analyzed using X-ray fluorescence spectrometry (XRF-1800, SHIMADZU, Japan).

**2.3. Stabilization of As-Contaminated Soil**

The source materials and stabilizers used in this study are presented in Section 2.2. A total of four different types of stabilized soils were prepared by mixing different stabilizers with the contaminated soil at 5% (w/w) of dry soil, as previously reported [8]. The 5% binder dosage is considered to meet the waste acceptance criteria [24]. The stabilizers used in this study were acid mine drainage sludge (AMDS), coal mine drainage sludge (CMDS), steel slag, and cement. The stabilizer samples were pounded and sieved using a #10 sieve (2 mm opening) prior to being homogeneously mixed by hand with the soil samples. A control sample of the soil was also prepared without the addition of any stabilizers. After mixing, the control and four different stabilized soils were transferred into five different acrylic columns.

**2.4. Up-Flow Percolation Column Test**

In this study, up-flow column percolation tests were performed following the procedure described in USEPA 1314 [23], with slight modifications. Briefly, each column was packed with the sample material (i.e., contaminated soil or one of five different stabilized soils). Each sample material included five subsamples with the column divided into five continuous layers of material. The packing of the column started from the top (outflow) and ended at the bottom (inflow), and the column was inverted prior to the experiment. Clean sand (20–30 mesh; Hi-Tech, Seongnam-Si, Korea) was compressed in both ends of the columns to provide an even flow pattern. In addition, filter papers (Whatman filter paper Grade 2) and plastic plates (thickness, 3 mm) containing several small holes were also placed at both ends (plates on the bottom and top positions) to prevent losing any packing materials from the column. We recorded the mass of the empty column and the end caps, tubing materials, packed materials (soils, clean sand, filter paper, and plastic
plates), and the total mass of completely packed columns. The experimental conditions, including the column dimensions and sample sizes are listed in Table 2.

Table 2. Column dimensions and sample size within the different columns. Sample packing involved light tamping of five layers from the top to the bottom of the column. The experimental setup followed the EPA Method 1314 with slight modifications (see the methods section for details).

| Parameters                            | Control          | AMDS   | Steel Slag | CMDS   | Cement |
|---------------------------------------|------------------|--------|------------|--------|--------|
| Column height (cm)                    | 30               | 30     | 30         | 30     | 30     |
| Column diameter (cm)                  | 5                | 5      | 5          | 5      | 5      |
| Sample dry mass in the columns (g)    | 616.8            | 539.6  | 549.4      | 533.7  | 519.4  |
| Height of the soil in the columns (cm)| 21               | 21     | 21         | 22     | 23     |
| Bulk density (g/cm$^3$)               | 1.46             | 1.33   | 1.33       | 1.32   | 1.20   |
| Flow rate (mL/min)                    | 0.5              | 0.5    | 0.5        | 0.5    | 0.5    |
| Initial equilibrium time (h)          | 24               | 24     | 24         | 24     | 24     |
| Eluent                                | 0.001 M CaCl$_2$ solution in deionized water |
| Sampling cumulative L/S               | 0.2, 0.5, 1, 1.5, 2, 4.5, 5, 9.5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 |

The inert tubes comprising polytetrafluoroethylene (PTFE) with 2 mm ID were connected to both end caps of the column. The tubes were connected with shut-off valves and tubes from the bottom end were connected to a peristaltic pump (Shenchen LabV1, China). The inlet tubes from the peristaltic pump were dipped into a 2 L glass beaker containing an eluent solution (1 mM CaCl$_2$). The top outlet tubes were connected to an eluate collection bottle. The eluent solution for the column percolation test was prepared following the USEPA Method 1314 [23]. Briefly, calcium chloride (1.0 mM CaCl$_2$) solution was prepared by dissolving 0.11 g of solid calcium chloride in 1 L of deionized water. The pH of the eluent was 5.8. The solution was freshly prepared before initiating the percolation tests. A peristaltic pump with five channels was used to supply the eluent throughout the columns. Nitrogen gas (an inert gas) was bubbled through the eluent (which was contained in a beaker) prior to release into the columns. A schematic diagram of the column percolation test is provided in Figure 1A (see Figure S1A for column setup).

After careful preparation of the experiment, the pump was turned on and columns filled with the eluent, wetting the packed materials as the eluent reached the top of the columns. Once the column packing was completely wet, the pump was stopped, and the columns were allowed to equilibrate. The original procedure in USEPA Method 1314 required the column to be equilibrated for 21 ± 3 h. However, this study used stabilizing agents mixed with the soil. Therefore, to cure the soil–stabilizer mixture, we followed the equilibration time (21 ± 3 h) with a further 28 days of resting to ensure equilibrium was reached. After 28 days of curing, the pump was turned on and the experiment began. The eluent flow rate was controlled at approximately 0.75 ± 0.25 L/S per day [23]. The eluate fractions were collected at different L/S ratios (Table 2). All experiments were conducted at ambient room temperature (of approximately 25 °C). The pH, electrical conductivity (EC), and redox potential (Eh) of the collected eluates (at various L/S ratios) were measured immediately after collection. The eluates were preserved by the addition of nitric acid and stored in a refrigerator at 4 °C until required for analysis.
Figure 1. Schematic diagram of the experimental set-up for (A) percolation column test and (B) toxicity characteristic leaching procedure (TCLP) tumbling apparatus.

The percolation column test is usually carried out until a 10 L/S ratio is reached [17,19,23]. However, we also investigated long-term leaching (using a long exposure time) of a 50 L/S ratio. The exposure time or temporal horizon (years) was calculated using the formula provided in Equation (1) [25]:

\[
\frac{L}{S} \left( \frac{L}{kg} \right) = \frac{\text{net infiltration (mm/year)} \times \text{temporal horizon (years)}}{\text{bulk density (kg/m}^3\text{)} \times \text{thickness of the layer (m)}}
\]

(1)

The following parameters were employed in the estimation: L/S ratio for the collected eluate = 0.2–50 L/kg-dry soil; the average net infiltration of the water through the stabilized soil = 20% of annual precipitation (assumption based on a road scenario); the average precipitation was based on average annual rainfall in Korea = 1350 mm per year [26]; the dry bulk density in column = 1200–1460 kg/m\textsuperscript{3}; and the thickness of the layer = 0.21–0.23 m (Table 2). A literature review revealed the assumed average net infiltration of water passing through a road containing the soil was approximately 20% [27]. Most studies have estimated an infiltration rate in the range of 10% of the annual precipitation [25,28], but our assumption has an infiltration rate two-fold higher. Using Equation (1), the long-term exposure time was calculated to be 51.1 to 56.8 years for the different soil columns (see Table S2).

2.5. Toxicity Characteristics Leaching Procedure (TCLP)

The leaching of arsenic from contaminated and stabilized soils was conducted using the USEPA Method 1311 for TCLP [29]. In this experiment, two types of extraction fluids (labelled extraction fluid #1 and #2) were prepared based on the TCLP method for the stabilization material. Briefly, extraction fluid #1 (for the lower pH materials of AMDS, steel slag, and CMDS stabilized soil, and a control) was prepared by adding 5.7 mL of glacial acetic acid (Daejung, Siheung-Si, Korea) to a 1000 mL volumetric flask containing 500 mL of ultrapure water (Human Corporation, Seoul, Korea). Then 64.3 mL of 1 N NaOH (Samchun Chemical, Pyungtaek-Si, Korea) was added to the flask. Ultrapure water was added until the total volume reached 1 L, resulting in an extraction fluid pH of 4.93 ± 0.05. If the pH of the resulting extraction fluid was not 4.93 ± 0.05, the fluid was adjusted using dilute acid or alkali [30]. Similarly, extraction fluid #2 (for the higher pH material of the
cement-stabilized soil) was prepared by adding 5.7 mL of glacial acetic acid to a 1000 mL volumetric flask containing ultrapure water until the total volume reached 1 L. The pH was adjusted using dilute acid or alkali when required to ensure the fluid maintained a pH of 2.88 ± 0.05.

The TCLP test involved the addition of 20 g soil/stabilized-soil to different PTFE extraction bottles and 400 mL of the respective extraction fluids (at a solid–fluid ratio of 1:20). Blank samples were also prepared using both TCLP extraction fluids (extraction fluid #1 and #2) in different bottles. The bottles were tightly capped and fitted into a rotatory agitation apparatus (YKZ-08-2, Changsha Yonglekang Equipment Co., Ltd., Changsha, China). The bottles were vertically rotated (end over end) at a constant speed of 30 rpm for 18 ± 2 h. All experiments were performed in triplicate. A schematic diagram of the experimental setup of the TCLP test is provided in Figure 1B (see Figure S1B for column setup). After completion of the extraction period, the resulting mixture was filtered using a 0.7 µm glass microfiber filter (GF/F, Whatman, Hangzhou, China). All the experiments were conducted at ambient room temperature (approximately 25 °C). The pH, EC, and Eh of the TCLP leachate were measured immediately after filtration. The eluates were preserved by adding nitric acid and stored in a refrigerator (at 4 °C) until required for the arsenic analysis.

2.6. Chemical Analysis of Samples

As the eluate samples were collected from column percolation test or the TCLP leachate obtained after filtration, a small volume of the sample was immediately separated and placed in a conical tube before the acid preservation. The sample was used to measure the pH, electric conductivity (EC), and redox potential (Eh). The pH, EC, and Eh of the column eluates and the TCLP leachates were immediately measured using pH, EC, and oxidation-reduction potential (ORP) electrodes (iSTEK), respectively, with the aid of a multimeter (MultiMeter K5000-CP, NeoMet, iSTEK, Seoul, Korea). The samples were preserved in dilute HNO\textsubscript{3} for further metal analyses. The alkali metals (Na, Mg, K, and Ca) and iron (Fe) present in the eluate were analyzed using an atomic absorption spectrometer (AAAnalyst 200, PerkinElmer, Waltham, MA, USA).

The As analysis involved the samples being digested then reduced into the trivalent form of As (As\textsuperscript{5+} to As\textsuperscript{3+}) and, finally, the total arsenic concentration was quantified using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7800, USA). The acid-preserved or fresh samples (eluate or leachate) were analyzed for As by digestion following the nitric acid digestion procedure, as suggested in EPA Method 6020 and 3010A [31,32].

After the digestion procedure, the digested samples were pre-reduced to the trivalent form (As\textsuperscript{5+} to As\textsuperscript{3+}) before analysis, as suggested by, and modified from, EPA Method 7062 [33–35]. After reduction, the contents of each sample within the conical tube were brought to a consistent volume (50 mL) using deionized water. The total As concentration was measured using ICP-MS. A similar procedure was used to validate this method using standard reference materials in deionized water. The results showed a very high recovery rate of the metals (90–110%). The standard stock solutions (Cica Reagent, Kanto Chemical Co. Inc., Tokyo, Japan) were used as the certified reference materials for calibration and validation for each metal’s analysis using ICP-MS. The limit of the detection (LOD) for As, Cd, Cu, Ni, Pb, and Zn were 7.18, 0.32, 0.88, 2.96, 3.94, and 0.27 µg/L, respectively. All measurements were performed in triplicate.

3. Results and Discussion

3.1. Percolation Column Test Results

3.1.1. Change in pH, EC and Eh of Effluent

The column effluents were collected and the pH, EC, and Eh were measured immediately. The eluate pH varied from fairly neutral to an alkaline pH, ranging between 6.6 and 12.8, depending on the soil stabilizer (Figure 2). The eluent pH applied in the column was 5.8. The first collected eluates (at 0.2 L/S ratio representing a 0.2 year exposure) of
AMDS-, CMDS-, and steel slag-stabilized soil and the control soil columns resulted in similar slightly alkaline pH values of 8 (pH range: 8.1–8.3). However, the pH of the cement-stabilized soil was significantly higher (approximately 12) than that of the other stabilized soils. The higher eluate pH from the cement-stabilized soil is due to the alkaline nature of cement. Cement-based materials generally have higher pH values (of more than 12) because they contain oxide minerals and alkali metals [36,37]. The eluate concentration of calcium (Ca) in the cement-stabilized soil was 2–8 times higher than in the other eluates. A similar increase in soil pH occurs after the soil is stabilized with cement [38,39].

Figure 2. Eluate curves for the pH as a function of the L/S ratio in the column percolation test using different stabilizers within the contaminated soils.

The pH of the eluates gradually decreased (albeit only slightly) by one unit when the cumulative L/S ratio reached 50 (representing more than 50 years of exposure). The eluate pH of the control, steel slag-stabilized, and cement-stabilized soil column decreased by approximately one unit or more (8.2 to 7.3 in the control, 8.3 to 7.3 in the steel slag, 12.8 to 11.4 in the cement) while those of AMDS- and CMDS-stabilized soils did not decrease (8.1 to 7.7 in AMDS, and 8.3 to 8.1 in CMDS) over the entire experimental period (Figure 2). These results indicate that, in the initial stage of percolation, some alkaline components present in contaminated or stabilized soil are partially removed with the eluent.

The EC of the column effluent eluted from the AMDS-, steel slag-, and CMDS-stabilized soils sharply decreased during the initial elution phase (from a cumulative L/S ratio of 0.2 to 2) (Figure 3). However, it sluggishly decreased to an almost constant value after 2 L/S (i.e., after an exposure of 2 years or more). However, the EC of the cement-stabilized soil in the initial phase was approximately 6.5. A gradual decrease in the eluate EC was observed in the cement-stabilized soil until the end of the percolation test. The results imply that stabilized soils should be carefully monitored and groundwater use should be prohibited for the initial two years (or five years for cement-stabilized soil) if the ions are not treated before its use, because high levels of ionic species were leached from stabilized soil in this initial period.
The redox potential (Eh) measures the tendency of the environment to oxidize or reduce the substrate. The Eh was also assessed during the percolation test period. The Eh values for the various column effluents at 0.2 L/S were in the order of: cement (251.1 mV) < control (373.4 mV) < CMDS (411.0 mV) ≤ steel slag (412.2 mV) ≤ AMDS (419.2 mV) (Figure 4). Our results imply the contaminated or stabilized soils are in the categories of either oxidized (Eh; >400 mV) or moderately reduced (Eh; +100 to +400 mV) environments, regardless of their positive Eh values [40]. AMDS-, steel slag-, and CMDS-stabilized soil had a relatively higher oxidative strength than the control or the cement-stabilized soils.

The pH and Eh are the most important factors in controlling As species, because they affect the chemical characteristics of different arsenic forms (As$^{3+}$ and As$^{5+}$) [41]. As demonstrated by the Eh–pH diagram (Figure S2), the eluate samples were clustered in the As$^{5+}$ species under oxidizing conditions (HAsO$_4^{2-}$ for the control, AMDS, steel slag, and...
CMDS, and AsO$_4^{3-}$ for the cement). This result suggests the As in the soil changed to a relatively less toxic As$^{5+}$ species.

3.1.2. Release of Arsenic (As) from the Soil: An Up-Flow Percolation Column Test

The up-flow column percolation test was used to assess the As-contaminated soil (control soil) and stabilized soils created by mixing various stabilizers (AMDS, steel slag, CMDS, and cement) (see Figure 5 for a graphical representation of the results). The initial release of As from the contaminated and stabilized soils occurred early, at a low L/S ratio (0.2 L/S, representing 0.2 years of exposure); this leaching continued to decrease until 5 L/S (representing weathering over 5 year or more). Leaching remained almost constant as time progressed (the cumulative L/S). Similar results were obtained in the eluate concentrations for each of the alkali metals (Na, Mg, K, Ca) and Fe (see Figure S3), as described in Supplementary Text S4. The initial eluate collected by the up-flow percolation column test provided insight into the pore solution composition in the bed of the soil column. A noticeable volume of As was initially released from all of the stabilized soils; this result implies that, after stabilization, the soluble As constituents were flushed from the pores and collected in the eluate (0.2 L/S). The decrease in As release with L/S ratio (or time) supports the findings of previous research.

![Figure 5](image_url)

Figure 5. Eluate concentration curves of the released arsenic from contaminated (control) and stabilized soils as a function of L/S ratio using the column-percolation test.

This study demonstrates that stabilization can be achieved with an additional 5% of a stabilizer to greatly reduce As release from contaminated soil (see Figure 5 for details). The stabilized soils reduced the initial As leaching from 137.6 µg/L (control) to 43.5 µg/L (AMDS), 87.6 µg/L (steel slag), 42.7 µg/L (CMDS), and 56.1 µg/L (cement) in the initial stage of the percolation test (0.2 L/S), corresponding to approximately 0.2 of a year of exposure. After 5 L/S (corresponding to the first five years of weathering), the As releases from all of the stabilized soils reduced slightly until 10 L/S (10–11 years) and remained almost constant until 50 L/S (51.1–56.8 years) with approximately 10 µg/L or less. This result shows that As leaching into groundwater can be substantially reduced by mixing stabilizers into the soil. However, the results of this study suggest that groundwater near the stabilized soil should be monitored and initially prohibited for use for approximately five years.

The efficiency at mitigating As release by the different stabilizing agents can be compared using the column effluent. The order of effectiveness of the stabilizers was:
steel slag (55.0%) < AMDS (74.3%) < cement (78.1%) < CMDS (81.5%) (see Figure 5). The reduction in As leaching from stabilized soil increased with the calcium content in the stabilizers (i.e., AMDS, CMDS, and cement) (Figure S4).

3.1.3. Cumulative As Release as a Function of L/S

We analyzed the leaching of arsenic from contaminated soil or the stabilized soils for the cumulative mass release of As (see Figure 6). The maximum mass of the leached constituents under field conditions over long time periods can be estimated using the cumulative masses of the constituents released during a definite L/S range. The cumulative mass release of As per unit of solid material is calculated as follows [23]:

$$\Sigma M_i = \sum_{i=1}^{n} \left[ C_i \times (\Sigma L/S_i - \Sigma L/S_{i-1}) \right]$$

(2)

where \(\Sigma M_i\) is the cumulative mass released through the interval \(i\) (mg/kg-dry); \(C_i\) is the As concentration in the eluent collected during interval \(i\) (mg/L); \(\Sigma L/S_i\) is the cumulative L/S of eluate collected through interval \(i\) (L/kg-dry); \(\Sigma L/S_{i-1}\) is the cumulative L/S of eluate collected through interval \(i-1\) (L/kg-dry); and \(n\) is the total number of collected eluate fractions.

![Figure 6.](image)

Figure 6. The cumulative release of arsenic from contaminated (control) and stabilized soils as a function of L/S ratio by the column percolation test.

The slope of the cumulative As released from the control soil was steeper than the stabilized soils (see Figure 6). The mass concentration (mg/kg) of the cumulative As released reached 3.62 mg/kg (at 50 L/S or 56.8 years). The stabilizers AMDS, steel slag, CMDS, and cement had a reduced cumulative mass release of As when compared to the contaminated soil (control). The cumulative As released from the stabilized soils after 50 L/S was 0.49 mg/kg (CMDS stabilized), 0.6 mg/kg (cement stabilized), 0.87 mg/kg (AMDS stabilized), and 1.46 mg/kg (steel slag stabilized). Therefore, the As is gradually released in the eluate of the stabilized soils.

3.2. TCLP Test for Contaminated Soil/Stabilized Soils

The concentrations of As that leached with fluids after the TCLP extraction method were analyzed to provide a worst-case scenario (see Figure 7). The As concentration leached in the different soil leachates were: control soil (174.1 µg/L) > steel slag- (95.5 µg/L) > AMDS- (65.9 µg/L) > cement- (32.1 µg/L) > CMDS-stabilized soil (20.6 µg/L) (Figure 7A).
Similarly, the mass of As released per unit of soil mass (in terms of mg/kg) was in the order: control soil (3.48 mg/kg), steel slag (1.91 mg/kg), AMDS (1.32 mg/kg), cement (0.64 mg/kg), and CMDS (0.41 mg/kg) (see Figure 7B). The results showed the leaching of As was greatly reduced by stabilization, and the efficiency of As stabilization when compared to the control was in the order: steel slag (45.2%), AMDS (62.2%), cement (81.6%), and CMDS (88.2%). None of the soil TCLP leachates exceeded the USEPA toxicity characteristic (TC) limit of 5 mg/L for hazardous waste [30].

![Figure 7](image-url)

**Figure 7.** Leaching of arsenic from contaminated (control) and stabilized soils using the TCLP test, (A) leachate concentration (as µg/L); and (B) release of arsenic (as mg/kg) from different stabilized soils.

### 3.3. TCLP vs. Percolation Column Procedure: A Comparison for As Release

This study compared the leaching of As from contaminated and stabilized soil (mg/kg) based on a worst-case scenario (TCLP), and long-term As leaching from soil in a natural scenario (using a percolation test). The levels of As release in both leaching tests were compared using the same L/S ratio (20 L/S), because the TCLP was conducted with a liquid-to-solid ratio of 20. The order of efficiency at reducing As release by the stabilizers in the TCLP test was in accordance with the percolation tests (Figure 8). The As release curve by the TCLP test and the percolation column test showed a linear relationship with a strong correlation ($R^2 = 0.9547$). When compared to the percolation column test, the TCLP test resulted in a higher volume of As released from soils. The TCLP results for As release from the various soils were higher by 1.4–3.4 mg/kg. This result is due to the harsh condition (worst-case scenario) applied in the TCLP test, whereas the percolation column test represents natural field conditions. Although the release of As was not completely prevented, the stabilizing agents enhanced the reduction of As from being released from soil in both the percolation and TCLP tests, showing an improvement in preventing groundwater contamination by binding with As to reduce the risks to the environment. Moreover, this study identified CMDS and cement as the most effective stabilizers for arsenic stabilization in soil.
4. Conclusions

The performance of the stabilization treatment for As-contaminated soil using 5% of either AMDS, steel slag, CMDS, and cement with long-term (over 50 years) exposure was studied using an up-flow percolation column test. The results showed that the stabilization of As in the contaminated soil significantly reduced the release of As from the soil. The concentrations of As and other substances (Na, Mg, K, Ca, and Fe) were initially higher in the percolation test and gradually decreased to become almost negligible over time. Stabilizers improved the As binding capacity in the soil for longer than 50 years of exposure. The most effective stabilizers for average As reduction (or hindering efficiency) with respect to the control were: steel slag (55.0%) < AMDS (74.2%) < cement (78.1%) < CMDS (81.5%). In addition, the release of As from the stabilized soil towards the end of the percolation test was reduced to below 10 µg/L. Moreover, leaching of As in the TCLP test followed a similar trend to that in the percolation test. However, the TCLP leaching concentration was higher than that in the percolation column test. This study shows that a stabilization treatment can achieve satisfactory durability and is a reliable technique for the long-term remediation of heavy metal-contaminated soil. Although these results are highly promising, further studies are required to evaluate the optimal parameters (soil pH, organic matter, stabilizer content, stabilizer size, mixing process, and aging period) before this technique can be widely applied to contaminated soils.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/app11177859/s1, Text S1: Measurement of soil characteristics. Text S2: Reagent and materials. Text S3: Chemical analysis of samples. Text S4: Alkali metals and iron concentration in the effluents. Table S1: Major heavy metals present in the contaminated soil. Table S2: The exposure time (in years) at different liquid-to-solid (L/S) ratios calculated by using Equation (1) for each soil column. Figure S1: Performing leaching tests for arsenic release from soil during (A) column percolation test and (B) toxicity characteristic leaching procedure (TCLP). Figure S2: The eluates’ redox potential (Eh)
and pH values (obtained from Figures 2 and 4) plotted on a Pourbaix diagram for arsenic species. Figure S3: Eluate concentration curves for the release of various metals (Na, Mg, K, Ca, and Fe) from different soil columns as a function of L/S ratio in the percolation test (mean concentrations were obtained from three replicates). Figure S4: Percentage composition (%) of different stabilizing agents used in this study. The component portions were analyzed using X-ray fluorescence spectrometry (XRF-1800, SHIMADZU, Kyoto, Japan).

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