

Article

Utilization of the Finer Particle Fraction of Arsenic-Bearing Excavated Rock Mixed with Iron-Based Adsorbent as Sorption Layer

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Abstract: Excavated rocks generated during tunnel construction may pose an environmental hazard due to the release of acidic leachate containing potentially toxic elements (PTEs). Addressing this concern requires strategic countermeasures against mitigating the release of PTEs. This study investigated the efficacy of a novel approach for managing altered excavated rocks that generate acidic leachates with elevated arsenic (As) by utilizing the finer altered rock as a base material for the sorption layer. The proposed method involves classifying the altered excavated rocks into coarse (9.5–37.5 mm) and finer (<9.5 mm) fractions, with the finer fractions incorporated with iron (Fe)-based adsorbent to form a bottom sorption layer for the disposal of coarser rock samples. Leaching behavior and As immobilization efficiency were assessed through shaking, stirring leaching tests, batch sorption tests, and column tests under varying particle size fractions of the rock samples. Results indicate that altered finer rock fractions exhibit increased As leaching under shaking conditions due to enhanced dissolution. The addition of >1% of Fe-based adsorbent to the finer rock in the sorption layer effectively suppressed As leaching concentration, meeting the management criterion of <0.3 mg/L for specially controlled contaminated soils in Japan. Batch sorption tests using the finer rock samples with the Fe-based adsorbent confirmed their efficacy as effective adsorbents. This efficacy was further elucidated in column experiments consisting of the coarse rock samples and fine altered rock samples mixed with the Fe based adsorbent at the bottom as a sorption layer. Results showed that the sorption layer effectively decreased the As leached from the rock layer, utilizing the altered excavated fine rock as a base material in the sorption layer. This approach highlights the potential for repurposing excavated rocks as sorption media, enabling sustainable management strategies for As-contaminated rocks. This study provides an innovative framework for integrating adsorption-based remediation, contributing to sustainable countermeasure strategies for excavated rocks.

Keywords: acidic leachate; arsenic immobilization; column experiment; excavated rocks; leaching behavior; potentially toxic elements



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1. Introduction

Large-scale excavation projects, including tunnel construction, are essential for infrastructure development and underground space utilization. However, these activities

generate substantial volumes of the excavated rocks [1–4], some of which may pose environmental risk due to the presence of potentially toxic elements (PTEs). For example, marine-derived mudstone and hydrothermally altered rocks often contain PTEs, such as arsenic (As) and lead (Pb) [5–7]. Exposure to environmental conditions, particularly rainfall, accelerates weathering and oxidative reactions [8]. This mobilizes the PTEs and acidifies leachates, posing significant risks to the surrounding soil and aquatic environments [9,10]. Therefore, implementing strategic measures to prevent the release of PTEs into the environment is vital [11].

A commonly employed countermeasure is the use of an impermeable liner, widely adopted for industrial waste disposal [12,13]. Other techniques include encapsulation, which involve covering rocks with impermeable layers or coatings to prevent water from interacting with As-bearing minerals. These strategies have proven effective in decreasing the leaching of As [14]. However, the long-term effectiveness of these methods may be compromised by environmental conditions such as temperature and humidity fluctuations, as well as risks associated with incomplete coverage or incorrect application, which can undermine the integrity of the encapsulating materials or impermeable liners [15,16]. Moreover, physical disturbances can compromise the effectiveness of the containment barriers, facilitating As mobilization and increasing the long-term costs and resource demands of such projects. Recent advancements in immobilization techniques and sorption layer systems provide promising strategies for mitigating the environmental impact of PTE-rich excavated rocks [7,17–22]. Advection–dispersion modeling in risk assessment can offer insights into PTEs migration by incorporating sorption characteristics and buffering effects of the surrounding soils to evaluate their potential for attenuating PTEs [23–25]. This strategy is crucial for recycling the excavated materials. Moreover, excavated rock from ore deposits or hydrothermal altered regions require extensive disposal area, posing significant environmental challenges [26,27].

In Japan, a specific management criterion exists for what is considered specifically controlled contaminated soils such as <0.3 mg/L for As and Pb [28]. This standard value is based on the concentration in the filtrate obtained by mixing the prepared sample (<2 mm particle size fraction) with distilled water at a weight/volume ratio of 10%, shaking the mixture at 200 rpm for 6 hours, and filtering it through a $0.45\ \mu\text{m}$ filter [29]. Normally, in case of As, if the concentration in the leachate exceeds 0.01 mg/L, it can be recycled into embankments by using various countermeasures [18]; however, if As concentration in the leachate exceeds 0.3 mg/L, it must be disposed of in a waste disposal site or sealed in a concrete container. This means that excavated rocks that exceed the specific management criterion cannot be subjected to normal countermeasures. Should the leachate from excavated rocks surpass these thresholds, such rocks must be treated as specially controlled contaminated soils. Moreover, when the volume of such rocks becomes substantial, identifying efficient and cost-effective strategies for their management becomes crucial, particularly because they carry a significantly high potential for environmental pollution. Therefore, the importance of finding viable, cost-effective solutions for the management and disposal of this type of excavated rock cannot be overstated, given the limited options available and the critical need to mitigate environmental risks.

In this study, the development of appropriate countermeasures for highly contaminated excavated rocks is attempted. Initially, attention is paid to the particle size distribution of the excavated rocks. The mechanical excavation or powder blasting involved in tunnel construction produces a broad distribution of particle size fractions, ranging from smaller to larger particles. The finer particles, with their extensive specific surface area, are thought to originate from highly altered zones, and may pose a significant risk due to their potential to release PTEs along with acidic leachate [30–33]. Larger particles,

having less specific surface area, are assumed to present a reduced risk for leaching PTEs or generating acidity. Prioritizing the management of excavated rocks with finer particle sizes is critical, with a recommendation for their selective stabilization using a reagent of sorption/immobilization. Managing larger particle fractions also remains essential. For this reason, an effective embankment system for the excavated rocks is proposed.

This approach involves segregating the excavated rock based on the environmental risk associated with its grain size; classifying it into finer-grained rock, which poses a higher environmental risk, and coarser-grained rock, which presents a lower risk. The finer-grained rock is then stabilized and employed as an adsorptive layer beneath the coarser-grained rocks. This protocol leverages the differentiation between finer and coarser excavated rocks to construct a layered sorption system, wherein the finer-grained rock mixed with an adsorbent serves as a foundational layer that supports the coarser rocks. Furthermore, the construction of a sorption layer usually requires base materials that have a capacity for adsorbing PTEs [20]. In contrast, the studied system creates a sorption layer by adding an artificial adsorbent directly to the finer altered excavated rock, which can release PTEs or acidic leachate, eliminating the need to source additional base material for the sorption layer. This approach not only mitigates the environmental risks but also promotes the effective utilization of excavated rocks, aligning with sustainable management practices.

Thus, the development of an optimized sorption layer system, specifically targeting the treatment of hydrothermally altered rocks yielding elevated concentrations of As in acidic leachate is established by: (1) conducting three types of batch leaching tests with rock samples with four different particle size distributions; (2) evaluating the efficacy of immobilization of the As leached from finer rocks and the sorption efficiency of the finer rocks with an iron (Fe)-based adsorbent; (3) elucidating how the finer-grained rocks with an adsorbent at the bottom sorption layer decrease As concentration leached from the untreated coarser rocks; and (4) evaluating the performance of the integrated approach under intermittent/unsaturated flow mimicking field conditions using three cases of laboratory column tests consisting of rock layer with/without bottom sorption layer. The results of this research hold the potential to shape the development of cost-efficient and innovative countermeasures for managing highly contaminated excavated rocks, for which effective remedial measures have yet to be established.

2. Materials and Methods

2.1. Rock Samples and Fe-Based Adsorbent Used for This Study

Hydrothermally altered conglomerate rock samples were obtained from a tunnel construction project on the island of Hokkaido, Japan, as bored cores. The cored samples were obtained through diamond core drilling prior to the execution of blasting operations in the tunnel (Figure S1). The particle size classification was determined based on the criteria outlined in the Japanese sieve analysis standards [34] and adjusted for ease of handling in the stirring test and column test described later. The samples were air dried, crushed, and then sieved into four distinct particle size ranges: 37.5–19.0, 19.0–9.5, 9.5–2.0, and <2.0 mm (Figure S2a–d). These size fractions were selected to correspond with the batch shaking and stirring tests described in Section 2.2 and to evaluate differences in leachate properties between the upper and lower layers when a sorption layer is introduced, with coarser fractions placed in the upper layer and finer fractions mixed with adsorbent in the lower layer. Samples <2.0 mm were partially subjected to further grinding until reaching a particle size of <10 µm and subsequently used for chemical and mineralogical analyses. The bulk chemical composition and mineral constituents of the grinded rock samples were determined using X-ray fluorescence spectrometry (SPECTRO XEPOS, Rigaku Corporation,

Japan) and X-ray diffraction spectrometry (MULTIFLEX, Rigaku Corporation, Japan), respectively. Both analyses were done using pressed powders of the sample. The adsorbent used in this study was a Fe-based material composed of reduced Fe particles, Fe oxide, and calcium sulfate (CaSO_4). The Fe oxide and calcium sulfate were by-products of the titanium-making industry and steel-making industry [35,36]. The bulk chemical composition and mineral constituents of Fe-based adsorbent were analyzed using XRF and XRD, respectively. Both analyses were performed using pressed powder samples.

2.2. Batch Leaching Tests

Three types of batch leaching tests were conducted to evaluate the leaching characteristics of As from altered rock samples (Figure S3a–c). First, a batch shaking test was conducted following the Japanese Environmental Agency Notification No. 46 method for four particle size fractions (37.5–19.0, 19.0–9.5, 9.5–2.0, and <2.0 mm) [29,37]. Fifty grams of each size fraction were mixed with 500 mL of deionized water and agitated at 200 rpm under ambient conditions for 6 hours. After the shaking, the pH, electrical conductivity (EC), and oxidation-reduction potential (ORP) of the suspensions were measured. The leachates were then obtained by filtering the suspensions through 0.45 μm Millex Millex[®]-HA sterile membrane filters and used for chemical analysis. The ORP values were converted to Eh for geochemical calculations.

Since the particle size reduction occurs due to collisions between samples during shaking in the batch leaching test, the leaching concentration of As may be overestimated compared to the actual embankment environment. Therefore, the batch stirring tests were also conducted following the Japanese standards JIS K 0058, using the four particle size fractions (37.5–19.0, 19.0–9.5, 9.5–2.0, and <2.0 mm) [38]. Predetermined amounts of samples and deionized water were stirred at 200 rpm under ambient conditions for 6 hours. After stirring, the pH, EC, and Eh of the suspensions were measured and the leachates were obtained by filtering the suspensions through 0.45 μm membrane filters. By conducting leaching tests under both shaking and stirring conditions, the influence of test conditions on As leaching concentrations can be evaluated. Although leaching tests under shaking conditions are more commonly applied [5,8], both test methods were conducted with the aim of evaluating the difference in As leaching concentration and pH variation as a function of particle size, using a method more representative of field conditions.

Furthermore, serial batch leaching tests were conducted to evaluate the continuous leaching behavior of As from rock samples with a particle size of <2 mm [39]. The procedure followed the batch shaking test described above; however, after each test cycle, the residue sample was recovered and reused for subsequent batch shaking test. This cycle was repeated until the leaching concentration of As decreased to <0.3 mg/L, which corresponds to a management criterion for specially controlled contaminated soils. To enhance the precision of leaching concentrations, all tests were conducted in triplicate. Deionized water (18 M Ω ·cm) from a Millipore Milli-Rx 12 α system (Merck Millipore, Burlington, MA, USA) was used for all the experiments.

2.3. Batch Immobilization Tests

Batch immobilization tests were conducted by mixing the rock samples with Fe-based adsorbent (Figure S4). The rock samples used in these tests consisted of a mixture of 2.0–9.5 mm and <2.0 mm fractions at a 1:1 weight ratio. The Fe-based adsorbent was added to the rock sample at a mass ratio of 1, 3, 5, and 10%. After mixing, the samples were cured for one day at room temperature, then lightly crushed, and subjected to the batch shaking tests methodology described in Section 2.2. After the batch leaching tests, the filtered leachate was analyzed for As leaching concentrations and pH.

2.4. Batch Sorption Tests

Batch sorption tests were conducted by adding predetermined amounts of rock samples mixed with Fe-based adsorbent into prepared leachate (Figure S5). The rock samples comprised of a mixture of 2.0–9.5 mm and <2.0 mm fractions at 1:1 weight ratio. The primary objective of the sorption layer system was to reduce As leaching concentration from the fine rock particles while simultaneously suppressing As leached from larger particles of excavated rock from the upper layer. Based on batch immobilization tests, the Fe-based adsorbent was added to the rock samples at ratios of 5, 10, and 15% of the weight of the rocks; higher than those used in batch immobilization tests. The leachate used in this batch sorption test was obtained from the batch stirring test conducted at 200 rpm for 6 h. The adsorbent–rock mixtures were prepared under varying conditions as shown in Table S1 and subjected to continuous mixing at 200 rpm for 24 h. The suspensions were filtered through 0.45 µm membrane filters and then the As concentration in the filtrates was analyzed.

The sorption of As in the mixture of the Fe-based adsorbent and rock samples was calculated as follows [40]:

$$q = \frac{(C_0 - C) \cdot V}{W}, \quad (1)$$

where, q is adsorbed amount (mg/g), C_0 is initial As concentration (mg/L), C is final As concentration (mg/L), V is volume of solution (L), and W is weight of adsorbent (g).

Data from the experiments were fitted with a non-competitive Langmuir isotherm.

$$q = \frac{q_{max} \cdot K_L \cdot C}{1 + K_L \cdot C}, \quad (2)$$

where, q_{max} (mg/kg) is the maximum sorption capacity, and K_L is the Langmuir constant. Values of the sorption parameters K_L and q_{max} were obtained by transforming Equation (2).

Typically, Langmuir isotherm approximation is conducted by varying the initial liquid phase concentration and adjusting the solid-phase mass in the sorption tests [41]. However, in this study, to assess sorption performance against actual leachate derived from As-bearing rock samples, leachate obtained from batch stirring tests was directly used as the liquid phase, maintaining a fixed initial concentration. Consequently, conventional Langmuir isotherm approximation was not applicable. Nevertheless, to provide a rough estimation of sorption capacity, a provisional Langmuir approximation was performed for the Fe-based adsorbent-sieved rock mixture.

2.5. Column Experiments

Figure 1 illustrates the schematic of the experimental columns, designed to simulate the movement of water through packed granular materials. Water introduction into the columns vary, with options for both continuous and intermittent flow, and down-flow and up-flow directions [40,42,43]. Each configuration is tailored to suit different experimental needs or to replicate various environmental conditions. In this study, an intermittent down-flow approach was selected to replicate conditions analogous to rainwater infiltration and subsequent percolation, resulting in an unsaturated flow of water. To evaluate As migration from the rock layer and its attenuation by the bottom sorption layer, three experimental cases were constructed in the column setup.

- Case 1 (Control): Rock samples containing all particle sizes < 37.5 mm.
- Case 2: Rock samples only composed of particle size ranging from 9.5 to 37.5 mm, simulating the upper layer in the sorption system.
- Case 3: Rock samples < 9.5 mm in mixed with Fe-based adsorbent, forming a sorption layer at the bottom of the rock column.

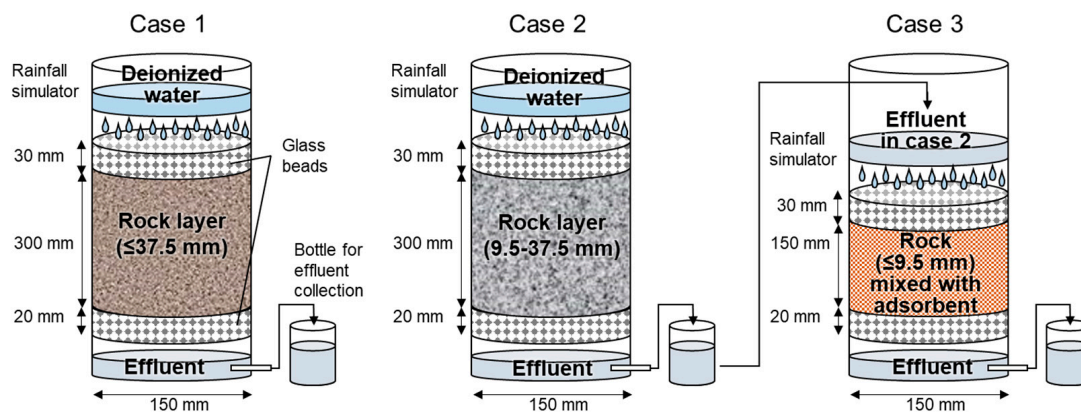


Figure 1. The schematic of column experiments.

Case 1 served as a control to evaluate As leaching behavior without intervention. Case 2 examined As leaching from coarse rock particles, while Case 3 assessed the effectiveness of the Fe-based sorption layer in suppressing As release.

Table S2 summarizes the condition of the column experiments. The Fe-based adsorbent dosages in the rock samples for the column experiments were determined by considering the results of the batch sorption tests and the serial shaking tests. The optimal mixing ratio (6%) was determined by calculating the cumulative As leaching until the concentration dropped below 0.3 mg/L in serial batch tests, followed by adsorption capacity calculations.

Acrylic rainfall simulators with small perforations were placed on top of each column to ensure uniform water distribution and prevent external contamination. Deionized water was introduced into Cases 1 and 2 at 2.06 L/day (Monday, Wednesday, and Friday) until reaching a cumulative liquid-solid ratio of 3, after which the flow rate was increased to 4.12 L/day. With a 3-h percolation time, the simulated rainfall intensity corresponded to 38.9 mm/h (up to a cumulative L/S ratio of 3) and 77.8 mm/h thereafter.

The concept of rainfall application for each column is as follows:

- The pore volume (PV) for Case 1 and 2 was 2057 cm³. Based on the following equation, 2.06 L (7200/1.75 × 0.40) was calculated;

$$PV = \frac{W_d}{\rho_d} \theta, \quad (3)$$

where, W_d (g) is the dry weight of rock sample, ρ_d is the dry density of the rock sample, and θ is the porosity in the column of rock layer.

- To supply deionized water equivalent to 1 PV per rainfall supply into the column, 2.06 L/day was applied. However, to accelerate the leaching process halfway through, the volume of deionized water supplied was doubled to 4.12 L/day after 3.0 of cumulative liquid–solid ratio (L/S) ratio.
- Approximately 200 L of deionized water was supplied to Case 1 and 2 throughout the experiment. This was equivalent to approximately 100 PV.
- Two hundred L of simulated rainfall was equivalent to 9–10 years of rainfall in an actual embankment environment (annual rainfall in Sapporo, Hokkaido (mm) × 10 years × column cross-sectional area of the column (mm²) = 1200 × 10 × 17,662 = 211(L)).
- After the sorption layer construction, the system's permeability was significantly reduced by covering the soil, suggesting that the 10-year simulation under nearly full infiltration conditions was sufficient to evaluate long-term stability.

For Case 3, 20 mL of the leachate obtained in Case 2 was collected for chemical analysis and the remaining leachate was recirculated through the rainfall simulator.

The leachate was collected 2 h after percolation, and then the pH, EC, and ORP of the suspensions were measured. Prior to chemical analysis, samples were filtered using 0.45 µm membrane filters.

The results were compiled using the L/S ratio, defined as the cumulative volume of collected effluent relative to the sample weight in the column. An increase in L/S ratio corresponds to an increase in simulated rainfall supply and experiment duration. The liquid–solid ratio was determined by the following equation;

$$L/S = \frac{\sum_{i=1}^n V_n}{W_C} \quad (4)$$

where V_n is the volume of the collected effluent from the column experiment in each sampling (mL) and W_c is the weight of the sample used for the column.

The simulated rainfall supply of 2.06 L/day corresponds to approximately L/S = 0.3, and by continuously supplying simulated rainfall, L/S increases cumulatively.

2.6. Chemical Analyses

Concentrations of As, Fe, and Al were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS-2030, Shimadzu Corporation, Kyoto, Japan) (margin of error = ±2–3%). All chemicals used in the preparation and analyses were reagent grade. Major cations, such as Na⁺, K⁺, Ca²⁺, Mg²⁺, and anions, such as a SO₄^{2−}, in the leachates were determined by ion chromatography (Dionex Integrion HPIC and Dionex Integrion RFIC, Thermo Fisher Scientific K. K., Waltham, MA, USA) (margin of error = ±2%) using nonacidified samples. The reagent grade standard solutions were used to prepare calibration curves for ICP and IC.

2.7. Principal Component Analysis

Multivariate principal component analysis (PCA) was performed to evaluate the major trends and interrelationships of the leachate analysis results obtained from the column tests. This approach has been applied in many studies to compare leachate properties generated from waste rocks containing PTEs and tailings generated in mining activities [44,45]. This study analyzed the following leachate components: pH, EC, Eh, As, Fe, Al, Na⁺, K⁺, Ca²⁺, Mg²⁺, and SO₄^{2−}. Origin Pro (OriginLab Corporation, Northampton, MA, USA) was used for PCA calculations.

2.8. Geochemical Modeling

To evaluate the stable phases of As and Fe under each test condition, Eh–pH diagrams were depicted using the Geochemist's Workbench® [46] based on their actual solute activities measured in the effluents. This modeling was applied to the results of column experiments for three cases. The activities used in this study were the initial water chemistry of the effluent from each three columns, Cases 1, 2, and 3.

3. Results and Discussion

3.1. The Mineral and Chemical Compositions of the Rock Samples and Fe-Based Adsorbent

The mineralogical and chemical compositions of the rock samples are summarized in Tables S3 and S4. XRD analysis revealed that the rocks predominantly contained quartz with minor amounts of plagioclase, illite, smectite, kaolinite, and pyrite. XRF analysis indicated a high content of SiO₂ (62.8 wt.%), Fe₂O₃ (14.7 wt.%), Al₂O₃ (9.20 wt.%), and SO₃ (3.74 wt.%). The significant presence of Fe₂O₃ and SO₃ is likely due to pyrite, which may act as a potential source of As in acidic leachate [47,48].

The XRD and XRF results for the adsorbent are also shown in Tables S3 and S4. The main chemical components of the Fe-based adsorbent were Fe_2O_3 (37.6 wt.%), SO_3 (34.5 wt.%), and CaO (23.5 wt.%). Major minerals, such as bassanite and gypsum, were detected with trace amounts of hematite, magnetite, and ferrihydrite. The Fe-bearing minerals, such as hematite, magnetite, and ferrihydrite, are known for As sequestration [49–51]. The adsorbent design leverages bassanite and gypsum to buffer pH fluctuations, preventing rapid pH shifts. Although XRD results showed low hematite intensity, the adsorbent contains substantial amorphous/low-crystalline Fe phases, which enhance As sorption efficiency.

3.2. Batch Leaching Tests of Rock Samples

The results of batch leaching tests for the rock samples under shaking and stirring for each particle size are illustrated in Figure 2. Under shaking conditions, As leaching concentrations were 2.1, 2.4, 1.2, and 1.0 mg/L for particle sizes < 2, 2.0 to 9.5, 9.5 to 19.0, and 19.0 to 37.5 mm, respectively. In contrast, under stirring conditions, the corresponding concentrations were lower at 1.3, 1.1, 0.2, and 0.15 mg/L, respectively. The results indicate that smaller particles exhibited elevated As concentrations irrespective of agitation conditions with shaking inducing significantly higher As concentrations of ca. 1.6, 2.2, 6.0, and 6.7 times greater than those observed under stirring. The increased agitation under shaking conditions likely caused more frequent collisions, leading to finer particles and enhanced As dissolution. As shown in Figure S6, 15 to 42% of the rocks were reduced to <2 mm under shaking (Figure S6a), whereas, during stirring (Figure S6b), <5% of the rocks were reduced to <2 mm.

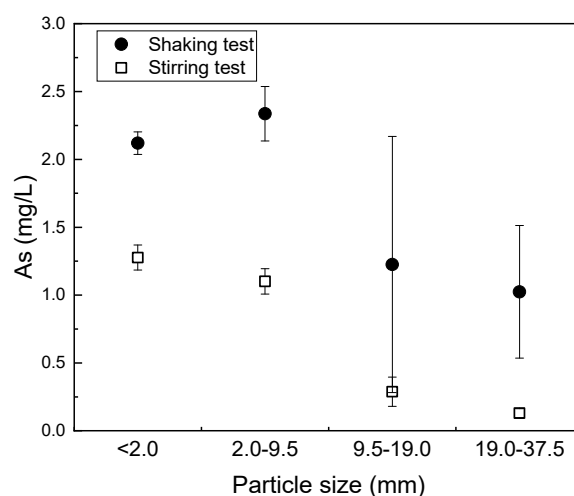


Figure 2. Arsenic leaching concentration under shaking and stirring conditions.

The changes of As leaching concentration in the serial shaking test are shown in Figure 3. The initial As leaching concentration was 0.58 mg/L, gradually decreasing with repeated shaking (Figure 3a). By the 10th cycle, the cumulative As leached reached up to 43.6 mg/kg (Figure 3b), with concentration dropping below Japan's threshold for specially controlled contaminated soil (<0.3 mg/L). These results suggest that the As leaching is strongly influenced by particle size, as smaller particles have a higher specific surface area, promoting greater As release into the leachate [31,52]. In addition, the decreasing trend in As concentration over multiple leaching cycles indicates the depletion of soluble and surface-bound As phases [6]. The serial batch tests also showed a continuous decline in pH, suggesting acidification of the leachate due to the gradual oxidation and dissolution of pyrite in the rock samples, which contributed to acid generation [53]. Based on these findings, fine-grained rock samples (<9.5 mm) were identified as major contributors to

As leaching. To mitigate this, these samples were mixed with Fe-based adsorbent and incorporated into the bottom sorption layer in the column experiments, aiming to reduce As mobility and enhance long-term stability.

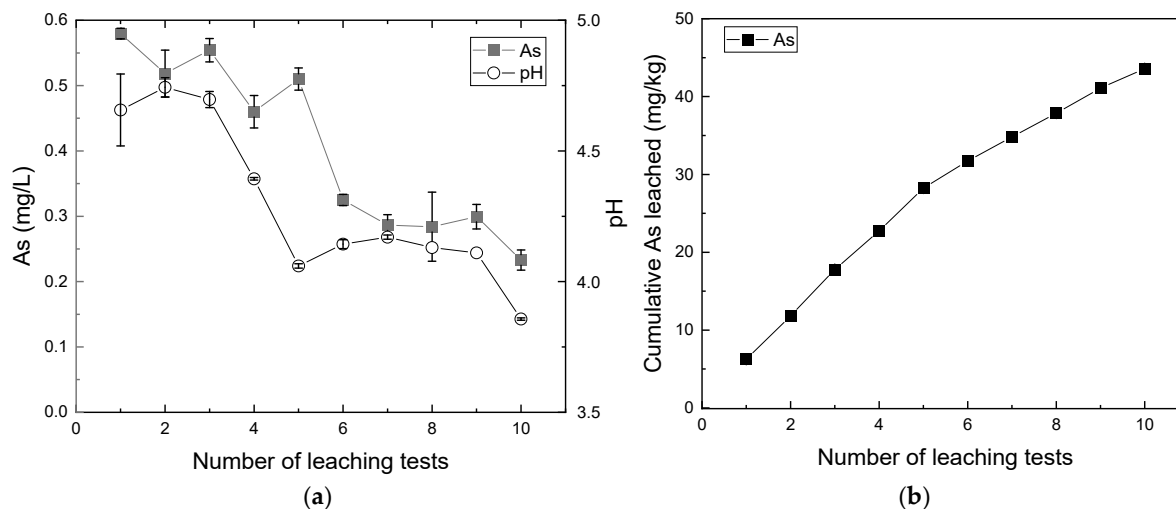


Figure 3. The changes of (a) As leaching concentration and pH and (b) cumulative leached As by serial leaching tests under shaking conditions.

3.3. Batch Immobilization and Sorption Tests

Figure 4 presents the results of the immobilization tests, demonstrating a significant reduction in As leaching concentrations with the addition of Fe-based adsorbent. Incorporating the Fe-based adsorbent into the rock sample at proportions of 1, 3, 5, 7, and 10% decreased As leaching concentrations to 0.098, 0.049, 0.026, 0.020, and 0.012 mg/L, respectively. These results confirm that even a 1% addition of Fe-based adsorbent effectively decreased As leaching from the As-bearing rock samples below Japan's regulatory threshold for specially controlled contaminated soil. Furthermore, it was found that the addition of Fe-based adsorbents into rock samples induced calcium sulfate component dissolution in the adsorbent and buffered the acidification of the pH (Figure 4).

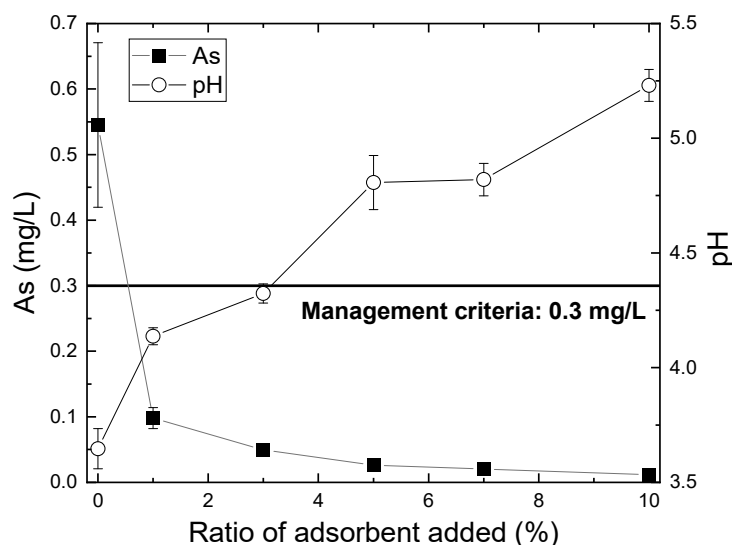


Figure 4. The reduction of As leaching and pH changes in immobilization tests using Fe-based adsorbent.

Figure 5a,b and Table S5 show the results of sorption test and provisional Langmuir isotherms approximation for batch sorption tests using the rock samples mixed with Fe-based adsorbent. The initial As concentration of 0.697 mg/L decreased with increasing

adsorbent dosage (Figure 5a). The determination coefficients for added ratios at 5, 10, and 15% were 0.73, 0.91, and 0.91, respectively (Figure 5b and Table S5). The corresponding q_{max} values increased to 246, 254, and 280 mg/kg. Although previous studies have reported variability in As leaching behavior; either increasing or decreasing upon the introduction of adsorbents [54]. In this study, the Fe-based adsorbent–rock mixture functioned effectively as adsorbents. This behavior aligned well with the Langmuir isotherm model, suggesting strong adsorption interactions and a high potential for As immobilization.

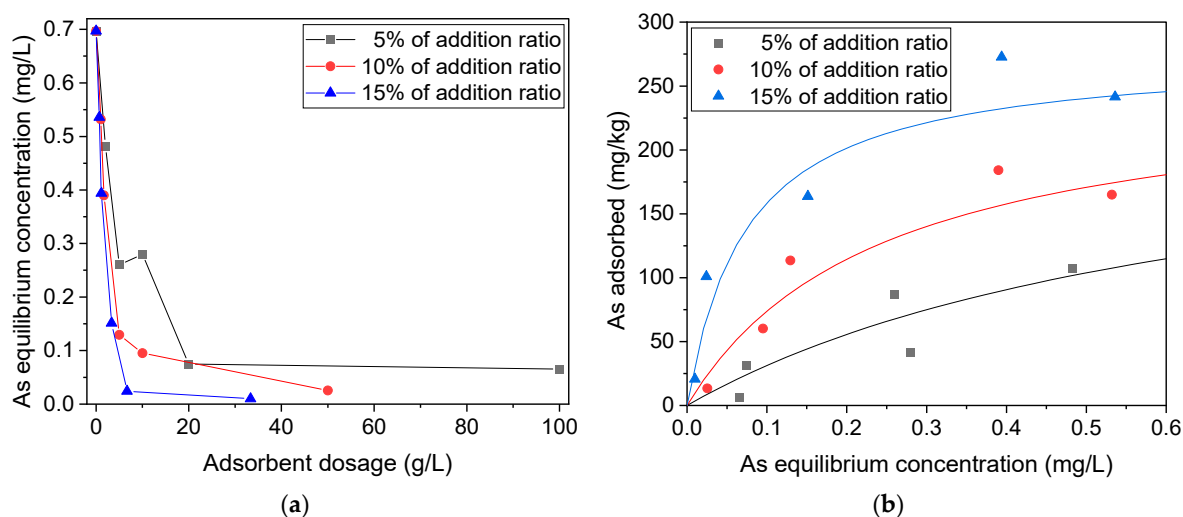


Figure 5. Equilibrium As concentration with adsorbent dosage (a) and As adsorbed onto the immobilized sieved excavated rock samples with Fe-based adsorbent with the provisional approximation of Langmuir isotherms (b) in sorption test.

3.4. Changes in the Quality of the Effluent in Column Experiments

The pH variations (Figure 6a) observed in Cases 1 and 2 followed a similar trend, initially at approximately 1.8, gradually increasing, and stabilizing around 3.0 when the L/S ratio reached 5. In Case 3, where the rocks were mixed with the Fe-based adsorbent, the pH remained stable at ~6.0 up to L/S of 10, beyond which it gradually declined, reaching approximately 3.0 at L/S of 20. The low pH could be attributed to the dissolution of pyrite contained in the rock samples [27,48], despite the pH buffering capability of the rock containing adsorbent. This suggests that to maintain long-term pH stability in leachate, it is necessary to evaluate threshold values not only for As but also for pH in immobilization tests, alongside the molar ratio of S and Ca in the adsorbent–rock mixture [27,55].

The Eh changes (Figure 6b) in Cases 1 and 2 indicated a similar trend ranging from 0.6 to 0.7 V. In Case 3, the Eh indicated reductive conditions, initially at around 0.2 V. This value fluctuated up to 0.4 V until the L/S reached 10. It gradually increased and fluctuated again between 0.4 and 0.6 V before stabilizing at an Eh value similar to those of Cases 1 and 2, observed at the L/S of 20. The reductive condition observed in Case 3 is likely due to the oxidation of easily reduced Fe particles in the Fe-based adsorbent, and Fe particles adsorbing As leached from the rock layer could be stabilized to be Fe oxide [56–58].

A significant difference in As leaching concentrations was observed among the three Cases at the initial stage, with concentrations of 340, 85, and 0.083 mg/L in Cases 1, 2, and 3, respectively (Figure 6c). In Cases 1 and 2, As concentrations declined rapidly at the beginning of the experiment, stabilizing after L/S = 5. The rapid decrease was attributed to the dissolution and washing out of water-soluble As fractions, coupled with the acidification of leachate. In contrast, Case 3, which contained the Fe-based sorption layer, maintained an initial As concentration of <0.1 mg/L until L/S = 15. After L/S = 20, As concentrations increased gradually, surpassing 0.3 mg/L and fluctuating between 0.20 and 0.95 mg/L. These

findings suggest that while the sorption layer effectively suppressed As release in the early stages, saturation of its adsorption capacity occurred beyond $L/S = 20$.

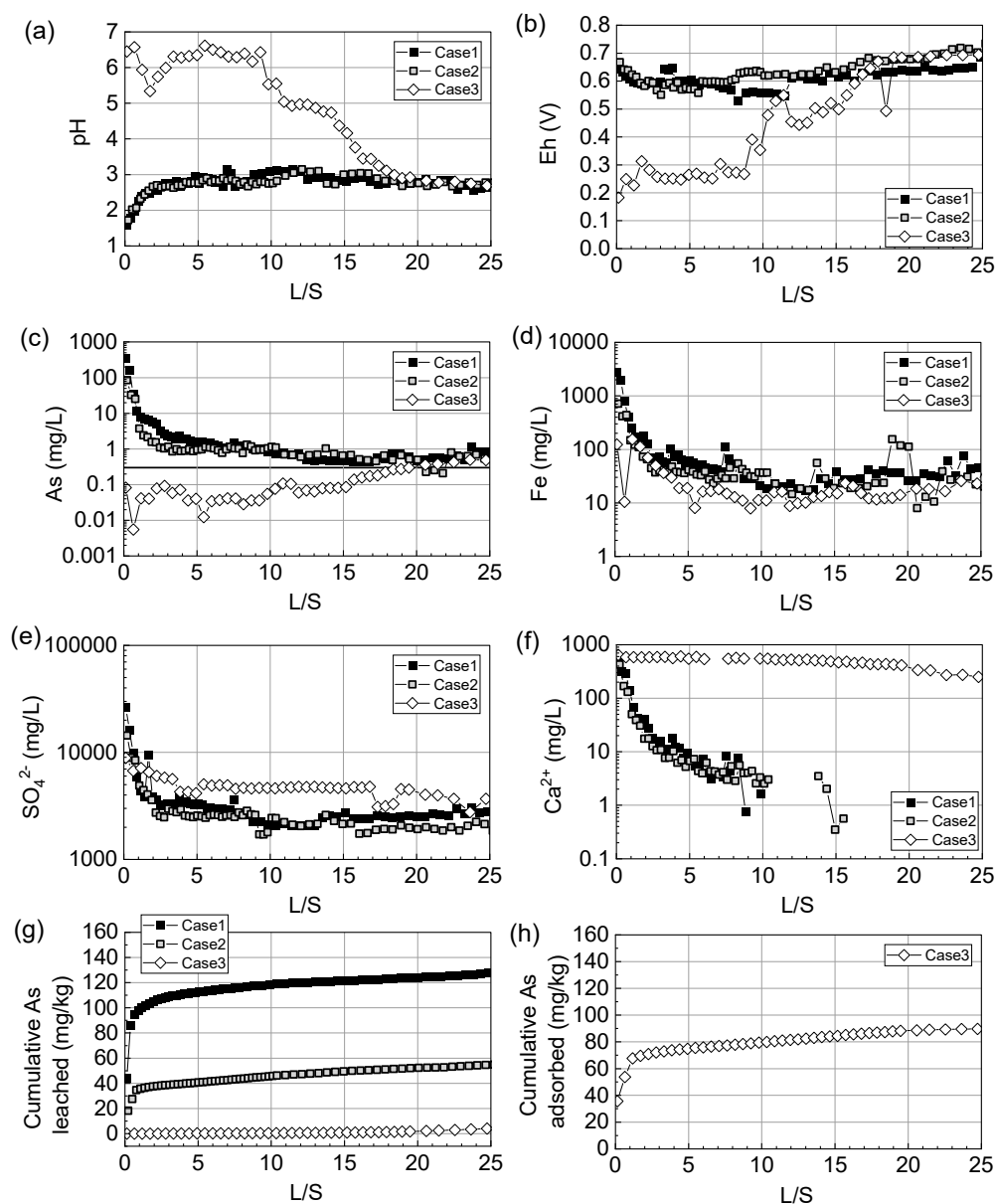


Figure 6. Effects of the sorption layer on the quality of the effluent; (a) pH changes with time, (b) Eh changes with time, (c) As concentration changes with time, (d) Fe concentration changes with time, (e) SO_4^{2-} concentration changes with time, (f) Ca^{2+} concentration changes with time, (g) cumulative As leached with time, and (h) cumulative As adsorbed with time.

The Fe leaching concentration (Figure 6d), in all cases, started at elevated levels, gradually declining thereafter, and stabilizing around 10 to 100 mg/L after $L/S = 5$. The highest initial Fe leaching concentrations were recorded as 2800 mg/L, 718 mg/L, and 154 mg/L in Cases 1, 2, and 3, respectively. The changes in SO_4^{2-} were very similar to those of Fe only in Case 1 and Case 2, showing high concentrations up to around $L/S = 3$, and then showing a constant leaching concentration without any significant changes (Figure 6e). Comparing Cases 1 to 3, the initial leaching concentrations in SO_4^{2-} were higher in Cases 1 and 2, but Case 3 showed a high leaching concentration over the long term, which is thought to be due to the dissolution of calcium sulfate minerals such as bassanite and gypsum. Meanwhile, the Ca in Cases 1 and 2 showed high concentrations in the early stages and

then dropped rapidly around $L/S = 5$. Case 3 showed high Ca leaching concentration from the early stage of leaching due to the influence of calcium sulfate minerals, and although it decreased slightly until the end of the test, around $L/S = 25$, it remained at a higher concentration than the other Cases (Figure 6f).

Considering the cumulative As leached (Figure 6g) in Case 1, a substantial quantity of As was leached from the beginning until $L/S = 2$, followed by a gradual increase until $L/S = 10$. The final cumulative As leached in Case 1 was 128 mg/kg. Case 2 exhibited a similar pattern, with a final cumulative As leached at 54.6 mg/kg at the end of the experiment. In Case 3, negligible As leaching was observed, resulting in a final cumulative As leached of 4.1 mg/kg at the end of the experiment.

Based on the cumulative As adsorbed by the sorption layer, the difference in the leached As between Case 2 and Case 3 was calculated, and the cumulative As adsorbed to the unit weight of the sorption layer is illustrated in Figure 6h. The results showed that As leached from the rock layer was highly adsorbed by the sorption layer in Case 3 before $L/S = 2$, and then continuous sorption occurred. At the end of the experiments, cumulatively, 89.7 mg/kg of As was adsorbed by the sorption layer.

The volume of collected effluent and the changes in EC, Na^+ , K^+ , Mg^{2+} , and Al in the effluent are shown in Figure S7a–f. Immediately after the simulated rainfall was supplied into the columns, not all of the effluent was recovered. This is because the simulated rainfall was retained in the dried sample in the column. However, after the second supply of the simulated rainfall into the columns, almost all of the supplied simulated rainfall was recovered as effluent. In the early stages of the column experiments, EC was high in all cases, followed by Cases 1, 2, and 3, and then gradually decreased. In Cases 1 and 2, Na^+ , K^+ , Mg^{2+} , and Al also gradually decreased in response to the change in EC. In case 3, the ion concentrations were slightly higher than those in Cases 1 and 2, which is thought to be due to the release of the components contained in the Fe-based adsorbent.

3.5. Mechanisms of As Sorption by Rock Sorption Layer with Adsorbent

To elucidate the mechanisms governing As migration from the rock layer and its sorption by the rock layer mixed with Fe-based adsorbent, the relationships between (a) As and pH, (b) Fe and pH, (c) Ca and pH, and (d) As and Fe as shown in Figure 7. Arsenic leaching concentration increased at $\text{pH} < 3$ but remained constant at <0.3 mg/L within a pH range from 3 to 7 (Figure 7a). Notably, at $\text{pH} < 3$, As leaching concentrations in Cases 2 and 3 were comparable, suggesting that the sorption layer had reached its maximum sorption capacity.

The Fe leaching concentration increased rapidly when the pH was <3 due to the dissolution of Fe minerals such as pyrite within the rock layer in Cases 1 and 2 (Figure 7b). In Case 3, Fe dissolution at $\text{pH} < 3$ may have resulted from either partial dissolution of Fe from the sorption layer or sorption saturation, potentially triggering secondary As release from the adsorbent layer [59,60]. At pH 3 to 5, Fe leaching concentration fluctuated between 8.8 and 23 mg/L, likely due to the formation of Fe oxide and/or oxyhydroxide [60,61]. At pH of 5 to 7, Fe leaching concentration remained relatively high, primarily derived from Fe-based adsorbent.

Figure 7c shows the relationship between Ca and pH. Calcium leaching remained above 400 mg/L within the pH range of 3–7 but declined sharply at $\text{pH} < 3$, indicating that Ca-based components were released from the Fe-based adsorbent. This depletion implies that the Ca-based component likely played a minor role in neutralizing acidic leachates. The simultaneous decrease in pH and Ca leaching concentrations further supports this inference [62].

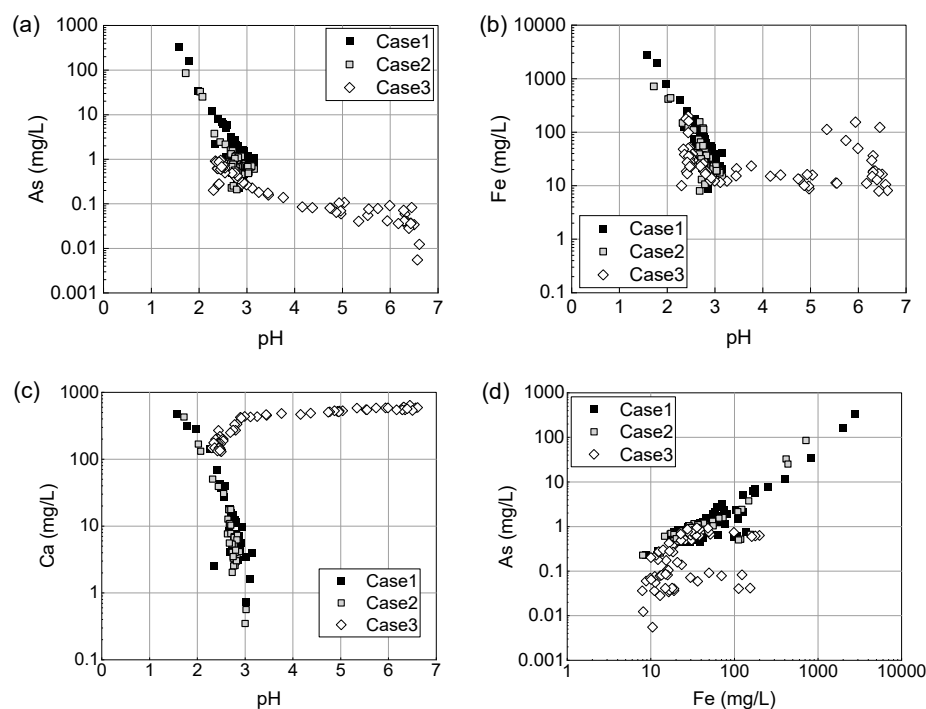


Figure 7. Relationship in effluent quality between; (a) As and pH, (b) Fe and pH, (c) Ca and pH, and (d) As and Fe.

Figure 7d shows the relationship between As and Fe. A strong positive correlation was observed in Cases 1 and 2, attributed to the dissolution of pyrite, which concurrently released Fe and As from the rock layer. This suggests that As mobilization was primarily driven by the oxidation and dissolution of As contained within the pyrite.

Principal component analysis (PCA) further supports these trends, showing strong correlations between As, EC, Fe, SO_4^{2-} and the major coexisting ions (Tables S6 and S7). In Case 3, however, pH, SO_4^{2-} , K^+ , and Ca^{2+} had high PC1 loadings (>0.33), while As and Eh exhibited strong negative correlations (<-0.36), suggesting that As reduction was primarily controlled by increasing pH and decreasing Eh. This highlights the critical role of the Fe-based sorption layer in pH stabilization and As immobilization.

In Case 3, As-Fe correlation was less distinct due to variations in their leaching patterns across different pH levels (Figure 7d). The pH remained neutral to slightly acidic up to $L/S = 15$ due to the effect of the Fe-based adsorbent containing the Ca-based component, favoring As sorption (Figure 6a,c). Beyond $L/S = 15$, pH gradually declined, leading to increased As and Fe leaching. At $L/S > 20$, pH dropped below 3, and As leaching exceeded 0.3 mg/L (Figure 6a,c,d). This trend suggests that while the Fe-based sorption layer was initially effective in As retention and pH buffering, the depletion of Ca-based components led to acidification and subsequent As release. This is thought to be the reason why a complex correlation between As and Fe was observed only in Case 3.

3.6. The Predicted Predominant Speciation of as and Fe in the Sorption Layer

To gain insights into the predominant speciation of As and Fe in Case 3, an Eh-pH diagram was depicted in Figure 8a–d. The Eh-pH diagrams for Cases 1 and 2 were also provided in Figure S8a–d. The As was predominately present as H_2AsO_4^- whereas Fe existed primarily as hematite (Fe_2O_3) (Figure 8a,b). XRD analysis confirmed the presence of magnetite and Fe hydroxide, such as ferrihydrite, in addition to hematite, prompting the inclusion of stability diagrams for magnetite and $\text{Fe}(\text{OH})_3$ (Figure 8c,d). Previous studies have demonstrated that H_2AsO_4^- exhibits strong affinity for Fe oxides and oxyhydrox-

ides [60,61,63,64]. Moreover, Eh-pH diagram described in this study showed that As in the effluent from the column in Case 3 exists mainly as H_2AsO_4^- . Insights gained from Eh-pH diagrams and previous studies suggest that, under experimental conditions, As released from the rock layers can be adsorbed by the sorption layer as arsenate.

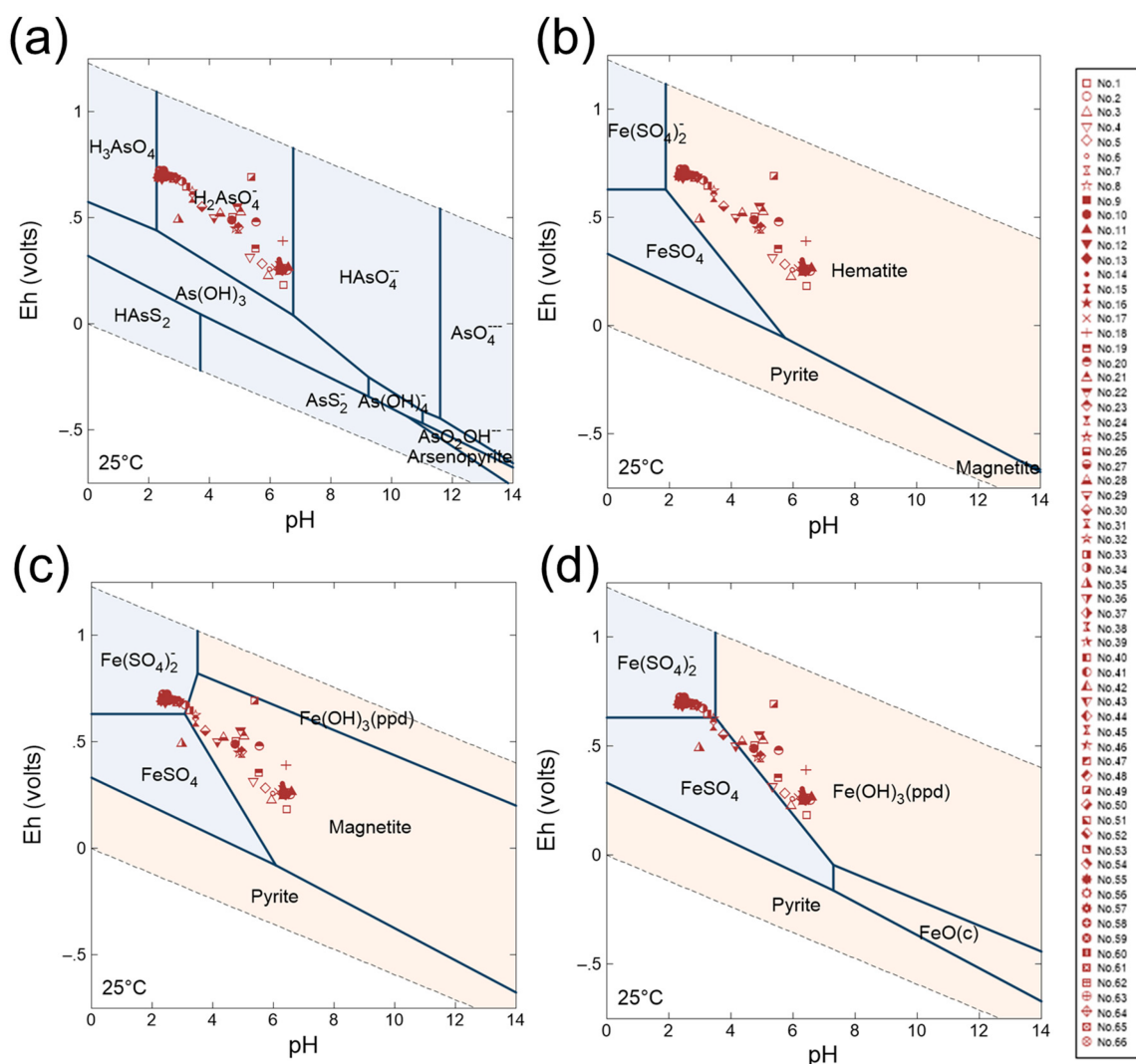


Figure 8. Eh-pH predominance diagram of (a) As, (b) Fe, (c) Fe suppressed hematite and goethite to show the stability of magnetite, and (d) $\text{Fe}(\text{OH})_3$ suppressed hematite, goethite, and magnetite to show the stability of $\text{Fe}(\text{OH})_3$ at 25 °C, 1.013 bars. Plots represent the actual Eh and pH measured during the column experiment in Case 3. No. 1 to No. 66 in the legends refer to the number of times leachate was collected in Case 3.

In addition, hematite, an Fe oxide, effectively adsorbs As even under acidic pH conditions [40,50,51]. Other Fe forms, such as magnetite and $\text{Fe}(\text{OH})_3$ also have good sorption performance for As [50,65]. However, magnetite and $\text{Fe}(\text{OH})_3$, having good performance for As sorption, may become soluble and less effective in reducing As under acidic environments, such as $\text{pH} < 3$, observed in column experiments for Case 3.

A slight increase in As leaching concentration in Case 3 was observed when L/S exceeded 15, attributed to the saturation of the Fe-based sorption layer (Figure 6c). This suggests that while hematite remained stable and As was retained as arsenate, sorption capacity diminished over time, leading to a plateau in As concentrations. The results underscore the importance of considering sorption capacity thresholds when using Fe-based adsorbents for As remediation in pH-variable environments. Additionally, the

decline in pH observed in the latter half of the experiment in Case 3 is believed to be due to the exhaustion of the Ca-based component within the Fe-based adsorbent. This component initially provided pH buffering capacity, reaching its limit, consequently diminishing its efficacy to neutralize pH, and leading to decreasing pH.

4. Conclusions

This study investigated the efficacy of the sorption layer system in which the As-containing excavated rock was classified into two fractions: the finer fraction of the rock was mixed with Fe-based adsorbent, which was utilized as a bottom sorption layer, while the coarser fraction was placed above it. This method aims to develop effective strategies for managing altered excavated rocks prone to producing acidic leachate with high As concentrations. The key findings are summarized as follows:

1. Batch leaching tests under both shaking and stirring conditions of four particle size distributions revealed a negative correlation between particle size and As leaching. Shaking conditions exacerbated As leaching since particle size decreased with time, whereas stirring conditions did not significantly affect As leaching nor alter particle size, highlighting the role of particle size in As leaching.
2. The addition of more than 1% Fe-based adsorbent to sieved rock with a particle size under 9.5 mm effectively reduced As leaching to below 0.3 mg/L. Additionally, this rock sample mixed with the Fe-based adsorbent demonstrated with the performance of As sorption, indicating their potential for As remediation.
3. Column experiments, designed based on As sorption performance by finer rock samples mixed with Fe-based adsorbent, confirmed the sorption layer's capability to sequester As over an extended period, suggesting that leached As primarily exists as H_2AsO_4^- and is reduced by Fe components inside the sorption layer. The depletion of the Ca component in the sorption layer likely leads to a shift from circumneutral to acidic pH in the leachate as well as partial remobilizing the As from the Fe minerals such as magnetite and $\text{Fe}(\text{OH})_3$, in the sorption layer.
4. Based on the results, the concept of the classification of grain size of excavated rock and sorption layer, consisting of fine rock with an adsorbent, is a promising method when only rock samples are available.

These results provide key insights into the system's design specifications, such as the particle size of the rock layer and the ratio of adsorbent added, as demonstrated in Figure S9. A significant outcome of this study is the demonstration that fine-classified As-containing excavated rock could be used as the base material for the sorption layer system, eliminating the need for a clean base material. Applying this system in construction projects suggests that excavated rocks could be repurposed as embankment materials with minimal adsorbent addition, complemented by other measures as impermeable sheets. This approach reduces the application of countermeasures to the entire excavated rocks and avoids disposal at waste disposal sites. This is expected to contribute to the utilization of excavated rocks as construction materials for embankments, as a resource, and promotes the reduction of waste, rather than treating the excavated rocks as waste.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min15030242/s1>, Figure S1: The borehole core sample used in this study. The core samples within the red frame were used for the experiments; Figure S2: Rock samples classified after air drying; (a) <2.0 mm, (b) 2.0–9.5 mm, (c) 9.5–19.0 mm, and (d) 19.0–37.5 mm; Figure S3: Conceptual schematic of batch tests; (a) shaking test using shaker, (b) stirring test using stirring device, and (c) serial batch leaching test; Figure S4: Conceptual schematic of batch immobilization test; Figure S5: Conceptual schematic of batch sorption test; Figure S6: Changes of particle size of the rock sample

after batch leaching experiments in triplicate under (a) shaking condition and (b) stirring condition; Figure S7: Effects of the sorption layer on the quality of the effluent; (a) volume of collected effluent, (b) EC changes with time, (c) Na^+ concentration changes with time, (d) K^+ concentration changes with time, (e) Mg^{2+} concentration changes with time, (f) Al concentration changes with time; Figure S8: Eh-pH predominance diagram of (a) As in Case 1, (b) Fe in Case 1, (c) As in Case 2, and (d) Fe in Case 2 at 25 °C, 1.013 bars. Plots represent the actual Eh and pH measured during the column experiment in Cases 1 and 2. No. 1 to No. 66 in the legends refer to the number of times leachate was collected in Cases 1 and 2; Figure S9: The flowchart for designing the combining of grain size classification of excavated rock and sorption layer consisting the mixture of rock and adsorbent; Table S1: The condition of the batch sorption tests; Table S2: The condition of the column experiments; Table S3: The mineral composition of used samples; Table S4: The chemical composition of used samples; Table S5: Fitted Langmuir isotherm parameters for the sorption of As into the excavated sieved rock samples with Fe-based adsorbent; Table S6: The results of principal component analysis of column experiments in Case 1 to 3; Table S7: Correlation of pH, EC, Eh, Al, As, Fe, SO_4^{2-} , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} of column experiments in Cases 1 to 3.

Author Contributions: Conceptualization, D.I. and T.I.; formal analysis, D.I., T.A., S.S. and Y.K.; methodology, D.I., T.A., S.S. and Y.K.; validation, D.I., T.A., S.S., Y.K., K.I., W.M. and T.I.; investigation, D.I., T.A., S.S. and Y.K.; resources, D.I., T.A., S.S., Y.K. and K.N.; data curation, D.I., T.A., S.S. and Y.K.; writing—original draft preparation, T.A.; writing—review and editing, D.I., T.S., K.N., W.M. and T.I.; visualization, D.I., T.A., S.S. and Y.K.; supervision, K.I. and T.I.; project administration, D.I. and T.A.; funding acquisition, D.I., T.A. and T.I. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: Daisuke Ishigami, Satoshi Shinohara, Yutaka Kamijima, Keijirou Ito, Tasuma Suzuki, Keita Nakajima are employees of companies. The paper reflects the views of the scientists and not the company.

Abbreviations

The following abbreviations are used in this manuscript:

PTEs	Potentially Toxic Elements
PV	Pore Volume
L/S	Liquid-to-Solid Ratio
PCA	Principal Component Analysis

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