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Leaching behavior of geogenic arsenic from marine sediments in chemical and biochemical batch leaching tests

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ABSTRACT

Soils containing geogenic arsenic (As) are widely distributed in Japan. With the amendment of soil contamination regulations, soils containing geogenic contaminants have been allowed to be utilized as geomaterials in limited conditions. However, a standard evaluation procedure on the long-term leaching behavior of As under anaerobic conditions has not been established. This research compared the leaching behavior of As from environmentally-qualified marine sediments in long-term batch leaching tests under reductive conditions brought about by chemical and biochemical methods to help improve the As leaching investigation procedure. Sodium ascorbate was employed as a chemical reducing agent with different concentrations. Glucose, ethanol, and sodium lactate were selected as biological nutrition sources. Testing results indicated that a reductive environment could significantly promote the leaching of As. The leaching of As was highly correlated with iron leaching. Under the chemical reducing conditions, a reductive environment could be realized in a short term and kept stable for the long term, and ORP varied with the concentration of the reducing agents. The concentration of leached As reached concentrations exceeding the environmental regulation of 0.01 mg/L. Under the biochemical reducing conditions, the leaching of As varied with the nutrition sources, and the release of As was followed by stronger resorption, indicating the effect of bio-activities on the leaching behavior of As.

Keywords: arsenic, marine sediments, reductive condition, chemical methods, biochemical methods

1 INTRODUCTION

The construction of large-scale infrastructure is always accompanied by a large amount of excavated soil. In Japan, the excavated soils are encouraged to be reused as geomaterials in landfill works on basis of environmental investigation. Since the amendment of Soil Contamination Countermeasures Act (SCCA) in 2017, soils containing designated geogenic heavy metals and metalloids have been allowed to be utilized as geomaterials in more conditions (Ito & Katsumi, 2020). Because of the wide distribution of geogenic toxic matters, such as lead (Pb), arsenic (As), and selenium (Se) (Okumura, et al., 2007), the risks in the disposal and reuse of excavated soils need more accurately investigation.

Currently, the appendix of No.46 Notification of the Ministry of the Environment issued in 1991 is referred as the standard soil leaching tests (No.46 Tests) to investigate the leaching condition of the designated hazardous matters in the soil. No.46 Tests are batch leaching tests using the mixture of distilled water and soil materials at an L/S ratio of 10:1 to shake for 6 hours. However, in the landfill works, an anaerobic environment tends to be formed because of a lack of access to oxygen and the activities of microorganisms, affecting the redox potential in the ground (Ivanov & Chu, 2008). As an experimental method conducted in the open condition, No.46 Tests are insufficient to investigate the long-term leaching behavior of heavy metals in a reductive condition. On the other hand, for As, Cr, and other elements of which chemical speciation is affected by redox potential, appropriate experimental methods are needed to quantitatively evaluate the leaching behavior under a reductive condition, so that promote a safe and reasonable utilization of the soils.

In the laboratory tests, reductive conditions can be realized by using chemical reducing agents or biochemical reducing processes (Chatain et al., 2005a; Chatain et al., 2005b). However, seldom

research has been made to compare these two methods by using the same material containing geogenic As. The objectives of this research were to (i) establish a reliable and convenient investigation procedure of geogenic As under reductive conditions, making the conditions controllable, and (ii) identify the changes in the chemical properties by using chemical reducing agents or biochemical reducing processes in the long-term tests. By realizing these targets, it is expected to help improve the reliability of As leaching investigation, promote the reuse of soil materials, and provide an example for other leaching tests under similar conditions.

2 MATERIAL AND METHODS

2.1 Material

The materials used in this research are As-containing marine sediments excavated from a depth of about 10 m in a coastal area of Hyōgo Prefecture, Japan. According to the sampling depth and the land use history, the As contained in the materials is considered geogenic rather than artificial-originated. The sediment was air-dried at room temperature for one day, sieved through 2 mm before conducting all the tests. The basic properties of the material are given in Table 1, of which total As and leaching As are below the environmental regulations in SCCA (Total As content< 150 mg/kg, As leaching concentration< 0.01 mg/L).

Table 1. *Basic properties of the material*

Soil particle density (g/cm^3)	pH[a]	Total As content[b] (mg/kg)	Leaching As concentration[a] (mg/L)	Major chemical components
2.69	8.2	11.0	0.0033	SiO_2: 52.3% Al_2O_3: 16.5% Fe_2O_3: 15.7% K_2O: 8.4% CaO: 3.6% TiO_2: 1.7%

[a] Determined by No.46 Tests.
[b] Determined according to JIS K 0470.

2.2 Batch leaching tests using chemical reducing agents and biochemical reducing processes

2.2.1 Experimental setups and procedure

The experimental setups are modified from a redox-pH control system developed by Masscheleyn et al. (1990) to realize sequential sampling, given in Figure 1. Sealed glass Erlenmeyer flasks of 1 L were employed to contain the samples, connecting with a gas pump to provide pure nitrogen gas, a sampling-recharging tube, and a liquid seal pot. Prepare suspension for each condition using 100 g of marine sediments with 1000 mL of chemical reducing agents or nitrogen sources (L/S ratio = 10). After sealing the flask, pump nitrogen gas for 20 minutes to remove the dissolved oxygen (DO) to lower than 0.5 mg/L. The suspensions were stirred with magnetic stirrer at 500 rpm for 5 minutes per day.

Sampling was conducted every two days until the fourth week. Inject nitrogen gas to provide stable air pressure and extract 20 mL of the supernatant in the depth of 60 cm by syringe as the test liquids for detection. Detect ORP value with electrode (HORIBA 9615s) immediately after sampling, and record the real-time value after 3 minutes. Then measure pH (by HORIBA 9300) and EC (by Laqua ES-71), pass the test liquids through a 0.45 μm membrane filter, and then analyze As, Fe, Al, Ca, and Mg using MP-AES (Agilent 4210 MP-AES). After sampling, recharge the same solution (or distilled water) through the charge tube to the former volume and bubble the suspension with nitrogen gas for 10 minutes.



Figure 1. *Diagram of the experimental setups (left). Photo of the actual test cases (right).*

2.2.2 Chemical reducing conditions

In this part, sodium ascorbate was chosen because it is a mild and common reducing agent. All the conditions were conducted under continuous natural light or lamp illumination (light condiition) at 20°C. Sodium ascorbate solutions in different concentrations were used and compared with a blank case using distilled water. The initial chemical properties of the solutions are given in Table 2.

Table 2. *Initial properties of the solutions*

Solvent	Concentration	pH	ORP (mV)	Note
Distilled water (DW)	0	7.1	190	Add 1 mg/L of resazurin as indicating medicine
Sodium ascorbate	0.1 M	6.9	-166	
	0.05 M	6.9	-155	
	0.02 M	7.1	-143	

A comparison tests were conducted in sealed plastic bottles to investigate the influence of the sampling and recharge operations. Distilled water and 0.02 M sodium ascorbate were used to mix up with the materials at an L/S ratio of 10 and fully filled 250 mL plastic bottles. After pumping nutrition gas for 20 minutes, the bottles were tightly sealed and incubated under light conditions at 20°C for 6h, 1 day, 3 days, 5 days, 7 days, 10 days, 14 days, 21 days and 28 days. The bottles were shaken at 200 rpm for 5 minutes every day (immediately after sealing for 6h cases). ORP and pH were immediately detected after open the bottles. The test liquids were prepared and the elements were analyzed using the same method in the section 2.2.1.

2.2.3 Biochemical reducing conditions

In this part, glucose and sodium lactate were chosen as nutrition resource, and ethanol was chosen as negative nutrition resource to incubate the soil-originated microorganisms to realize a reductive condition. This part was divided into two phases.

A pre-test phase was conducted to confirm the activation of the soil-originated microorganisms and the occurrence of biochemical reactions. Glucose solution (1 wt%) and sodium lactate solution (1.25 wt%) were used to mix up with the materials at an L/S ratio of 10 and fully filled 250 mL plastic bottles (maximum volume about 305 mL) and sealed them in the dark. A UV light sterilizer box was used to restrain the activity of microorganisms. According to the curing conditions, set three groups as a normal group, a sterilization group, and a blank group, as shown in Table 3.

Table 3. *The test conditions of the pretest in biochemical conditions*

Group	**Normal**		**Sterilization (UV)**		**Blank**	
Solvent	**Glucose**	**Na-lactate**	**Glucose**	**Na-lactate**	**Glucose**	**Na-lactate**
L/S ratio	10:1 (290 mL / 29 g)		10:1 (290 mL / 29 g)		No soil	
Sterilization	×		√		×	
Incubation	20°C in the dark for 14 days, turn upside down for 1 min every day					

After the pre-test, batch leaching tests using biochemical reducing processes were conducted. All the conditions were conducted in the dark at 20°C. Glucose solution (1 wt%), sodium lactate solution (2.49 wt%), ethanol solution (9.77 μL/g) were used, and compared with sodium ascorbate solution (1.1 wt%≈0.0055M). The concentrations were determined to ensure a same carbon content of 0.40 g/L. The initial chemical properties of the solutions are given in Table 4.

Table 4. *Initial properties of the nutrition resource*

Solvent	Concentration	pH	ORP (mV)	Note
Glucose	1 wt%	7.1	98	Add 1 mg/L of resazurin as indicating medicine
Sodium lactate	2.49 wt%	7.2	124	
Ethanol	9.77 μL/g	6.9	156	
Sodium ascorbate	1.1 wt%	7.0	-89	

3 RESULTS AND DISCUSSION

3.1 Chemical reducing conditions

3.1.1 Batch leaching tests using chemical reducing agents

The changes in pH, ORP, and leaching concentration of As with time are shown in Figure 2. In DW condition, the leaching concentration of As increased from 1.4 μg/L to 5.0 μg/L, which was close to the result of the No.46 Test, and mainly influenced by leaching time. The changes in ORP indicated that removing dissolved oxygen can reduce the redox potential, but the drop is not enough to show reductivity in the suspension.
On the other hand, in sodium ascorbate conditions, pH decreased with similar trends, while ORP distributed with the concentrations. The As concentrations exceeded the environmental regulation of 10 μg/L. The peak As concentrations appeared to be negatively correlated with reducing agents concentration, which were 22.9 μg/L, 23.6 μg/L, and 32.1 μg/L in 0.1 M, 0.05 M, and 0.02 M conditions.

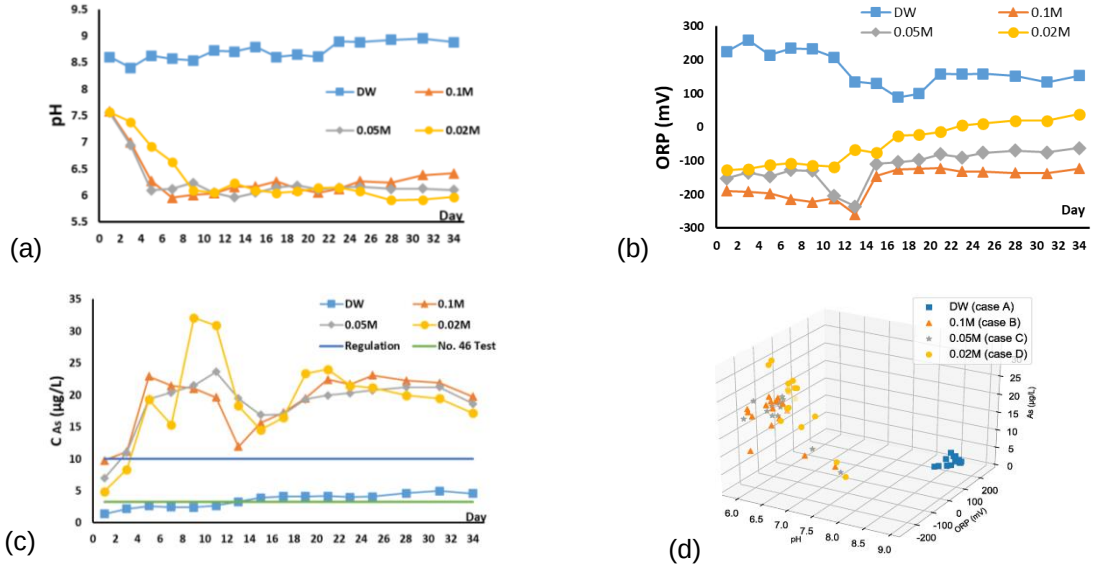


Figure 2 *Changes in (a) pH, (b) ORP, (c) As concentrations with time using reducing agents, and (d) pH-ORP-As concentration relationship*

Figure 2(d) shows the relationship of As concentration with pH-ORP system. The As concentrations were linearly correlated with pH (R=0.93, 0.97, 0.96 in 0.1 M, 0.05 M, 0.02 M) before reaching the peak. A range from -200 mV to -20 mV is beneficial for As leaching. This result indicates that As concentration was controlled by both pH and ORP.

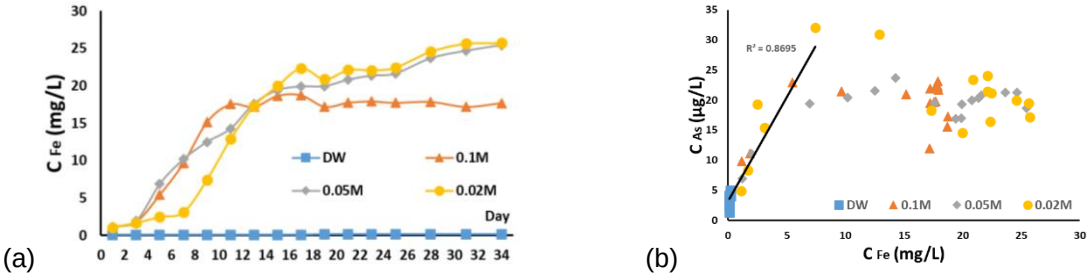


Figure 3 *(a) Changes in Fe concentrations with time and (b) Fe-As concentration relationship*

The concentrations of Fe, Ca, and Mg in DW condition were much lower than the sodium ascorbate conditions during the whole test period. Fe concentrations increased and balanced respectively in sodium ascorbate conditions. The concentrations of As and Fe were positively correlated (R^2=0.87) before the peak concentration of As, showing in Figure 3. This result indicated that under the reducing conditions of chemistry, the leaching of As is mainly associated with the changes in the chemical form of Fe. With the leaching of Fe increases, the As concentration no longer changes significantly, indicating

that As is mainly adsorbed on the surface of Fe oxide and can be adsorbed/desorbed again on the surface of the remaining Fe oxide with the progress of time. Ca and Mg concentrations increased with pH change (Figure 4), but the long-term stable concentrations were distributed into three levels with the concentration of sodium ascorbate solutions, which indicate that the leaching behavior of cations were affected by salt effect. As reported in previous researches (Bothe & Brown, 1999; Camacho et al., 2009), the existence of Ca can promote the sorption of As, reducing agents of high concentrations should be avoided when there are no significant differences in ORP and pH.

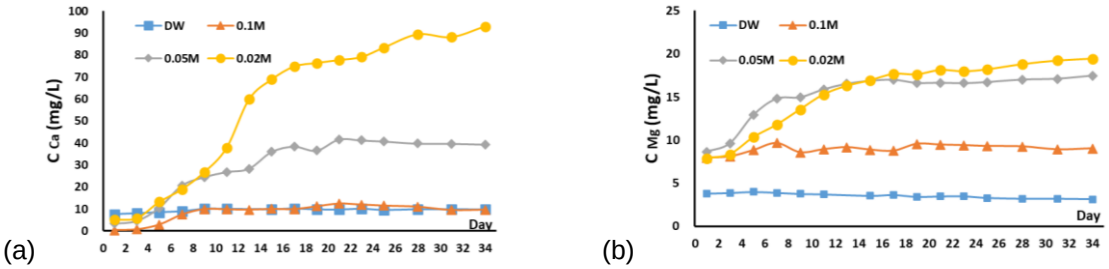


Figure 4 *Changes in (a) Ca and (b) Mg concentrations with time using reducing agents*

3.1.2 Comparison tests using 0.02 M sodium ascorbate

In comparison tests, the changes in pH and ORP with time in the two conditions matched the results in the batch leaching tests. As concentration kept a stable level after reaching the peak, reflecting the influence of sampling and recharging in the batch leaching tests. The positive linear correlation between As and Fe before the peak concentration of As was also observed, shown in Figure 13. The results of the comparison tests confirmed the reliability of the setups of the batch leaching tests, but the sampling times and interval should be well controlled to reduce the effect on As concentrations.

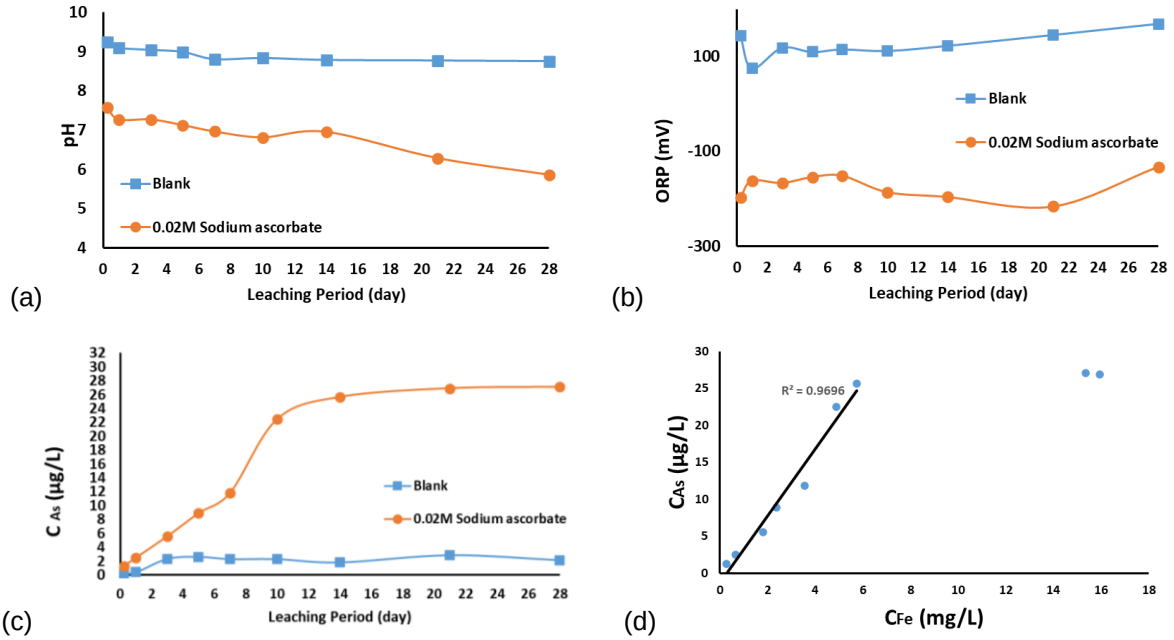


Figure 5 *Changes in (a) pH, (b) ORP, (c) As concentrations with time using reducing agents, and (d) As-Fe concentration relationship*

3.2 Biochemical reducing processes

3.2.1 Pretests to confirm microorganism activities

The results of pH, ORP, EC and leaching concentration of As after 14 days incubation in the pretest are shown in Figure 6. The results indicated that (i) glucose solution and sodium lactate solution did not directly act as strong reducing agents; (ii) The activity of soil-originated microorganisms not only consumed oxygen but also utilizes carbon-based nutrients to complete proliferation, producing byproducts with certain reducing properties; (iii) Under continuous sterilization, the activity of soil-

originated microorganisms is suppressed, manifested as a decrease in the generation of reductive substances and a reduction in the increment of EC.

3.2.2 Batch leaching tests using biochemical reducing processes

The changes in pH, ORP, EC and leaching concentration of As in different incubation conditions with time are shown in Figure 7. Generally, decrease in pH occurred in all the conditions, indicating the activation of microorganisms and production of bio-acid. The changes in ORP varied significantly with the nutrition resource. In conditions with sodium lactate and ethanol, ORP continuously decreased with time to around -260 mV. While in conditions with glucose and sodium ascorbate, ORP experienced a sharp decrease, increase and rebalance process. The reasons for the different trends in ORP in each condition may be attributed to differences in the microbial activity or variability of dominant species with varying resources of nutrients. It is noteworthy that the lowest and rebalanced ORP value in the sodium ascorbate group were lower than that in the chemical reducing groups, and a pungent smell also occurred in the solution, indicating a dark condition allowed sodium ascorbate to act as a nutrition resource and the biochemical factors may be dominant in the later stage.

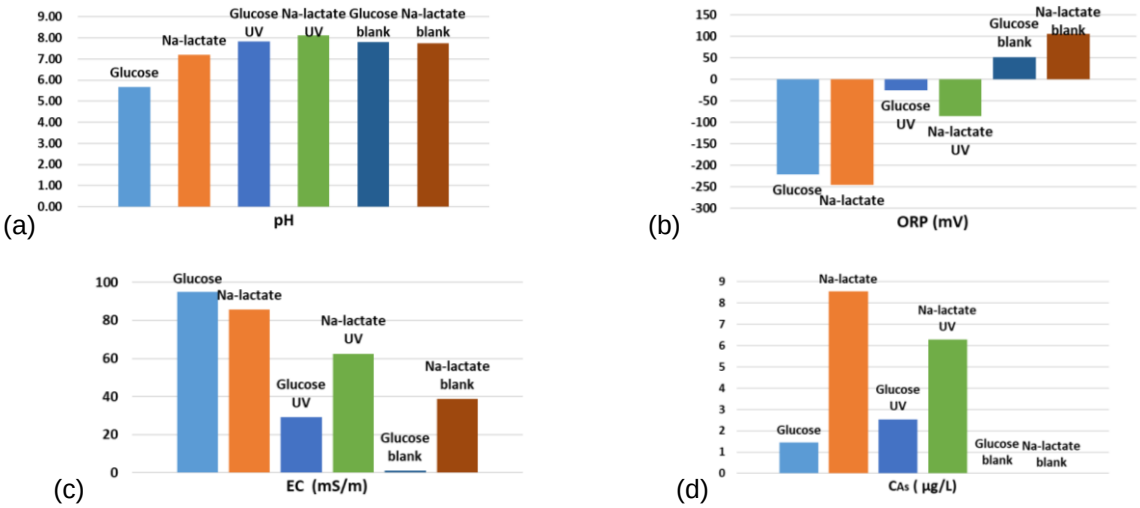


Figure 6 *Results of (a) pH, (b) ORP, (c) EC and (d) As concentration in different incubation conditions*

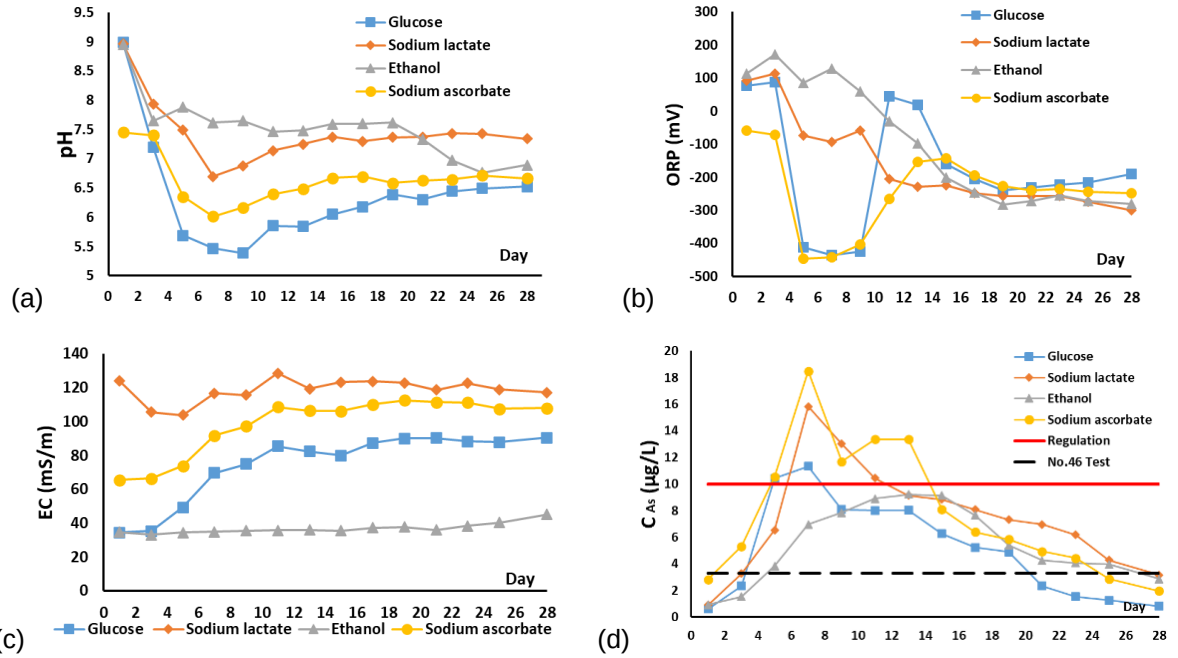
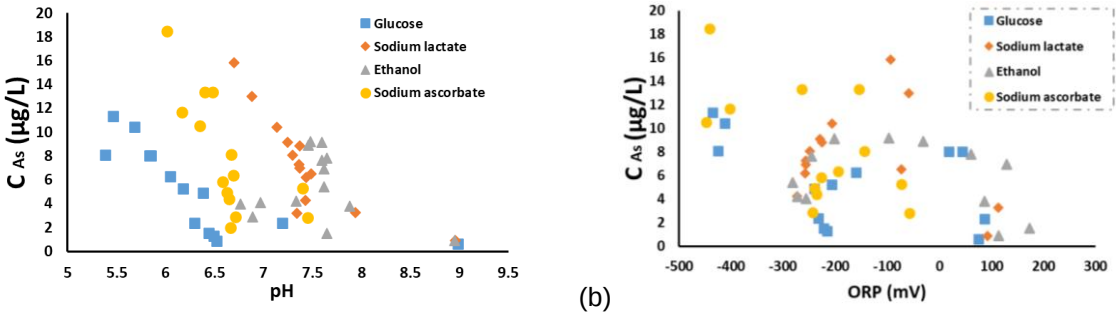


Figure 7 *Changes in (a) pH, (b) ORP, (c) EC and (d) As concentrations with time in different incubation conditions*

The changes in As concentration during the whole leaching period significantly differed with the chemical reducing agent groups, shown in Figure 7(d). A peak followed by a decrease in As concentration was observed in all the conditions, of which three peaks exceeded the regulation value (C_{As}=11.3 μg/L, 15.8 μg/L and 18.5 μg/L in condition glucose, sodium lactate and sodium ascorbate). The final concentrations of As in all the conditions were lower than the result of No.46 Test.

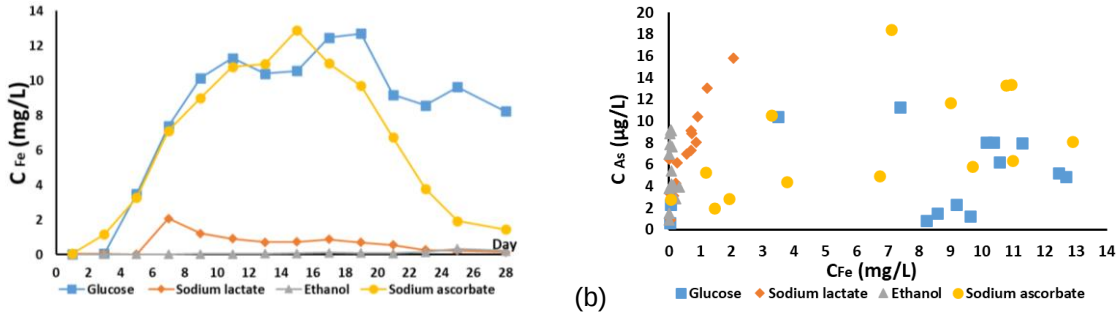
Before reaching the peak, negative correlations between As concentration and pH were observed in condition glucose (R=0.92), sodium lactate (R=0.94) and sodium ascorbate (R=0.92), shown in Figure 8(a). Similarly, negative correlations between As concentration and ORP were observed in condition glucose (R=0.96), sodium lactate (R=0.84) and sodium ascorbate (R=0.87), shown in Figure 8(b). The relationships were not clear in condition ethanol. These results confirmed the effect of pH and ORP on the leaching of As during the initial leaching out stage. On the other hand, considering the correlation varied with the additives, and no direct correlation was observed between As concentration with ORP or pH during the resorption period, biotic factors have been working during the whole leaching period and dominated the sorption of As.



(a) (b)

Figure 8 *Relationships of As concentration with (a) pH and (b) ORP*

The concentration of Fe with As also varied with the nutrition resources. In the glucose condition, As had similar increase and decrease trend with Fe, but no linear correlation was observed. In the sodium lactate condition, As was positively correlated with Fe (R=0.93) during the whole period. In the ethanol condition, Fe was not sufficiently released. In the condition with sodium ascorbate, As was positively correlated with Fe during the leaching period (R=0.99 until the 7th day) and the resorption period (R=0.97 from the 15th day to the end) respectively. These results indicated the highly co-releasing relationship between Fe and As in the pH range from 5.0 to 7.5.



(a) (b)

Figure 9 *(a) Changes in Fe concentrations with time and (b) relationship between Fe and As concentrations in different incubation conditions*

4 CONCLUSIONS

An experimental procedure and the setups for investigating the leaching behavior of geogenic As from marine sediments using chemical reducing agents and biochemical reducing processes were established. The leaching behavior of As and related elements was investigated by using distilled water, sodium ascorbate, glucose, sodium lactate, and ethanol in this research. The results reflected that this method can realize long-term batch leaching tests under reductive conditions, and allow sequential sampling and detection. Real-time control of chemical conditions is also expected to be realized in further tests. Considering the effects of sampling and recharging, improvements should be made in terms of total sample volume and sampling interval.

Chemical reducing agents can quickly and stably realize a predictable pH-ORP condition with less resorption. Biochemical reducing processes are expected to simulate the actual biochemical condition, but the mechanisms will be more complicated and vary with the nutrition sources, making the chemical condition unpredictable. The reducing agents or the nutrition resources should be added in low concentrations to minimized the effects on ion balance. The light condition is a key factor to initiate a biochemical reducing process. For organic reducing agents, a dark condition should be avoided when the bio-activity factors are not needed.

The results in both chemical-reducing conditions and biochemical conditions confirmed the importance of reductive conditions in investigating the contamination risk of a soil sample, especially for those which were considered environmentally qualified in common leaching tests. Under reductive conditions, linear correlations of As concentrations with pH and As concentrations with Fe concentrations were observed in conditions of sodium ascorbate, glucose, and sodium lactate before reaching the peak, indicating the pathway of As releasing from Fe-related chemical fractions.

In biochemical reductive conditions, stronger resorption processes dominated As concentrations because of bio-activities. Although the mechanisms remain uncertain, different pH-ORP trends indicate that differences in the microbial active or variability of dominant species with varying resources of nutrients can greatly affect the leaching behavior of As.

5 ACKNOWLEDGEMENTS

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REFERENCES

Ito, H., & Katsumi, T. (2020). Leaching characteristics of naturally derived toxic elements from soils in the western Osaka area: considerations from the analytical results under the Soil Contamination Countermeasures Act. Japanese Geotechnical Journal, 15 (1), 119–130.

Okumura, K., Sakurai, K., Nakamura, N., & Morimoto, Y. (2007). Environmental impacts of naturally-occurring heavy metals and countermeasures. Journal of Geography (Chigaku Zasshi), 116(6), 892-905.

Ivanov, V., & Chu, J. (2008). Applications of microorganisms to geotechnical engineering for bioclogging and biocementation of soil in situ. Reviews in Environmental Science and Bio/Technology, 7(2), 139-153.

Chatain, V., Sanchez, F., Bayard, R., Moszkowicz, P., & Gourdon, R. (2005). Effect of experimentally induced reducing conditions on the mobility of arsenic from a mining soil. Journal of hazardous materials, 122(1-2), 119-128.

Chatain, V., Bayard, R., Sanchez, F., Moszkowicz, P., & Gourdon, R. (2005). Effect of indigenous bacterial activity on arsenic mobilization under anaerobic conditions. Environment international, 31(2), 221-226.

Bothe, J. V., & Brown, P. W. (1999). Arsenic immobilization by calcium arsenate formation. Environmental Science & Technology, 33(21), 3806-3811.

Camacho, J., Wee, H. Y., Kramer, T. A., & Autenrieth, R. (2009). Arsenic stabilization on water treatment residuals by calcium addition. Journal of Hazardous Materials, 165(1-3), 599-603.