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Effects of changes in oxidizing and reducing environments on the characteristics of arsenic elution from excavated rocks

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ABSTRACT

The arsenic that occurs in rocks excavated during tunnel construction is a common issue in Japan. A landfill site in which arsenic-containing excavated rocks is deposited must deploy anti-diffusion measures to contain the eluate. Landfill designs generally do not account for excavation or landfill operations or changes in the environment to which these rocks are exposed once deposited. Typically, after excavation, the characteristics of the environment surrounding rocks change from reducing to oxidizing before reverting to a reducing environment when the rocks are deposited in a landfill site. Our study examined various methods for evaluating the effects of the changing oxidizing/reducing (redox) environment on arsenic elution based on elution tests using reducing agents. The arsenic in the rock samples used for this testing occurs in pyrrhotite. We confirmed that arsenic elution increases with pyrrhotite oxidation and that adding a reducing agent accelerates this elution. This tendency was observed in both batch and unsaturated column tests. This result shows that elution tests using reducing agents are at least somewhat effective in reproducing the arsenic elution from pyrrhotite that occurs naturally. In the future, we plan to verify whether tests using reducing agents can reproduce the elution that occurs at actual excavation sites and landfills.

Keywords: arsenic elution characteristics, redox environment, landfill, reducing agent, excavated rock

1 INTRODUCTION

The amount of an element contained in the Earth's crust and upper continental crust is known as abundance or Clarke number. It has been reported that the abundance of arsenic in the upper crust of the Japanese archipelago is 6.7-7.1 mg/kg, which is two to three times higher than the average abundance in the upper crust (Togashi et al. 2000). In addition, the ground that forms the Japanese archipelago is located in a place where the oceanic plate subducts into the continental plate, so complex strata are spreading. Among them, many strata containing arsenic due to hydrothermal alteration associated with volcanic activity have also been confirmed. Arsenic occurring in excavated rocks generated by tunnel construction in Japan, poses numerous issues. Arsenic in excavated rocks diffuses via water (typically, rainwater). For this reason, the landfills in which excavated rock is deposited must incorporate measures to prevent heavy metal diffusion.

Anti-diffusion measures fall into several categories. One such measure encapsulates arsenic in a water impermeable material—for example, bentonite mixed soil and a water impermeable sheet. Another absorbs the arsenic eluted from excavated rock into a layer at the bottom of a landfill to prevent outflow into the environment (Kamon et al., 2015). Landfill designs are based on geological surveys carried out in advance. Preliminary surveys and countermeasures are often carried out based on the "Manual for dealing with rocks and soil such as naturally occurring heavy metals in construction work (provisional version)". In this manual, the elution characteristics of hazardous substances are evaluated by conducting multiple types of tests on excavated rocks and other materials. On the other hand, these tests do not consider the change to an oxidizing environment due to atmospheric exposure from excavation to landfill disposal, or the change to a reducing environment due to biological or chemical action within the repository. Therefore, we think that a new evaluation method is necessary. In particular, arsenic is known to change its form according to changes in the redox environment, and its ease of

elution is known to change (Hiroshiro et al., 2008), so it can be said that it is important to consider the above environmental changes when considering disposal methods.

As a previous study, an elution test utilizing oxygen consumption by aerobic bacteria has been reported (Kamata et al. 2022). As a test method, it is highly likely that changes close to actual phenomena can be reproduced. On the other hand, we believe that there is a problem in that it is difficult to adjust the reducing power of the solvent. Our study examined the effectiveness of elution tests with reducing agents (sodium formate and sodium ascorbate) in evaluating the effects of changes in oxidizing/reducing (redox) environments on arsenic elution.

2 SAMPLES

The samples used in this study are rocks excavated during the construction of a mountain tunnel in Iwate Prefecture. Since these rocks contain arsenic, they had been encapsulated at a landfill in a bentonite mixed soil, from which we obtained the samples. The tunnel site lies in an accretionary complex formed from the Jurassic to the Cretaceous periods of the Mesozoic Era (Takahashi et al., 2016); the rock samples are primarily shale and sandstone from this stratum.

The samples were collected with a backhoe from the landfill on June 19, 2019. To preserve the grain size composition inside the embankment, the excavated rocks were promptly sealed in flexible containers. In addition, for the convenience of the handling anticipated in laboratory tests, the samples in each flexible container were separated with a 100-mm mesh sieve into large and small rocks. They were placed separately in flexible containers once again and stored (Figure 1: Particle size distribution of samples).

Certain samples contained quartz or calcite veins, apparent traces of the passage of hot water. The sandstone was tinged an overall green indicating a slight metamorphism. No correlation was observed between rock type and the amount of arsenic eluted. We found samples characterized by high elution among all rock types (Iwamoto et al., 2020).

Shale was randomly selected from a flexible container and crushed into particles of 2 mm or smaller. These crushed samples were subjected to the arsenic elution test (Manual for dealing with earth and sand containing naturally derived heavy metals in construction work, Review Committee, 2010). The resulting concentration was 0.015 mg/L. We also performed total arsenic content analysis by Japan's sediment survey method, which returned a result of 9.5 mg/kg. Specimens of sandstone and shale cut into thin slices and subjected to EPMA analysis showed that arsenic occurred in pyrrhotite with a maximum content of 0.17%.

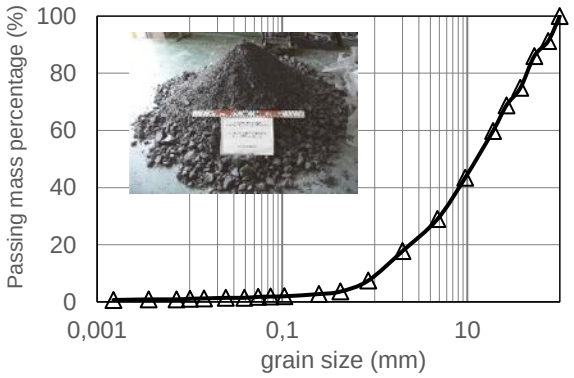

Figure 1. *Particle size distribution of samples*

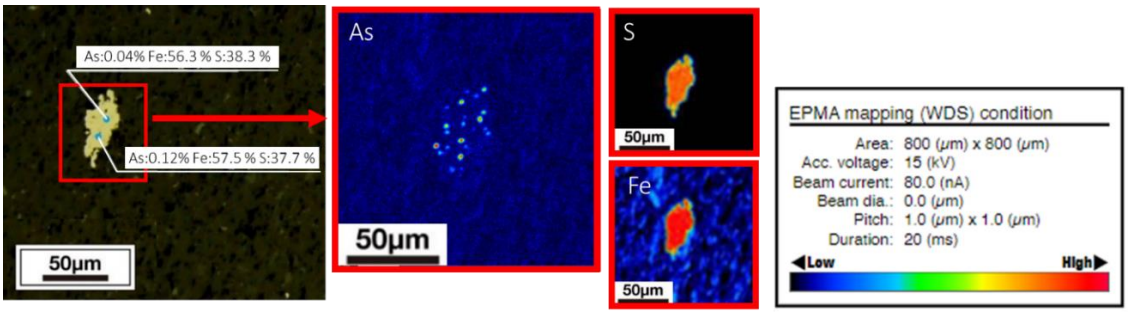

Figure 2. *Results of EPMA analysis*

3 TEST METHOD

We first performed a batch test to determine whether changes in redox environments affect the amount of arsenic eluted. Next, we performed column test, whose conditions were closer to field conditions, to evaluate arsenic elution in a landfill. Since the environment inside the landfill is not saturated, the arsenic in the rocks is eluted by the infiltrated rainwater. Therefore, an unsaturated column test in which water was sprinkled from the upper part of the column was adopted.

3.1 Batch test

After rocks are excavated, their surrounding environment becomes oxidizing; when they are buried in a landfill, the environment becomes reducing. To evaluate this process, we crushed and cured rock samples at 20°C. Specimens were taken from these samples at regular intervals and subjected to the elution test with a reducing agent. The reducing agents used here were sodium formate and sodium ascorbate. The test was performed as follows:

(1) Randomly take several samples ranging from 70 mm to 100 mm from a flexible container.
(2) Cut and separate about 1 cm of material from the surface of the samples. (Figure 3)
(3) Crush the surfaces and internal rock separately into 2.0 mm or smaller pieces.
(4) Add the specified quantity of a reducing agent to purified water to prepare a reducing agent solution (Table 1: Reducing agent solution concentrations).
(5) Place 30 g of the test specimens created in (3) above and 300 ml of the reducing agent solution prepared in (4) into a plastic bottle.
(6) Shake for six hours at 200 rpm/min over a span of 4 cm to 5 cm.
(7) Take the supernatant of (6) and centrifuge for 20 minutes at 3,000 rpm/min.
(8) Filter the supernatant in (7) with a 0.45-μm membrane filter.
(9) Using (8) as a test solution, measure the redox potential, arsenic concentration (ICP-MS), total iron concentration (ICP-AES), and sulfate ion concentration (IC).
(10) Cure the remaining specimens of the internal rock created in (3) in a room at 20°C. Take specimens from them at regular intervals and repeat steps (4) to (9) using the specimens.

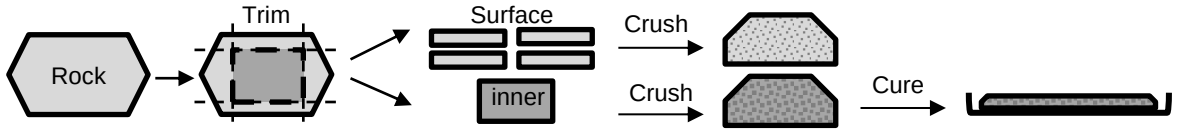

Figure 3. *Sample processing flow*

Table 1. *Reducing agent solution concentrations*

Reducing agent type	Reducing agent concentration (mg/L)	Solvent Eh (mV)	Sample name
Not used	-	460.0	Non
Sodium formate	0.05	316.3	Sf-0.05
	0.1	265.8	Sf-0.1
	0.2	222.2	Sf-0.2
Sodium ascorbate	0.05	86.7	Sa-0.05
	0.1	59.7	Sa-0.1
	0.2	29.7	Sa-0.2

3.2 Unsaturated column test

We randomly removed several rock samples from a flexible container. The samples were crushed and separated with 2.0 mm and 10 mm sieves to obtain test specimens ranging from 2.0 mm to 10.0 mm in diameter. Columns, each made of a PVC tube with a diameter of 50 mm and a height of 500 mm, were filled with the specimens up to a height of 300 mm. When the sample was filled, the water content was about 2.7% and the porosity was about 35%. A reducing agent solution was drizzled at a rate of 180 mL/hour from a sprinkler equipped with nine plastic needles, each with a bore of 0.19 mm (Figure 4: Unsaturated column test apparatus). We prepared the reducing agent solution used here by dissolving a reducing agent in purified water, generated by removing impurities with a water purifier (Kuribomber KB made by Kurita Water Industries). (Table 2: Reducing agent solution concentrations) We then measured the redox potential of the eluate from the test apparatus and measured arsenic concentration (ICP-MS), total iron concentration (ICP-AES), and sulfate ion concentration (IC) by collecting water at regular intervals. Since the iron concentrations of most specimens were below the quantitation limit, this paper shows only the measurement results for arsenic and sulfate ion concentrations.

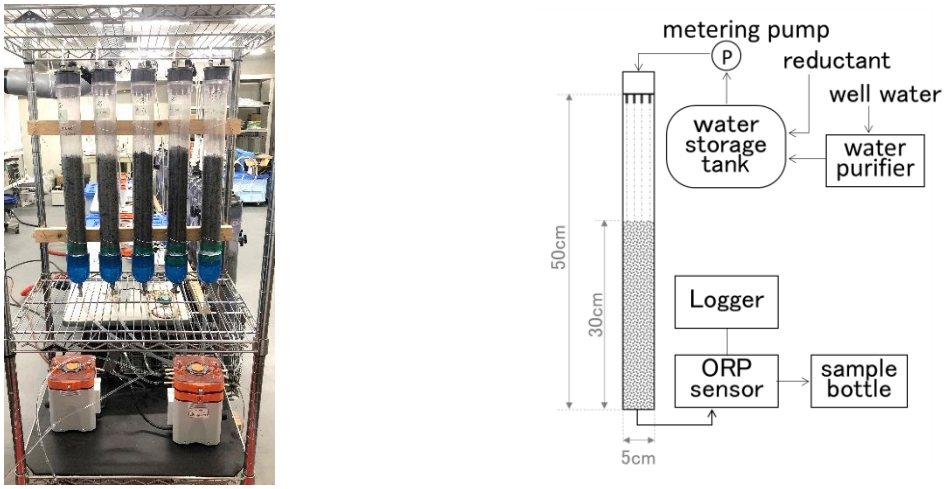

Figure 4. *Unsaturated column test apparatus*

Table 2. *Reducing agent solution concentrations*

Reducing agent type	Reducing agent concentration (mol/L)	Solvent Eh (mV)	Sample name
Not used	-	460	C-Non
Sodium formate	0.005	350	C-Sf-0.05
	0.05	278	C-Sf-0.1
	1.0	195	C-Sf-0.2

4 RESULTS

4.1 Batch test

Since the arsenic in the sample rocks occurred in pyrrhotite, we measured the amounts eluted of arsenic, iron, and sulfate ions.

4.1.1 Arsenic

Figure 5 shows the relationship between the amount of arsenic eluted and redox potential. Figure 6 shows the relationship between the amount of arsenic eluted and length of exposure to the atmosphere after crushing.

The correlation observed between the amount of arsenic eluted and the redox potential was negative. When Eh was about the same, samples exposed longer to the atmosphere tended to exhibit higher arsenic elution concentrations. The lower the Eh, the more widely arsenic elution concentrations varied.

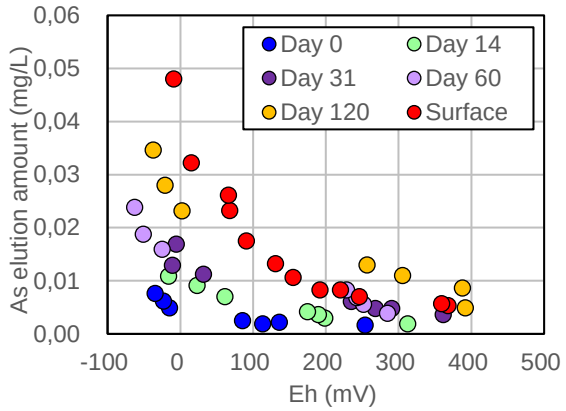

Figure 5. *As elution amount - curing period*

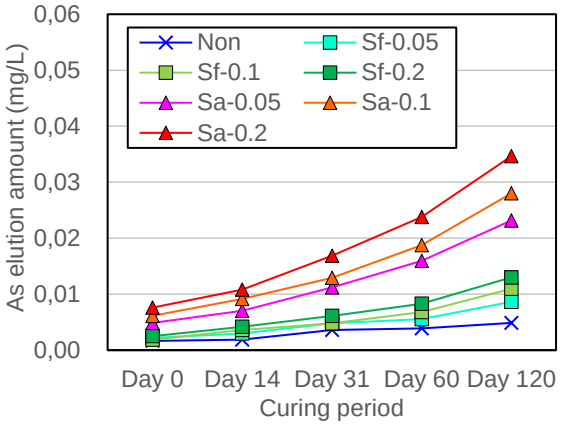

Figure 6. *As elution amount - redox potential*

4.1.2 Iron

Figure 7 shows the relationship between the amount of iron eluted and redox potential. Figure 8 shows the relationship between the amount of iron eluted and length of exposure to the atmosphere after crushing. Figure 8 excludes the results of the test using a sodium formate solution and purified water as a solvent because the amounts eluted of all specimens were below the quantitation limit.

As shown in Figure 7, the amount eluted increases when the redox potential falls below approximately 100 mV. Figure 8 shows that the amount of iron eluted declines with longer exposure to the atmosphere. The extent of this decline did not differ for different solvents. In contrast, the highest amount of iron eluted was observed with the surface sample considered to be most oxidized. This result suggests that the amount eluted is likely to increase as oxidation further progresses or that surface samples were previously altered by factors other than oxidation.

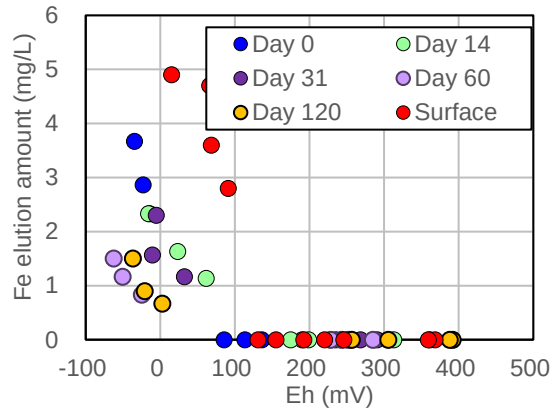

Figure 7. *Fe elution amount - redox potential*

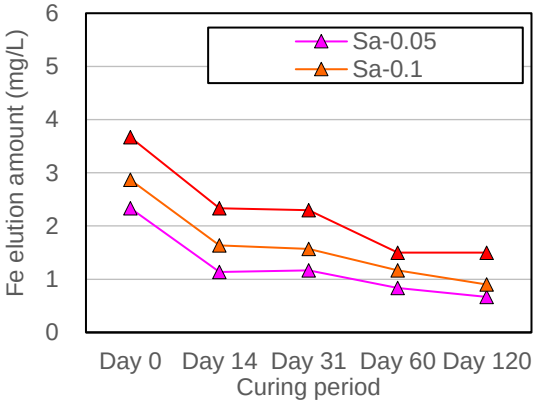

Figure 8. *Fe elution amount - curing period*

4.1.3 Sulfate ions

Figure 9 shows the relationship between amounts of sulfate ion eluted and the redox potential. Figure 10 shows the relationship between amounts of sulfate ion eluted and length of exposure to the atmosphere after crushing. The concentrations could not be determined in the test using a sodium ascorbate solution as a solvent, except for the surface samples, because the peaks overlapped those of other substances.

With the surface samples, the correlation between the redox potential and amounts of sulfate ion eluted was negative. However, no significant differences were confirmed in the other samples because the amounts eluted were too small. The sulfate ion amounts eluted tended to increase with longer exposure. The amount eluted of the surface sample considered most oxidized was 200 times greater than the amount eluted immediately after crushing.

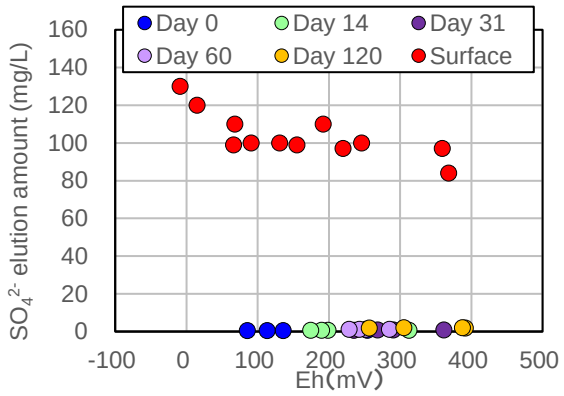

Figure 9. SO_4^{2-} *elution amount - redox potential*

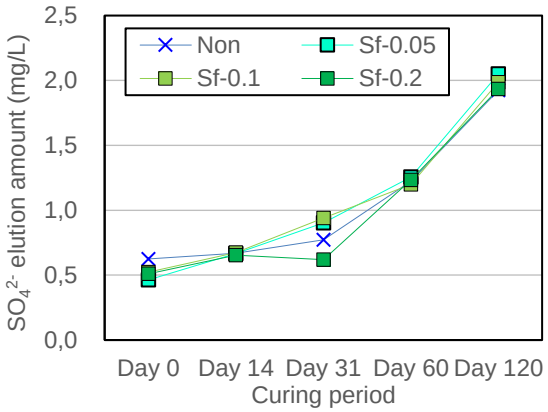

Figure 10. SO_4^{2-} *elution amount - curing period*

4.2 Unsaturated column test

4.2.1 Arsenic

Figure 11 shows the relationship between the arsenic concentration of the eluate and the liquid to solid ratio of the solvent to the sample in a column. Figure 12 shows the relationship between the arsenic concentration of the eluate and the redox potential of the eluate.

In all tests, regardless of solvent, the arsenic concentration of the eluate decreased immediately after the addition of the solvent. As with the batch test, in the unsaturated column test, the amount of arsenic eluted tended to increase as the redox potential decreased. The difference in amount eluted between the first measurement (liquid to solid ratio: approx. 0.3) and the second measurement (liquid to solid ratio: approx. 1.0) was larger with redox potentials of 200 mV to 100 mV than redox potentials of 300 mV to 200 mV. Batch tests showed similar tendencies.

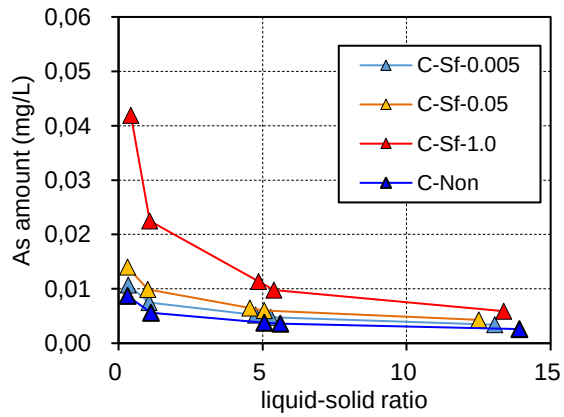

Figure 11. As *amount - redox potential*

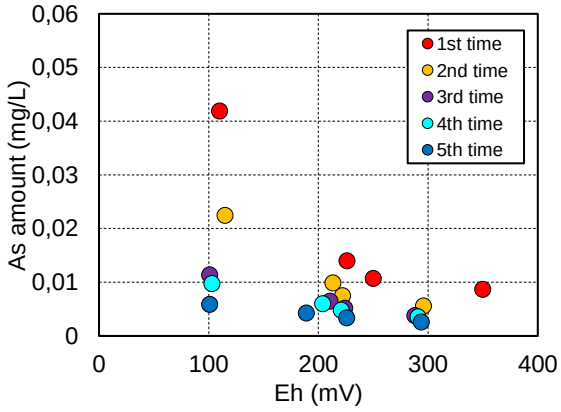

Figure 12. As *amount - curing period*

4.2.2 Sulfate ions

Figure 13 shows the relationship between the sulfate ion concentration of the eluate and the liquid to solid ratio of the solvent to the sample in a column. Figure 14 shows the relationship between the sulfate ion concentration of the eluate and the redox potential of the eluate.

As with arsenic, sulfate ion concentrations immediately declined after the addition of the solvent. Sulfate ion concentrations were higher when the redox potential was lower, a finding confirmed in batch tests of surface samples.

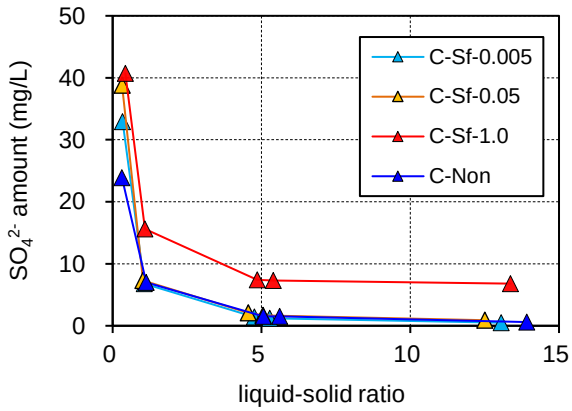

Figure 13. SO_4^{2-} *elution amount - redox potential*

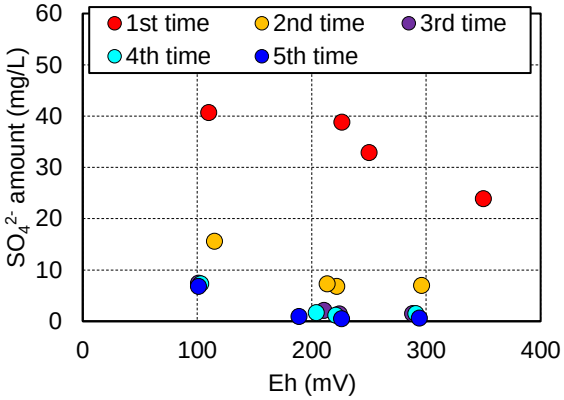

Figure 14. SO_4^{2-} *elution amount - curing period*

5 CONCLUSIONS

We performed elution tests (batch and unsaturated column tests) using reducing agents to evaluate the effects on arsenic elution characteristics of changes in the redox environments of arsenic-containing rocks excavated during mountain tunnel construction. In both tests, a similar tendency was confirmed between the redox potential and the elution amount of arsenic.

The arsenic in these sample rocks occurred in pyrrhotite. Our tests confirmed that the amount of arsenic eluted increased as oxidation of pyrrhotite progressed and that elution accelerated following the addition of a reducing agent. This was believed to be attributable to the oxidative decomposition of pyrrhotite following exposure to the atmosphere (Equation 1), which released arsenic occurring as impurities in pyrrhotite. In addition, while arsenic coprecipitated with iron hydroxide, in tests involving the addition of a reducing agent, the dissolution of iron hydroxide with decrease in redox potential (Equation 2) appears to have reduced arsenic coprecipitation (Figure 15: Image of behavior of arsenic, iron, and sulfur) (Hayase et al., 1957; Okumura et al., 2007).

$$FeS + 3O_2 + H_2O \rightarrow Fe(OH)_3 + SO_4^{2-} + H^+ \quad (1)$$

$$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O \quad (2)$$

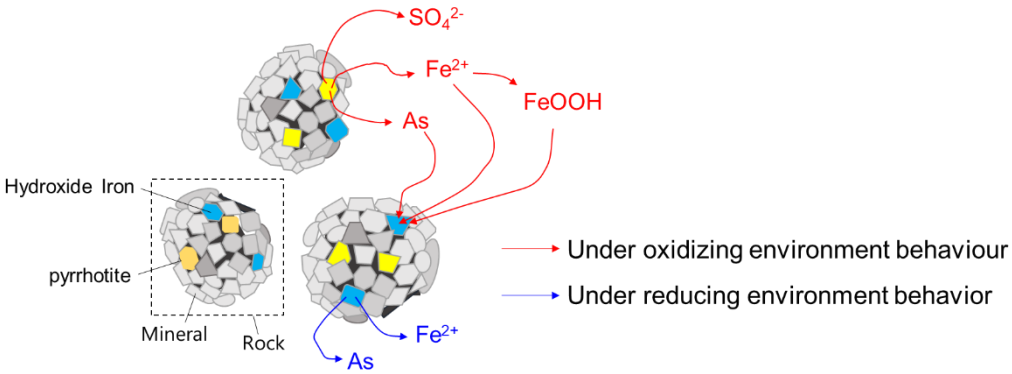

Figure 15. *Image of behavior of arsenic, iron, and sulfur*

The positive correlation between sulfate ion concentrations and length of exposure to the atmosphere indicates the reaction of Equation 1. Even on Day 0 of the exposure, adding a reducing agent increased the amounts eluted of arsenic and iron. In addition, Sulfate ion concentrations were higher when the redox potential was lower. These suggests that unoxidized pyrrhotite also dissolved. In contrast, the amount of iron eluted declined with length of exposure. This is believed to result from an increase in crystallinity of iron hydroxide (from amorphous to crystalline) due to exposure to the atmosphere. However, the amount eluted was high in the most oxidized surface sample, a finding we plan to investigate and confirm in the future.

The oxidation-reduction potential of the leachate from the disposal site where the rock samples were taken in this test is 200-300mV. This redox potential could be reproduced in both batch and column tests. Furthermore, when confining rocks rich in carbonate minerals or soil rich in organic matter, the redox potential becomes lower, but It is considered that this can be dealt with by increasing the reducing agent concentration. Furthermore, the batch test and the column test solutions pH is about 9.0, and the oxidation-reduction potential (Eh) is 50 mV to 400 mV. Arsenic under this environment is considered to exist as pentavalent $HASO_4^{2-}$ in a large proportion. However, it is considered that the addition of a reducing agent lowers the oxidation-reduction potential and increases the proportion of trivalent H_3AsO_3. Since trivalent arsenic is less likely to be adsorbed to iron hydroxide than pentavalent arsenic, this is also considered to be one of the factors that increase the arsenic elution amount due to the reduction in redox potential.

Our study confirmed that a elution test using a reducing agent is at least somewhat effective in reproducing the elution of arsenic from sulfide mineral in natural settings. On the other hand, the amount of water sprayed in the column test was set at 180 mL/hour, which is the minimum amount of water that can be stably sprinkled with the water sprinkler used this time. This is high compared to the rainfall intensity in Japan. Therefore, we believe that verification with a watering amount that is closer to the actual rainfall is necessary. In the future, we plan to verify whether tests using reducing agents can reproduce the elution that occurs at actual excavation sites and landfills.

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