

Sorption Behavior of Iodine on Allophane under Acid and Alkaline Conditions -12203

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ABSTRACT

In the safety assessment of TRU geological disposal, Iodine-129 (I-129) is considered a key radionuclide. In Japan the reference buffer material within the repository is a bentonite based sand mixture, which is lacking in iodine adsorbent capacity. Additives or alternative buffer materials that can enhance iodine adsorption are desired. Allophane, a common soil material in Japan, is a potential candidate to aid in iodine retention. In order to assess the potential for improvement of buffer and backfill material to limit release of I-129, the sorption behavior of iodine (IO_3^- and I^-) on allophane was examined in this research. The sorption behavior of IO_3^- by allophane is strong in acidic conditions, and markedly reduced in alkaline conditions. The K_d values of IO_3^- are approximately 0.4 m^3/kg (pH=5), 0.03 m^3/kg (pH=8), 0.011 m^3/kg (pH=9), 0.005 m^3/kg (pH=10). Conversely, the K_d value of I^- is as small as 0.01 m^3/kg in acidic conditions, and much smaller in alkaline conditions. The numerical analysis shows that a maximum release rate of I-129 from the engineered barrier in the geological disposal system decreased approximately one order of magnitude and the K_d of the buffer increased up to 0.1 m^3/kg by applying allophane soils to engineered barriers.

INTRODUCTION

Iodine-129 (I-129) is considered a key radionuclide in the safety assessment of TRU geological disposal because of its long half-life (1.57×10^7 y), high mobility, and the risk of internal exposure to the human body. Accordingly, advanced solidified waste forms that limit release of I-129 have been studied [1]. In Japan's TRU repository, the Engineered Barrier System (EBS) consists of the waste form, concrete pit and buffer and backfill region. The Japanese reference buffer and backfill material is a bentonite based sand content material [1], which lacks iodine adsorbent and retardation capacity.

Allophane is a poorly-crystalline hydrous aluminium silicate contained in volcanic ash soils, typically comprised of hollow spherical particles with diameters of 3.0~5.5 nm and pores of 0.3~0.5 nm. The structure is composed of an outer round alumina octahedral layer and the inner silica tetrahedral layer. It is a weathering or hydrothermal alteration product of volcanic glass and feldspars and is a very common soil material in Japan. Allophane's chemical formula is $\text{Al}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ($m=1\sim 2$, $n=5\sim 6$) and it has a composition similar to kaolinite [2] [3]. The anion exchange capacity (AEC) of allophane is 0.1-0.2 eq/kg (pH=5.4), and it is known that allophane has a high anion adsorbent capacity in acidic conditions. The solid to liquid distribution coefficient value (K_d) for iodine (I-125) has been reported as $3.07 \times 10^{-3} \text{m}^3/\text{kg}$ (pH5.9) [4].

In this research, in order to improve the I-129 release rate of the buffer and backfill material, the sorption behavior of iodine on allophane was examined and the retardation effects were estimated by numerical analysis.

EXPERIMENTAL METHODS

Batch sorption and desorption experiments were carried out using 'Tachikawa loam' soil sampled from 1.1 m below the ground surface in Tokyo University Tanashi Farm. It is typical loam in Japan; the sediment period is 10,000-30,000 y. The materials sampled have been very scarcely affected by human- and bio-activities, that is, they are composed of pure allophane.

In the sorption experiments, 1.0 and 3.0 ml of 60 ppm KIO_3 (IO_3^-) aqueous solution and 1.0 ml of 30 ppm KI (I^-) aqueous solution were introduced to soil samples of 0.5 g after adding 1 ml of 0.1 M KNO_3 aqueous solution and adjusted to pH of 5, 6, 7, 8, 9 and 10 using distilled water and KOH solution of 0.01 M and 0.1 M. The reaction time was 24 hrs and 20 days to study the strength of adsorption. In the desorption experiments, 10 ml of 0.01 M KNO_3 solution was added to IO_3^- adsorbed samples and 0.5 ml of 100 ppm KNO_2 solution was added to I^- adsorbed samples. The reaction time for desorption was 24 hrs. Under each of the conditions, the sorption and desorption experiments were performed in triplicate ($n=3$). After the prescribed sorption or desorption reaction time, the samples were centrifuged at 3,000 rpm for 10 minutes and solid/liquid separation was performed by passing the samples through a 0.22 μm membrane filter. The concentration of IO_3^- and I^- in the solutions was measured by ICP atomic emission spectroscopy (Shimazu ICP-8100).

EXPERIMENTAL RESULTS

Sorption experiment

The results on the sorption of IO_3^- and I^- onto allophane are shown in Figure 1 as a function of pH. The influence of reaction time appeared only in IO_3^- adsorption in the high alkaline conditions. Up to pH9, the sorption of IO_3^- after 24 hrs was equal to that adsorbed over the period of 20 days and at pH10, the sorption of IO_3^- after 20 days decreased. The extremely high alkaline conditions may have led to the dissolution and collapse of the structure of allophane minerals [5].

About 20 mg I^- /kg sorbed on allophane in acidic conditions, but in alkaline conditions the sorption was not detected. On the other hand, the sorption behavior of IO_3^- by allophane is significantly greater than I^- , except under the most alkaline conditions. Specifically, about 100-350 mg/kg IO_3^- was sorbed on allophane at the lowest pH levels, and reduced linearly to about 20-70 mg/kg at the highest pH levels.

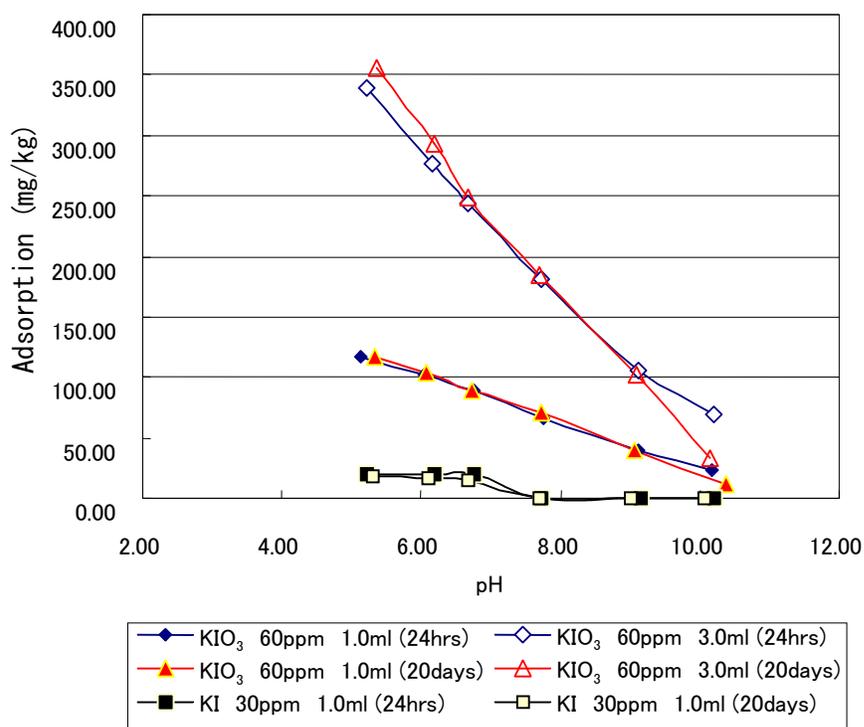


Fig.1 Relationship between adsorption onto allophane and pH (24 hours and 20 days)

Desorption experiment

The results on desorption of IO_3^- and I^- after sorption experiment is shown in Figure 2. The ratio (%) of desorption to the amount of adsorption is shown in Figure 3. Desorption of I^- is minimal or not detected in all conditions, but the desorption ratio of IO_3^- increased as pH increased. Figure 3 shows that up to pH9, IO_3^- desorption ratio is independent of the sorption reaction time (24 hrs and 20 days) and the initial amount of IO_3^- . The desorption ratio of IO_3^- after 20 days sorption, are 5.3% (pH5.5), 14.2% (pH6.3), 16.7% (pH6.8), 25.6% (pH7.7) and 40.3% (pH9.1). But under strong alkaline conditions (pH>10), desorption ratio increased up to over 80% and the desorption ratio of 20 days sorption specimen are 20% higher than that of 24 hrs sorption specimen. The reason for this is considered the same as in the sorption experiment; that is, the dissolution or collapse of the allophane structure may have occurred on 20 days adsorption specimens in high alkaline conditions.

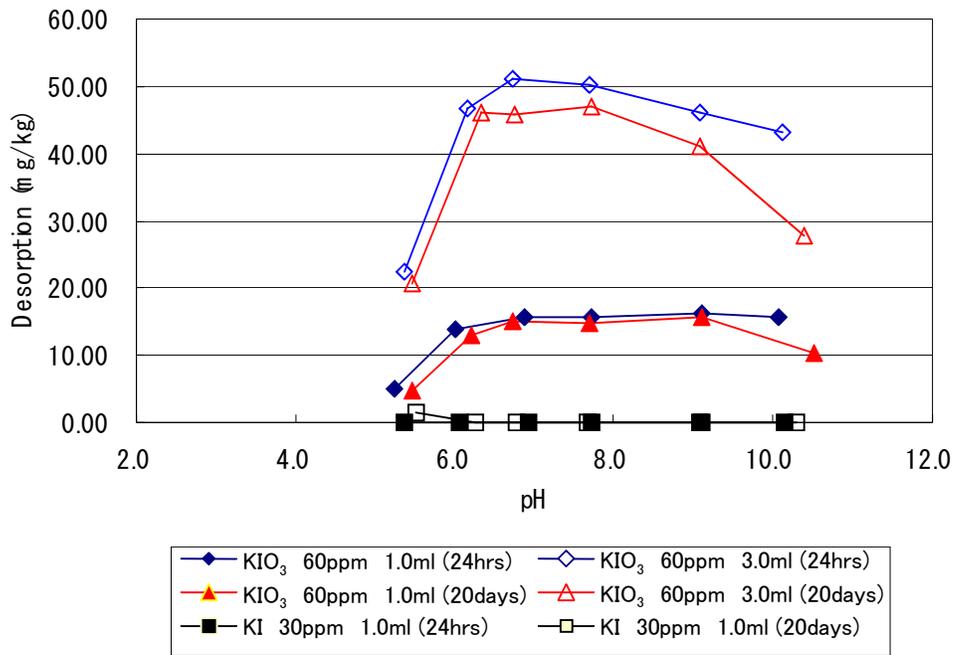


Fig.2 Relationship between desorption from allophane and pH

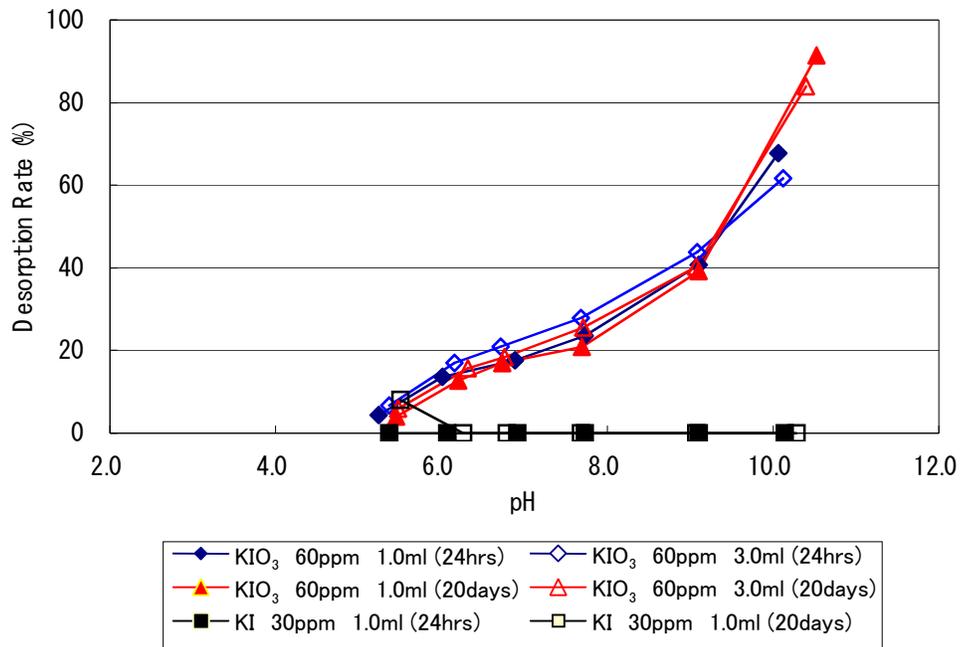


Fig.3 Relationship between desorption ratio (desorption/adsorption) and pH

Solid to liquid distribution coefficient value (Kd)

Kd values can be calculated from the results of these sorption and desorption experiments using Equation 1.

$$K_d = C_{sorb} / C_{solution} \quad (Eq. 1)$$

where C_{sorb} is the amount of ion sorbed in the soil (g/kg), $C_{solution}$ is the amount of remaining ion in the solution (g/m³).

Figure 4 shows the Kd value for IO₃⁻ and I⁻ in allophane as a function of pH in sorption processes. In alkaline conditions, the Kd for IO₃⁻ showed the same value regardless of reaction time (24 hrs or 20 days). The approximate Kd value was 0.03 m³/kg at pH8, 0.005 m³/kg at pH10, in acidic conditions 0.28-0.45 m³/kg at pH5 and 0.05 m³/kg at pH7. The Kd for I⁻ is 0.01 m³/kg in acidic conditions and in pH>8 Kd equals zero. The reaction time had no effect on the Kd value.

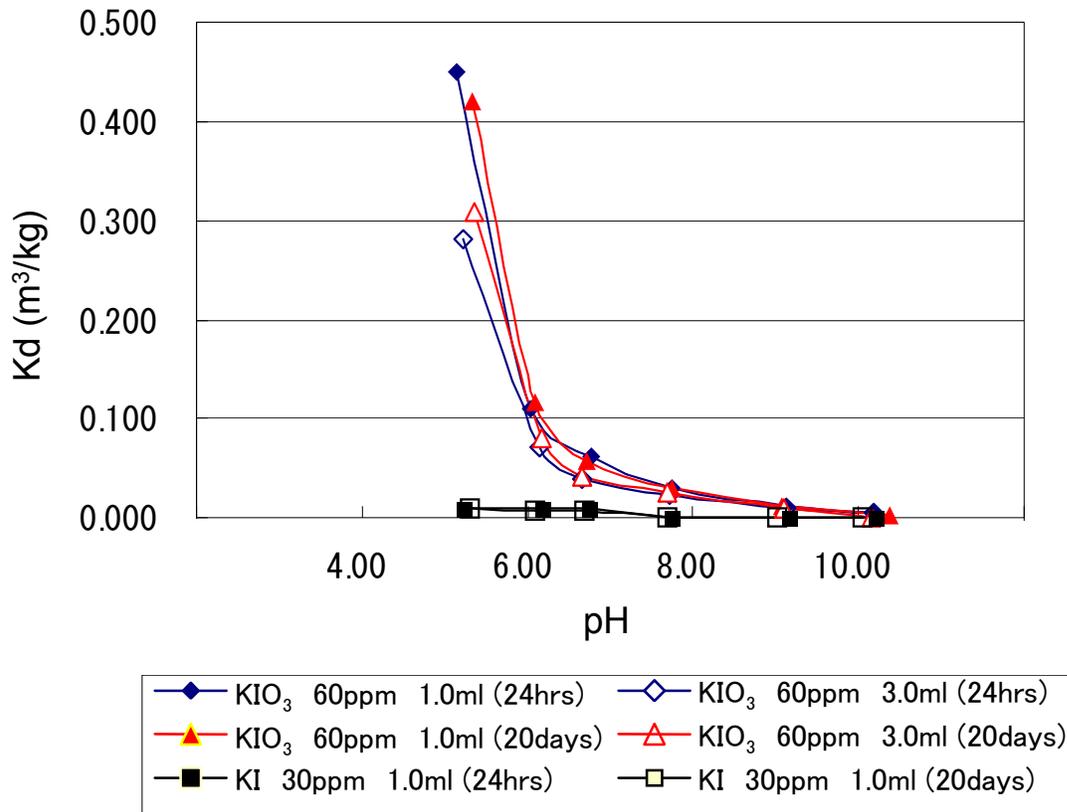


Fig.4 Kd for iodine (I-125) in allophane

NUMERICAL ANALYSIS ON TRANSFER OF I-129

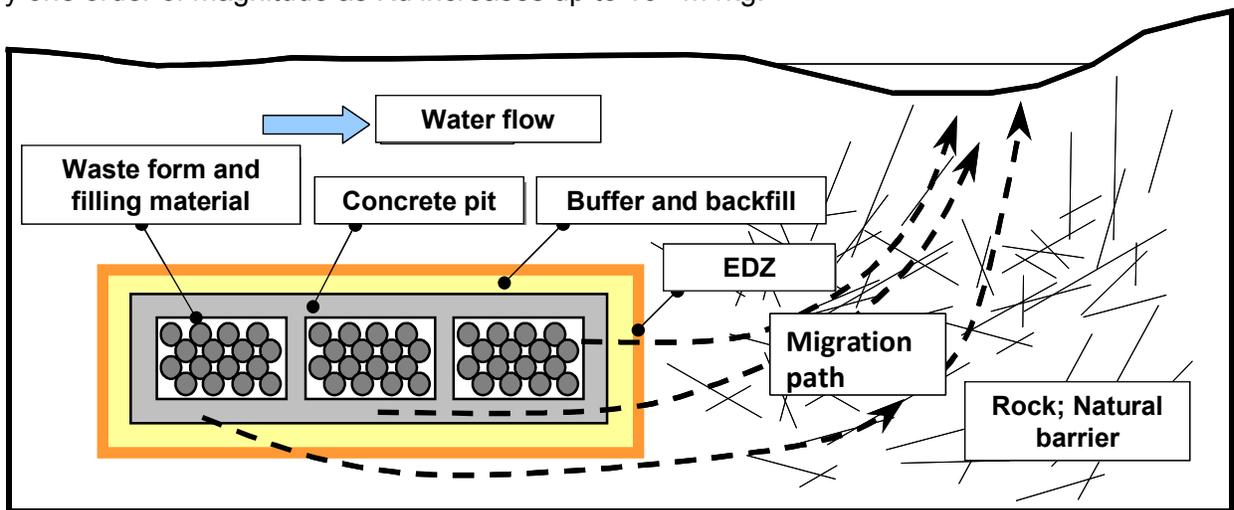
The effect of iodine sorption capacity of the buffer material on radionuclide transport into the environment can be estimated by a numerical analysis. In general, the radionuclide transport in fully saturated porous materials is shown as Equation 2. The conceptual model for I-129 transport is shown in Figure 5

$$\left(1 + \frac{\rho_d^i}{\varepsilon^i \rho_w} K_d^i\right) \frac{\partial A^i}{\partial t} = \frac{\partial}{\partial x} \left(\varepsilon^i D^i \frac{\partial C^i}{\partial x} \right) - \frac{\partial}{\partial x} (\varepsilon^i q^i C^i) - \lambda A^i \quad (\text{Eq.2})$$

where superscript i refers to waste form, concrete and buffer, and

- A^i : Nuclide concentration in EBS [mol/m^3]
- C^i : Nuclide concentration in pore water of EBS [mol/m^3]
- λ : Decay constant [$1/\text{s}$]
- ε^i : Porosity
- ρ_d^i and ρ_w : Bulk density of materials and density of water, respectively [Kg/m^3]
- D^i : Diffusion coefficient [m^2/s]
- q^i : Velocity of pore water
- t and x : Time and space coordinate

Table 1 shows the conceptual data used in numerical simulations, in which the data for waste form, concrete and buffer materials are included. The analysis has been performed for 5 different K_d values of I-129 in the buffer, ranging from 0 to $10^{-1} \text{ m}^3/\text{kg}$, based on the range of measurements obtained by sorption experiments on allophane under the conditions of $\text{pH} > 6$. Figure 6 shows the release rate of I-129 from the EBS. Each analysis shows that the migration of I-129 was retarded as the K_d value of the buffer was increased. The peak released time is later every few 100,000 years, and consequently the maximum release rate of I-129 decreases nearly by one order of magnitude as K_d increases up to $10^{-1} \text{ m}^3/\text{kg}$.



EDZ; Excavation Damaged Zone

Fig 5. Conceptual model for I-129 migration analysis

Table I. Conceptual data used for numerical analyses

| Region | Description | Symbol | Unit | Value |
|------------|--------------------------------|-----------------|----------|---|
| Waste Form | Inventory:I-129 | M | Bq/ton | 6.2 |
| | Waste weight | - | Kg | 100,000 |
| | Waste volume | V^s | m^3 | 40,000 |
| | Distribution coefficient:I-129 | Kd^s | m^3/kg | 0.0001 |
| | Leaching rate | L | y^{-1} | 10^{-5} |
| | Porosity | ε^s | - | 0.15 |
| | Surface area | X^s | m^2 | 8.8 |
| | Velocity of water | q^s | m/y | 0.01 Same as concrete |
| Concrete | Distribution coefficient:I-129 | Kd^c | m^3/kg | 0.0001 |
| | Diffusion coefficient:I-129 | D^c | m^2/s | 1.4×10^{-9} |
| | Porosity | ε^c | | 0.15 |
| | Density | ρ^c | Kg/m^3 | 2500 |
| | Cross sectional area | X^c | m^2 | 10 |
| | Hydraulic gradient | i | - | 0.0001 |
| | Hydraulic conductivity | k^c | m/s | 4.76×10^{-6} |
| | Velocity of water | q^c | m/y | 0.01 |
| | Length | l | m | 2.0 |
| Buffer | Distribution coefficient:I-129 | Kd^b | m^3/kg | $0, 1 \times 10^{-4}, 1 \times 10^{-3}, 1 \times 10^{-2}, 1 \times 10^{-1}$ |
| | Diffusion coefficient:I-129 | D^b | m^2/s | 10^{-10} |
| | Porosity | ε^b | | 0.4 |
| | Density | ρ^b | Kg/m^3 | 2680 |
| | Cross sectional area | X^b | m^2 | 12 |
| | Hydraulic gradient | i | - | 0.0001 |
| | Hydraulic conductivity | k^b | m/s | 1.27×10^{-6} |
| | Velocity of water | q^b | m/y | 0.01 Same as concrete |
| | Length | l | m | 1.0 |

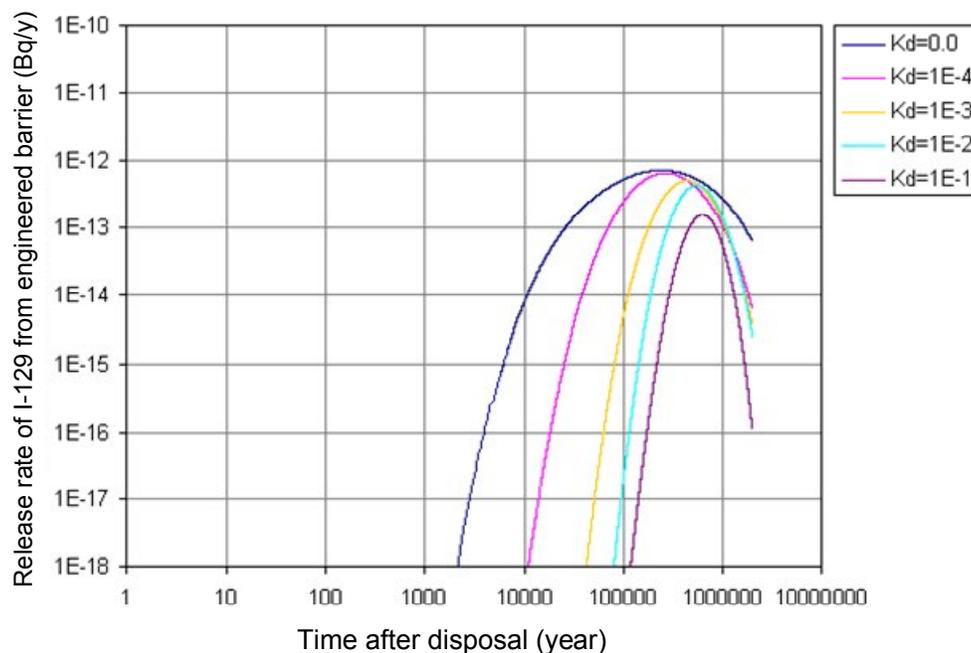


Fig 6. Release rate of I-129 from EBS (the effect of Kd of buffer)

DISCUSSION AND CONCLUSIONS

Our study shows that IO_3^- is adsorbed on allophane not only in acidic conditions but also in alkaline conditions. But I^- is slightly adsorbed by allophane only in acid conditions. Such sorption capacity of allophane may reduce the maximum release rate of I-129 from the repository. Under anoxic/reducing conditions in deep underground environment, I-129 might be I^- as chemical species [2]. In cases where the chemical species released from iodine waste could be controlled to IO_3^- or the chemical conditions of allophane used as backfill material could be kept acidic, application of allophane as a backfill material for iodine waste might be helpful.

Allophane exhibits both pH-dependent negative and positive charge since Al-OH_2^+ appears on surface of allophane in acidic conditions and Al-OH^- and Si-O^- in alkaline conditions, respectively. Consequently, CEC (cation exchange capacity) and AEC (anion exchange capacity) are dependent on pH. CEC is in a range of 0.2 to 1.3 eq/kg^{-1} and AEC is in a range of 0.1 to 0.2 eq/kg^{-1} [3] [6]. The results in Figure 1 demonstrate the sorption behavior of IO_3^- and I^- owing to such pH-dependent charges on allophane surface. Regarding desorption behavior, it might be worthy to note that the amounts of IO_3^- desorption are smaller in 20 days adsorption than that in 24 hrs adsorption in a case with large amount of adsorption. However, the amount of desorption is independent of reaction time and pH in the case with small amount of adsorption (Figure 2). It might suggest that weak adsorption promptly operates in a short reaction time (24 hrs) and strong adsorption is performed during a long time (20 days).

The numerical analyses demonstrate the schematic pattern of release rate of I-129 to the environment from the EBS by applying Kd values obtained from adsorption experiments for IO_3^- and I^- (Figure 6). Kd values are dependent on pH. Accordingly, the results indicate that the

release of I-129 in acidic conditions (pH6, $K_d=0.1 \text{ m}^3/\text{kg}$) is delayed ($\sim 100,000$ years) and the maximum release rate is reduced. In alkali conditions (pH10, $K_d=10^{-3}$ to $10^{-4} \text{ m}^3/\text{kg}$), I-129 release starts tens of thousands years earlier and the maximum release rate is higher. Consequently, it is proposed that I-129 be prepared to the form of IO_3^- in waste treatment and buffers are managed so that they maintain acidic conditions when allophane soil is used as a buffer material. The pH of ground-water, rainfall and soils are different in different regions. Results of this work suggest that disposal of I-129 waste may be improved in regions with acidic soils formed by much rainfall and with volcanic ash soils.

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