Synthesis and Characterization of Hydrous Zirconia
as an Ion-exchanger for Removal of Radioactive Iodine

Master’s thesis

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In terms of nuclear waste management, the behavior of radionuclides with long half-lives, such as I-129, is of special concern especially for the final depository of nuclear waste. In addition, generally speaking, iodine is highly mobile and easily transferable to the natural environment. Furthermore, because iodine is an essential element for the synthesis of thyroid hormones, it accumulates in the human thyroid. Thus, radioactive iodine can also be the greatest potential danger of dose uptake for humans.

Among many kinds of iodine species, it is rather challenging to separate iodate selectively from other anions and thus it is necessary to investigate new materials which can adsorb iodate efficiently for the removal of radioactive iodine.

In this study, the iodate adsorption ability of hydrous zirconia has been investigated. Hydrous zirconia has been reported as an anion-exchanger, and because of its stability, this material is a promising candidate for selective iodate removal from radioactive waste solutions.

White solid of hydrous zirconia was successfully synthesized with an amorphous structure. Its surface showed a character in between amphoteric and basic. The isotherm indicated that the material has a preference to adsorb iodate and the saturation value of adsorption was estimated to 1.8 mmol/g.

The material showed lower uptakes as pH got higher. Among several competing anions tested, divalent sulphate ions suppressed the iodate adsorption to some extent due to higher affinity to the material surface. In a basic environment, boric acid also suppressed strongly the adsorption probably because of the formation of tetrahydroxyborate with hydroxide sites on the material surface. These suppressions of iodate adsorption became stronger as the concentration got higher.

Post-heating at 400 °C resulted in the transformation of the material structure to tetragonal and a slight improvement of iodate adsorption rate. As the temperature of post-heating got higher, the structure became more monoclinic and showed the lower uptakes, which may be due to the loss of hydroxide sites.

A column setup of the material with simulant of wastewater from Fukushima Daiichi Nuclear Power Plant has been operating and approximately 11,000 bed-volume of the solution has been gone through, but still, the column is yet to reach a 100% breakthrough.

Based on the results presented in this study, it can be concluded that synthesized hydrous zirconia showed clear iodate preference and a possible high performance for the waste treatment from nuclear power plants.
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1. Introduction

Up until now, nuclear industries have been produced and stored large volumes of radioactive waste solutions.\cite{1} In addition, previous nuclear accidents resulted in a massive discharge of radioactive waste. For example, in the case of Fukushima Daiichi Nuclear Power Plant accident which happened on March 12th in 2011, so far 2,090,670 m$^3$ of the waste solution has been treated and 23,740 m$^3$ of the untreated highly-radioactive waste solution is still stored as of May 9th, 2019.\cite{2} Selective removal of radionuclides from the nuclear waste effluents is therefore necessary and important to reduce the radioactive discharges into the environment and the final volumes of waste to be disposed of. Since most waste solutions contain trace concentrations of radioactive elements and much higher concentrations of other inactive ions, materials with high selectivity of the target elements are needed for the successful removal of radionuclides.\cite{1,3,4}

In terms of nuclear waste management, the behavior of radionuclides with long half-lives is of special concern especially for the final depository of nuclear waste. In case of iodine, among the many radioactive fission product isotopes, I-129 has the longest half-life of $1.6 \times 10^7$ years and thus it becomes a predominant radionuclide in the final repositories in the long run.\cite{4,5}

In addition, iodine in general is highly mobile in aqueous solutions and easily transferable to the natural environment. Because iodine is an essential element for the synthesis of thyroid hormones, it accumulates in the human thyroid and thus it can also be the greatest potential danger of dose uptake for humans.\cite{5}

Iodine is found mainly as forms of iodide ($\Gamma^-$), iodate (IO$^{3-}$), molecular iodine ($I_2$), or organic iodine compounds, and is easily transformed between these forms responding to the surrounding conditions.\cite{5,6} In water, the majority of iodine species exists as either iodide or iodate ions.\cite{7} The iodide ion has a strong affinity to monovalent silver ion (Ag$^+$) and AgI salt shows an extremely low solubility to water.\cite{8} Therefore, methods for iodide removal have
been established and industrial materials are available for this purpose.\cite{9} However, it is still necessary to investigate new materials which can adsorb iodate ions efficiently for the removal of whole radioactive iodine.

In this study, the iodate adsorption ability of hydrous zirconia has been investigated. Hydrous zirconia has been reported as an anion-exchanger, and because of its stability, this material is a promising candidate for selective iodate removal from radioactive waste solutions.\cite{10}

2. Theories

2.1. Ion exchange

2.1.1. General mechanism

Ion exchange is the process in which ions are exchanged usually between an electrolyte solution and an insoluble solid. Cation exchangers carry exchangeable cations and anion exchangers anions. Those ions (i.e. counterions) can be exchanged for other ions of the same type of charge: negative or positive. These exchange phenomena occur as a rule stoichiometrically and reversibly. Also, ion exchange is essentially a diffusion process and usually has little relation to chemical reaction kinetics. In general, ion exchangers have a preference on certain counter ions to others and electively adsorb them.\cite{1}\cite{11}\cite{12}

An ion exchange reaction in a binary ion system (ion A and B) may be written as:

\[ Z_B A^{Z_A} + Z_A B^{Z_B} \leftrightarrow Z_A B^{Z_B} + Z_B A^{Z_A} \]  \hspace{1cm} (1)

where

\[ Z_A, Z_B = \text{charge of the ions} \]
\[ A, B = \text{the ion in the solution} \]
\[ \bar{A}, \bar{B} = \text{the ion in the solid exchanger} \]
Various properties and quantities at the equilibrium state are used to characterize the efficiency of the ion exchangers.

2.1.2. Selectivity coefficient

A selectivity coefficient is the property which is usually used to measure the equilibrium state of the ion exchange reaction. The selectivity coefficient $k_{A/B}$ is defined as:

\[ k_{A/B} = \frac{[A]_S^{Z_A} [B]_L^{Z_B}}{[A]_L^{Z_A} [B]_S^{Z_B}} \]

where

- $[A]_S$, $[B]_S$ = the concentration of the ion in the solid exchanger
- $[A]_L$, $[B]_L$ = the concentration of the ion in the liquid phase
- $Z_A$, $Z_B$ = charge of the ion

Selectivity coefficient may depend on the loading amount of the ion $A$ in the exchanger and also change with the ionic strength of solutions especially at high concentrations. In fact, selectivity is one of the key factors to determine the maximum processing capacity of the material. In a context of ion exchange, a capacity means the amount of ions which a material is able to exchange.

2.1.3. Distribution coefficient

Especially in radionuclide removal, the efficiency of an ion exchanger is often measured by the distribution coefficient $K_d$. In general, $K_d$ is defined as a concentration ratio of the ion in the solid exchanger and the liquid phase.
Generally speaking, \( K_d \) depends on the ionic composition of the exchanger and the solution, which means pH of the liquid phase is one of the important parameters for ion exchange processes.

For a binary exchange, from the equation (2) and (3), \( K_d \) of ion \( B \) can be written as:

\[
K_d = \frac{[A]_S}{[A]_L} \quad (3)
\]

\[
K_d = k_{A/B}^{1/Z_B} \left( \frac{[B]_S}{[B]_L} \right)^{Z_A/Z_B} \quad (4)
\]

When the ion \( A \) is present in the solution and in exchanger at a much lower concentration than the ion \( B \), \( k_{A/B} \), and \([B]_S \) can be considered as constant. \([B]_S \) can be also considered to be nearly equal to the ion exchange capacity of the column (\( Q \)). Therefore, the equation (4) can be written as follows:

\[
\log K_d = \frac{1}{Z_B} \log (k_{A/B} \cdot Q^{Z_A}) - \frac{Z_A}{Z_B} \log [B]_L \quad (5)
\]

In this condition, it can be said that \( K_d \) depends only on the concentration of ion \( B \) and the slope on a logarithmic scale equals to the ratio of charges (\(-Z_A/Z_B\)).

To study adsorption mechanisms, a series of experiment to determine graphs of \( \log K_d \) as a function of \( \log [B]_L \) are frequently carried out. Taking a binary uni-univalent exchange, which is also applied to the exchanger material in this study, as an example, the equation (5) can be translated as follows:

\[
K_d = \frac{Q}{k_{A/B} + [A]_L} \quad (6)
\]
When $[A]_L << [B]_L/k_{A/B}$ (in this study $A = IO_3^-$ is much smaller than other anions $B$), the equation (6) can be written as:

$$\log K_d = \log (k_{A/B} \cdot Q) - \log [B]_L$$

(7)

This equation is true only if the selectivity coefficient is low, and shows that $K_d$ is inversely proportional to the concentration of ion $B$ in the solution. If the selectivity coefficient is very large, even if $[A]_L << [B]_L$, the dependence may not be linear. In addition, when one common macro-ion is present in the solution, the other ions that are present at trace level have a negligible effect on equilibriums, and therefore the equation (7) is still valid under the condition where several trace-ion exchange reactions occur in parallel.

The calculated $K_d$ values are shown in Fig. 1. When the selectivity coefficient is low, $K_d$ falls linearly with the concentration of ion $B$ on a logarithmic scale. However, as the selectivity coefficient becomes higher, the $K_d$ starts to become less linear and ultimately becomes independent of $[B]_L$ when the selectivity is very high. Fig. 1 also shows that in diluted solutions, the $K_d$ tend to be a common value, which is determined by $Q/[A]_L$.

Distribution coefficients can be determined by static batch experiments. In this study, they are determined by a series of batch experiments as well. Also, the distribution coefficient can be measured by a dynamic column experiment. $K_d$ that is measured under batch conditions can be used to estimate the performance of the ion exchanger in a column if these two kinds of operations are carried out under the same equilibrium conditions. The distribution coefficient gives the maximum theoretical processing capacity of the ion exchanger. For example, when the concentration of ion $A$ in the exchanger is expressed in mol/kg and in solution in mol/L, $K_d$ means how many liters of liquid can be maximally treated with one kilogram of the exchanger. This maximum capacity is reached when the ratio between the concentration of the target ion in effluent and in influent of the column becomes 100%, and at this point, it can be said the column is completely exhausted.
Fig. 1: Calculated values for the distribution coefficient $K_d$ for trace ion $A$. ($[A]_L = 10^{-6}$ mol·L$^{-1}$) in binary univalent $A^+/B^+$ exchange as a function of macro-ion concentration $[B]_L$ at different values of the selectivity coefficient $k_{A/B}$ (Dotted line, $k_{A/B} = 5,000,000$; dashed line, $k_{A/B} = 50,000$; continuous line, $k_{A/B} = 500$. Ion exchange capacity of the exchanger: 2.0 mmol/g).$^{[12]}$

In this study, graphs of log $K_d$ as a function of pH were employed. It is because the ion B in the system is hydroxide ions (the detailed information can be found in section 2.2.2) and in dilute aqueous solutions the following relation holds.$^{[13]}$

$$pOH = pK_w - pH$$  \hspace{1cm} (8)$$

where

$$pA = -log_{10}[A]$$

$K_w$ = ionic product of water

Since when the temperature is constant $K_w$ also remains constant, the adsorption mechanism can be also evaluated by pH instead of pOH.
2.1.4. Ion exchange isotherm

An ion exchange isotherm shows the ionic composition of the exchanger as a function of the ionic composition of the solution at a constant temperature.\[11][12] In the isotherm graph, the equivalent ionic fraction of the ion A in the exchanger is plotted as a function of the equivalent ionic fraction in the liquid phase, while the other variables are kept constant. The equivalent ionic fractions are defined by the following equations:

\[
[A]_{S,E} = \frac{Z_A[A]_S}{Z_A[A]_S + Z_B[B]_S} \tag{9}
\]
\[
[A]_{L,E} = \frac{Z_A[A]_L}{Z_A[A]_L + Z_B[B]_L} \tag{10}
\]

where

\[ [A]_{S,E} = \text{the equivalent ionic fraction of ion A in the solid exchanger} \]
\[ [A]_{L,E} = \text{the equivalent ionic fraction of ion A in the liquid phase} \]

From the plot, the selectivity of the exchanger can be estimated qualitatively. If the isotherm lies on the diagonal, the exchanger has no preference for either ion A or B. If the ion A is preferred, the isotherm is negatively curved towards the axis of the ion concentration in the exchanger and lies above the diagonal. If ion B is preferred, the isotherm is positively curved and falls below diagonal. This can be explained by employing the separation factor:

\[
a_{A/B} = \frac{[A]_S[B]_L}{[B]_S[A]_L} = \frac{[A]_{S,E}[B]_{L,E}}{[B]_{S,E}[A]_{L,E}} \tag{11}
\]

where

\[ a_{A/B} = \text{the separation factor} \]

If ion A is preferred, the separation factor is larger than 1, and if B is preferred, the factor is smaller than 1. Also, from the definition described above, the separation factor is given by the ratio of the two rectangular areas which lie above and below the isotherm, which can explain the relationship between the shape of isotherm and selectivity. The detailed explanation can
be found in Fig. 2 below.

Fig. 2: Ion exchange isotherm and separation factor. (The isotherm is shown as a heavy line).
For any ionic composition, the separation factor equals to the ratio of the two rectangular areas of I and II touching one another in the corresponding point on the isotherm. The broken line is the isotherm of a fictitious ion exchanger which has no preference for either counterion.\[11\]

The essential difference between the separation factor and the selectivity coefficient is that the latter contains the ionic valences as exponents. As a comparison, the relationship between the equivalent ionic fractions and the selectivity coefficient can be described as follows:

$$k_{A/B} = \frac{[A]_{S,E}^{Z_A} [B]_{L,E}^{Z_B}}{[B]_{S,E}^{Z_A} [A]_{L,E}^{Z_B}} \cdot [T]_{L}^{(Z_A - Z_B)}$$  \hspace{1cm} (12)$$

where

$$[T]_{L} = \text{the total ion concentration in the liquid phase}$$
Therefore, the separation factor is usually quite different from the selectivity coefficient especially when \( Z_A \neq Z_B \). Also, in such cases, the selectivity coefficient cannot be estimated from the isotherm, because the isotherm depends on the total ion concentration in the solution.

In this study, the ionic fraction in the liquid phase is estimated by the concentration of ion A (more specifically, iodate) in the solution \( C_A \), which is described as follows:

\[
C_A = \frac{v_A \cdot c_A}{V_{total}}
\]  

(13)

where

\[
\begin{align*}
    v_A &= \text{volume of the original solution containing ion A} \\
    c_A &= \text{molar concentration of ion A in the original solution} \\
    V_{total} &= \text{total volume in a batch operation}
\end{align*}
\]

As a definition, \( C_A \) is a sum of the concentration of radioactive and non-radioactive iodate ions in the liquid phase. However, the concentration of radioactive iodate is negligible and thus only that of non-radioactive iodate is taken into account. Further discussion about the concentration of radioactive iodate can be found in section 6.1.

The ionic fraction in the exchanger is estimated by the amount of adsorbed I-125-iodate tracer with the exchanger \( I_A \), which is described as follows:

\[
I_A = \frac{v_A \cdot c_A}{m_{exc}} \cdot \frac{R_{n,ref} - R_{n,sample}}{R_{n,ref}}
\]  

(14)

where

\[
\begin{align*}
    m_{exc} &= \text{mass of the exchanger material} \\
    R_{n,sample} &= \text{net count rate of the sample} \\
    R_{n,ref} &= \text{net count rate of the reference}
\end{align*}
\]

The definition of a net count rate is explained in section 2.4.1.3.
2.1.5. Ion Exchange Kinetics

The various diffusion processes in the system govern the rate of ion exchange reactions. In general, purely statistical diffusion of ions is driven by the concentration gradient, and can be described by Fick’s first law as follows:\(^{12}\)

\[
J_A = -D \cdot \text{grad}[A]_L
\]  \(15\)

where

\[
J_A = \text{the flux of ion A} \\
D = \text{the diffusion coefficient}
\]

To argue the kinetics of ion exchangers, it is usually necessary to consider also the electric potential. In this case, the flux of ion A is given by the combination of Fick’s first law and the Nernst-Planck equation, which can be written as follows:

\[
J_A = -D(\text{grad}[A]_L + Z_A[A]_L \frac{F}{RT} \cdot \text{grad}\psi)
\]  \(16\)

where

\[
F = \text{Faraday constant} \\
R = \text{gas constant} \\
T = \text{temperature} \\
\psi = \text{the electric potential}
\]

Most commonly, the kinetics of ion exchange reactions are interpreted in terms of two different kinds of diffusion: external or internal diffusion.

The external diffusion which contributes mainly to the ion-exchange process is called film diffusion. When the external solution is agitated, the concentration gradients are not observed as bulk, but arise only within a thin layer of solution adhering to the surface of the exchanger particle. The film diffusion occurs across this thin layer at solid-solution interfaces.
On the other hand, the internal diffusion is called particle diffusion, which is a diffusion of the ions in the exchanger phase. The exchanger particle is usually considered homogeneous, and therefore the different kinds of diffusion process within the particle, such as pore diffusion or matrix diffusion, can be represented by a single particle diffusion coefficient.

In general, film diffusion may dominate at early stages of exchange when the concentration gradient in the particle is large. However, as the exchange reaction proceeds, particle diffusion may dominate because the concentration gradients in the particle decrease and the contribution of film diffusion also decrease.

### 2.1.6. Basic Ion Exchange Operations

#### 2.1.6.1. Batch operation

Batch operations are a technique, which are mainly used for laboratory purposes, because their experimental set up is rather simple and a large number of operations can be carried out simultaneously.[14]

In batch operations, a given amount $m$ of ion exchanger and a given volume $V$ of a solution are simply mixed together in a container such as a vial. The mixture is then agitated until the system reaches equilibrium. Considering the simple uni-univalent exchange, the ratio of ion concentrations at equilibrium is given by:[12]

$$\frac{[A]_S}{[B]_S} = k_{A/B} \frac{[A]_L}{[B]_L}$$  \hspace{1cm} (17)

In general, to achieve a high conversion of the exchanger to the A form, the selectivity coefficient $k_{A/B}$ and the ratio $[A]_L/[B]_L$ must be high.
The degree of conversion to the $A$ form is controlled by adjusting the initial concentration of $A$ in the solution and the batch factor ($BF$):

$$[A]_S = ([A]_{L,0} - [A]_L) \cdot BF$$  \hspace{1cm} (18)

where

$$[A]_{L,0} = \text{the initial concentration of ion A in the liquid phase}$$

The batch factor is determined by:

$$BF = \frac{\text{volume of solution (mL)}}{\text{mass of exchanger (g)}}$$  \hspace{1cm} (19)

In this study, the distribution coefficient $K_d$ is determined by the following equation:

$$K_d = \frac{R_{n,\text{ref}} - R_{n,\text{sample}}}{R_{n,\text{ref}}} \cdot BF$$  \hspace{1cm} (20)

Adsorption rate $A$, which describes how much percent of target ions the material can adsorb, is another useful concept to describe the ability of the ion exchanger. The rate is calculated by the following equation:

$$A \% = \frac{R_{n,\text{ref}} - R_{n,\text{sample}}}{R_{n,\text{ref}}} \cdot 100$$  \hspace{1cm} (21)

The main disadvantage of batch operations is that it cannot separate the ions completely if the material has a moderate affinity since the reaction reaches equilibrium when the phases are separated. Also, batch operations sometimes require complicated phase-separation operations.\cite{14}
2.1.6.2. Column operation

In column operations, when the solution goes through the column, it comes subsequently in contact with fresh portions of the material, which can be considered effectively as a large number of successive batch operations. Therefore, unlike batch operations, column operations can achieve complete ion-exchange reactions.\(^\text{[14]}\)

In the binary exchange, a solution containing the target ions $A$ is passed through the column, in which the exchanger material contains ion $B$. The $A$ ions are then taken up by the exchanger and $B$ ions are released into the solution. Ideally, at the beginning, the column effluent is free of ion $A$, but its concentration increases gradually up to that in the influent solution, which is called a breakthrough.\(^\text{[1]}\)[12]

When the concentration of $A$ in the effluent is plotted as a function of effluent volume, the area above the curve gives the total volume of solution, from which ion $A$ has been removed. Dividing this volume by bed volume gives the theoretical capacity ($Q_T$) of the column (L·L\(^{-1}\)). In general, $Q_T$ is equal to $K_d$.

The reason why ion-exchange removal of ion $A$ is carried out is usually because the ion $A$ is harmful, and thus an operation is normally not continued until total processing capacity has been reached in order for those harmful ions not to flow out a lot. Therefore, the feed is stopped before the concentration of $A$ in the effluent reaches 100% of that of influent. This limit is called the breakthrough capacity ($Q_B$). Therefore, the ratio $Q_B/Q_T$ is smaller than 1.

The breakthrough capacity of the column depends on the process conditions and on the diffusivity of the ions in the system. Various theoretical approaches have been developed in order to determine the breakthrough capacity. Among them, models based on the theoretical plates are commonly used.
According to the model currently presented,[15] the plate number $N$ depends on the operational conditions such as flow rate and exchanger’s particle size. The flow rate contributes to longitudinal diffusion and usually becomes important only when the flow rates are very low. The particle size, on the other hand, contributes to particle diffusion and it is likely to dominate when the system is close to equilibrium. For particle diffusion controlled exchange, the plate number $N_p$ can be presented as follows:

$$N_p = 60D_p \cdot s \cdot d^{-2} \cdot u_0^{-1}$$  \hspace{1cm} (22)

where

- $s$ = the column length
- $d$ = the particle diameter
- $u_0$ = the linear flow rate
- $D_p$ = the diffusion constant

In general, the breakthrough capacity increases as the number of theoretical plates increases. And as it can be seen from the equation (22), the number of plates can be increased by increasing diffusion coefficients, by decreasing the flow rate, and by decreasing the exchanger particle size.

In this study, the breakthrough behavior is estimated by tracking the activity ratio of the effluent against influent $B$ defined as follows:

$$B \% = \frac{R_{n,\text{eff}}}{R_{n,\text{inf}}} \cdot 100$$  \hspace{1cm} (23)

where

- $R_{n,\text{inf}}$ = count rate of gamma rays in the influent
- $R_{n,\text{eff}}$ = count rate of gamma rays in the effluent
2.2. Hydrous zirconia

2.2.1. Physical and chemical properties

Zirconium is the 40th element on the periodic table, whose electron configuration is [Kr]4d²5s². Due to two electrons from the inner 4d-shell and two electrons from the outer 5s-shell, zirconium can be divalent and quadrivalent in its compounds.[6][16]

When an excess of alkali is added to a solution of a Zr(IV) salt, a gelatinous white precipitate is formed. This precipitate is called hydrous zirconia. Although this hydrous zirconia is often represented as ZrO₂ as the same formula of “normal” zirconium oxides or zirconia, it is very difficult to predict the exact composition and it has not been well-defined, because the composition is strongly influenced by synthesizing process and post-treatment. One example of its expressions is ZrO₆(OH)₄₋₂b·H₂O, or more simply ZrO₂·nH₂O.[17][18]

Most of the precipitation procedures by neutralization of Zr(IV) salts produce amorphous forms of hydrous zirconia. During the precipitation, significant amounts of anions are incorporated, and these anions cannot be removed completely by washing the precipitate with water. Since ammonia does not interfere significantly with the ion exchange properties of the precipitate, precipitation by diluted ammonia solution gives better results,[17][19] and therefore ammonia was used in this study as well.

Transformation of amorphous hydrous zirconia into a crystalline form is possible by heating during the synthesis. Post-heating in the air also triggers the transformation into a crystalline form. However, during the post-heating, the material loses its incorporated water and becomes more similar to zirconium oxide. Hydrous zirconia has three crystalline forms: cubic, tetragonal and monoclinic.[20][21] Zirconium oxide also has those three forms and the interplanar distances of the crystal structure of zirconium oxide are similar to those of the hydrous zirconia.[20][21] Hydrous crystalline zirconia contains approximately 11% of water, and it can be said that it is probably on the surface of the particles since hydrous zirconia and
zirconium oxides have similar interplanar distances.\textsuperscript{[20]}

### 2.2.2. Hydrous zirconia as an ion exchanger

Hydrous zirconia in all of the precipitated forms exhibits ion-exchange abilities to some extent. It can behave both as a cationic and anionic ion exchanger.\textsuperscript{[17]} The hydroxyl groups on the surface of hydrous zirconia can be exchanged with anions in acid solutions at a pH below the isoelectric point (IEP, the definition is explained in section 2.4.3.3) which is reported as 6.7,\textsuperscript{[22]} while in basic solutions for the higher pH protons on the surface can be exchanged with cations. There is no clear limit for both processes, from which it can be said that the exchange sites may be heterogeneous. Since in the anion exchange process, the hydroxyl groups are exchanged, and therefore the ion exchange capacity of hydrous zirconia depends on the number of hydroxyl groups on the surface.

### 2.3. Iodine

#### 2.3.1. General characters

Iodine is an essential element for the synthesis of thyroid hormones, and it can accumulate in the human thyroid. In addition, iodine is easily transferable to the natural environment. Also, there are several radioactive isotopes of iodine, which are mainly produced through a process of nuclear fission at a nuclear power plant. These iodine isotopes are therefore responsible not only for an external dose but also for internal dose; since they are easily transported into the body through respiration and/or via food. In addition, one of them has a long half-life and a high fission yield, and thus the behavior of radioactive iodine released from nuclear facilities is of special concern.\textsuperscript{[4][5]}
Iodine is found mainly as forms of iodide (I\textsuperscript{−}), iodate (IO\textsuperscript{3−}), molecular iodine (I\textsubscript{2}) or organic iodine compounds, and is easily transformed between these forms responding to the surrounding conditions. The chemical forms of iodine often change rapidly, and each species behave differently.\cite{5\cite{6}}

2.3.2. Isotopes

Iodine has many fission product nuclides, such as I-129, I-131, I-132, I-133, I-134, and I-135, and all of them have been released into the environment from nuclear facilities.\cite{5} I-129 and I-131 are especially released into the environment from nuclear facilities, such as nuclear fuel reprocessing plants. The isotopes of I-131, I-132, I-133, I-134, and I-135 are short-lived, and therefore they are hazardous to humans only during the first few months following a fresh nuclear fallout. On the other hand, I-129 has a very long half-life of $1.6 \times 10^7$ years.\cite{23}

In addition to the release from nuclear facilities, I-129 naturally exists in the environment, being generated from nuclear reactions of xenon induced by cosmic radiation and from fission of uranium in the soil. The activity level of natural I-129 in the environment was very low, but it has risen as a result of nuclear weapons tests, nuclear accidents, and emissions from nuclear facilities since the early 1990s.

At present, most of the I-129 nuclides generated in the nuclear facilities are in the spent nuclear fuel. In the long run, I-129 becomes a predominant radionuclide in the final repositories and thus will be a long-term concern. Also, due to the high mobility of iodine, I-129 could enter not only the geosphere and soil but also the biosphere from spent fuel repositories. Therefore, it is essential to control the behavior of radioiodine in the environments for the safety of the final disposal of spent nuclear fuel.\cite{1\cite{4}\cite{5}}
In this study, I-125 is used as a tracer. I-125 is a radionuclide, which decays in electron capture mode, with a half-life of about 59 days. It emits 35.5 keV gamma rays with the intensity of 6.7% and this gamma ray is used to measure the activity. Several other X-rays are also emitted in the energy range of 27–31 keV with intensities of 4–74%.[23]

Table 1: Major isotopes of iodine and their characters.[5][23]

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life</th>
<th>Decay mode</th>
<th>Gamma emission</th>
<th>Source or use</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{125}$I</td>
<td>59.4 d</td>
<td>EC</td>
<td>yes</td>
<td>Tracer</td>
</tr>
<tr>
<td>$^{129}$I</td>
<td>$1.57 \times 10^7$ y</td>
<td>$\beta^-$</td>
<td>yes</td>
<td>fission product, cosmogenic</td>
</tr>
<tr>
<td>$^{131}$I</td>
<td>8.03 d</td>
<td>$\beta^-$</td>
<td>yes</td>
<td>fission product</td>
</tr>
<tr>
<td>$^{132}$I</td>
<td>2.30 h</td>
<td>$\beta^-$</td>
<td>yes</td>
<td>fission product</td>
</tr>
<tr>
<td>$^{133}$I</td>
<td>20.8 h</td>
<td>$\beta^-$</td>
<td>yes</td>
<td>fission product</td>
</tr>
<tr>
<td>$^{134}$I</td>
<td>52.5 m</td>
<td>$\beta^-$</td>
<td>yes</td>
<td>fission product</td>
</tr>
<tr>
<td>$^{135}$I</td>
<td>6.58 h</td>
<td>$\beta^-$</td>
<td>yes</td>
<td>fission product</td>
</tr>
</tbody>
</table>

Table 2: Characters of the tracer nuclide I-125.[23]

<table>
<thead>
<tr>
<th>Parent Nucleus</th>
<th>Parent Half-life</th>
<th>Decay Mode</th>
<th>Daughter Nucleus</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{125}_{53}$I</td>
<td>$59.400 \pm 0.010$ d</td>
<td>EC: 100 %</td>
<td>$^{125}_{52}$Te</td>
</tr>
</tbody>
</table>
Table 3: Gamma rays of I-125.[23]

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Intensity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.77</td>
<td>14.8 ± 0.6</td>
</tr>
<tr>
<td>27.202</td>
<td>39.6 ± 1.1</td>
</tr>
<tr>
<td>27.472</td>
<td>73.1 ± 1.9</td>
</tr>
<tr>
<td>30.944</td>
<td>6.74 ± 0.18</td>
</tr>
<tr>
<td>30.995</td>
<td>13.0 ± 0.3</td>
</tr>
<tr>
<td>31.704</td>
<td>3.75 ± 0.09</td>
</tr>
<tr>
<td>35.493</td>
<td>6.68 ± 0.13</td>
</tr>
</tbody>
</table>

2.3.3. Speciation

Since the ion-exchange material in this study shows an affinity to only one species of iodine-related ions, careful speciation was required.

The major species of iodine can be described as follows:[5][6][7]

\[ I^- (-1) \leftrightarrow I_2 (0) \leftrightarrow IO_3^- (+5) \]

The numbers in the parentheses represent the oxidation states of iodine. Table 4 shows the most relevant oxidation/reduction reactions and their conditions to obtain the desired oxidation state. The redox reactions between iodide and molecular iodine are fast since only electron transfer is involved. However, reactions between iodide or molecular iodine and iodate are relatively slow because these reactions require re-formation of a covalent bond between iodine and oxygen atoms. In this study, iodate is the preferred species and therefore NaClO solution is used to maintain enough oxidative condition for iodate.
The iodide ion has a strong affinity to monovalent silver ion (Ag\textsuperscript{+}) and their salt, AgI, shows a extremely low solubility to water (1.22×10\textsuperscript{-8} mol/L at 25°C).\textsuperscript{[8]} Therefore, methods for iodide removal have been established and industrial materials are available for this purpose. For example, Silcarbon Aktivkohle GmbH has been producing activated carbon granules with impregnated Ag\textsuperscript{+}, which adsorbs iodide ions efficiently.\textsuperscript{[9]} In this study, this material was used for the quality control of the radioactive iodate tracer solutions. However, on the other hand, the iodate ion does not show a strong affinity to ordinal cations to form insoluble salts, and therefore it is necessary to investigate new materials which can adsorb iodate efficiently for the removal of whole radioactive iodine in a solution.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Oxidation / Reduction</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>I\textsuperscript{-} → I\textsubscript{2}</td>
<td>Oxidation</td>
<td>H\textsubscript{2}O\textsubscript{2} or NaNO\textsubscript{2} in acid</td>
</tr>
<tr>
<td>I\textsuperscript{-} → IO\textsubscript{3}\textsuperscript{-}</td>
<td>Oxidation</td>
<td>NaClO in base or KMnO\textsubscript{4} in acid</td>
</tr>
<tr>
<td>I\textsubscript{2} → I\textsuperscript{-}</td>
<td>Reduction</td>
<td>HSO\textsubscript{3}\textsuperscript{-} or SO\textsubscript{3}\textsuperscript{2-} or SO\textsubscript{2}</td>
</tr>
<tr>
<td>IO\textsubscript{3}\textsuperscript{-} → I\textsubscript{2}</td>
<td>Reduction</td>
<td>NH\textsubscript{2}OH-HCl in acid.</td>
</tr>
</tbody>
</table>

### 2.3.4. Tracer solution

In this study, a carrier-free Na\textsuperscript{125}I solution in 1.0×10\textsuperscript{-5} M NaOH solvent purchased from PerkinElmer was used as a tracer. Its radionuclidic purity was 99.95\% and radiochemical purity was 99.8\%. In order to convert iodide ions to iodate, NaClO (0.14\% active chlorine) solution was used.
2.4. Characterization methods

2.4.1. Gamma counter

Gamma counters are instruments used to measure gamma rays emitted by radionuclides. Gamma-ray measurement is a chief experimental technique to study the high energy photons which are characteristic of the specific initial- and final-state nuclear energy levels of the radioactive decays.\(^{[24][25][26][27][28]}\)

2.4.1.1. Gamma ray

Gamma rays are energetic, short-wave electromagnetic radiations. The waves are emitted as photons by the excited nuclei of radioactive atoms such as daughter nuclides of alpha and beta decay, or products of fission and nuclear reactions that are induced by particle bombardments. The emitted photons have radiation levels that vary in energy between \(10^{-15}\) and \(10^{-10}\) J corresponding to a wavelength of \(10^{-10}\) to \(10^{-14}\) m and are highly penetrating. They are stopped by materials with a high density such as lead, concrete, and steel.\(^{[24][25][26][27]}\)

Importantly, gamma rays are usually considered to be emitted by the parent nuclides, although they are from the transition states of the daughter nuclides. Since the de-excitations usually occur in a short period where the half-life is in nanosecond order, they can be considered as a part of decay of the parent nuclides.

2.4.1.2. Principle of gamma counting

The energy state structure of a nucleus varies depending on the number of protons and neutrons, also on the shape and motion state of the nucleus. Therefore, each atom has a characteristic energy state structure. The energy of a gamma ray corresponds to the energy between the excited states and ground or relaxed states of daughter nuclides. Thus, each
radionuclide shows a characteristic gamma-ray spectrum, and therefore it is possible to measure the activity of one certain radioactive species by setting target energy of radiations.\textsuperscript{[28]}

In addition, since gamma rays are highly penetrating, the measurement can be carried out directly from the original sample without radiochemical separations.

### 2.4.1.3. Calculation of activities

Radioactivity is determined by counting a number of decays within a unit time (i.e. count rate). Gross count rate is a count rate, in which all the detections by a counter are taken into account, and is defined as follows:\textsuperscript{[29]}

\[
R_g = \frac{x}{t}
\]  
\hspace{1cm} (24)

where

\begin{align*}
R_g &= \text{gross count rate of the sample} \\
x &= \text{counts of gamma rays} \\
t &= \text{measurement time}
\end{align*}

Net count rate is a count rate, in which background radiations are also taken into account, and is calculated as:

\[
R_n = R_g - R_{bg}
\]  
\hspace{1cm} (25)

where

\begin{align*}
R_n &= \text{net count rate of the sample} \\
R_{bg} &= \text{gross count rate of background}
\end{align*}

The detailed discussion about background radiations can be found in section 2.4.1.5. In this
study, count rates are always referred to net count rates and presented in the unit of count-per-minute (cpm).

### 2.4.1.4. NaI detector

In this study, gamma counting was performed with a scintillation detector, which is made of thallium-doped sodium iodide (NaI(Tl)). The mechanism of gamma counting is as follows; the gamma rays which enters the NaI(Tl) crystal excites electrons, and photons are emitted at the transition from the excited state to the ground state. Those photons are captured by a photocathode and converted to a flow of electrons, which form an electric pulse. Then the pulses are amplified at the electron multiplying dynodes, and the final pulses are detected as voltage signals. By counting the number of the voltage signals, the radioactivity of the sample can be estimated.\(^{[30]}[31]\)

### 2.4.1.5. Background

In radiation measurements, there are always some effects from the background which may cause inaccuracy if it is not taken account.\(^{[32]}\) The background count rate originates from such as cosmic rays and radioactive substances in nature. Especially when samples with low activities are measured, it is important to know about the background radiation in the measurement area, so that the background can be subtracted. Also, background radiation can affect the lower limit of detection. Therefore, when the count rate of a sample is calculated, the background counts always need to be subtracted from the measured value.
2.4.2. **X-ray Diffraction (XRD)**

X-ray diffraction is one of the non-destructive analytical techniques, which reveals the crystal structures and atomic spacing of samples, based on the scattered intensity of an X-ray beam hitting a sample as a function of angles.[34]

### 2.4.2.1. Principles

X-ray diffraction is based on an interference of X-rays on a crystalline sample. Incident X-rays are diffracted depending on what atoms are in the crystal lattice and how these atoms are aligned. The interaction between the incident and diffracted X-rays produces constructive interference when conditions satisfy Bragg's Law, which can be written as follows;[34][35][36]

\[ 2d \sin \theta = n\lambda \]  

(26)

where

- \( d \) = distance between lattice planes (d-spacing)
- \( \lambda \) = wavelength of the X-ray
- \( \theta \) = scattering angle (Bragg angle)
- \( n \) = integer representing the order of the peak

This law relates the wavelength of X-ray to the diffraction angle and the distance between lattice planes in a crystalline sample. The diffracted X-rays from different atoms can interfere with each other, which causes strongly modulated intensity distribution. If the atoms are arranged in a periodic manner, such as forming crystal lattices, the diffracted rays create sharp peaks corresponding to d-spacings. Amorphous materials can also be recognized by the absence of peaks. Therefore, by measuring the diffraction pattern, the underlying structures of the samples can be determined.
In addition, the Bragg's Law can be applied not only to atoms but also scattering centers consisting of any periodic distribution of electron density, such as a collection of molecules.

![Lattice planes and Bragg's law](image)

**Fig. 3:** Schematic image of lattice planes and Bragg’s law.

### 2.4.2.2. Powder Diffraction

In a powder sample, crystalline domains are randomly oriented. Therefore, the 2-dimensional diffraction pattern appears like concentric rings. Those rings are the scattering peaks, which are corresponding to the various distances $d$ of the lattice planes.\[^{34}\]

Powder diffraction data can be collected using either transmission or reflection geometry, as shown in Fig. 5. Because the particles in the powder sample are randomly oriented, these two methods will yield the same data. In either method, the angle between the incident and diffracted X-rays is $2\theta$, because the angle $\theta$ is defined between a lattice plane and an incident or a diffracted ray. Therefore, the patterns are measured as a function of $2\theta$. In this study, the data were obtained by $2\theta$-scanning of the reflection mode with a 1-dimensional detector.
2.4.2.3. Miller indices

Since the peaks of an XRD pattern are due to the diffraction on parallel lattice planes, it is necessary to distinguish a set of parallel lattice planes from another. Miller indices are the labels, which are used to define a set of parallel planes in a crystal so that nonparallel planes can be distinguished.\textsuperscript{35}\textsuperscript{36}\textsuperscript{37} Miller indices are determined by three smallest integers \((h, k\) and \(l)\) whose ratio is equal to the reciprocal of the intercept on the axes along the unit cell by the plane of concern. Miller indices are used to identify the peaks of XRD patterns in order to know the lattice structure.
2.4.2.4. Simulation by CaRIne Crystallography

CaRIne Crystallography (CaRIne) is software which deals with different geometrical characters of crystals including 3D images of lattices and X-ray diffraction patterns. In this study, this software was used for XRD pattern simulation, and the simulation method is as follows.

The calculation of the X-rays diffraction is done from the parameters of a unit cell, for randomly orientated powder. The diffraction angle is calculated from the interplanar distance and from the incident wavelength $\lambda$:

$$\lambda = 2 \sin \left( \frac{d_{hkl}}{n} \right)$$  \hspace{1cm} (27)

where

- $d_{hkl}$ = the interplanar distance of 2 parallel planes with Miller indice $(hkl)$

For each $(hkl)$ plane, the structure factor is computed using equation below:

$$F_{hkl} = \sum_{n=1}^{N} f_n \cdot f_{occ} \cdot \exp \left[ 2\pi i (h \cdot x_n + k \cdot y_n + l \cdot z_n) \right]$$  \hspace{1cm} (28)

where

- $f_n$ = the atomic diffraction factor for X-rays
- $x_n, y_n, z_n$ = the coordinates of the nth atom of the cell
- $f_{occ}$ = the occupation factor of the site $(0 < f_{occ} \leq 1)$

The atomic scattering factors vary as a function of the Bragg angle or the angle which satisfies Brag’s Law, and the wavelength of X-ray. CaRIne uses the following approximation:
\[ f \left( \frac{\sin \theta}{\lambda} \right) = \sum_{i=1}^{4} a_i \cdot \exp \left[ -b_i \cdot \left( \frac{\sin \theta}{\lambda} \right)^2 \right] + c \]  

(29)

where

\[ a_i, b_i, c = \text{fitting coefficients} \]

To compute the peak intensities, CaRIne takes into account the following factors:

- The Lorentz factor:

\[ f_{\text{Lorentz}} = \frac{1}{4 \sin^2 \theta \cos \theta} \]  

(30)

- The polarization factor:

\[ f_{\text{Polarization}} = \frac{1}{2} (1 + \cos^2 \theta) \]  

(31)

- The temperature factor (supposed to be constant for all atoms of the cell):

\[ f_{\text{Temperature}} = \exp \left[ -2B \left( \frac{\sin \theta}{\lambda} \right)^2 \right] \]  

(32)

where

\[ B = \text{Debye–Waller factor}^{[38]} \]

The temperature factor is given manually.

In addition, the multiplicity factor \( f_{\text{Multiplicity}} \), which depends on the \((hkl)\) plane and on the unit cell, is taken into account as well.

Finally, the intensities of the peaks are computed as:
\[ I = \|F\|^2 \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \exp \left[ -2B \left( \frac{\sin \theta}{\lambda} \right)^2 \right] \cdot p \quad (33) \]

where

\[ F = \sum f_i \text{ (the sum of all the factors in concern)} \]

And these intensities are relatively normalized to the highest peak.

### 2.4.3. Zeta potential

#### 2.4.3.1. Principles

The zeta potential is the energy potential at the interface between a surface of a charged particle and liquid medium, which describes the charging behavior at the interface.\(^{[39]}\) It is a valuable parameter to compare the states of material surfaces in terms of their charging behavior at different conditions.

The definition of the zeta potential is explained by the model of the electrochemical double layer (EDL) shown in Fig. 6. When charged particles are suspended in an aqueous solution, ions of the opposite charge are attracted to the surface of the particles, which causes a surface charge. The surface charge affects the charge distribution in the interfacial region, increasing the concentration of counterions close to the surface. Then a surface potential of the solid particles rises furthermore, which decays with the distance from the surface. As a result of these phenomena, an electrochemical double layer is formed at the interface.

This EDL model distinguishes two layers: a stationary immobile layer and a diffuse mobile layer. The stationary immobile layer is an inner region, in which ions are bound relatively tightly to the particle surface, and the diffuse mobile layer is an outer region, in which the distribution of counterions that compensate the surface charge is determined by a balance of
electrostatic forces and random thermal motion. Between the stationary layer and the diffuse layer, there is a boundary, inside which any ions move with the particle when it moves in the liquid. On the other hand, outside the boundary, any ions stay where they are. This boundary is called a shear plane where the zeta potential exists.

Fig. 6: Model of the electrochemical double layer at the solid-liquid interface (Ψ\(_S\): surface potential, ζ: zeta potential).\(^{[39]}\)

### 2.4.3.2. Surface charge formation

The charge formation at the solid-liquid interface arises by different mechanisms. Among them, the acid-base reaction between the solid surface and an aqueous solution and the physical adsorption of water-originated ions are dominant processes.\(^{[39]}\)

The surface charges generated by acid-base reactions are derived by the functional groups of the material surface. For this acid-base reaction, the pH of an aqueous solution is one of the driving forces. For example, a high pH enhances the dissociation of acidic groups but
suppresses the protonation of basic groups. Therefore, from the pH dependence of zeta potential, the type and strength of the functional groups which are present on the solid surface can be known.

Meanwhile, material surfaces without functional groups behave hydrophobically in aqueous solutions. By these hydrophobic surfaces, some of the water molecules are affected and get replaced by hydroxide and hydronium ions. Hydroxide ions prefer hydrophobic conditions more than hydronium ions or water, and thus they substitute water molecules, which are adsorbed at the hydrophobic surfaces. This process makes the solid-liquid interface behave more acidic than the bulk water phase. As pH becomes higher, the concentration of hydroxide ions increases, which render the surface charge negative. However, at a low pH, the concentration of hydronium ions becomes high and the surface gets positively charged, and thus the dissociation of water molecules is suppressed. Therefore, it can be said that the charging of hydrophobic surfaces or surfaces without functional groups also strongly depends on the pH.

Since both the acid-base reaction and the physical adsorption processes strongly depend on the pH of the solution, pH is the most important parameter which contributes the zeta potential.

2.4.3.3. pH dependence of the zeta potential

The pH dependence of the zeta potential reveals important information about the nature of the charges and thus the chemistry of the surface. The different pH dependences of the zeta potential on the different charging mechanism are shown in Fig. 7. At a certain pH, the zeta potential becomes 0 mV and reverses its sign when moving from high to low pH. The pH is known as the isoelectric point (IEP). At this point, equilibrium between negative and positive charges on the surface, which in average gives zero net charge, is reached. IEP can be
determined from the analysis of zeta potential at different pH, and since different kinds of charging of the surfaces return different values of IEP, it can be used to describe the acidic or basic characters of the material surface.

Fig. 7: pH dependences of the zeta potential for material surfaces with acidic, basic and amphoteric behavior.\textsuperscript{[39]}

2.4.4. Uncertainty

Any kinds of experimental results include some uncertainties. Uncertainties associated with measurements are divided into two categories: random and systematic uncertainties. All uncertainties are summed up to form the total uncertainty.\textsuperscript{[40]}
2.4.4.1. Systematic uncertainties

In this study, uncertainties of measurements due to instruments are estimated as Table 5 shows. The estimation is based on the user’s manual of each instrument. The systematic uncertainty of the gamma counter was not taken into account because only the ratio of the count rates of samples is employed to characterize the material and therefore the uncertainty factor of the gamma counter is cancelled during the calculations.

<table>
<thead>
<tr>
<th>Property</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>0.0002 g</td>
</tr>
<tr>
<td>pH</td>
<td>0.1</td>
</tr>
<tr>
<td>Volume (pipette)</td>
<td>1.0%</td>
</tr>
<tr>
<td>Concentration of solution</td>
<td>2.0%</td>
</tr>
<tr>
<td>Time (for kinetics)</td>
<td>1.0 minute</td>
</tr>
</tbody>
</table>

2.4.4.2. Uncertainty of radioactivity measurements

Radioactive decay is random phenomena, and therefore the uncertainty from the randomness is described with the Poisson distribution. However, when the number of decays is large enough (> 100), the Poisson distribution can be approximated as Gaussian distribution given by the following equation: \[ \text{[40][41]} \]
\[ P_x = \frac{1}{\sqrt{2\pi} \sigma^2} e^{-\frac{(x-M)^2}{2\sigma^2}} \]  \hspace{1cm} (34)

where

\[ P_x = \text{the probability of decays at a unit time} \]
\[ M = \text{the mean (average) ratio} \]
\[ \sigma = \text{the standard deviation} \]

The standard deviation can be written as follows:

\[ \sigma \approx \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}} \]  \hspace{1cm} (35)

where

\[ x_i = \text{the number of pulses observed} \]
\[ \bar{x} = \text{the arithmetic mean value} \]
\[ n = \text{the number of measurements} \]

Also, the standard deviation of the average can be written as follows:

\[ \sigma_{\bar{x}} = \frac{\sigma_x}{\sqrt{n}} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n(n - 1)}} \]  \hspace{1cm} (36)

Usually, instead of several measurements, only one single measurement is carried out. The uncertainty, i.e. standard deviation \( \sigma_x \), of a single measurement is calculated as follows:

\[ \sigma_x = \sqrt{x} \]  \hspace{1cm} (37)
2.4.4.3. The propagation law of uncertainty

If a physical property is calculated with several variables, each of which has own uncertainty, the overall uncertainty of the property can be derived by the propagation law as:  

\[ \sigma = \sqrt{\sum_k \left( \frac{\partial f(k)}{\partial k} \sigma_k \right)^2} \]  

(38)

According to the propagation law, the uncertainties of the physical properties used for characterization of the material in this study are calculated by following equations. Firstly, the uncertainty of count rate can be described as follows:

\[ \sigma_{R_n} = \frac{x_g}{t_g^2} + \frac{x_{bg}}{t_{bg}^2} \]  

(39)

where

- \( x_g \) = gross counts of gamma ray
- \( x_{bg} \) = gross counts of background radiation
- \( t_g \) = measurement time of gross counts
- \( t_{bg} \) = measurement time of background

For isotherm, the uncertainty of the concentration of ion A in the solution (equation (13)) and the amount of adsorbed tracer with the exchanger (equation (14)) is expressed respectively as follows:

\[ \sigma_{c_A} = \left[ \left( \frac{c_A}{V_{total} \cdot \sigma_{c_A}} \right)^2 + \left( \frac{v_A \cdot c_A}{V_{total} \cdot \sigma_{total}} \right)^2 + \left( \frac{v_A}{V_{total} \cdot \sigma_{c_A}} \right)^2 \right]^{\frac{1}{2}} \]  

(40)
\[ \sigma_{\text{IA}} = \left( \frac{c_A}{m_{\text{exc}}} \cdot \frac{R_{n,\text{ref}} - R_{n,\text{sample}}}{R_{n,\text{ref}}} \cdot \sigma_{v_A} \right)^2 + \left( \frac{v_A}{m_{\text{exc}}} \cdot \frac{R_{n,\text{ref}} - R_{n,\text{sample}}}{R_{n,\text{ref}}} \cdot \sigma_{c_A} \right)^2 \\
+ \left( - \frac{v_A^2 \cdot c_A^2}{m_{\text{exc}}^2} \cdot \frac{R_{n,\text{ref}} - R_{n,\text{sample}}}{R_{n,\text{ref}}} \cdot \sigma_{m_{\text{exc}}} \right)^2 \\
+ \left( - \frac{v_A \cdot c_A}{m_{\text{exc}}} \cdot \frac{1}{R_{n,\text{ref}}} \cdot \sigma_{R_{n,\text{sample}}} \right)^2 + \left( \frac{v_A \cdot c_A}{m_{\text{exc}}} \cdot \frac{R_{n,\text{sample}}}{R_{n,\text{ref}}^2} \cdot \sigma_{R_{n,\text{ref}}} \right)^2 \right]^{1/2} \quad (41) \\

For a batch operation, the uncertainty of the distribution coefficient (equation (20)) and the absorption rate (equation (21)) is expressed respectively as follows:

\[ \sigma_{K_d} = \left[ \left( \frac{1}{M} \left( \frac{R_{n,\text{ref}}}{R_{n,\text{sample}}} - 1 \right) \right)^2 V \left( \frac{R_{n,\text{ref}}}{R_{n,\text{sample}}} - 1 \right) \right] \sigma_M \]
\[ + \left( \frac{V}{M \cdot R_{n,\text{sample}}} \cdot \sigma_{R_{n,\text{ref}}} \right)^2 + \left( - \frac{V \cdot R_{n,\text{ref}}}{M \cdot R_{n,\text{sample}}^2} \cdot \sigma_{R_{n,\text{sample}}} \right)^2 \right]^{1/2} \quad (42) \\

\[ \sigma_A = \left[ \left( - \frac{1}{R_{n,\text{ref}}} \cdot 100 \cdot \sigma_{R_{n,\text{sample}}} \right)^2 + \left( \frac{R_{n,\text{sample}}}{R_{n,\text{ref}}^2} \cdot 100 \cdot \sigma_{R_{n,\text{ref}}} \right)^2 \right]^{1/2} \quad (43) \\

For a column operation, the uncertainty of the activity ratio of the effluent against influent B (equation (23)) is calculated as follows:

\[ \sigma_B = \left[ \left( \frac{1}{R_{n,\text{inf}}} \cdot 100 \cdot \sigma_{R_{n,\text{eff}}} \right)^2 + \left( - \frac{R_{n,\text{eff}}}{R_{n,\text{inf}}^2} \cdot 100 \cdot \sigma_{R_{n,\text{inf}}} \right)^2 \right]^{1/2} \quad (44) \]
3. Experimental

3.1. Synthesis of hydrous zirconia

Firstly, 1000 mL of 6 M HNO$_3$ solution was prepared in a 3L-beaker, and 100.0124 g (0.3443 mol) of zirconium carbonate basic hydrate ([ZrO$_2$]$_2$·CO$_2$·xH$_2$O, produced by Alfa Aesar) was added gradually while stirred. After all the salts were dissolved, the solution was stirred for 1 hour. The approximate pH was checked by Macherey-Nagel Universal pH indicator papers, and it was less than 1 at this point.

After that, 6 M NH$_3$ solution was added slowly with a separatory funnel to neutralize up to pH 7.8 (the actual pH was 7.82). The pH was monitored by pH paper when it was between less than 1 to around 3, and by pH meter when it was over 3. In total, approximately 1220 mL of NH$_3$ solution was added.

After the pH reached 7.8, the solution was settled overnight while stirring. Then the supernatant was removed with a suction pipette. Deionized water was added to rinse the precipitates and the mixture was stirred for 10-15 min and then settled. After that, the supernatant was removed by a suction pipette again. This rinsing step was repeated 17 times in total until the conductivity becomes less than 3 mS/cm at room temperature (actual conductivity was 2.94 mS/cm, which was measured by Hanna Instruments HI-99301 EC/TDS/Temperature Meter - High Range). The pH of the supernatant was monitored by a pH meter and the final pH was 5.43.

The precipitates were transferred into ceramic dishes and dried in an oven at 70 °C for 3 days. The dried sample was ground into a powder and sieved through 100-mesh and 200-mesh screens to the particle-size of 74-149 μm.
3.2. Physical characterization

3.2.1. Crystallinity

The crystallinity of synthesized hydrous zirconia was characterized by powder XRD measured by Malvern Panalytical X’Pert$^3$ Powder. The X-rays were produced with a Cu anode and their wavelength was 1.5405980 Å.

3.2.2. Zeta potential

10 mL of 10 mM NaNO$_3$ and 20 mg of hydrous zirconia, 50 μL of I-125 tracer solution, and various amount of 0.5 M NaOH solution to adjust equilibrium pH were added into a 20-mL scintillation vial, and the mixture was equilibrated by a rotary mixer for 24 hours. The amount of NaOH solution to be added was estimated by titration experiments beforehand. After the equilibration, the zeta potential of at different pH values from 3.5 to 10 was measured by Malvern Panalytical Zetasizer Nano ZS.

3.3. Evaluation of the ion-exchange ability

3.3.1. Batch operation

As a general procedure after the 24-hour equilibration, all the batch samples were centrifuged by Thermo Fisher Scientific Heraeus Megafuge 1.0R with 2773 ×g for 10 minutes and filtered with Pall Laboratory Acrodisc Syringe Filters (13 mm). After those steps, pH of each solution was measured by Thermo Scientific Orion Star A211 pH Benchtop Meter, and the count of gamma rays from I-125 was measured for 1200 seconds by PerkinElmer Wallac Wizard 3” 1480 Gamma Counter. For gamma measurement, reference samples are prepared with 10 mL of the same solution and 50 μL of the same tracer without the addition of hydrous zirconia and bases or acids to adjust pH. Distribution coefficients ($K_d$) and adsorption rates were then calculated.
3.3.1.1. Quality control of I-125 tracer solutions

Quality control measurements were carried out first to know how long the conversion from iodide to iodate takes, and secondly to make sure most of the I-125 nuclides exist as iodate stably in the tracer solution,

First, to convert iodide ions to iodate, 6 mL of the Na\textsuperscript{125}I solution, 0.2 mL of 1 M NaOH solution, 0.2 mL of NaClO (0.14% active chlorine) solution, and 13.6 mL of deionized water were mixed (reference number: 856-1-4) and settled for 3, 5, and 10 days. After the settlement, 10 mL of 10 mM NaNO\textsubscript{3}, 20 mg of hydrous zirconia, or silver-impregnated granular activated carbon produced by Silcarbon Aktivkohle GmbH, hereinafter called Ag-C, and 50 μL of the I-125 tracer solution were added into a 20-mL scintillation vial, and the mixture was equilibrated by a rotary mixer for 24 hours.

For the purpose of quality control, batch operations in the same procedure were carried out on all the other tracer solutions (reference number: 856-1-3, 856-1-5 and 885-1-1), which were all used in this study. The measurement was carried out multiple times to track if I-125 iodate ions stably exist.

3.3.1.2. Kinetical behavior

In order to know how long it takes for the ion exchange system to reach equilibrium, the kinetical behavior of the material was investigated by 2 different methods.

3.3.1.2.1. With vials (Normal batch operation)

10 mL of 10 mM NaNO\textsubscript{3}, 20 mg of hydrous zirconia, 50 μL of I-125 tracer solution, and 20 μL of 0.5 M NaOH solution to adjust equilibrium pH to 4 were put into a 20-mL scintillation vial, and the mixture was equilibrated for the target length, such as 15 minutes, 30 minutes, 1
hour, 2 hours, 4 hours, 6 hours, 1 day, 2 days, 4 days, and 7 days.

### 3.3.1.2.2. With a beaker

200 mL of 10 mM NaNO\(_3\), 0.1 g (the actual amount was 0.1003 g) of hydrous zirconia, and 2 mL of I-125 tracer solution were added into a 400-mL beaker. The mixture was stirred by a magnetic stirrer and approximately 4 mL of supernatant was taken for measurement at every time point of 15 minutes, 30 minutes, 1 hour, 2 hours, 4 hours, 6 hours, 1 day, 2 days, 4 days, and 7 days. The taken supernatant was filtered with syringe filters. 2 sets of 1 mL of filtered solution were used for the gamma-ray count measurement and the rest of the taken solution was used to measure pH.

### 3.3.1.3. Ion exchange capacity (isotherm)

The ion exchange capacity (isotherm) was investigated. 10 mL of 10 mM NaNO\(_3\), 20 mg of hydrous zirconia, various amount of 0.2 M KIO\(_3\) solution, various amount of 0.5 M NaOH or 0.5 M HNO\(_3\) solution to adjust equilibrium pH to 4, and 50 μL of I-125 tracer solution were added into the scintillation vial, and the mixture was equilibrated by a rotary mixer for 24 hours. The amount of NaOH or HNO\(_3\) solution to be added was estimated by titration experiments beforehand. Further information about the pH adjustment can be found in section 6.2.1. Then the gamma count-rate and pH were measured for each sample.

### 3.3.1.4. Competition of anions

The competition effect of different anions was investigated. 10 mL of 10 mM NaNO\(_3\), NaCl, NaSO\(_4\) or H\(_3\)BO\(_3\), 20 mg of hydrous zirconia, 50 μL of I-125 tracer solution, and various amount of 0.5 M NaOH or 10 mM corresponding acid solution to adjust equilibrium pH were added into a 20-mL scintillation vial, and the mixture was equilibrated by a rotary mixer for
24 hours. The amount of NaOH solution to be added was estimated by titration experiments beforehand. Further information about the pH adjustment can be found in section 6.2.2.

3.3.1.5. Effect of concentration of competing anions

The competition effect of different anions of the various concentrations was investigated. 10 mL of 0, 1, 10, or 100 mM NaNO₃, NaCl, NaSO₄, or H₃BO₃, 20 mg of hydrous zirconia, 50 μL of I-125 tracer solution, and various amount of 0.5 M NaOH solution to adjust equilibrium pH to 4 or 8 were added into a 20-mL scintillation vial, and the mixture was equilibrated by a rotary mixer for 24 hours. The amount of NaOH solution to be added was estimated by titration experiments beforehand. Further information about the pH adjustment can be found in section 6.2.2.

3.3.1.6. Effect of post-heating

The effect of post-heating on the crystal structure of hydrous zirconia and its ion-exchange ability was investigated. Approximately 0.5 g of hydrous zirconia was heated at 200, 400, 600, 800, or 1000 °C in an oven for 24 hours. 10 mL of 0, 1, 10, or 100 mM of NaNO₃, NaCl, NaSO₄, or H₃BO₃, 20 mg of treated hydrous zirconia, 50 μL of I-125 tracer solution, and 20 μL of 0.5 M NaOH solution to adjust equilibrium pH to 4 were added into a 20-mL scintillation vial, and the mixture was equilibrated by a rotary mixer for 24 hours. The amount of NaOH solution to be added was estimated by titration experiments beforehand. Further information about the pH adjustment can be found in section 6.2.3. The crystal structures of hydrous zirconia heated at each temperature were measured by XRD. To identify the crystal structure, XRD patterns as references were simulated with CaRIne Crystallography by adopting the lattice parameters of ZrO₂ which were previously reported.^[46]
3.3.2. Column operation

The iodine removal ability of the material under simulated wastewater from Fukushima Daiichi Nuclear Power Plant was investigated, by measuring the breakthrough curve of the column set up.

3.3.2.1. Preparation of Fukushima simulant

6.6937 g of CaCl$_2$, 4.2208 g of Mg(NO$_3$)$_2$·6H$_2$O, 2.0007 g of Na$_2$SO$_4$, 90 mL of 3 M HCl, and 14 mL of 5 M NaOH solution were added to a 5-L volumetric flask, and the volume was adjusted up to 5 L by deionized water. The solution was left overnight to make sure all the salts were dissolved. To adjust the pH between 7 and 7.5, in total 620 μL concentrated HCl (37%) solution and 13.5 mL of 15 M NaOH were added. After the equilibration of 24 hours, the pH of the solution was 7.491 and the conductivity was 10.30 mS/cm at room temperature.

Another 5 L of Fukushima simulant was prepared in the same method with 6.7011 g of CaCl$_2$, 4.2223 g of Mg(NO$_3$)$_2$·6H$_2$O, 2.0084 g of Na$_2$SO$_4$, 54 mL of 5 M HCl, and 14 mL of 5 M NaOH solution and deionized water. To adjust pH, 10 mL of 15 M NaOH, 10 mL of 5 M NaOH, 100 μL of 0.5 M NaOH, and 660 μL of 5 M HCl solutions were added. After 24-hour equilibration, pH was 7.175 and the conductivity was 9.27 mS/cm.

After the preparation of the simulant, I-125 tracer was added. The count rates of 5 mL of the solution were adjusted to 1000–1500 cpm by changing the amount of the tracer added.

3.3.2.2. Operation

1.0210 mL (approximately 1.2 g) of the hydrous zirconia was loaded to a column tube. The column was connected through tubes to a tank of an influent (Fukushima simulant radio-labeled with an I-125 tracer solution), a pump and a sample collector as Fig. 8 shows. The influent went through the hydrous zirconia particles, while I-125 iodate ions were
removed by the material. Sample fractions were collected hourly and the pump speed was adjusted to where the volume of each fraction was about 10.5-11 mL. For every ten fractions, pH and the count rate were measured.

![Fig. 8: The picture of the column system.](image)

4. Results and Discussion

4.1. Synthesis

During the neutralization of the starting solution, a white gelatinous precipitation was obtained. After the drying in an oven, 48.5667 g of white solids were obtained. This weight is corresponding to 0.3941 mol of pure ZrO$_2$, although the amount of the starting material ([ZrO$_2$]$_2$·CO$_2$·xH$_2$O) was 0.3443 mol. This excess of mass may be because the obtained material is hydrous zirconia, which has incorporated water in the structure of ZrO$_2$. 
4.2. Physical characterization

4.2.1. Crystallinity

The powder XRD pattern of the obtained material is shown in Fig. 9. It can be said that the material was amorphous, which is corresponding to the results previously reported.[17][20][21]

Fig. 9: Powder XRD pattern of the synthesized hydrous zirconia.

4.2.2. Zeta potential

According to the linear approximation of the pH dependence of zeta potential (Fig. 10) from pH 7 to 8, the IEP is estimated at about 7.9, although the reported value is 6.7.[22] The IEP of ZrO₂ is reported as 10-11,[22] and thus it is assumed that existence of ZrO₂ contributed to the high IEP.

In addition, by comparing Fig. 10 to Fig. 7, it can be concluded that the material surface shows a character in between amphoteric and basic.
Fig. 10: pH dependence of zeta potential of the material in 10 mM NaNO$_3$ solution. (The error bars represent uncertainties of pH and standard deviations of the potential measurement. The blue broken line is a linear approximation line around pH 7-8).

### 4.3. Evaluation of the ion-exchange ability

#### 4.3.1. Batch operation

##### 4.3.1.1. Quality Control of I-125 tracer solutions

Basically, hydrous zirconia adsorbs only iodate and Ag-C only iodide. Since the purchased Na$^{125}$I solution is carrier-free, the low adsorption rate and $K_d$ of hydrous zirconia and the high adsorption rate and $K_d$ of Ag-C indicate the major existence of iodide ions. In order to carry out experiments, the ratio of iodate to iodide has to be high enough, or in other words, the adsorption rate of hydrous zirconia has to be high enough (> 95%).
According to the graph of the time dependence of adsorption rates and distribution coefficients of both materials for the tracer solution 856-1-4 (Fig. 11), it can be said that it took 10 days to convert most of the iodide ions to iodate until the ratio reached to the desirable level. On day 10, the adsorption rate of hydrous zirconia was 95.74 ± 0.02% and $K_d$ was 11,400 ± 200 mL/g, and those of Ag-C was 9.13 ± 0.07% and 49.5 ± 0.8 mL/g respectively.

Fig. 11: the time dependence of the adsorption rate and distribution coefficient in 10 mM NaNO$_3$ solution for the tracer solution 856-1-4. (“ZrO$_2$”stands for hydrous zirconia).
Fig. 12: The adsorption rates and distribution coefficients of hydrous zirconia and Ag-C in 10 mM NaNO₃ solution for different tracer solutions measured on different dates. (ZrO₂ stands for hydrous zirconia. The measurement dates are written as dd/mm in 2019).
The same measurements on different tracer solutions on different dates (Fig. 12) indicates that once the ratio of iodate becomes high enough, the iodate ions stably exist in the solution and the quality of I-125 iodate tracer solution has been successfully maintained. The measurement results of 856-1-3 even showed it was stable for at least 82 days.

4.3.1.2. Kinetical behavior

According to the graphs of the time dependence of pH and the iodate uptakes (Fig. 13 and Fig. 14), the ion-exchange reaction reaches equilibrium within 24 hours for normal batch operations with vials.

For the beaker operation, since the batch factor of the beaker operation changes every time the sample is taken, it is difficult to say when the reaction exactly reaches equilibrium. However, from Fig. 14, it can be said that the adsorption rate became high enough after 24 hours, which was similar to the results of the normal batch operation.

![Fig. 13: The time dependence of pH of the liquid phase.](image-url)
Fig. 14: The time dependence of the adsorption rates and distribution coefficients of hydrous zirconia in 10 mM NaNO₃ solution.
4.3.1.3. Ion exchange capacity (isotherm)

In the graph of the dependence of adsorption on the iodate concentration (Fig. 15), the curve of isotherm lies above the diagonal, it can be said that iodate ions are preferred to be adsorbed onto the surface of the material.

However, sometimes adsorption process is not reversible; once ions are adsorbed onto the material surface, they cannot be replaced by other ions in the liquid phase. In this experiment, 0.2 M KIO$_3$ solution was added to the vial and came into contact with the material before 50 μL of I-125 iodate tracer solution was added. Therefore, although from the graph it seems the iodate adsorption of the material saturates at around 1.8 mmol/g, the estimated value is not necessarily correct because the adsorption of nonradioactive iodate ions may interfere the later adsorption of radioactive iodate. To determine the saturation value, other experiments need to be carried out to take the possible irreversible adsorption process into account; 0.2 M KIO$_3$ solution and I-125 iodate tracer solution should be mixed before the contact to the material.

Fig. 15: Iodate concentration dependence of adsorption by the material at pH 4.
4.3.1.4. Competition of anions

As seen in the graph of the pH dependence of the iodate uptake with various competing anions (Fig. 16), the material showed smaller adsorption rates and distribution coefficients as pH got higher with any anions. This may be because at high pH, hydroxide ions in the liquid phase suppress desorption of hydroxide ions or incorporated water from the surface of hydrous zirconia.

In the range from pH 3 to 6, the samples in NaNO$_3$, NaCl, and H$_3$BO$_3$ showed similar adsorption rates and $K_d$ values. NaNO$_3$ and NaCl are salts of a monovalent acid and virtually all the salts are ionized, which can be concluded based on pKa values shown in Table 6 and the relation between pKa and pH which can be described as the following equation:[6][8]

$$\log \frac{[A^-]}{[HA]} = pH - pK_a$$

(45)

Applying the same logic, most of the H$_3$BO$_3$ molecules, on the other hand, are not ionized. It seems that the existence of monovalent anions of NO$_3^-$ and Cl$^-$ and H$_3$BO$_3$ molecules does not affect the iodate adsorption ability of the material in pH 3-6.

The samples in Na$_2$SO$_4$ solution showed lower adsorption rates and $K_d$ values compared to other anions especially in the range of pH 3-6. In this pH range, all the salts of Na$_2$SO$_4$ are virtually fully ionized, which results in the major existence of SO$_4^{2-}$ ions in the liquid phase. Since SO$_4^{2-}$ ions are divalent, they may have a larger affinity to the material surface than monovalent anions or unionized molecules and suppress the adsorption of iodate, which may explain the lower adsorption rates and $K_d$ values.
Fig. 16: pH dependence of the adsorption rates and distribution coefficients of hydrous zirconia in 10 mM solution of various anions.
When pH is higher than 6, the samples in H$_3$BO$_3$ solution showed a significant decrease in adsorption rate and $K_d$ values. This phenomenon may be due to the unique character of boric acid; unlike other protonic acids, it acts as a Lewis acid and accepts hydroxide ions.$^{[47]}$ Therefore, H$_3$BO$_3$ can be expressed as B(OH)$_3$ and its ionization in water can be written as:

$$\text{B(OH)}_3 + \text{H}_2\text{O} \rightleftharpoons \text{B(OH)}_4^- + \text{H}^+$$

Since pKa value of this reaction is 9.236 as shown in Table 6, it is likely to happen in the basic condition and this may result in the association of H$_3$BO$_3$ and hydroxide ions of the material surface and suppression of iodate adsorption, which is consistent with the result.

<table>
<thead>
<tr>
<th>Acid</th>
<th>pKa$_1$</th>
<th>pKa$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_3$</td>
<td>−1.37</td>
<td>-</td>
</tr>
<tr>
<td>HCl</td>
<td>−6.2</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>−3.59</td>
<td>1.99</td>
</tr>
<tr>
<td>H$_3$BO$_3$</td>
<td>9.236</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6: Dissociation constants of inorganic acids in water.$^{[48][49]}$

4.3.1.5. Effect of concentration of competing anions

Similarly to what is discussed in the previous section, the existence of monovalent anions of NO$_3^-$ and Cl$^-$ and H$_3$BO$_3$ molecules does not affect the iodate adsorption ability of the material irrespective of the concentration at pH 4 (Fig. 17, Fig. 18 and Fig. 19). And since divalent SO$_4^{2-}$ ions may have a larger affinity to the material surface, the adsorption of iodate is suppressed more when the concentration is higher.
Because H$_3$BO$_3$ is likely to be ionized at higher pH and affect the iodate adsorption, the same experiment was carried out at pH 8 as well for H$_3$BO$_3$ solutions, the result of which is presented in Fig. 20. Here it can be seen that the high concentration of H$_3$BO$_3$ solution drastically suppress the iodate adsorption, indicating that the affinity of H$_3$BO$_3$ toward hydroxide ions on the material surface is extremely high.

The adsorption rates and $K_d$ values for 100 mM H$_3$BO$_3$ recorded even below zero, which is probably partly due to a loss of iodine. Reference count rates were measured with samples of I-125 iodate tracer in 100 mM H$_3$BO$_3$ solution without addition of hydrous zirconia and pH adjustment (the equilibrium pH was approximately 2.9). Although iodate ions are basically stable, acidic condition triggers slight reduction of iodate into molecular iodine, and therefore the reference sample showed lower count rates than the samples at pH 8, which resulted in the negative adsorption rate and $K_d$. Further investigation of iodine loss depending on pH can be found in the supplement section 0.
Fig. 17: Adsorption rates and distribution coefficients of hydrous zirconia in 0, 1, 10, and 100 mM solution of various anions at pH 4. (Uncertainties are not indicated for simplicity).
Fig. 18: Adsorption rates of hydrous zirconia in 0, 1, 10, and 100 mM solution of various anions at pH 4.
Fig. 19: Distribution coefficients of hydrous zirconia in 0, 1, 10, and 100 mM solution of various anions at pH 4.
4.3.1.6. Effect of post-heating

Since hydrous zirconia is assumed to have a similar structure with ZrO$_2$,\textsuperscript{[20]} the simulation of XRD patterns was carried out with the lattice parameter of each crystal structure of ZrO$_2$.\textsuperscript{[46]}

As mentioned in section 4.2.1, the untreated material showed an amorphous pattern, which was also observed with the sample post-heated at 200 °C (Fig. 21). On the other hand, the one heated at 400 °C showed a crystalline structure, which can be identified as tetragonal. As the temperature of post-heating increased, the crystalline structure of samples became more monoclinic and the one heated at 1000 °C showed a pattern of nearly pure monoclinic structure. The detailed identification of peaks can be seen in Fig. 22. Overall, the peaks of the simulations are well-corresponding to those of the samples.

The native and adjusted equilibrium pH values in correlation to the post-heating temperatures can be found in Fig. 23. Native equilibrium pH stands for the pH value at equilibrium without
pH adjustment, meaning only the NaNO₃ solution and the material were added to a vial, which was measured during the titration. The samples heated at a higher temperature than 600 °C showed higher native pH around 5.8, which is close to equilibrium pH 5.7 of pure water exposed to the atmosphere. Also, from XRD patterns, those samples were assumed to have a monoclinic structure. Thus it can be said when hydrous zirconia is heated at a higher temperature than 600 °C, it becomes monoclinic and loses the sites for hydroxide ions and water to be incorporated, which results in less abstraction of hydroxide ions from the liquid phase and higher native equilibrium pH. Losing of the adsorption sites may also result in suppressing iodate adsorption, and actually, this assumption corresponds to the decrease of adsorption rate of samples which were post-heated at high temperatures, as shown in Fig. 24.

On the other hand, the material with tetragonal structure seems not to have lost the adsorption sites, which can be concluded from the native equilibrium pH and the iodate adsorption rate. Even the sample that was post-heated at 400 °C showed the highest adsorption rate and $K_d$ value of 96.07 ± 0.02% and 12,100 ± 200 mL/g respectively.
Fig. 21: Simulated XRD patterns of ZrO$_2$ and measured XRD patterns of untreated and post-heated hydrous zirconia at various temperatures.
Fig. 22: Identification of peaks on XRD patterns of post-heated hydrous zirconia at 400 and 1000 °C. (M: monoclinic, T: tetragonal).

Fig. 23: Native and adjusted equilibrium pH of the batch samples with untreated and post-heated hydrous zirconia at various temperatures.
Fig. 24: Adsorption rates and distribution coefficients of untreated and post-heated hydrous zirconia at various temperatures.
4.3.2. Column operations

From the calculated concentration of each ionic species in Fukushima simulants (Table 7), it can be stated that the first simulant had the almost same ionic composition as that of the second simulant. According to the results of the previous sections (section 4.3.1.4 and 0), the species which may cause the suppression of adsorption of iodate was only the \( \text{SO}_4^{2-} \) ion and its concentration was approximately 270 ppm or 2.8 mM in both solutions.

As of May 22 in 2019, the column has been operating for 42 days and approximately 11,000 bed-volume of the solution has gone through the column (Fig. 25). The pH of effluent became stable at around 5.8-5.9 after approximately 3,000 bed-volumes had gone through (Fig. 26). As for the activity ratio, it is predicted that the iodate adsorption may be suppressed gradually by the \( \text{SO}_4^{2-} \) ions in the Fukushima simulant and this tendency actually can be seen in Fig. 25. However, the iodate concentration is still around 50% and has not reached 100% breakthrough yet. The operation will be continued until the 100% breakthrough is reached.

Table 7: The concentration of each ionic species in 2 different Fukushima simulants in ppm and mM. (Uncertainties were calculated based on the values in Table 5).

<table>
<thead>
<tr>
<th>Ionic species</th>
<th>1st simulant ppm</th>
<th>1st simulant mM</th>
<th>2nd simulant ppm</th>
<th>2nd simulant mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^-)</td>
<td>2820 ± 60</td>
<td>79.4 ± 1.5</td>
<td>2790 ± 60</td>
<td>78.8 ± 1.5</td>
</tr>
<tr>
<td>NO(_3)^-</td>
<td>407 ± 5</td>
<td>6.57 ± 0.07</td>
<td>408 ± 5</td>
<td>6.59 ± 0.07</td>
</tr>
<tr>
<td>SO(_4)^{2-}</td>
<td>270 ± 3</td>
<td>2.81 ± 0.03</td>
<td>272 ± 3</td>
<td>2.83 ± 0.03</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>482 ± 5</td>
<td>12.03 ± 0.13</td>
<td>484 ± 5</td>
<td>12.08 ± 0.13</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>79.8 ± 0.8</td>
<td>3.28 ± 0.04</td>
<td>80.0 ± 0.9</td>
<td>3.29 ± 0.04</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>1380 ± 30</td>
<td>60.0 ± 1.2</td>
<td>1370 ± 30</td>
<td>59.7 ± 1.1</td>
</tr>
</tbody>
</table>
Fig. 25: The activity ratio of the effluent against influent in correlation to bed volume.

Fig. 26: pH of the effluent depending on bed volume.
5. Conclusion

In this study, synthesis and characterization of hydrous zirconia as an ion exchanger for radioactive iodate were carried out.

White solid of hydrous zirconia was successfully synthesized with the starting material of [ZrO$_2$]$_2$-CO$_2$-xH$_2$O solution by adding NH$_3$ solution. The obtained material had an amorphous structure, which was determined by powder XRD. By measuring the pH dependence of zeta potential of the material, the isoelectric point was approximated about 7.9, and the material surface showed a character in between amphoteric and basic.

After the physical characterization of the material, evaluation of the ion-exchange ability was carried out by using I-125 iodate tracer solutions, whose quality, in other words, the iodate/iodide ratio was inspected regularly.

For batch operations, the system of the material in contact on a solution reached equilibrium within 24 hours. Isotherm curve indicated that the material has a preference to adsorb iodate. The saturation value of adsorption was estimated to 1.8 mmol/g, although further investigation to reveal if the adsorption process is reversible.

A series of batch operation experiments at various pH and with different competing anions was carried out. The material showed lower uptakes as pH got higher with any anions, because of suppression of desorption of hydroxide ions or incorporated water from the surface of the material in a basic environment. In an acidic environment, monovalent NO$_3^-$, Cl$^-$ and unionized H$_3$BO$_3$ did not affect the iodate adsorption ability of the material with any concentration between 0 mM to 100 mM. However, divalent SO$_4^{2-}$ suppressed to some extent due to higher affinity to the material surface, and the suppression became stronger as the concentration got higher. In a basic environment, H$_3$BO$_3$ solution showed a significant decrease in adsorption rate and $K_d$ values probably because of the formation of B(OH)$_4^-$ with
hydroxide ions on the material surface. This suppression of iodate adsorption also became stronger as the concentration got higher.

Post-heating at 400 °C for 24 hours resulted in the transformation of the material structure from amorphous to tetragonal and a slight improvement of iodate adsorption rate. As the temperature of post-heating got higher, the structure of treated samples became more monoclinic and the sample heated at 1000 °C had nearly fully monoclinic. The more monoclinic the structure became, the lower the iodate adsorption rate the material showed, which may be due to the loss of hydroxide sites.

In order to evaluate if the material can be used for the actual waste treatment, the column operations with simulant of wastewater from Fukushima Daiichi Nuclear Power Plant was carried out. The iodate adsorption may be suppressed gradually by the SO$_4^{2-}$ ions in the simulant. However, the column has been operating for 42 days and approximately 11,000 bed-volume of the solution has been gone through the column, and still, the column is yet to reach a 100% breakthrough.

As a summary, the synthesized hydrous zirconia showed a clear iodate-preference and a possible high performance for the waste treatment from nuclear power plants.

A further research is needed to understand the precise composition of the material. The certificate of analysis of the starting material says there are at least sodium and iron as impurities.$^{[51]}$ Also, hafnium might exist as impurity as well because of its chemical and physical similarity to zirconium.$^{[16][52]}$ Thus, a composition analysis such as a series of the inductively coupled plasma - mass spectrometry (ICP-MS) should be carried out. The precise mechanism of adsorption of iodate to the materials is another interest, which might require such as a analysis by X-ray absorption spectroscopy. Furthermore, to confirm the breakthrough capacity, the column operation, which is currently ongoing, will be continued until the breakthrough is reached.
6. Supplemental

6.1. Iodine concentration in a tracer solution

The concentrations of I-125 nuclides were determined through the following procedure. 5 mL of deionized water and 25 μL of I-125 tracer solution were added into a 20-mL scintillation vial, and the activity of the mixture was then measured by a gamma counter. The ratio of the amount of the added tracer solution and a background solution is the same as that of all the samples in batch operations in this study.

The relation of the radioactivity and the number of radioactive nuclides in the sample is written as follows:

\[ A_R = \frac{\ln 2}{t_{\frac{1}{2}}} \cdot N \]  

(46)

where

\[ A_R = \text{radioactivity} \]
\[ t_{\frac{1}{2}} = \text{half-life} \]
\[ N = \text{number of radioactive nuclides} \]

In this study, the activity is measured as a net count rate \( R_n \) in a unit of cpm. Therefore, the concentration of the tracer I-125 nuclides is calculated as follows:

\[ C_t = \frac{t_{\frac{1}{2}} (\text{min.})}{\ln 2} \cdot \frac{R_n}{N_A \cdot V_G} \]  

(47)

where

\[ C_t = \text{concentration of the tracer I-125 nuclides} \]
\[ V_G = \text{total volume of a solution for the gamma measurement} \]
\[ N_A = \text{Avogadro constant} \]
The activities and the calculation results of the concentrations of I-125 nuclides in each tracer solution can be found in Table 8. Here it can be concluded that the concentration of I-125 is extremely low (~$10^{-13}$ M) and thus it is negligible.

Table 8: Concentrations of I-125 nuclides in each tracer solution. (“Date” stands for the measurement date in a dd/mm/yy form).

<table>
<thead>
<tr>
<th>Tracer</th>
<th>cpm</th>
<th>Date</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>856-1-3</td>
<td>2814.7</td>
<td>19/02/19</td>
<td>$1.15 \times 10^{-13}$</td>
</tr>
<tr>
<td>856-1-4</td>
<td>4527.5</td>
<td>12/02/19</td>
<td>$1.86 \times 10^{-13}$</td>
</tr>
<tr>
<td>856-1-5</td>
<td>2785.5</td>
<td>13/03/19</td>
<td>$1.14 \times 10^{-13}$</td>
</tr>
<tr>
<td>885-1-1</td>
<td>15376.8</td>
<td>02/05/19</td>
<td>$6.30 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

6.2. pH adjustment

6.2.1. For the isotherm determination

To adjust equilibrium pH for the isotherm determination, the amount of acid or base to be added was estimated by titration experiments. First, 10 mL of 10 mM NaNO$_3$, 20 mg of hydrous zirconia, 50 µL of I-125 tracer solution, 20 µL of 0.5 M NaOH solution to adjust the initial pH (i.e. pH before equilibration) to 4, and various amount of 0.2 M KIO$_3$ solution were added into a 20-mL scintillation vial, and the mixture was equilibrated by a rotary mixer for 24 hours. After the equilibration, pH of each sample was measured, and based on these results, a further titration was carried out.

Based on the graph of the equilibrium pH of the samples (Fig. 27), it can be concluded that pH was successfully adjusted around 4. The volume of acid or base added to each sample for the adjustment can be found in Table 9.
Fig. 27: Equilibrium pH of the samples with different iodate concentrations.

Table 9: List of volumes of acid or base to adjust equilibrium pH for isotherm determination.

<table>
<thead>
<tr>
<th>0.2 M KIO₃</th>
<th>Adjustment</th>
<th>Volume (μL)</th>
<th>Acid / Base</th>
<th>Volume (μL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+ 0.5 M NaOH</td>
<td>20</td>
<td>0.5 M NaOH</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.5 M NaOH</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.5 M NaOH</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.5 M HNO₃</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.5 M HNO₃</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.5 M HNO₃</td>
<td>14.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>0.5 M HNO₃</td>
<td>17.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>0.5 M HNO₃</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>0.5 M HNO₃</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>0.5 M HNO₃</td>
<td>29</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.2.2. For normal batch operations

Based on a series of titration experiments, the correlation between volumes of acid or base and approximate equilibrium pH values for different background solutions were determined. 10 mL of deionized water, NaNO₃, NaCl, NaSO₄ or H₃BO₃ solution in different concentrations (i.e. background solutions), 20 mg of hydrous zirconia, and various amount of acid or base to adjust equilibrium pH were added into a 20-mL scintillation vial, and the mixture was equilibrated by a rotary mixer for 24 hours. After the equilibration, pH of each sample was measured. The results of the titration can be found in Table 10. The pH adjustment for all the normal batch operations was carried out based on these results.

6.2.3. For post-heating effect analysis

To adjust equilibrium pH for the post-heating effect analysis, the amount of acid or base to be added was estimated by titration experiments. 10 mL of 10 mM NaNO₃, 20 mg of post-heated hydrous zirconia and various amount of acid or base to adjust equilibrium pH were added into a 20-mL scintillation vial, and the mixture was equilibrated by a rotary mixer for 24 hours. After the equilibration, pH of each sample was measured. The results of titration can be found in Table 11.
Table 10: List of volumes of acid or base to adjust equilibrium pH for each background solution. (“Approx. pH” stands for approximate equilibrium pH).

<table>
<thead>
<tr>
<th>Background Solution</th>
<th>Conc. (mM)</th>
<th>Acid / Base</th>
<th>Volume (μL)</th>
<th>Approx. pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>-</td>
<td>0.5 M NaOH</td>
<td>20</td>
<td>3.9</td>
</tr>
<tr>
<td>Deionized water</td>
<td>-</td>
<td>0.5 M NaOH</td>
<td>50</td>
<td>8.4</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>1</td>
<td>0.5 M NaOH</td>
<td>20</td>
<td>4.0</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>3.3</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>10</td>
<td>3.6</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>20</td>
<td>4.2</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>30</td>
<td>5.1</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>40</td>
<td>6.4</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>45</td>
<td>7.1</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>50</td>
<td>8.5</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>100</td>
<td>0.5 M NaOH</td>
<td>10</td>
<td>4.1</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>100</td>
<td>0.5 M NaOH</td>
<td>20</td>
<td>4.9</td>
</tr>
<tr>
<td>NaCl</td>
<td>1</td>
<td>0.5 M NaOH</td>
<td>20</td>
<td>4.0</td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>10</td>
<td>3.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>20</td>
<td>4.3</td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>30</td>
<td>5.1</td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>40</td>
<td>5.9</td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>45</td>
<td>6.4</td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>47</td>
<td>7.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>50</td>
<td>8.3</td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>60</td>
<td>9.2</td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>70</td>
<td>9.8</td>
</tr>
<tr>
<td>NaCl</td>
<td>100</td>
<td>0.5 M NaOH</td>
<td>10</td>
<td>4.0</td>
</tr>
<tr>
<td>NaCl</td>
<td>100</td>
<td>0.5 M NaOH</td>
<td>20</td>
<td>4.9</td>
</tr>
</tbody>
</table>
Table 10: (continued).

<table>
<thead>
<tr>
<th>Background Solution</th>
<th>Conc. (mM)</th>
<th>Acid / Base</th>
<th>Volume (μL)</th>
<th>Approx. pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>1</td>
<td>0.5 M HNO₃</td>
<td>25</td>
<td>3.0</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>4.0</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>10</td>
<td>0.2 M H₂SO₄</td>
<td>40</td>
<td>3.9</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>10</td>
<td>0.2 M H₂SO₄</td>
<td>25</td>
<td>4.4</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>10</td>
<td>-</td>
<td>0</td>
<td>5.6</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>10</td>
<td>5.9</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>20</td>
<td>6.1</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>30</td>
<td>6.8</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>40</td>
<td>8.0</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>60</td>
<td>9.5</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>100</td>
<td>0.5 M HNO₃</td>
<td>35</td>
<td>4.1</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>6.1</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>1</td>
<td>0.5 M NaOH</td>
<td>25</td>
<td>4.1</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>1</td>
<td>0.5 M NaOH</td>
<td>49</td>
<td>8.5</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>2.9</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>20</td>
<td>3.4</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>30</td>
<td>3.9</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>40</td>
<td>5.0</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>45</td>
<td>6.0</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>48</td>
<td>6.9</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>50</td>
<td>7.6</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>60</td>
<td>8.2</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>70</td>
<td>8.4</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>10</td>
<td>0.5 M NaOH</td>
<td>85</td>
<td>8.6</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>2.8</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>100</td>
<td>0.5 M NaOH</td>
<td>38</td>
<td>3.9</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>100</td>
<td>0.5 M NaOH</td>
<td>215</td>
<td>8.0</td>
</tr>
</tbody>
</table>
Table 11: List of volumes of acid or base to adjust equilibrium pH for each post-heating temperature. ("Approx. pH" stands for approximate equilibrium pH).

<table>
<thead>
<tr>
<th>Post-heating Temperature (°C)</th>
<th>Acid / Base Volume (μL)</th>
<th>Aprx. pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.5 M NaOH 20</td>
<td>4.2</td>
</tr>
<tr>
<td>200</td>
<td>0.5 M NaOH 38</td>
<td>4.1</td>
</tr>
<tr>
<td>400</td>
<td>0.5 M NaOH 5</td>
<td>4.0</td>
</tr>
<tr>
<td>600</td>
<td>0.5 M HNO₃ 5</td>
<td>3.8</td>
</tr>
<tr>
<td>800</td>
<td>0.5 M HNO₃ 5</td>
<td>3.8</td>
</tr>
<tr>
<td>1000</td>
<td>0.5 M HNO₃ 5</td>
<td>3.8</td>
</tr>
</tbody>
</table>

6.3. Iodine loss

The pH dependence of the loss of I-125 during the procedure of a normal batch operation was investigated. 10 mL of 10 mM NaNO₃, 50 μL of I-125 tracer solution, and various amount of 0.5 M NaOH solution to adjust the equilibrium pH (can be found in Table 12) were added into a 20-mL scintillation vial, and the mixture was equilibrated by a rotary mixer for 24 hours. The amount of NaOH solution to be added was estimated by titration experiments beforehand. Fig. 28 shows the count rates of gamma rays at various pH. It can be stated that the higher pH became, the more gamma rays were detected. This may be because of the likelihood of reduction of iodate ions. Although iodate ions are basically stable, acidic condition may triggers reduction of iodate into molecular iodine. The standard electrode potentials of the reduction processes in an acidic and a basic condition are expressed as follows.[53]

\[
\begin{align*}
2I_\text{O}_3^- + 12H^+ + 10e^- & \rightarrow I_2 + 6H_2O, & E^0 &= 1.210 \text{ V} \\
2I_\text{O}_3^- + 6H_2O + 10e^- & \rightarrow I_2 + 12OH^-, & E^0 &= 0.216 \text{ V}
\end{align*}
\]
In acidic conditions (48), since the standard electrode potential is higher than in basic ones (49), the reduction of iodate is more likely to occur. Once molecular iodine is formed, it may escape from the liquid phase to atmosphere. Because of the coordination between a sample and the detector which is described schematically in Fig. 29, gamma rays from molecular iodine in the atmosphere cannot be detected as efficiently as those of iodate ions in the liquid phase.\textsuperscript{[28]} Therefore, the formation of molecular iodine in acidic conditions is assumed to derive lower count rates.

Table 12: List of volumes of acid or base to adjust equilibrium pH. ("Approx. pH" stands for approximate equilibrium pH).

<table>
<thead>
<tr>
<th>Acid / Base</th>
<th>Volume (μL)</th>
<th>Approx. pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 M HNO\textsubscript{3}</td>
<td>300</td>
<td>1.2</td>
</tr>
<tr>
<td>5 v/v% HNO\textsubscript{3}</td>
<td>100</td>
<td>2.1</td>
</tr>
<tr>
<td>5 v/v% HNO\textsubscript{3}</td>
<td>10</td>
<td>3.1</td>
</tr>
<tr>
<td>0.1 M HNO\textsubscript{3}</td>
<td>10</td>
<td>4.6</td>
</tr>
<tr>
<td>0.1 M HNO\textsubscript{3}</td>
<td>5</td>
<td>5.9</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>6.8</td>
</tr>
<tr>
<td>0.1 M NaOH</td>
<td>5</td>
<td>7.3</td>
</tr>
<tr>
<td>0.1 M NaOH</td>
<td>10</td>
<td>8.5</td>
</tr>
</tbody>
</table>
Fig. 28: Count rates of gamma rays from I-125 at various pH. (The count rates are corrected by total volume of each sample. The broken line is a linear fitting based on all the results).

Fig. 29: Schematic image of coordination of the gamma detector and a sample.
7. References


[16] Reference [6], p. 339-340
[29] Reference [25], p. 156.

[33] Reference [24], chap.10.


[40] Reference [25], p. 157-163.

[41] Reference [24], p. 233-236.


