Measurement of ^{129}I in an Inorganic Adsorbent

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A separation and recovery method for ^{129}I in an inorganic adsorbent (Ag^{129}I-zeolite) was used as a trapping filter to remove fission products and nuclear fission-generated gas. ^{129}I was added to the AgX-exchanged zeolite and the radioactivity of the Ag^{129}I-zeolite was determined as a reference substance for ^{129}I. The recovery rate for ^{129}I after alkali fusion was 76.3 ± 2.8 %. To investigate the influence of ^{129}I in the ^{99}Tc (Re)-containing inorganic adsorbent on separation and quantification, the recovery rate for ^{129}I was measured after adding Re to the adsorbent. Furthermore, the recovery rate for ^{129}I was evaluated to identify the influence of ^{14}C in the eluted solution on ^{129}I measurement. The results show that separation and quantification of ^{129}I was not influenced by ^{14}C in the eluted solution.

Key Words: ^{129}I, Separation, Inorgnic adsorbent, Re, ^{14}C.

INTRODUCTION

Research and case studies have clarified the effect of iodine on the environment and people. Representative examples have shown that iodine is accumulated in mammalian thyroid and causes thyroid gland cancer as well as contributes to destruction of the ozone layer[1-4]. ^{129}I has the longest half-life ($T_{1/2} = 1.57 \times 10^7$ y) among volatile radionuclides and a large amount of iodine is produced through man-made nuclear activity. However, it is also generated from cosmic rays[5]. In particular, large quantities of iodine are produced from reprocessing spent nuclear fuel and in nuclear experiments involved in nuclear weapon production. Furthermore, for a nuclear power plant, the ^{129}I yield is 0.8 %[6,7]. Thus, iodine is emitted directly or indirectly through many paths into the natural environment. In particular, iodine can form a highly volatile compound through bonding with an organic solvent (tributyl phosphate), which is extracted in the PUREX process for reprocessing spent fuel[8]. Organic iodine with these methyl groups can be easily removed when it will otherwise be released into the environment or absorbed inside the containment building[9,10]. In addition, human health may be threatened because it is highly volatile.

Therefore, more methods to suppress the release of volatile iodine into the external environment are necessary. In facilities for processing or dismantling spent fuel, a device to remove the fission radionuclides and dust must be constructed. The filtration membrane or inorganic adsorbent must remove or effectively collect fission products. In particular, iodine removal equipment can effectively remove iodine from this released media because dusted or gaseous CO_2, inert gas, nitrogen oxide, tributyl phosphate, elemental iodine and organic iodine are in the "off-gas"[11,12]. In general, radioiodine removal through an adsorption method using Iodox, Mercurex washing methods and an inorganic solid adsorbent are well-known methods for reprocessing spent fuel[13]. Iodine-friendly silver or another metal-substituted zeolite are an excellent adsorbent for the iodine produced in nuclear facilities. In particular, zeolite is non-combustible and is a low explosion hazard. Furthermore, the absorption efficiency is good at high temperatures[12]. ^{129}I , which is a fission product, is difficult to directly assay because the specific activity of its radiation is low[6,14]. Therefore, pretreatment and separation of iodine must be preceded by separation using inorganic adsorbents installed at the outlet of a radioactive waste facility. Well-known chemical separation methods for iodine include an acid-leaching elution[15], alkali fusion[14], low-temperature distillation[16] and ion-exchange resin separation methods[17,18]. Acid-leaching is a method to separate iodine in extracts through oxidation and reduction and alkali fusion is a method for melting samples with alkali fusion agents and oxidants. Furthermore, the low-temperature distillation and ion-exchange resin separation methods use characteristics particular to iodine.

In this study, a chemical separation and quantitative analysis method was developed for ^{129}I using Ag^{129}I-zeolite as an inorganic adsorbent (AgX-zeolite) and trapping filter. Trapping filters are installed to remove fission products and gas released during high-temperature oxidation of spent fuels. For

this process, [129]I was absorbed on an AgX-exchanged zeolite to prepare a standard sample and various separation methods for iodine were applied and reviewed[19]. In addition, the influence of iodine separation on volatile β-emitting radionuclides (^{99}Tc and ^{14}C) with [129]I was investigated.

EXPERIMENTAL

Reagent grade KOH and KNO$_3$ (Aldrich) were used as the alkali fusion agent and KI was added as a [129]I carrier. The [129]I used to trace radioiodine was first diluted in 2,138 Bq/mL, NaI/0.1 M Na$_2$S$_2$O$_3$ (NIST-SRM-4949 c). Anion exchange resin (AG 1x2, 50-100 mesh, Cl$^-$ form, Bio-rad Co.) for iodine absorption was used after it was washed with a dilute acid. The organic solvent used for extraction was a Merck product. For radiological [129]I monitoring, a low-energy γ-ray spectrum analyzer (model GLP 36360/13P4, AMETEC) was used.

Preparation of AgX (X = [129]I) zeolite: In a glove box (90 cm, W × 180 cm, H) that had been charged with N$_2$ gas, 5 g of AgX-exchanged zeolite was added to a pH 10 carbonate buffer solution in a plastic beaker; 10.0 Bq of [129]I was then added into the beaker. Then, 20 mL of H$_2$O and 6 mL of NaI (1.5 g NaI) were added to the beaker. The contents of the beaker were stirred with a magnetic bar to facilitate radioiodine absorbance with the AgX-exchanged zeolite. After filtering with Whatman filter paper #42, the residue was dried under an IR lamp. Finally, the [129]I radioactivity in the AgI-zeolite was measured using a radioactivity counter.

Application of the alkali fusion method: The dried AgI-zeolite (2.0 g) was placed into a 50 mL platinum crucible, into which 0.5 g of KNO$_3$ (oxidant), 5 g of KOH (fusion agent) and 1.0 mL of standard KI solution (μg/mL) were added. After mixing well, the crucible was covered with a lid and the furnace temperature was adjusted to 100-120 ℃ for drying. The temperature was then maintained at 200 ℃ for *ca.* 1 h and was then raised slowly to 450 ℃. The fused solid was dissolved in a dilute acid for a stock solution.

Application of the acid leaching method: The 2 g dried AgI-zeolite was placed into a 250 mL plastic bottle; 50 mL distilled water and 10 mg KI (carrier) were added. Finally, 50 mL of 10 M HNO$_3$ (leaching agent) was added. Iodine was then leached by shaking the plastic bottle for 4-5 h. After leaching, the leached solution was filtered using a suction filter device. The filtrate was used as a stock solution for the chemical separation of [129]I.

Separation of the [129]I using the anionic exchange resin: The pH 10 buffer solution (5 mL), 10 mg of KI and 5 g of anionic resin (AG1-X 4 Resin) were placed into a plastic beaker and stirred with a magnetic bar for 12 h to absorb the iodine. Thereafter, it was filtered with Whatman #42 filter paper and the aqueous solution was discarded. The resin was then used to fill a polyethylene tube 10 mm in diameter and 140 mm long. Next, the resin was washed with 10 mL distilled water 2 times. Iodine was then eluted with 20 mL of 10 % NaOCl at a 0.4 mL/min flow rate.

The 10 mL eluted solution was poured into a 50 mL extraction tube and 1 mL of HNO$_3$ and 1,000 mg of NH$_2$OH·HCl were added. Thereafter, by adding 10 mL of CHCl$_3$, iodine was extracted for 3 min. In the extraction solution, the aqueous

phase was discarded and only 5 mL organic phase was placed into a new extraction tube. After adding 5 mL of 0.1 N NaHSO$_3$ solution into the separated organic phase in the tube, the solution was back-extracted to the aqueous phase. The precipitate formed by 0.1 M AgNO$_3$ in the aqueous phase was aged for 5 min at 70 ℃. After centrifuging, the sample was transferred to a Planchet; the final sample in the Planchet was dried below 70 ℃ and its activity was measured for 10,000 s with a low-energy level gamma spectrometry system.

RESULTS AND DISCUSSION

Standardization of the reference AgX (X = [129]I) zeolite: An inorganic adsorbent and Ag-substituted AgX-exchanged zeolite can be used to remove the volatile fission gas generated from highly oxidative spent fuel processing and can be installed in the exhaust facilities of a spent fuel reprocessing plant or nuclear fuel processing facilities.

As a reference concentration of [129]I, AgX (X = [129]I) was synthesized to develop a separation method for [129]I in the inorganic absorbent. For homogeneity of the inorganic absorbent, the absorbent was ground and added to buffer solutions at pH 4, 7 and 10. Next, ungrounded absorbent was added to the buffer solutions to identify the effect of grinding. Finally, the concentrations of radioiodine (to use as a reference substance) were determined through measurement of [129]I in the residue and filtrate. Table-1 shows the measurement results for [129]I adsorption on the AgX-zeolite in the buffer solutions and the [129]I adsorbed in the pH 10 buffer solution was selected as the reference substance.

TABLE-1
CUMULATIVE YIELD OF IODINE ON AgX EXCHANGE-ZEOLITE

Adsorption buffer solution	Recovery (%)			
	Not grinding		Grinding by agate mortar[a]	
	Filtrate	Solid	Filtrate	Solid
pH 4, phthalate	33.3±3.5	40.8±4.5	30.1±3.5	55.5±3.2
pH 7, phosphate	30.0±2.3	43.1±2.7	29.5±2.3	58.2±2.0
pH10, carbonate	29.5±2.7	45.8±3.6	24.8±2.0	60.4±2.2[b]

[a]Adopting as the decomposition method of the AgX exchange-zeolite used as the reference substance of this research. [b]It selects as the reference concentration of the AgI-zeolite for the analysis method development.

Sample pretreatments for [129]I separation and quantitative analysis: A flowchart on the analysis process for separation and quantification of [129]I in the AgI-zeolite is shown in Fig. 1. In Fig. 1, the reference substance is determined through radioactivity measurements of [129]I in the synthesized zeolite. If the concentration of the reference iodine is determined, the alkali fusion and leaching-based [129]I separation methods can be compared. In the alkali fusion method, isolated I$^-$ is oxidized to I$_2$ and eventually fused when KOH, KNO$_3$ and KI are added to Ag[129]I zeolite and heated in a furnace. In the acid leaching method, iodine can be leached when 1:1 nitric acid is added to Ag[129]I-zeolite and slowly stirred. After pretreatment, the separated fusion solution and leachate are bound to the anionic resin (AG 1 x2, 50-100 mesh Cl$^-$ form), placed in the column and eluted. The I$^-$ bound to the anionic exchange resin is oxidized to nonvolatile iodine oxidation products, such as
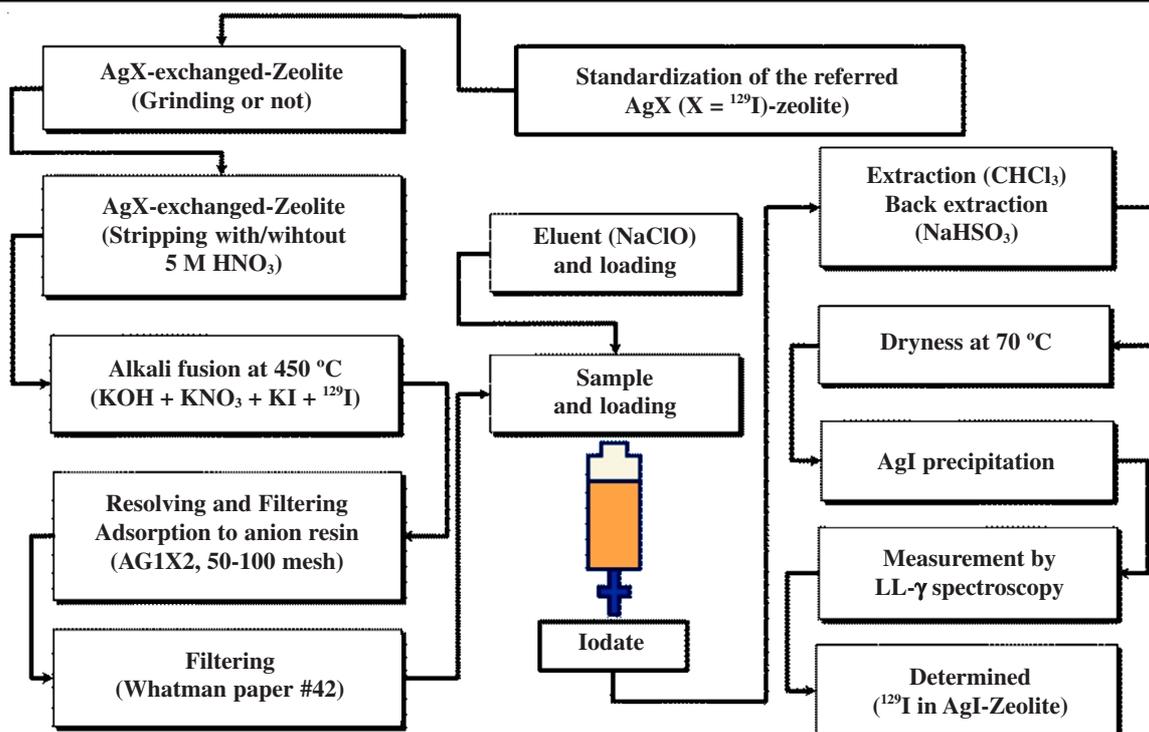
Fig. 1. Schematic diagram for chemical analysis of ^{129}I in an inorganic absorbent (AgI-zeolite)

IO$_3^-$ or IO$_4^-$, when NaClO is used to elute. These nonvolatile oxidation products were then easily eluted from the resin (AG 1 x2, 50-100 mesh Cl$^-$ form) because they have a relatively low affinity compared with other anions, such as Cl$^-$, Br$^-$ and NO$_2^-$, HSO$_3^-$ and NO$_3^-$. After adding the NH$_2$OH·HCl and reducing, the remaining I$_2$ in the eluted solution was extracted by adding an organic solvent (CHCl$_3$) and then back-extracted with NaHSO$_3$ to an aqueous layer; I$^-$ was used for the determination of the recovery rate. The recovery rates for iodine in the two separation methods are shown in Table-2. As shown in the results (Table-2), the recovery rate from the acid leaching method was low compared with the alkali fusion method, which is why the iodine complex with Ag in the zeolite was primarily not decomposed and most of the iodine complex remained in the zeolite.

Influence of the other volatile radionuclides: The inorganic adsorbent can also absorb volatile ^{14}C, ^{99}Tc and radioactive gas generated from a spent fuels reprocessing facility and volatile ^{129}I. Thus, the influence of other volatile radionuclides for the separation and measurement of ^{129}I must be considered. First, Re, which is used as a monitoring nuclide for ^{99}Tc, was added to the Ag^{129}I-zeolite.

To identify the stripping efficiency of nitric acid, AgX (X = ^{129}I, Re) zeolite was used to strip before application of the alkali fusion method. For 0.5-10.0 M nitric acid, the recovery rate of Re was measured after stripping and the result is presented in Table-3. As shown in Table-3, the recovery rates when using higher concentration than 5 M of nitric acid were found to be close each other compared with when using lower than 5.0 M nitric acid. The measured recovery rates for the added Re and iodine were tabulated in Table-4. As can be seen in Table-4, the recovery rate for separation through alkali fusion after Re stripping with nitric acid is 72.3-72.5 % and the recovery rate for ^{129}I without adding Re is 76.3 ± 2.8 %, which is similar to the Re added sample. For Re detection at 2.26 ± 9.2 %, the removal ratio of Re is 77.4 %, which is why ^{129}I easily reacts with Ag to form a stable AgI compound and the compound is easily dissolved in alkali-containing solutions but not in water or below 5 M acid.

TABLE-2
RECOVERY RATE FOR ^{129}I IN AgI-ZEOLITE
AFTER SAMPLE PRETREATMENT

Number of experiment	Sample treatment method[a]	
	Alkali fusion[b]	Acid leaching[c]
	Recovery (%)	Recovery (%)
1	78.5	43.5
2	74.6	48.2
3	77.5	44.6
4	73.5	45.8
5	77.2	42.3
Ave, (RSD) %	76.3, (2.8)	Ave, RSD) %, 4.9 (5.0)

[a]I-zeolite does not strip with HNO$_3$. [b]Alkali fusion agents; flux (KOH), oxidant (KNO$_3$) and iodine carrier (KI); temperature, 450 ℃. [c]Acid leaching agent; 50 mL H$_2$O + 50.0 mL10.0 M HNO$_3$, leaching time, 4 to 5 h.

TABLE-3
RECOVERY RATE FOR Re-AgX-ZEOLITE[a] CONFIRMED
USING NITRIC ACID AFTER STRIPPING[a]

Concentration of HNO$_3$ (M)	10.0 mg Re added	
	Identified Re[b]	Recovery (%)
0.5	5.32	53.2
1.0	6.80	68.0
3.0	8.02	80.2
5.0	8.53	85.3
8.0	8.61	86.1
10.0	8.50	85.0

[a]In the zeolite used in this experiment, the standard ^{129}I was not added. [b]By using ICP-AES, the concentration of the Re measured.

TABLE-4
RECOVERY RATE FOR ^{129}I AND Re IN AgI-ZEOLITE[a]

No. of experiment	10.0 mg Re added	
	Recovery of ^{129}I (%)	Removing rate (%)[d]
1	72.5	77.0
2	73.4	80.0
3	70.7	79.0
4	71.8	75.0
5	73.0	76.0
Ave. (RSD) %	72.3 (1.5)	77.4 (2.6)

[a]The reference concentration of ^{129}I in AgI-zeolite was 3.58 Bq/mL. [b]Stripping and alkali fusion were performed before measurement using LL-γ spectroscopy. [c]Stripping and alkali fusion were performed before measurement with ICP-Aes. [d]Removing rate of Re = Re (10 mg) added - Found Re x 100 (%).

Effect of (^{14}C) on iodine measurement: Radioactive waste liquid produced from a nuclear power plant contains high concentrations of ^{14}C, which may be several ten times higher than iodine. Therefore, the effect on the measurement of activity of ^{129}I from the β-emission nuclide, such as ^{14}C, which is not separated and remains with iodine during pretreatment was studied. Fig. 2 shows β-spectra for several volatile radioactive nuclides (^{3}H and ^{14}C and ^{129}I) using a liquid scintillation counter. As shown in Fig. 2, since the spectra of ^{14}C and ^{129}I are overlapped in the range of 250-450 channel band, ^{14}C has to be removed for the determination of ^{129}I.
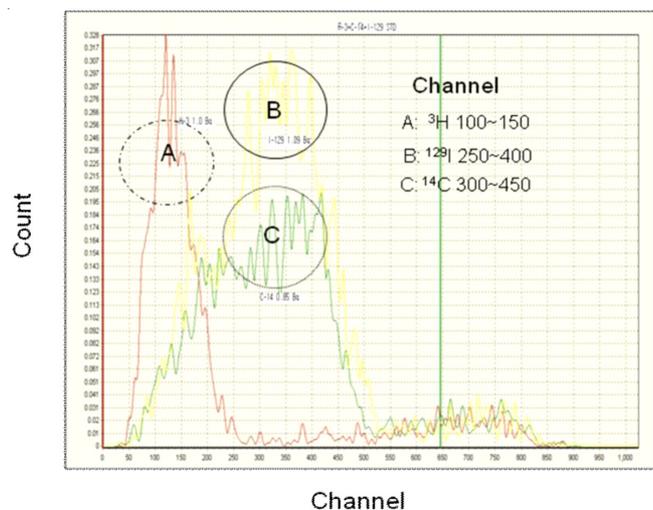

Fig. 2. β-Spectra for several volatile radioactive nuclides using a liquid scintillation counter

^{14}C was removed by evaporation at a temperature lower than 70 ℃ after stripping the iodine in the organic phase to an aqueous phase. The radio-activities for ^{129}I before and after ^{14}C removal were compared in Table-5. As shown in Table-5, the evaporation procedure for ^{14}C did not induce co-evaporation of ^{129}I, while the temperature was below 70 ℃. In addition, the recovery rates for the samples containing ^{129}I were compared and the results indicate that the effects from β-emission nuclide such as ^{14}C can be removed using an evaporation procedure for the aqueous phase after the stripping procedure.

TABLE-5
INTERFERENCE OF ^{14}C IN ^{129}I MEASUREMENT[a]

^{129}I added	^{14}C added	Measured (Bq/mL)	Recovery (%)	Remark
4.36	0	3.34 (^{129}I)	76.5	^{14}C removed through evaporation[b]
4.36	0	3.37 (^{129}I)	77.2	No evaporation
0	50	0.04 (^{14}C)	< 0.1	^{14}C removed through evaporation
4.36	50	18.60 (^{14}C)	37.2	No evaporation
4.36	50	3.21 (^{129}I)	73.8	^{14}C removed though evaporation

[a]As to the recovery rate of ^{14}C, measuring with the liquid scintillation counting method. [b]As to the temperature of the evaporative dry, performing in the water bath under 70 ℃.

Conclusion

The separation and quantification method for ^{129}I in an inorganic adsorbent (Ag^{129}I -zeolite) was used as a trapping filter to remove fission products and nuclear fission-generated gas. To identify the recovery of ^{129}I, Ag^{129}I-zeolite was prepared by adding ^{129}I to AgX-exchanged zeolite and ^{129}I in the zeolite was determined by radiochemical analysis. The average recovery rate for ^{129}I was 76.3 ± 2.8 % for the reference Ag^{129}I-zeolite prepared using alkali fusion. Furthermore, the influence of ^{99}Tc (Re) and ^{14}C-inclusion on the inorganic adsorbent for separation and recovery of ^{129}I was studied. It was found that there's no interference of ^{99}Tc (Re) for the measurement of ^{129}I after stripping by the nitric acid. It was also found no interference of ^{14}C, when measuring ^{129}I of the evaporation of the separated solution at the temperature below 70 ℃.

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