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Title page

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Development of the separation method of Zr in the rubble waste generated at the Fukushima Daiichi Nuclear Power Station

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Abstract

Separation method of Zr using *tr*ans *u*ranium resin (TRU resin) and *te*tra *va*lent actinide resin (TEVA resin) was developed for the analysis of ^{93}Zr contained in the rubble waste. Zr, Nb, and U were quantitatively extracted on the TRU resin from 3 M HNO_3 and striped with 0.01 M HF, in addition, some part of Mo, Hg, Bi, and Th were also included in the stripping solution. The stripping solution was evaporated to eliminate HNO_3 and the residue was dissolved in 0.1 M HF. Finally, Zr was separated from Nb and Mo with the TEVA resin.

Keywords

TRU resin, TEVA resin, ^{93}Zr, Fukushima Daiichi Nuclear Power Station, rubble

Introduction

The reactor buildings at the Fukushima Daiichi Nuclear Power Station (FDNPS) were severely damaged by the hydrogen explosion and the structural material were reduced to rubble. For the safety disposal of the radioactive rubble waste and understandings of the progress of the accident, characterization of the radionuclides attached to the rubble is indispensable. Based on the ORNL isotope generation and depletion code 2 (ORIGEN2), ^{3}H, ^{14}C, ^{36}Cl, ^{60}Co, ^{79}Se, ^{90}Sr, ^{94}Nb, ^{99}Tc, ^{129}I, ^{137}Cs, ^{152}Eu, ^{154}Eu, ^{238}Pu, ^{239}Pu, ^{241}Am, ^{244}Cm were estimated as main radionuclides and analyzed [1-3]. As the results, ^{3}H, ^{14}C, ^{60}Co, ^{90}Sr, and ^{137}Cs were detected for the rubble samples collected around reactor buildings unit 1, 2, 3, and 4 at the FDNPS [1-3], and ^{3}H, ^{14}C, ^{60}Co, ^{79}Se, ^{90}Sr, ^{99}Tc, ^{129}I, ^{137}Cs, ^{154}Eu, ^{234}U, ^{235}U, ^{238}U, ^{238}Pu, $^{239+240}$Pu, ^{241}Am, and ^{244}Cm were detected for the rubble collected inside of the reactor buildings [4]. This result implies that the rubble waste is possibly contaminated by both of fission products and activated nuclides. Furthermore, boring cores were sampled from wall and floor inside of reactor building 1, 2, and 3 to estimate the type of the contamination, that is, loose, fixed, and penetrated contaminations [5]. For the unit 1 and 3, radioactive contamination of ^{134}Cs, ^{137}Cs and ^{110m}Ag was detected of which had characteristics of loose contamination. On the other hand, radioactive contamination of ^{134}Cs, ^{137}Cs, ^{110m}Ag, and ^{125}Sb was detected for the unit 2 of which had characteristics of fixed contamination. Almost all fixed contamination was remained on the epoxy coating surface.

In the early stage of the characterization, gamma-ray emitting nuclides and relatively large radioactivity nuclides were mainly analyzed. However, characterization of long-lived nuclides was also important for the safety disposal of the radioactive waste. ^{93}Zr is one of the long-lived nuclide (the half-life is 1.53×10^{6} y) produced in a reactor (fission of ^{235}U and activation of ^{92}Zr in structural material) and its contribution to the radioactivity of high-level radioactive waste will be the second largest after 1000 years. When a nuclear power plant was under control, ^{93}Zr was mainly existed in the irradiated fuel and cladding tube, hardly existed in concrete structual materials. On the other hand, it is unknown whether concrete structual materials were contaminated by ^{93}Zr or not under the accidental condition at the FDNPS. In order to dispose the contaminated rubble generated at the FDNPS, evaluation of ^{93}Zr level is also required.

P. Cassette et al [6] and F. Chartier et al [7] determined ^{93}Zr contained in an irradiated zircaloy sheath with isotope dilution method using multi-collector inductively coupled plasma mass spectrometer and liquid scintillation counting after rigorous separation of Zr with co-precipitation, solvent extraction, and anionic exchange resin. Whereas, simplified separation methods of Zr using anionic exchange resin [8], UTEVA resin [9], TEVA resin [10], TRU resin, and TODGA resin [11] were also developed so far. In our laboratory, separation method of Zr using TEVA resin was developed for the contaminated water generated at the FDNPS. In this method, sample solution was adjusted to diluted HF solution (0.01 or 0.1 M HF) to extract Zr on the TEVA resin. However, it is difficult to dissolve the rubble sample in diluted HF solution, typically, it was adjusted to a few molar of HNO_3 solution. As the separation methods of Zr for HNO_3 media sample solution, UTEVA resin method (8 M HNO_3), TODGA resin method (3 M HNO_3 for sample solution and 11 M HNO_3 for the separation solution from Ca), and TRU resin method (2 M HNO_3) were reported. Because usage of a few molar of HNO_3 is preferable for all process, TRU resin method was considered suitable method. However, Gautier et al pointed out that eluting solution of Zr from the TRU resin, 0.02 M HNO_3-0.05 M $NH_4HC_2O_4$ solution, make trace level contamination and emphasize memory effect for the measurement of inductively coupled plasma mass spectrometer (ICP-MS). Therefore, modification of eluting solution was studied in the present study. In addition, separation of Zr from Nb and Mo was also studied because these separation was indispensable for the measurement of ^{93}Zr using ICP-MS to avoid isobaric interference.

Experimental

The *tr*ans *u*ranium resin (TRU resin) and the *te*tra *va*lent actinide resin (TEVA resin) were purchased from Eichrom Technologies, USA (particle size 50-100 μm). Multi-element plasma standard (XSTC-13) was purchased from SPEX Industries, Inc., USA. That is 5% HNO_3 solution containing 10 mg/L of Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, In, Cs, Ba, Hg, Tl, Pb, Bi, Th, U. The following metal standard solutions (1 mg/mL) were purchased from Wako, Japan: Mo in 0.4 M HCl–0.2 M HNO_3, Nb in 1 M HF, and Zr in 1 M HNO_3.

XSTC-13 (25 mL) and metal standard solutions of Zr, Nb, and Mo (each 0.25 mL) were taken into a PTFE beaker and mixed, and then, evaporated to dryness. The residue was dissolved in 3 M HNO_3 solution (approximately 10 mL). Because trace amount of insoluble was observed in the bottom of the PTFE beaker, the solution was filtered with mixed cellulose membrane (pore size: 0.1 μm). 3 M HNO_3 was added into the filtrate to make the total volume 25 ml. This solution was assigned the control solution. The concentrations of metal ions in the control solution were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Shimadzu ICPS-7500 sequential plasma emission spectrometer) or inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Co.). The dissolution of metals into the control solution was evaluated by a comparison with a diluted mixture solution of XSTC-13 and metal standard solutions without evaporation. Although most of the metal ions were remained and dissolved in the control solution (approximately 10 mg/L), the concentrations of Hg, Nb, and Mo were decreased (approximately 3.3, 1.1, and 8.6 mg/L, respectively). Because vapor pressure of Hg is low, Hg may be lost during evaporation. Nb is well known to loss by precipitation in HNO_3 solution. When dissolved solution was standed for one night before filter, approximately 100% dissolution of Mo was obtained. However, dissolution was carried out in 5 min in this experiment, loss of Mo was observed.

It is known that most of the radioactive contaminants derived from the reactor components were attached to the rubble surface. In this work, a painted concrete surface was simulated. The detail of the simulated concrete surface and its dissolution were described in the reference [12]. The dissolved concrete surface solution containing correspomding amount of 0.0272 g of the material and metal standard solutions of Zr, Nb, and Mo were taken into a PTFE beaker, and then, evaporated to near dryness. The residue was dissolved in 3 M HNO_3 solution to make the simulated rubble sample solution.

The TRU resin and TEVA resin (0.37 g and 0.35 g, respectively) were suspended in ultrapure water and the slurry were packed into a polyethylene column. A frit was set above the resins.

The column chromatgraphic scheme is summarized in Fig.1. First, 5 mL of 3 M HNO_3 solution was loaded to the TRU resin column to condition. After then, 3.4 mL of the sample solution (the control solution or the simulated rubble sample solution) was loaded into the column. Subsequently, the column was rinsed with 3 M HNO_3 solution. The extracted Zr was recovered with 0.01 M HF solution. Further stripping of the extracted metal ions on the TRU resin using 0.1 M HNO_3/ 0.025 M oxalic acid solution was performed for the control solution.

Aliquot of the 0.01 M HF effluent, Zr recover fraction, was evaporated to dryness, and then, the residue was dissolved in 0.1 M HF solution. The 0.1 M HF solution was loaded into the TEVA resin conditioned by 5 mL of 0.1 M HF solution. The TEVA resin column was rinsed with 0.1 M HF. The extracted Zr, Nb, and Mo were eluted by 7 M HCl/0.5 M HF solution, 4 M HF solution, and 1 M HNO_3, respectively.

Aliquot of the effluents from the TRU and TEVA resins were diluted with appropriate solution to measure the metal ion concentrations using ICP-AES or ICP-MS.

Elution behaviors of metal ion were evalutaed with recovery (%). The recovery was obtained following equation:

$$\text{recovery (\%)} = \frac{metal\ amount\ \ in\ the\ fraction}{metal\ amount\ in\ the\ sample\ solution}$$

Results and discussion

Elution behaviors of 32 elements in the control solution from TRU resin were summarized in Table 1. Although Na and K were also contained in the control solution, these data were not included in the Table1. Most of the elements were eluted during sample loading and rinsing with 3 M HNO_3, they were not contained in the Zr fractions. On the other hands, 100% of Zr, Nb, and U, 10% of Mo, 7% of Hg, 77% of Bi and 20% of Th were contained in the first Zr recovery fraction with 0.01 M HF. It is reported that Zr and U were hardly to recover with HNO_3/HF (0.5 M/0.005 M, pH=0.3) from the TRU resin [11]. The use of 0.01 M HF made the recovery of these elements improved. Because the extraction agent of the TRU resin, octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide, is an neutral ligand, neutral species are extracted on the TRU resin and anion species are eluted from the TRU resin. It is reported that main species of Zr in HNO_3/HF (0.5 M/0.005 M) solutions at pH 0.3 were ZrF_4 and ZrF_3^+ and those at pH 2 were ZrF_5^{-} and ZrF_6^{2-} [11]. It is possibly that anion species were dominant in the 0.01 M HF (pH >2), allowing Zr eluted.

Table 1 Elution behavior of multi elements in the control solution from the TRU resin.

	Load/rinse1 3 M HNO_3 (3.4/6.8 mL =5/10 FCV) %	Rinse2 3 M HNO_3 (6.8 mL =10 FCV) %	Zr1 0.01 M HF (6.8 mL =10 FCV) %	Zr2 0.01 M HF (6.8 mL =10 FCV) %	Others 0.025 M $(COOH)_2$ /0.1 M HNO_3 (10 mL =14.7 FCV) %
Li	95±9	<0.1	<0.1	<0.1	<0.1
Be	98±5	<0.1	<0.1	<0.1	<0.1
Mg	104±5	<0.5	<1	<0.5	<0.5
Al	104±1	<0.1	<0.1	<0.1	<0.2
Ca	110±2	<8	<8	<8	12
V	100±4	<0.7	<2	<0.7	<0.1
Cr	99±4	<2	<3	<2	<0.2
Mn	99±5	<0.1	<0.2	<0.1	<0.1
Fe	93±2	9±1	<3	<3	<4
Co	98±5	<0.1	<0.1	<0.1	<0.1
Ni	103±5	<9	<9	<9	<13
Cu	99±6	<0.1	<0.1	<0.1	<0.1
Zn	104±10	9±1	<0.8	<0.4	<0.1
Ga	102±7	<0.1	<0.1	<0.1	<0.1
As	99±3	<0.4	<0.7	<0.4	<0.1
Se	97±4	<0.5	<0.9	<0.5	<0.1
Rb	98±5	<0.1	<0.1	<0.1	<0.1
Sr	99±7	<0.1	<0.1	<0.1	<0.1
Zr	1±1	<0.3	100±3	1±1	1±1
Nb	2±1	1±1	100±2	1±1	2±1
Mo	36±2	56±1	10±1	<0.1	<0.1
Ag	104±3	<5	<5	<5	<8
Cd	99±5	<0.1	<0.1	<0.1	<0.1
In	99±6	<0.1	<0.1	<0.1	<0.1
Cs	99±5	<0.1	<0.1	<0.1	<0.1
Ba	105±1	1±1	<0.1	<0.1	<0.1
Hg	70±18	5±1	7±1	3±1	<0.1
Tl	100±3	<0.1	<0.1	<0.1	<0.1
Pb	101±3	<0.1	<0.1	<0.1	<0.1
Bi	<0.3>	<0.1	77±6	1±1	27±7

Th	<0.1>	<0.1	20±1	19±5	59±1
U	<0.1>	<0.1	102±3	1±1	<0.1

The column cromatography experiment was carried out twice, and the uncertainty was quantified by the dispersion in these two experiments. Free column volume =FCV

When the sample solution was adjusted to 3 M HNO_3, 89% of Nb and 14% of Mo were lost from the added amount in this experiment. It is well known that Nb shows deficient dissolution in HNO_3 solution. However, dissolved Nb behaved similar to Zr at the separation using the TRU resin, and a part of Mo was also included in the Zr fraction. Zr has to be separated from Nb and Mo for the ICP-MS measurement of ^{93}Zr to avoid isobaric interference although Hg, Bi, U and Th do not intherfere the measurement. Therefore, further purification process using a TEVA resin to separate Zr, Nb, and Mo was added according to the Ref [13]. Because both of the solutions to recover Zr from the TRU resin and to load into the TEVA resin are 0.01 M HF, direct loading of the eluent from the TRU resin into the TEVA resin was examined. However, this examination was unsuccessful because considerable amount of Zr was passed through the TEVA resin without retention. It is considered that NO_3^- remained on the TRU resin was contained in the loading solution to the TEVA resin, consequently, Zr was eluted. Hence, evaporation of the eluent from the TRU resin to dryness and dissolution of the residue in diluted HF solution was needed to condition the loading solution to the TEVA resin. Eventually, 0.1 M HF, instead of 0.01 M HF, was used as the loading solution to assist the dissolution of Zr. The difference of the HF concentration was not effect on the elution behavior of Zr, Nb, and Mo with the TEVA resin [13]. Elution of Zr during sample loading and rinsing was eliminated by the complete evaporation. The elution behavior of Zr, Nb, Mo, Bi, Th, and U from TEVA resin was summarized in Table 2. Because the sample solution of the TEVA resin was prepared from the Zr fraction from the TRU resin, Zr, Nb, Mo, Bi, Th, and U were contained. However, Hg was not contained in the solution. It would be evaporated. Bi was eluted during sample loading and rinsing. Zr and Th were recoverd in the Zr recover fraction. Mo and U were recovered in the Mo recover fraction. Nb was recovered in the Nb recover fraction in which 8% of Mo was also contained. The elution behavior of Zr, Nb, and Mo was comparable to that reported in Ref [13].

Table 2 Elution behavior of Zr, Nb, Mo, Bi, Th, and U from the TEVA resin.

	Load/rinse 0.1 M HF (3.4/10.2 mL =5/15 FCV) %	Zr recover 7 M HCl-0.5 M HF (6.8 mL =10 FCV) %	Mo recover 4 M HF (6.8 mL =10FCV) %	Nb recover 1 M HNO_3 (6.8 mL =10FCV) %
Zr	<0.05	101±2	<0.02	<0.02
Nb	<0.04	<0.07	<0.07	100±2
Mo	<0.6	<0.3	96±5	8±0.3
Bi	94±2	<0.05	<0.03	<0.03
Th	<0.08	103±3	<0.4	<0.2
U	<0.003	3±0.1	101±3	<0.3

The sample solution was prepared with Zr recover fraction from the TRU resin. The column cromatography experiment was carried out once and measurement was carried out 3 times for each solution. Standard deviation was evaluated by the measurements. For the calculation of the recovery, the standard deviation was synthesized by considering propagation.

The developed method was applied for the simulated rubble sample solution in which the concentrations of major elements (Na, Al, Ca, Fe), Zr, Nb, and Mo were 132, 180, 941 53, 40, 41, 41 μg/mL, respectively. Elution behavior of Na, Al, Ca, Fe, Zr, Nb, and Mo from the TRU resin was shown in Table 3. The percentage of each fraction was calculated by dividing the concentration of elements in each fraction with that of the sample solution. The concentration of the sample solution and load fraction would be measured lower than actual concentration because of the higher concentration of the salt. Therefore, the total percentage was over 100% and that is the reason why separation is needed. However, the tendency of the metal elution is able to know. Most of the major elements were eluted from the TRU resin (1 mL) during sample loading and rinsing. 3±4% of Na in the Zr recovery fraction might be caused by contamination of the instrument. On the other hand, it is reported that Fe^{3+} is slightly extracted on the TRU resin and when the concentration of Fe^{3+} was higher than that of the target element, the extraction of Fe^{3+} competes with that of the target element. The elution of Zr in the load/rinse fraction and of Fe in the Zr recover fraction would be caused by the competition of the extraction of Zr and Fe. It is reported that reduction from Fe^{3+} to Fe^{2+} with ascorbic acid is useful to improve the extraction of the target elements (Am is the target element in the report) on the TRU resin [14,15]. Therefore, this method was applied to improve the extraction of Zr on the TRU resin. However, extraction of Zr was decreased rather than increased.

Table 3 Elution behavior of major elements of the simulated rubble sample solution, Zr, Nb, and Mo from the TRU resin.

	Load/rinse 3 M HNO_3 (3.4/10.2 mL =5/15 FCV) %	Zr recover 0.01 M HF (6.8 mL =10 FCV) %
Na	91±1	3±4
Al	100±2	<5
Ca	115±6	<0.1
Fe	105±2	4±1
Zr	22±1	87±2
Nb	60±1	41±1
Mo	17±1	80±2

The column cromatography experiment was carried out twice, and the uncertainty was quantified by the dispersion in these two experiments.

It is reported that the capacities of the TRU resin for Nd and Am were 5.49 and 9.18 mg per mL of bed, respectively [14], that is, approximately 38 μmol of metal ion. The simulated rubble sample solution contained approximately 1.5 μmol of Zr, Nb, Mo and 3.2 μmol of Fe. The total amount of possible extracted metal ions was approximately 20% to the capacity. The sample solution contains also 20 μmol of Na, 23 μmol of Al, and 80 μmol of Ca and other ions. Because they are hardly to be extracted on the TEVA resin, the amount of the TRU resin in this experiment, 1 mL, was considered sufficient amount to extract Zr. However, it could be too small to avoid interfere of the other elements, consequently, Zr might be eluted. In addition, F^-, which was contained in the stock solution of dissolved rubble sample, was possibly remained in the sample solution and caused the elution of part of Zr in the load/rinse fraction. Even though the elution of Zr in load/rinse fraction was observed, it is clear that most of Zr was recovered in Zr recover fraction. Therefore, we employed this separation method to separate Zr from major elements of the simulated rubble sample solution.

1.5 ml of the Zr recover fraction from TRU resin loaded the simulated rubble sample solution was evaporated to dryness and the residue was dissolved in 10 ml of HF (0.1 M) solution, and 3.4 ml of the disolved solution was loaded to the TEVA resin. The concentrations of Zr, Nb, and Mo in the loaded solution were 2.437±0.115 μg/ml, 1.106±0.076 μg/ml, and 2.197±0.108 μg/ml, respectively. All fractions from the TEVA resin were diluted 100 times to measure with ICP-MS. 6.872±0.921 ng/ml of Na and 2.026±0.503 ng/ml of Al were constantly contained in the all fractions and sample. They are contamination from experimental environment. The concentrations of Ca, Cr, and Fe in all fractions and sample were less than the detection limit. The measured concentration at the m/z of 90(Zr), 93(Nb), and 98(Mo) in the Zr recover fraction from the TEVA resin were 12.37±0.0091, 0.006325±0.00330, 0.01261±0.01481 ng/ml, respectively. The detection limits obtained from the measurement of dilutant were 0.078, 0.011, and 0.0053 ng/ml for Zr, Nb, and Mo, respectivery. The separation factor for Nb, $([\mathrm{Nb}]/[\mathrm{Zr}])_{\mathrm{TRU\ sample}} / ([\mathrm{Nb}]/[\mathrm{Zr}])_{\mathrm{TEVA\ Zr\ fraction}}$, was 2005 (If detection limit value for Nb was used for the calcuration, the separation factor was 1153), that for Mo, $([\mathrm{Mo}]/[\mathrm{Zr}])_{\mathrm{TRU\ sample}} / ([\mathrm{Mo}]/[\mathrm{Zr}])_{\mathrm{TEVA\ Zr\ fraction}}$, was 1005. It is considered that Zr was successfully separated from Nb and Mo. The elution behavior of Zr, Nb, and Mo from the TEVA resin was shown in Table 4. Where, recovery was calculated by dividing the amount of element in each fraction with that in the loaded solution. Quantitative recovery of Zr was obtained in the Zr fraction. Bcause chemical properties of ^{93}Zr are the same to the other Zr isotopes, ^{93}Zr will be quantitatively recovered in the Zr fraction.

Table 4 Elution behavior of Zr, Nb, and Mo from the TEVA resin

	Load/rinse 0.1 M HF (3.4/10.2 mL 5/15 FCV)	Zr recover 7 M HCl-0.5 M HF (6.8 mL =10FCV)	Mo recover 4 M HF (6.8 mL =10FCV)	Nb recover 1 M HNO_3 (6.8 mL =10 FCV)
	%	%	%	%
Zr	3±1	102±5	<0.5	<0.5
Nb	<0.4	<0.2	<0.2	105±7
Mo	<0.1	0.1	97±1	5±4

The column cromatography experiment was carried out twice, and the uncertainty was quantified by the dispersion in these two experiments.

Conclusions

Extraction agents impregnated in the TRU resin are octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and tri-n-butyl phosphate (TBP). It is reported that extraction mechanism of Zr with CMPO from nitric acid is as follows [16]:

$$Zr^{4+}_{aq} + 4NO_{3}{}^{-}_{aq} + 2CMPO_{org} \rightleftarrows Zr(NO_3)_4 \cdot 2CMPO_{org}.$$

The equilibrium constant of $1.13\times10^{5}\pm1.48\times10^{4}$ was also reported for the reaction. As expected from the high equilibrium constant, Zr was extracted on the TRU resin from 3 M HNO_3 solution. In addition, Zr was successfully recovered with 0.01 M HF solution which is able to avoid trace level contamination and emphasis of memory effect for the measurement of ICP-MS. Most of the elements such as major elements of the rubble sample were separated from Zr by passing through the TRU resin. However, a part of Nb and Mo, which were the interfering elements for the measurement of Zr with ICP-MS, was observed in the Zr fraction. It was reported that Zr, Nb, and Mo were mutually separated with the TEVA resin [13]. Extraction agent impregnated in the TEVA resin is a mixture of trioctyl and tridecyl methyl ammonium chlorides. It works like an anion exchanger, that is, anionic species were extracted on the TEVA resin. Zr, Nb, and Mo form anionic species depending on the concentrations of HF, HCl and HNO_3. Therefore, extraction and elution of Zr, Nb, and Mo on the TEVA resin are controlled by the concentrations of these acid. Based on this theory, separation of Zr from Nb and Mo was accomplished by the sequential separation using the TEVA resin.

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