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Development of determination method of ^{93}Mo content in metal waste generated at the Japan Power Demonstration Reactor

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Abstract

A separation method of Mo from Nb, Zr, and the matrix elements of rubble waste was modified to determine the content of ^{93}Mo in metal waste. A separation scheme to treat 1 g of metal waste was established by optimizing the amount of ascorbic acid, the rinsing solution, and repeating of the procedure. A thin-layer source was prepared using direct drop deposition and evaporation to measure ^{93}Mo content. Finally, ^{93}Mo content in the metal waste generated at the Japan Power Demonstration Reactor was analyzed using the developed method.

Keywords

^{93}Mo, TEVA resin, low-level radioactive waste, metal waste, Japan Power Demonstration Reactor

Introduction

The international Atomic Energy Agency proposed the application of scaling factors (SF) method, which is established by a correlation between the difficult to measure and easy to measure nuclides, for waste characterization in nuclear power plants [1]. Accordingly, the applicability of the SF method is being studied for the metal waste generated at the research reactors in the Japan Atomic Energy Agency. Therefore, samples were obtained from the waste generated in the Japan Power Demonstration Reactor (JPDR), and important nuclides for the safety assessment have been analyzed [2-6].

Molybdenum-93 (with half-life 4000 y) is one of the difficult to measure nuclide, and is mainly produced by the neutron irradiation of ^{92}Mo contained in metal structural materials. Molybdenum-93 decays to ^{93m}Nb (with half-life 16.13 y) through an electron capture reaction, followed by the emission of a specific X-ray of Nb (the intensities of L (2.17 keV), KA2 (16.521 keV), KA1 (16.6151 keV), and KB (18.6 keV) are 6.0, 21, 40, and 12%, respectively) [7]. The daughter nuclide, ^{93m}Nb, decays to stable Nb via an IT decay, and this process also emits a specific X-ray of Nb (the intensities of L, KA2, KA1, and KB are 2.82, 3.24, 6.2, and 1.84%, respectively) [8]. Since ^{93m}Nb is produced by not only the EC decay of ^{93}Mo but also the β^- decay of ^{93}Zr, Mo has to be separated from Zr and Nb to detarmine ^{93}Mo using the X-rays. Moreover, the X-ray energy of ^{93}Mo is sufficiently low to be absorbed by the sample matrix and/or glass vial; further, the chemical separation of Mo from the matrix elements and the preparation of thin-layer source are indispensable.

Recently, a chemical separation method of Mo from Zr, Nb, and the matrix elements of rubble sample using a tetra valent actinide resin (TEVA resin) was developed in our laboratory to analyze a small amount of rubble samples from Fukushima Daiichi Nuclear Power Station [9]. In order to use this method for the analysis of the metal waste from the JPDR, it should be modified because the sample amount is large (approximately 0.2 g of Fe) and the metal waste contains a large amount of Fe, which interferes with the extraction of Mo on the TEVA resin. In the present study, the amount of ascorbic acid of the sample solution, rinse solution, and duplication of the separation were elucidated to optimize the separation of Mo. Finally, ^{93}Mo in the metal waste from JPDR was analyzed.

Experimental

Materials

TEVA resin was purchased from Eichrom Technologies, USA (particle size 100-150 μm). Standard materials of stainless steel (SUS304, JSS 651-10) and carbon steel (CS, JSS 050-2) were purchased from the Japan Iron and Steel Federation. Hydrochloric acid (35-37%) and nitric acid (60-62%) for the analysis of poisonous metal and perchloric acid (70%) and hydrofluoric acid (47%) of analytical grade were purchased from Wako Pure Chemical Industries, Ltd., Japan.

Dissolution of metal samples and preparation of sample solutions

Grained SUS304 and CS were used in the experiments to optimize the separation method. One gram of SUS304 or CS was placed in a beaker, and 15 mL of HCl and 5 mL of HNO_3 were added; subsequently, the beaker was heated on a hot plate. The addition of these acids and subsequent heating were repeated several times. Subsequently, the concentrated solution was transferred into a PTFE beaker, and 10 mL of HF and 20 mL of HNO_3 were added to evaporate Si. This process was also repeated several times. After the evaporation of the solution, the residue was treated with 10 mL of $HClO_4$ and 20 mL of HNO_3 to eliminate F completely. The residue was dissolved in HCl solution and filtered. Finally, the solution was adjusted to obtain a 4 M HCl/0.1 M HF solution. Sample solutions to load the TEVA resin column were prepared by adding ascorbic acid and 0.5 mg of Mo into the digested solutions containing 0.5 g of SUS304 or CS. The digestion method of metal waste generated at the JPDR was described in ref [2]. The metal surface was digested by using acid.

Modification of the separation scheme

The basic separation scheme is shown in Fig. 1. The sample solution consisted of 0.5 g of SUS304 or CS, 0.1 M HF, 4 M HCl, and ascorbic acid. The concentration of ascorbic acid in the sample solution was changed from 0.3 M to 1 M. The TEVA resin column (5 mL) was conditioned with 25 mL of a solution whose composition is the same as the sample solution but without SUS304 or CS. Subsequently, the sample solution was loaded into the TEVA resin column and rinsed with the solution containing 0.1 M HF, 4 M HCl and the same concentration of ascorbic acid as the sample (hereafter referred as “rinse1”). Subsequently, the column was rinsed with a solution containing 0.1 M HF and 4 M HCl

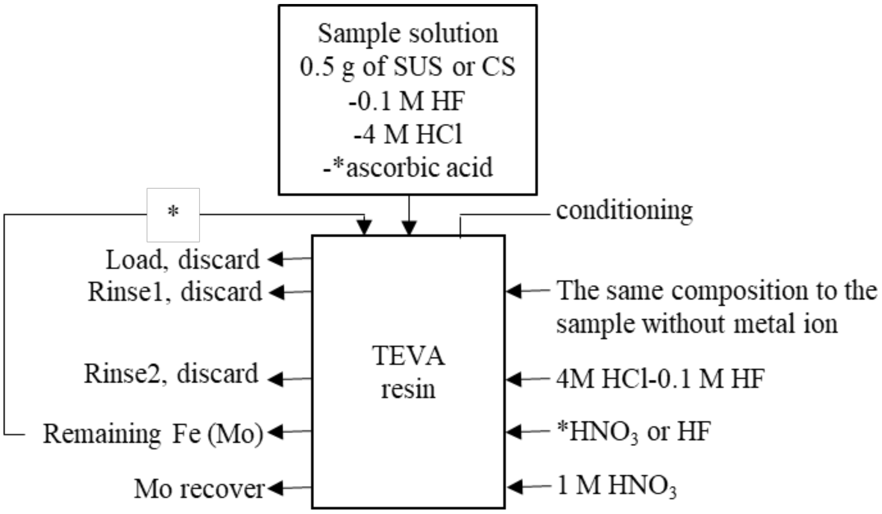

Fig 1 Basic chromatographic scheme to optimize the separation of Mo from Fe

(hereafter referred to as “rinse2”). The remaining Fe was rinsed with “rinse3” solution. Where, 0.01 M HNO_3, 0.1 M HF, and 2 M HF were examined as rinse3 solution to decrease the elution of Mo. Finally, the extracted Mo was recovered with 1 M HNO_3 and the total volume was adjusted to 50 mL. Moreover, the procedure was repeated for the selected rinse3 (0.1 M HF) to improve the total Mo recovery. The concentration of Mo in the Mo recovery fractions was measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES) system (Shimadzu ICPS-7500 sequential plasma emission spectrometer). The percentage of recovery was calculated using the following formula:

$$\text{Recovery percentage} = \frac{Metal\ amount\ in\ the\ fraction\ \times 100}{Metal\ amount\ in\ the\ sample\ solution}$$

Loss of Mo during the preparation of thin-layer source

The loss of Mo during direct drop deposition was evaluated because some Mo compounds have low boiling points. A standard solution containing 0.05 mg of Mo was placed on a Ta disk and evaporated on a hot plate until it was dry. Subsequently, the deposit was dissolved with 10 mL of 1 M HCl to measure the concentration of Mo using the ICP-AES.

Measurement of ^{93}Mo in the metal waste generated at the JPDR

Stable Mo (0.5 mL of 1000 ppm Mo solution in 0.4 mol HCl-0.2 mol HNO_3) was added to the dissolved solution of the metal waste generated at the JPDR (corresponding amount of the metal waste was 1 g, for dissolved amounts of the waste was 0.2±0.3 g, 0.05-1 g), and the solution was adjusted as 25 mL of 4 M HCl-0.1 M HF-0.6 M ascorbic acid to load into the conditioned TEVA resin (5 mL). After rinsing with 4 M HCl-0.1 M HF-0.6 M ascorbic acid (rinse1) and 4 M HCl-0.1 M HF (rinse2), the remaining Fe was rinsed with 0.1 M HF (rinse3), and Mo was recovered with 1 M HNO_3 (Mo). Since a part of Mo was eluted in the rinse3 fraction, the fraction was adjusted to 4 M HCl/0.1 M HF/0.6 M ascorbic acid solution to repeat the chromatographic separation process. The Mo recovery fractions of the first and second operations were combined and evaporated until they were dry. The residue was dissolved in 3 M HNO_3 (0.5 mL). A part of the dissolved solution was diluted to determine the concentration of Mo using the ICP-AES. The percentage of recovery of Mo was calculated using the concentration. A thin-layer source was prepared according to ref [3]. X-rays of ^{93}Mo were detected using a low-energy photon detector (GLP-36360/13-P, Seiko EG&G).

Results and discussion

Modification of the separation scheme

In this study, the sample solution contained 0.5 g of SUS304 or CS. These amounts are equivalent to approximately 6.6 mM and 7.5 mM of Fe, respectively; whereas, 25 mL of 0.3 M ascorbic acid solution contains 7.5 mM of ascorbic acid. In theory, 2 mole equivalent of Fe is reduced by 1 mole equivalent of ascorbic acid. Therefore, 0.3, 0.6, and 1 M ascorbic acid are equivalent to 2, 4, and 6.7 times the amount of required ascorbic acid to reduce Fe in the sample solution, respectively. Table 1 presents the percentage of recovery of Mo in the recovery fraction of Mo when the concentration of ascorbic acid in the sample solution was changed from 0.3 to 1 M. When the concentration of ascorbic acid was 0.3 M, the percentage of recovery was low (6% and 11% for SUS304 and CS, respectively). However, the percentage of recovery was more than 50% for both SUS304 and CS when the concentration of ascorbic acid was more than 0.6 M. An increase in the concentration of ascorbic acid from 0.6 to 1 M did not cause an increase in the percentage of recovery. Moreover, the dissolution of ascorbic acid is a time-consuming process. Therefore, the concentration of ascorbic acid was optimized to 0.6 M.

Table1 The percentage of recovery of Mo in the recovery fraction of Mo.

Concentration of ascorbic acid	SUS304	CS
0.3 M	6%	11%
0.6 M	62%	53%
1 M	67%	50%

The sample consisted of 0.5 g of stainless steel (SUS304) or carbon steel (CS), 4 M HCl, 0.1 M HF, and ascorbic acid. The concentration of ascorbic acid was varied from 0.3 to 1 M.

The elution behavior of Mo in each fraction is summarized in Fig. 2, wherein 0.6 M ascorbic acid-4 M HCl-0.1 M HCl solution containing 0.5 g of SUS304 or CS was loaded into the TEVA resin. The subsequent rinse with rinse2, i.e., 4 M HCl-0.1 M HF, was skipped in this evaluation.

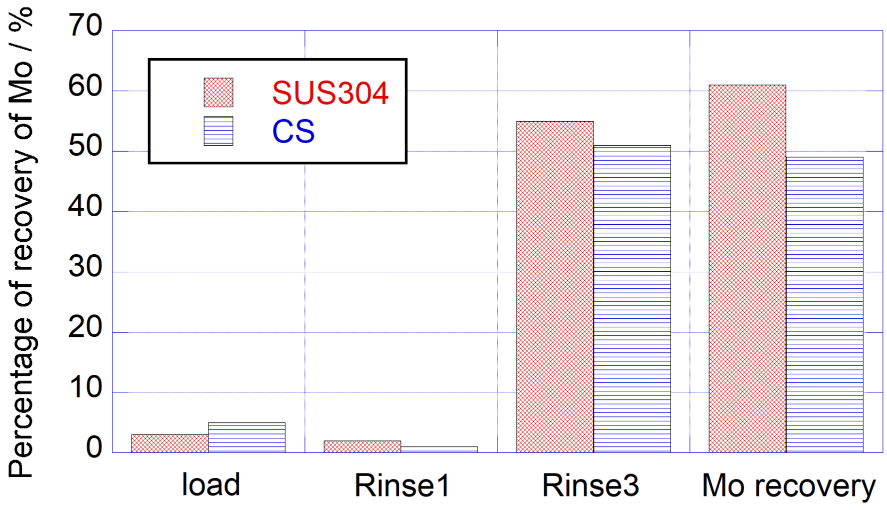

Fig.2 Elution behavior of Mo in each fraction

The Mo elution during the sample loading and rinsing with 0.6 M ascorbic acid-4 M HCl-0.1 M HCl solutions is small, 1-5%, and blue-green band was observed on the upper side of the TEVA resin column. This indicates that Mo was extracted on the TEVA resin regardless the sample solution contained a large amount of Fe. However, approximately half of the total amount of Mo was eluted by the 0.01 M HNO_3 solution, and the blue-green band disappeared followed by the elution of red-brown solution. It was reported that most of Fe was eluted during the sample loading and the extracted Fe was eluted with 0.01 M HNO_3 with remaining of the extraction of Mo on the TEVA resin when a rubble sample solution containing 52 µg/mL of Fe and 40 µg/mL of Mo was analyzed [9]. However, a large amount of Fe (approximately 0.37 g for SUS304 and 0.5 g for CS) in the sample solutions elutes Mo together with the extracted Fe. Molybdenum may form a complex with Fe in the sample solution and the formation is facilitated by the high concentration of Fe. If the Mo-Fe complex is extracted on the TEVA resin, the elution of Fe from the TEVA resin column may induce the accompanying elution of Mo.

Analogous column separation experiments were performed with different rinse 3 solutions, 0.01 M HNO_3, 2 M HF, and 0.1 M HF. Table 2 presents the percentages of recovery of Mo in the Mo recovery fraction. This result suggests that 0.1 M HF slightly suppressed the elution of Mo with the extracted Fe. Moreover, the eluate with 0.1 M HF was adjusted to 0.6 M ascorbic acid-4 M HCl-0.1 M HF solution to load the TEVA resin column again. It was confirmed that more than 80% of Mo was recovered via duplication of the column separation.

Table2 The percentage of recovery of Mo in the Mo recovery fraction when the composition of rinse3 was changed

Composition of Rinse 3	SUS304	CS
0.01 M HNO_3	62%	53%
2 M HF	19%	29%
0.1 M HF (first tern)	58%	81%
0.1 M HF (second tern)	26%	23%
0.1 M HF (total)	84%	104%

Finally, the following conditions were selected to analyze ^{93}Mo content in the metal waste of JPDR: 0.6 M ascorbic acid-4 M HCl-0.1 M HF for the sample solution, 0.1 M HF for rinse 3 solution, and the eluate of rinse3 solution was adjusted to 0.6 M ascorbic acid-4 M HCl-0.1 M HF to repeat the column separation procedure.

Loss of Mo during the preparation the thin-layer source

The direct drop deposition method was originally developed to prepare a thin-layer source for the measurement of α-ray [10]. Although tetraethylene glycol was used as a spreading agent, it was not used in this case because the self-absorption of X-rays is considered to be smaller than that of α-rays. It was confirmed that the percentage of recovery of Mo deposit was approximately 100%; in other words, the loss of Mo during the deposition was negligible.

Measurement of ^{93}Mo in the metal waste from JPDR

The analytical results of ^{93}Mo content in the metal waste of JPDR are summarized in Table 3. A high percentage of recovery (88±8%, 72-105%) was obtained in the analysis. All the ^{93}Mo concentrations were less than the detection limit of 2×10^{-2} Bq/g. It was shown that ^{93}Mo concentration in the metal waste of JPDR is at least 500 times less than that of the exclusion value of ^{93}Mo, i.e., 10 Bq/g [11].

Table 3 The analytical results of ^{93}Mo content in the metal waste of JPDR

Sample	Sample No.	Percentage of recovery (%)	^{93}Mo concentration (Bq/g) [5]
Pipe from feed-water system	M-926-1-2	82	$<2\times10^{-2}$
Reactor building	NY-926-557-2	105	$<1\times10^{-2}$
Pipe from forced circulation system (exit)	NY-926-558-1	72	$<2\times10^{-2}$
Pipe from forced circulation system (exit)	NY-926-558-2	86	$<2\times10^{-2}$
Pipe from purification demineralizer system	NY-927-1030-1	95	$<2\times10^{-2}$
Pipe from liquid waste treatment system	NY-927-1047-1	91	$<2\times10^{-2}$
Pipe from liquid waste treatment system	NY-927-1050-1	90	$<2\times10^{-2}$
Pipe from liquid waste treatment system	NY-927-1050-2	92	$<2\times10^{-2}$
Filter from fuel pool	NY-927-976-1	94	$<2\times10^{-2}$
Pipe from liquid waste treatment system	NY-927-946-2	84	$<2\times10^{-2}$
Pipe from liquid waste treatment system	NY-924-225-1	80	$<2\times10^{-2}$
Valve from liquid waste treatment system	NY-922-1730-1	82	$<2\times10^{-2}$
Pipe from liquid waste treatment system	NY-927-957-1	97	$<2\times10^{-2}$
Pipe from purification demineralizer system	NY-927-932-1	85	$<2\times10^{-2}$
Device used for decommissioning	NY-923-1949-1	91	$<2\times10^{-2}$
Pipe from feed-water system	NY-91Y-989-1	89	$<9\times10^{-3}$
Pipe from purification demineralizer system	NY-919-372-1	88	$<2\times10^{-2}$

Conclusions

The existing analytical method of ^{93}Mo was successfully modified to treat a metal waste sample. The concentration of ascorbic acid was increased from 0.3 M to 0.6 M to ensure the reduction of Fe^{3+} to Fe^{2+}, and 0.1 M HF was used as a rinse solution for the extracted Fe instead of 0.01 M HNO_3 to suppress the Mo elution with Fe. By repeating the separation procedure for the rinse solution of Fe, the percentage of recovery obtained was more than 80%. Finally, the concentrations of ^{93}Mo in the metal waste of the JPDR were analyzed using the modified method, and it was confirmed that they were lower than the exclusion level.

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