

Study on volatilization mechanism of ruthenium tetroxide from nitrosyl ruthenium nitrate by using mass spectrometer



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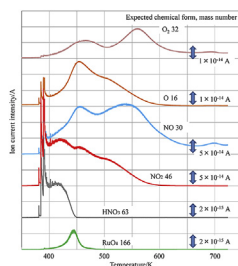
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HIGHLIGHTS

- Nitrosyl Ru nitrate ($\text{Ru}(\text{NO})(\text{NO}_3)_3$) dissolved in nitric acid (HNO_3) was dried and heated up to 723 K.
- Release of ruthenium tetroxide (RuO_4) was detected between 390 K and 500 K by means of the mass spectrometer.
- The experimental results suggest that Ru could be oxidized to form RuO_4 by the nitrate ion as well as HNO_3 .

GRAPHICAL ABSTRACT



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ABSTRACT

In a cooling malfunction accident of a high-level liquid waste (HLLW) tank, behavior of ruthenium (Ru) attracts much attention, since Ru could be oxidized to a volatile chemical form in the boiling and drying of HLLW, and part of radioactive Ru can potentially be released to the environment. In this study, nitrosyl Ru nitrate ($\text{Ru}(\text{NO})(\text{NO}_3)_3$) dissolved in nitric acid (HNO_3), which is commonly contained in a simulated HLLW, was dried and heated up to 723 K, and the evolved gas was introduced into a mass spectrometer. The well-known volatile species, ruthenium tetroxide (RuO_4) was detected in a temperature range between 390 K and 500 K with the peak top around 440 K. Various gases such as HNO_3 , nitrogen dioxide (NO_2), nitrogen monoxide (NO) also evolved due to evaporation of the nitric acid and decomposition of the nitrate ions. The ion current of RuO_4 seems to increase with the increasing decomposition of nitrate, while the evaporation of HNO_3 decreases. More volatilization of RuO_4 was observed from the HNO_3 solution containing not only $\text{Ru}(\text{NO})(\text{NO}_3)_3$ but also cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) which was added for extra supply of nitrate ion, compared with that from the HNO_3 solution containing only $\text{Ru}(\text{NO})(\text{NO}_3)_3$. These experimental results suggest that Ru could be oxidized to form RuO_4 by the nitrate ion as well as HNO_3 .

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1. Introduction

Cooling system malfunction of a high-level liquid waste (HLLW)

tank is regarded as one of major accidents in reprocessing business [1]. The tank is equipped with the cooling system to always remove the decay heat in the HLLW. However, if the cooling system is lost and is not recovered for a long term, it is presumed that the HLLW would slowly heat up, boil, evaporate to dryness. Some radioactivity would be then released out of the tank and the barriers. For instance, ruthenium (Ru), of which radioactive isotopes are

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generated as fission products, could be oxidized to the volatile ruthenium tetroxide (RuO_4) in a boiling and drying HLLW made of a hot and concentrated nitric acid (HNO_3). Therefore, chemical behavior of Ru attracts much attention.

M. Philippe et al. conducted the evaporation experiment to dryness using a genuine HLLW with approx. 0.04 mol L^{-1} of the Ru concentration and 1.8 mol L^{-1} of the HNO_3 concentration [2]. The genuine HLLW of 400 mL was slowly evaporated for 70 h and finally heated up to about 433 K. The amount of Ru released out of the heated vessel and collected in the condensate was found to increase significantly in a late stage of the evaporation particularly above 403 K, at which temperature the acidity in the condensate was 9 mol L^{-1} . They finally found that about 12% of Ru initially contained in the HLLW had been released. The other experiments were carried out by A. Sasahira et al. to distil a nitric acid dissolving nitrosyl Ru nitrate ($\text{Ru}(\text{NO})(\text{NO}_3)_3$) at the nitric acid concentration of 9 mol L^{-1} [3] and 453 K. Finally they determined the equation for the formation rate of volatile octavalent Ru, which is related with the activity and the concentration of nitric acid [4]. Recently, Y. Yamane et al. have performed the experiments to heat a genuine high active liquid waste up to 573 K and observed the Ru volatilization from a drying material in the temperature range over 400 K [5]. However, even reaction formula for RuO_4 formation has not been clarified and further experimental data is still necessary to know radioactive Ru release behavior at a late stage of the evaporation and the dryness, in particular. Another matter is the experimental method to clarify the Ru release behavior that would depend on various conditions as nitric acid concentration, solute concentrations and composition, heating rate and time, and so on. The release of Ru from nitric acid solution has been mainly investigated by recovering and analyzing the condensed volatile Ru. Such a method is not very efficient to examine complicated behavior of the Ru release.

In this study, volatilization of Ru was studied by using mass spectrometer. A nitric acid solution dissolving $\text{Ru}(\text{NO})(\text{NO}_3)_3$, which is commonly contained in a simulated HLLW, was dried and heated up to 723 K, and the evolved gas was introduced into the mass spectrometer. Few study has been reported on mass spectrometry of Ru volatilized from the drying nitric acid and nitrate in such a low temperature range. Much information on other evolved gases obtained by the mass spectrometry is possibly helpful for the consideration about the oxidation reaction to form the volatile Ru. Mass spectrometry can also potentially give an effective and helpful method for study on the Ru release from acid solutions.

2. Experimental

A quadrupole type mass spectrometer, which is a part of SHIMADZU gas chromatograph-mass spectrometer GCMS-QP2010 Ultra, was used in this study. A direct sample inlet unit can be attached to the mass spectrometer. Sample contained in a glass pot (1.9 mm in an inner diameter, 10 mm in a length) was settled at the rod end of the unit and then inserted to just touch the ion source box and close to the quadrupole in a vacuum chamber below 10^{-3} Pa . The reagent of $\text{Ru}(\text{NO})(\text{NO}_3)_3$ containing 32.0 wt % of Ru was purchased from RARE METALLIC Co., LTD. It was dissolved in a concentrated nitric acid solution at approx. 61 wt % of HNO_3 . The molar ratio of Ru: HNO_3 in the solution was calculated to be 1:8.5, compared with 1:22 in a typical simulated HLLW [6]. In order to examine an effect of coexisting nitrates on volatilization of Ru, mass spectrometry was carried out for sample solution containing not only $\text{Ru}(\text{NO})(\text{NO}_3)_3$ but cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). The reagent of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, of which assay is minimum 98%, was purchased from Wako Pure Chemical Industries, Ltd.. It was dissolved in a pure water at the ratio of 1 g-

$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}/2 \text{ mL-H}_2\text{O}$ and then the water solution containing 10.4 wt % of Ce was added to the Ru initial nitric acid solution. Thus, the molar ratio of Ru: HNO_3 was kept to be 1:8.5 even in the Ce-Ru mixed solution.

The solutions less than $15 \mu\text{L}$ were injected in the small glass pot by using a micro syringe. Before it was inserted into the vacuum chamber, the sample solution was warmed up and dried at 353 K to avoid a violent evaporation of an excess liquid in heating under the vacuum. The dried sample was heated up to 723 K at a constant heating rate of 5 K min^{-1} and the evolved gas was directly analyzed in situ by means of the mass spectrometer through the ion source box and the quadrupole. The ionization voltage was set at 70 eV and the mass spectrum was obtained by scanning the mass number from 2 to 390.

The evolution of gas was also observed by using Burker Optics Fourier transform infrared spectrometer (FTIR) ALPHA series fixed on NETZSCH thermo-gravimetric analyzer (TG) STA 449 F3. The powder remaining in the alumina crucible of TG-FTIR was analyzed by means of X-ray diffraction (XRD).

3. Results and discussion

3.1. Volatilization of Ru from $\text{Ru}(\text{NO})(\text{NO}_3)_3$

As a result of the mass spectrometry for the dried nitric acid solution containing the $\text{Ru}(\text{NO})(\text{NO}_3)_3$ reagent, ion current intensities of the mass number concerning with RuO_4 were obtained with respect to the temperature as shown in Fig. 1. There are seven natural isotopes of Ru, of which mass numbers are 96, 98, 99, 100, 101, 102, and 104 corresponding to 160, 162, 163, 164, 165, 166, and 168 of RuO_4 . The intensities of all mass numbers in Fig. 1 have obvious peaks in the temperature range from 400 K to 470 K and the peak tops were observed at the same temperature around 440 K. The intensity ratio (IR) of ion current among the seven isotopes was defined as Eq. (1) and the average values for the temperature range are summarized in Table 1.

$$\text{IR}_M (\%) = I_M / I_{\text{sum}} \times 100 \quad (1)$$

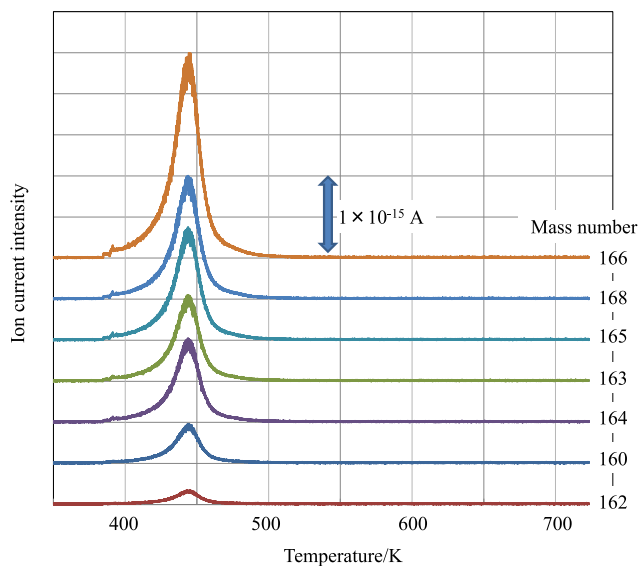


Fig. 1. Ion current intensities of the mass numbers concerning with RuO_4 obtained in mass spectrometry for dried nitric acid solution containing $\text{Ru}(\text{NO})(\text{NO}_3)_3$. Heating rate: 5 K min^{-1} , sample solution weight: 6.61 mg, contained Ru weight: 0.56 mg.

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