# Ruthenium Behavior at Phase Separation of Borosilicate Glass-12259

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## ABSTRACT

The Rokkasho reprocessing plant (RRP) located in Aomori, Japan, vitrifies high level waste (HLW) into a borosilicate glass.   The HLW is generated from the reprocessing of spent fuel and contains ruthenium (Ru) and other platinum group metals (PGMs).   Based on the recent consequences after a huge earthquake that occurred in Japan, a hypothetical blackout was postulated for the RRP to address additional safety analysis requirements.   During a prolonged blackout, the borosilicate glass could phase separate due to cooling of the glass in the melter. The Ru present in the glass matrix could migrate into separate phases and impact the durability of the borosilicate glass.   The durability of the glass is important for quality assurance and performance assessment of the vitrified HLW.   A fundamental study was performed at an independent university to understand the impact of a prolonged blackout. Simulated HLW glasses were prepared for the RRP, and the Ru behavior in phase separated glasses was studied.   The simulated HLW glasses contained nonradioactive elements and PGMs.   The glass compositions were then altered to enhance the formation of the phase-separated glasses when subjected to thermal treatment at 700 $^{\circ}$C for 24 hours.   The synthesized simulated glasses contained 1.1 % Ru by weight as ruthenium dioxide ($RuO_2$).   A portion of the $RuO_2$ formed needle-shaped crystals in the glass specimens.   After the thermal treatment, the glass specimen had separated into two phases.   One of the two phases was a $B_2O_3$ rich phase, and the other phase was a $SiO_2$ rich phase.   The majority of the chemical species in the $B_2O_3$ rich phase was leached away with the Material Characterization Center-3 (MCC-3) protocol standardized by the Pacific Northwest National Laboratory using an aqueous low-concentrated nitric acid solution, but the leaching of the Ru fraction was very limited; less than 1% of the original Ru content. The Ru leaching was much less than those of the other elements, and the needle-shaped crystals of $RuO_2$ were observed in the $B_2O_3$ rich phase in the specimen after the leaching test.   Another experiment was performed using another glass specimen which had been prepared with the same frits, but used reagent $RuO_2$ of granular shape at lower content (0.0073% by weight as $RuO_2$).   The leached  fractions of elements for the latter specimen increased to almost the same fraction (more than 10% of the original Ru content) as observed for boron and sodium, when the phase separated glass was leached using the MMC-3 protocol with non-acidic de-ionized water.   Based on the results of this study, it was concluded that needle-shaped $RuO_2$ crystals are contained in the $B_2O_3$rich phase after phase separation of the borosilicate glass after a hypothetical blackout.   The leaching fraction for the needle-shaped $RuO_2$ present in the phase separated glass is much lower than those for boron or sodium.

## INTRODUCTION

Ruthenium (Ru) is one of the major fission products, obtained from the reprocessing of spent fuel, and is contained in high-level radioactive waste (HLW).   The HLW is immobilized in a borosilicate glass matrix [1] for long term storage.

Sedimentation of the PGMs in a vitrification process triggered a temporary shutdown of the RRP. Needle-shaped crystals of $RuO_2$ have been confirmed to exist in the bottom of the liquid-fed ceramic melter (LFCM) in the RRP [2-3]. The needle-shaped crystals of $RuO_2$ found in the vitrification process have been scientifically reported in Germany [4-6], but in the German vitrification plant, no significant sedimentation of the PGMs has been reported [7].   Since a

limited number of studies have been conducted concerning the formation mechanisms of the crystals, the authors investigated how the needle-shaped crystals of $RuO_2$ are formed in the LFCM and performed leaching tests on these glasses using the MCC-3 protocol [2-3].

The operator of the RRP facility has concluded that a failure to control temperature in the LFCM was the major cause of the sedimentation of PGMs in the melter. RRP engineers have completed modifications to the process equipment and operating procedures in order to restart the final stage of the testing campaign in the RRP [8]. Prior to finishing the final step of the test campaign at the RRP facility, the tragic nuclear accident in Fukushima occurred (in March, 2011) due to a station blackout (SBO). The SBO was due to the tidal waves caused by the historic earthquake that ravaged northern Japan. The SBO had lasted more than 10 days whereas it had been assumed to be only half an hour for previously performed safety assessments.. Based on the extended SBO period experienced, additional safety analyses are now required to be performed not only for nuclear power plants, but also for the reprocessing plant in Japan.

During a prolonged blackout in the RRP facility, the borosilicate glass could phase separate due to cooling of the glass in the melter. The Ru present in the glass matrix could migrate into the separated phases and impact the durability of the glass. The durability of the borosilicate glass is important for quality assurance and the performance assessment of the vitrified HLW. Generally, the compositions of the HLW borosilicate glass are chosen to avoid any phase separation which may cause deleterious effects on the glass durability, i.e. leachability with groundwater. In addition to having a composition that favors phase separation, both temperature and time play a significant role in whether the phase separation will be noticeable. In the present work, we assumed that the composition, temperature, and time were hypothetically favored for phase separation of the HLW glass. Then, our research efforts focused on identifying the Ru migration into the separated phases and its leachability by an aqueous solution.

From an experimental perspective, the time available in a laboratory for achieving a phase separated glass is limited. Thus, the glass formulation was altered to favor a phase separated glass by considering the phase diagram illustrated in Fig. 1. This diagram represents the phase separation of borosilicate glass in order to obtain phase separated glass specimens in a reasonable time [9]. In this figure, the compositions plotted with open circles numbered 11 through 15 were found to produce glass specimens that can be separated into binary phases within 24 hours. Those plotted with "x" numbered 1 through 10 were not able to be separated. The data point from Fig. 1 that showed the most favorable conditions, based on composition and temperature, for the binary phase separation was number 15.
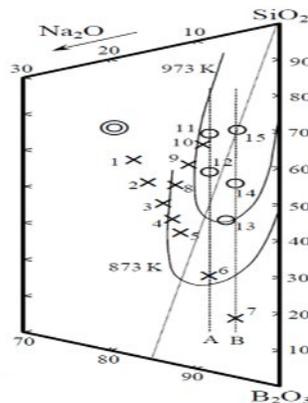


Fig. 1.   An example of a diagram of phase separation for borosilicate glass [9].

## EXPERIMENTAL

### Reference Glass Fabrication and Glass Dissolution Methods

Spent fuels of 45,000MWd/t burn-up were assumed to be averagely reprocessed in the RRP [12], and the composition of the spent fuel was calculated using the Origen-2 computer code, and a reference glass composition was assumed to have the same contents of silicon, aluminum, boron, sodium, lithium, calcium, and zinc in the glass as that from the Tokai Vitrification Plant operated by the Japan Atomic Energy Agency [13].   The total loading of simulated wastes was 15% by weight as their oxides.   Actinides were simulated by neodymium for uranium and cerium for the transuranic elements.   The target simulated composition is listed in Table I.

Table I.   Target Composition of Simulated HLW Glass.

| component | Content by weight as oxide, % | Subtotal, % |
|---|---|---|
| $SiO_2$ | 46.7 | |
| $B_2O_3$ | 14.3 | |
| $Al_2O_3$ | 5.0 | |
| $Na_2O$ | 10.0 | 85 |
| $Li_2O$ | 3.0 | |
| CaO | 3.0 | |
| ZnO | 3.0 | |
| $P_2O_5$ | 0.3 | |
| $Fe_2O_3$ | 2.0 | |
| NiO | 0.2 | 15 |
| $Cr_2O_3$ | 0.1 | |
| FPs as oxides | 9.9 | |
| Actinides oxides | 2.5 | |

All chemical reagents used for the simulated HLW glass preparation were of reagent grade and purchased from Wako Pure Chemical Industries, Ltd., Japan, and used as received.   The glass oxides were weighed and placed into a high purity alumina crucible (SSA-S, 500 cm$^3$ in volume, Purity >99.5%, Nikkato Co., Japan).   The sample was then well mixed and heated to 1400 $^o$C in a tubular electric furnace (KTF433N1, Koyo Thermos Co., Ltd., Japan) and held at temperature for 12 hours.   The sample was then quenched at room temperature to obtain the reference glass sample.   All elements in the simulated glass sample were introduced by this procedure, but one exception was Ru.   Ruthenium was introduced through additional contact of the glass melt with the prepared salt of trisodiumruthenate in sodium nitrate as previously described in the literature [2,3].   All specimens used in the current study were taken from this batch of glass and some chemical reagents were added to modify compositions in order to meet the objectives set in each experiment as described below.

To determine the glass composition of the prepared reference sample, the sample was dissolved using two dissolution methods.   The two dissolution methods used were an alkali fusion with sodium carbonate and an aqueous dissolution with hydrofluoric acid.   The resulting dissolution solutions were then analyzed by an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES).   For the alkali fusion method, a 100 mg sample of the prepared glass was mixed with 500 mg of reagent grade sodium carbonate purchased from Wako Pure Chemical Industries, Ltd., Japan, heated at 1000 $^o$C for 20 minutes in a platinum crucible and quenched at room temperature.   The salt remaining in the crucible was then dissolved in a 5 mol dm$^{-3}$ hydrochloric acid solution. This solution was analyzed for silicon, boron, and Ru by ICP-AES (ICPE-9000, Shimadzu Corp., Japan).   The hydrofluoric acid method was used to obtain the concentration of

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the remaining elements of concern in the glass.   For the hydrofluoric acid method, 100 mg of the prepared glass was dissolved with 3 cm$^3$ a 2:1 in volume mixture of 46% hydrofluoric acid and 60% perchloric acid and evaporated to dryness.   The obtained solid was dissolved in a 1 mol dm$^{-3}$ hydrochloric acid solution.   The resulting solutions were the analyzed by ICP-AES.

**Thermal Treatments and Formulation Modification to Produce Phase Separated Glasses**

In the current study, seven glass specimens were prepared and subjected to thermal treatment described below and then analyzed.   Table II summarizes the glass composition, crystal shape of the ruthenium dioxide, and thermal conditions for the phase separation.   The glass specimens, 1 through 5, were subsamples of the original reference glass sample as described above.

Table II.   Summary of the Prepared Glass Specimens and Thermal Conditions for Phase Separation.

| Glass Specimen Number | Glass Composition | $RuO_2$ Crystal Shape | Subjected Thermal Condition and Time |
|---|---|---|---|
| 1 | Reference | needle-shaped | 550 $^o$C for 1-4 days |
| 2 | Reference | needle-shaped | 600 $^o$C for 1-4 days |
| 3 | Reference | needle-shaped | 650 $^o$C for 1-4 days |
| 4 | Reference | needle-shaped | 700 $^o$C for 1-4 days |
| 5 | Reference | needle-shaped | 750 $^o$C for 1-4 days |
| 6 | separation favored | needle-shaped | 700 $^o$C for 1 day |
| 7 | separation favored | granular | 700 $^o$C for 1 day |

Since the reference composition of the prepared glass sample was significantly different from that as of the favored condition for the binary phase separation, we modified the formulation of the specimens 6 and 7 by the addition of $SiO_2$ and $B_2O_3$ in order to match the composition of number 15 in Fig. 1.   A 65 g sample of $SiO_2$ (Reagent Grade, Wako Pure Chemical Industries, Ltd., Japan) and 35 g sample of $B_2O_3$ (Reagent Grade, Wako Pure Chemical Industries, Ltd., Japan) were added to 100 g of the prepared glass after being ball-milled. The mixture was heated in an alumina crucible (Purity >99.5%, SSA-S, Nikkato Co., Japan) at 1400 $^o$C in a tubular electric furnace (KTF433N1, Koyo Thermos Co. Ltd., Japan) for one hour and then quenched at room temperature.

The specimen 7 was prepared with the same glass composition as the reference composition and ruthenium dioxide granular-shaped which was of reagent grade and purchased from Wako Pure Chemical Industries, Ltd., Japan. By preparation of this specimen, we expect that it contained no needle-shaped $RuO_2$ of a lower content (0.0073%) and the ruthenium was dissolved in the glass matrix homogeneously.

As a part of the current study, a series of small-scale experiments were performed for specimens 1 through 5 to confirm the phase stability of the prepared glass sample with the reference composition at temperatures of 550 $^o$C, 600 $^o$C, 650 $^o$C, 700$^o$C and 750$^o$C for 24 to 96 hours. The heat treatments for the phase separation for the specimens 6 and 7 were performed at 700 $^o$C for 24 hours.   The heat treatments for the phase separation for the all specimens were performed in an electric muffle furnace (FUH600, Advantec Toyo Kaisya, Ltd., Japan).

**Glass Leaching Test**

A part of each phase separated specimen and the original sample were separately pulverized and sieved into fragments of 5 to 10 mm in size and 0.1 g of the fragments were then placed in a

Teflon® container with 20 cm$^3$ of 1 mol dm$^{-3}$ nitric acid solution or ultrapure water, i.e., de-ionized water produced by Elix Advance System provided by Japan Millipore Corp., Japan, for the leaching test for 24 hours based upon the MCC-3 test protocol [11]. The leached solution was analyzed using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (SPQ-9700, Seiko Instruments Nanotechnologies, Inc., Japan).

**RESULTS AND DISCUSSION**

The compositions of the prepared borosilicate glass specimens 1 through 5 were determined and tabulated in Table III. When the values of elemental contents in Table III are compared with those in Table I, and the expected measurement errors (±3% of each value) are taken into account, the targeted contents for the glass sample to simulate the HLW glass in the RRP were successfully prepared.   The observations using a scanning electron microscope (SEM) (JEOL Ltd., JSM-7001F, Japan) followed by energy dispersive x-ray spectroscopy (EDX) showed the existence of needle-shaped crystals of Ru species as observed in previous studies [2,3].

Table III.   Glass Composition Determined for the Reference Sample Used in this Study.

| component | Content by weight as oxide, % | Subtotal, % | component | Content by weight as oxide, % | Subtotal, % |
|---|---|---|---|---|---|
| SiO$_2$ | 45 | | TeO | 0.24 | |
| B$_2$O$_3$ | 15 | | BaO | 0.71 | |
| Al$_2$O$_3$ | 5.1 | | La$_2$O$_3$ | 1.2 | |
| Na$_2$O | 8.9 | | Pr$_2$O$_3$ | 0.73 | |
| Li$_2$O | 3.0 | | Sm$_2$O$_3$ | 0.31 | |
| CaO | 3.2 | | CdO | 0.035 | |
| ZnO | 3.4 | | Eu$_2$O$_3$ | 0.052 | |
| Sub-total for glass frits | | 83.6 | Gd$_2$O$_3$ | 0.24 | |
| P$_2$O$_5$ | -$^a$ | | SeO | - | |
| Fe$_2$O$_3$ | 0.60 | | SnO$_2$ | 0.092 | |
| NiO | 0.19 | | Sb$_2$O$_3$ | 0.024 | (2.9) |
| Cr$_2$O$_3$ | 0.085 | | RuO | 1.1 | |
| Sub-total for corrosion products, | | 0.88 | Rh$_2$O$_3$ | 0.14 | |
| ZrO$_2$ | 2.5 | | PdO | 0.62 | |
| MoO$_3$ | 1.8 | | Sub-total of PGMs | | 1.9 |
| CeO$_2$ | 2.4 | | Sub-total of FPs and actinides | | 14.6 |
| Nd$_2$O$_3$ | 2.0 | | Total loading of waste | | 15.5 |
| MnO$_2$ | 0.41 | | Total | | 99.1 |
| SrO | 0.45 | | | | |
| Y$_2$O$_3$ | 0.20 | (9.8) | | | |

$^a$ under detection limit.

Based on the thermal treatments outlined in Table II, the specimens were very stable up to 96 hours against phase separation; no phase separation was observed by visual appearance or by observation with a scanning electron microscope (SEM) (JSM-7001F, JEOL Ltd., Japan).

On the other hand, the glass formula modification performed for glass specimens 6 and 7 successfully yielded a binodal-type phase separation of the $B_2O_3$ rich and $SiO_2$ rich phases. This is illustrated in Fig. 2 by comparing pictures of the glass specimen thermal treatment at 700 $^\circ$C for 24 hours. Whether the phase separation was observed or not is summarized in Table IV.



|  (a)  |  (b)  |

Fig. 2. Photographic images of glass specimen 6 (a) before and (b) after phase separation

Table IV.    Observation of Phase Separation for Experiment Specimens

| Specimen number | Occurrence of phase separation | $RuO_2$ present phase after phase separation |
|---|---|---|
| 1 | No | - |
| 2 | No | - |
| 3 | No | - |
| 4 | No | - |
| 5 | No | - |
| 6 | Yes | $B_2O_3$ |
| 7 | Yes | $B_2O_3$ |

When subjected to the leach test, almost all the components for the simulated fission products are known to be removed from the glass having the similar silicon, sodium and aluminum contents as specimens 6 and 7.   This is due to the phase separation that occurred from the heat treatment of glass based on the altered glass formulation of the reference composition [9]. In agreement with previous results, more than half of the sodium (79%) and boron (54%) originally contained in the glass were leached out of the specimen, but the fraction of the leached Ru was less than 1%. A needle-shaped crystal containing Ru was found in the $B_2O_3$ phase as illustrated in Fig. 3.
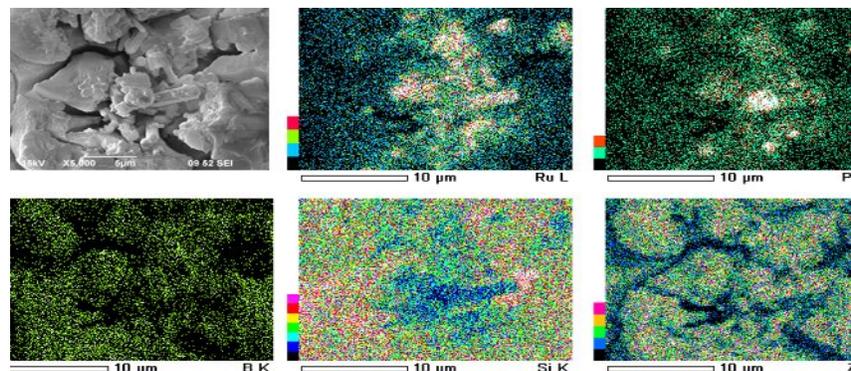


Fig. 3.    Microscopic photograps and results of energy dispersive X-ray spectroscopy.

In addition to this experimental observation, black granular materials were found, and an X-ray diffraction analysis showed the existence of $RuO_2$ in the #6 pulverized glass specimen after the leaching test. This implied that granular ruthenium dioxide can be a morphological form of ruthenium after bimodal-type phase separation of the vitrified high level waste with borosilicate glass media. These experimental results showed that both needle-shaped and granular-shaped crystals of $RuO_2$ remain in the glass matrix without dissolution even after an acid leaching with 1 mol $dm^{-3}$ $HNO_3$ for the phase separated glasses. These results agree well with the result that leaching fraction for the specimen 7 prepared from granular $RuO_2$ and with a lower Ru content (0.0073%) was also very low. On the other hand, we should note that the fraction of leached Ru increased to almost the same fraction (more than 10%) as observed for boron and sodium when the phase-separated glass was leached with ultrapure water, i.e., non-acidic de-ionized water. This is because the leached solution in contact with the glass specimen became basic after the dissolution of sodium from the glass matrix, and $RuO_2$ is easier to dissolve in a basic solution rather than in an acidic one. The results of the leaching tests for specimens 6 and 7 are shown in Table V.

Table V. The Leaching Test Results for the Phase Separated Specimens.

| Specimen number | Leaching solution | Original Ru content by weight as its oxide in specimen,% | Leached elemental fraction by weight, % | | |
|---|---|---|---|---|---|
| | | | Ru | B | Na |
| 6 | 1 mol $dm^{-3}$ $HNO_3$ | 1.1 | 0.7 | 54 | 79 |
| 7 | 1 mol $dm^{-3}$ $HNO_3$ | 0.0073 | <0.3[b] | 45 | 39 |
| 7 | UPW[a] | 0.0073 | 11 | 20 | 12 |

[a] Ultrapure water
[b] The detection limit for Ru with ICP-MS under this condition.

## CONCLUSIONS

Ruthenium behavior has been studied for a hypothetical loss of cooling in the liquid fed ceramic melter for high level waste by taking into account the phase separation of borosilicate glass. The needle-shaped crystal of ruthenium dioxide after binodal-type phase separation of the borosilicate glass at 700°C migrated into the $B_2O_3$ rich phase, but remained without dissolution by an acidic aqueous solution. Additionally, granular ruthenium dioxide can be a morphological form of ruthenium after bimodal-type phase separation of the vitrified high level waste with borosilicate glass media. After the phase separation of the borosilicate glass, the crystal shape of the ruthenium dioxide is either needle-shaped or granular, and the leachable fraction of ruthenium is relatively much lower than those of major components (boron and sodium) in the vitrified borosilicate glass. The fraction of leached ruthenium increased to almost the same fraction as observed for boron and sodium when the phase-separated glass was leached with ultrapure water.

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