

**The Countermeasure for the Noble Metal in the HLW Vitrification  
- the Removal Technology of Ru, Rh and Pd from the System –  
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**ABSTRACT**

In this study, the system to separate ruthenium (Ru) in High-level radioactive liquid waste (HLLW), which has negative impact for the vitrification system, was investigated. It consists of three main parts. One is the process to remove Ru in HLLW by oxidizing Ru to RuO<sub>4</sub> using ozone (O<sub>3</sub>) and by heating to make RuO<sub>4</sub> vaporize. Second one is the process collecting gas RuO<sub>4</sub> vaporized from HLLW in the previous process. Final one is a degradation process of O<sub>3</sub> which still remains. Several experiments were carried out to evaluate each process using the liquid waste simulating HLLW (SHLLW). As results of them, we found out bellows. (1) Approximately 100% of Ru could be removed from SHLLW by adding O<sub>3</sub> to heated SHLLW in 80 degree C. (2) Over 80% of gas RuO<sub>4</sub> was destructed to RuO<sub>2</sub> particle in over 300 degree C without O<sub>2</sub>/O<sub>3</sub>. And nearly 100 % O<sub>3</sub> gas was also degraded in the same condition. From those results, the system to remove Ru from HLLW before putting it into the glass melter must be realized by setting additional HLLW heating process with O<sub>3</sub> supplying equipment and additional heating process of gas exhausted from the previous HLLW heating process. In the system, additional waste is not generated because of no additional solid and liquid chemicals. Moreover, we confirmed that DBP (di-butyl phosphate) which was added in SHLLW, was also degraded adding O<sub>3</sub>.

In addition, it was found that rhodium (Rh) and palladium (Pd) remained in glass make a low melting point alloy by adding TeO<sub>2</sub> and its fluidity can be improved.

**INTRODUCTION**

The high-level radioactive waste which is separated by spent nuclear fuel reprocessing is melted with the borosilicate glass beads for the vitrifying radioactive waste, in Japan. LFCM (Liquid Fed Joule-heated Ceramic Melter) is used for high-level radioactive waste vitrification. This type melter is heated by passing an electric current for the molten glass, but the noble metal particle sediment in the melter which increases glass viscosity and is high conductivity, negatively affects such as the drop of heating defectiveness and glass

fluidity for the melter operation. And the induction heat melter also has the same issue about glass fluidity lowering caused by the noble metal. Therefore, the various countermeasures have been performed for the issue of the noble metal. As physical countermeasure, melter shape modification for LFCM has been performed. However this physical approach can't be applied to the induction heat melter. As chemical countermeasures which can be applied to both melter, separation methods of the noble metal from HLLW using chromatography [1,2] and electro-oxidation [3] technology have been developed. But these have not been realized in commercial scale. Therefore, in this study, we tried to solve the issues of the noble metal in chemical approach which is different from methods described above. Especially, we focused on Ru which is included most in the HLLW among the noble metal.

It will be reported by K.Nakano et al in this conference that Ru negatively affects glass fluidity [4], therefore we have investigated technology for separating Ru from HLLW before putting it to the glass melter. In this technology, we tried to make Ru oxidize  $\text{RuO}_4$  using ozone ( $\text{O}_3$ ) and heating it to be vaporized. And the possibility of DBP degradation was also tested. This technology can be applied to the induction heat melter.

## DISCRIPTION

We assumed the system shown in Fig.1 as the system to remove Ru from HLLW. This system consists of three main processes. One is the process to remove Ru in HLLW by oxidizing Ru to  $\text{RuO}_4$  using  $\text{O}_3$  and by heating to make  $\text{RuO}_4$  vaporize. Second one is the process collecting gas  $\text{RuO}_4$  vaporized from HLLW in the previous process. Final one is a degradation process of  $\text{O}_3$  which still remains. Feasibility of each process was evaluated by experiments using the liquid waste simulating HLLW (SHLLW).

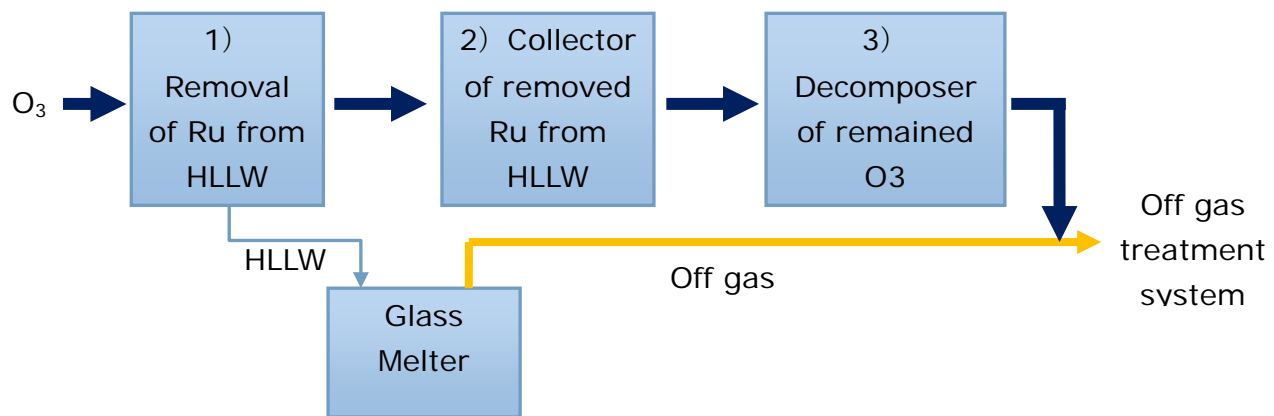


Fig. 1. Imagined process for removing Ru from HLLW

### Evaluation of Ru removal condition from SHLLW by oxidizing and heating

Experiments to make Ru in SHLLW oxidize to  $\text{RuO}_4$  and to vaporize  $\text{RuO}_4$  from SHLLW were done using the experimental apparatus shown in Fig.2.  $\text{N}_2$  was not used during experiments. It was used as purge gas after finishing experiment.

At first, experiments to oxidize Ru to  $\text{RuO}_4$  were done in several conditions shown in TABLE I. In these experiments, gas volume including  $\text{O}_3$  and SHLLW temperature were changed. And SHLLW diluted with 1:10  $\text{HNO}_3$  in 10 times was used. To evaluate the experimental result, concentration of Ru except for  $\text{RuO}_4$  in SHLLW was measured in predetermined time interval, and the amount of oxidized Ru was calculated from the difference of initial concentration of Ru in SHLLW and the measured concentration of Ru.

Fig. 3 shows temporal change of the amount of Ru in SHLLW. Time 0 is the start time when  $\text{O}_3$  was supplied to SHLLW. And the value of vertical axis is normalized value by the amount of Ru in SHLLW at time 0.

The amount of un-oxidized Ru in SHLLW decreases rapidly since when  $\text{O}_3$  was supplied to SHLLW. And decreasing rate of un-oxidized Ru becomes large as the SHLLW temperature becomes high. In the case that SHLLW temperature is between 30 and 50 degree C, un-oxidized Ru is still existed in 240 minutes. On the other hand, in the case of 80 degree C SHLLW temperature, un-oxidized Ru hardly exists in 60 minutes. This means that approximately 100% Ru in SHLLW is oxidized to  $\text{RuO}_4$ . Therefore an experiment shown in TABLE II was done using non diluted SHLLW to confirm if oxidizing Ru and vaporization of  $\text{RuO}_4$  could be done at the same time.

Fig. 4 shows temporal change of the amount of Ru in SHLLW heated in 80 degree C. Vertical axis and horizontal axis are as same as Fig. 3. The amount of Ru in SHLLW decreased to 20% from the initial amount of Ru in 45 minutes since ozone supplied, and decreased to below 10% after 90 minutes since ozone supplied.

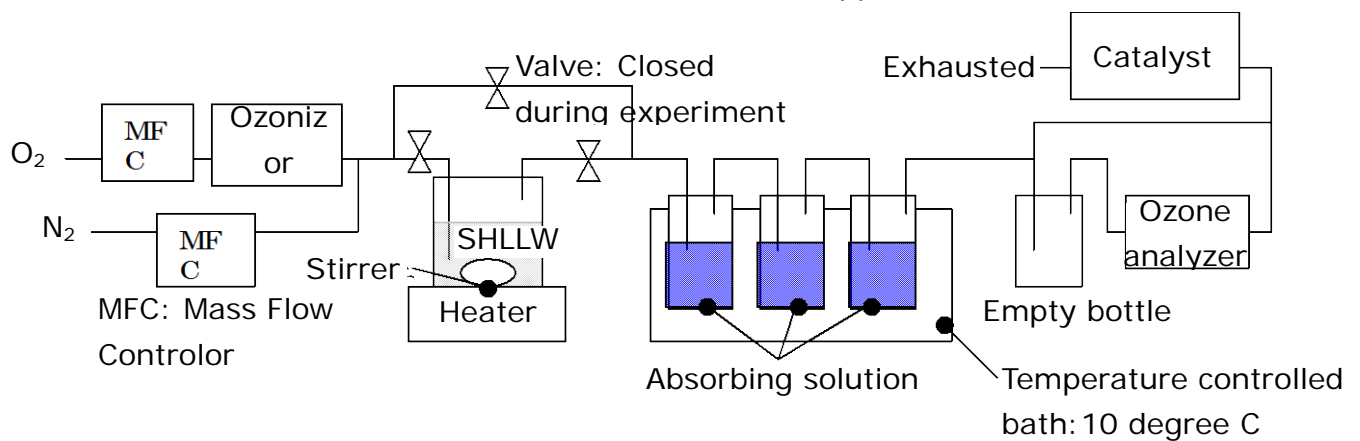


Fig. 2. Experimental apparatus for oxidizing Ru and vaporizing RuO<sub>4</sub>

TABLE I. Experimental conditions for oxidizing

Tested SHLLW	Diluted SHLLW* Ru : 200mg/l
Ozone Gas	Flow rate : 1, 0.5 L/min Concentration of ozone : 4vol%
Temp. of SHLLW	30, 40, 50, 80 degree C

\*Diluted with 1:10 HNO<sub>3</sub>aq in about 10 times

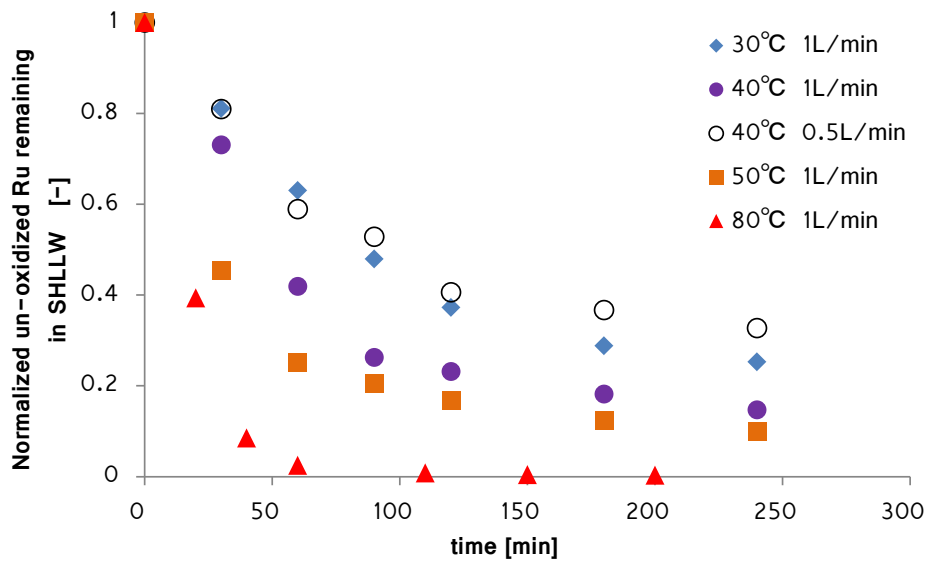


Fig. 3. Temporal change of the amount of un-oxidized Ru in SHLLW in the conditions shown TABLE I

TABLE II. Experimental condition for oxidizing and heating

Tested SHLLW	SHLLW Ru: 2300 mg/l
Ozone Gas	Flow rate : 0.3L/min Concentration of ozone : 6.7vol%
Temp. of SHLLW	80 degree C

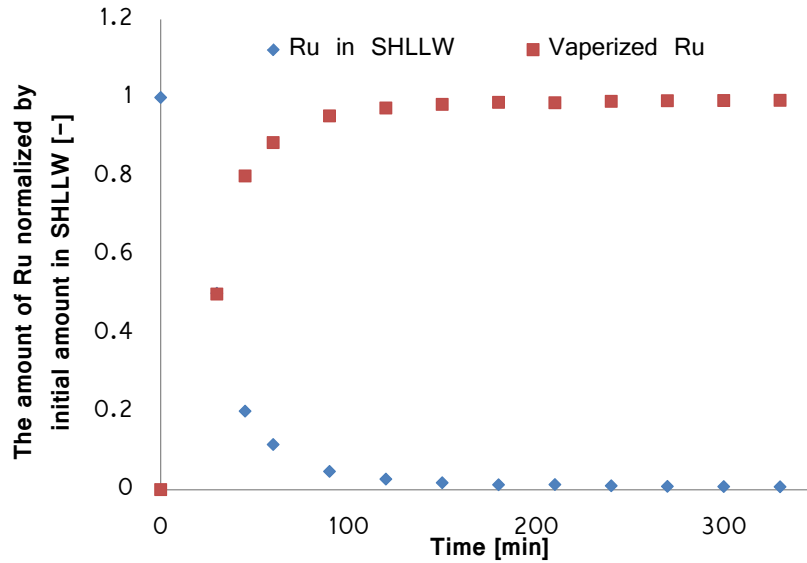


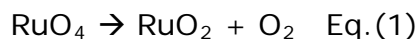
Fig. 4. Temporal change of the amount of T-Ru in SHLLW and vaporized Ru in the condition shown TABLE II

### Investigation of the way to collect vaporized RuO<sub>4</sub>

If gas RuO<sub>4</sub> is changed to RuO<sub>2</sub> particles, it will be easily collected by dust collector existed in off gas system with the melter. Therefore we tried to decompose RuO<sub>4</sub> vaporized from HLLW to RuO<sub>2</sub> particles in heating. Fig. 5 shows the experimental apparatus equipped with RuO<sub>4</sub> gas generator. In the RuO<sub>4</sub> gas generator, the carrier gas and the solution including RuO<sub>4</sub> are constantly supplied to RuO<sub>4</sub> gas generator and RuO<sub>4</sub> gas is generated.

Experiments were done in the conditions shown in TABLE III. Heating temperature was only changed up to 500 degree C during these experiments. Decomposition ratio of RuO<sub>4</sub> to RuO<sub>2</sub> was calculated from the difference between supplied RuO<sub>4</sub> gas and RuO<sub>4</sub> absorbed in absorbing solution set after heater.

Fig. 6 and 7 show the relation between destruction rate of RuO<sub>4</sub> and heating temperature in the experiments with/without ozone. As shown in Fig. 6, in the case without ozone, RuO<sub>4</sub> is destructed in over 200 degree C and approximately 100% RuO<sub>4</sub> is destructed in 300 degree C. On the other hand, the behavior of destructed RuO<sub>4</sub> with ozone gas is quite different. As shown in Fig. 7, only 80% of RuO<sub>4</sub> is destructed even though temperature is in 500 degree C. RuO<sub>4</sub> is destructed with eq. (1).



From the equation, it is clear that O<sub>2</sub> inhibits RuO<sub>4</sub> destruction. In the experiments with ozone, much amount of O<sub>2</sub> exists in carrier gas because ozone is generated from pure O<sub>2</sub>

gas. However, in the case of experiments without ozone, only  $N_2$  was used as the carrier gas. Therefore, it is estimated that the different result with/without ozone caused by existing/non-existing  $O_2$ .

In the experiments, residence time in  $RuO_4$  decomposer was short, 0.3-0.5 second. If it becomes longer, destruction ratio of  $RuO_4$  must be higher although  $O_2$  exists.

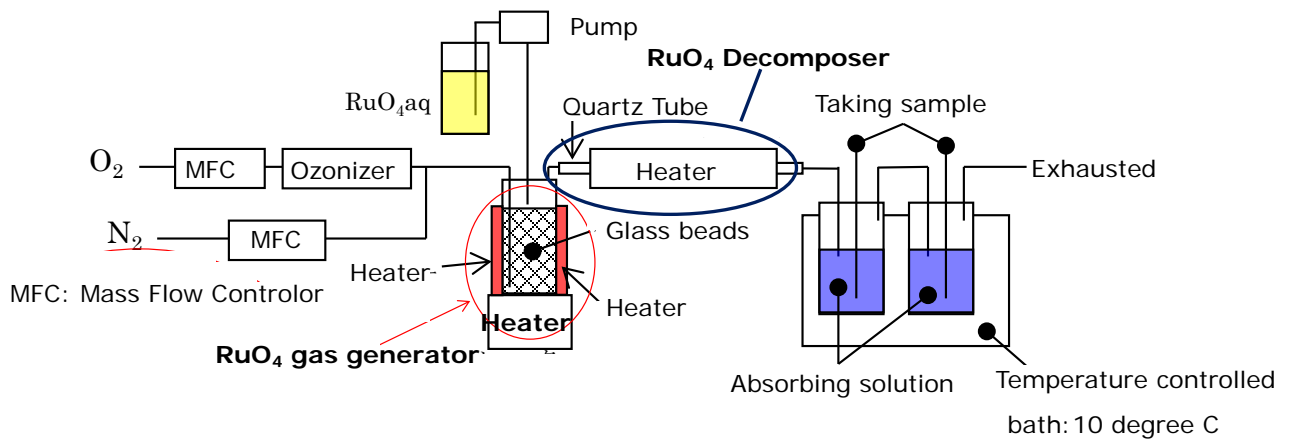


Fig. 5. Experimental apparatus to decompose  $RuO_4$  to  $RuO_2$  particle  
 TABLE III. Experimental conditions to decompose  $RuO_4$  to  $RuO_2$  particle

Supplied condition of $RuO_4$ gas	<ul style="list-style-type: none"> <li>• Conc. of <math>RuO_4</math> in solution : About 60mg/l as Ru</li> <li>• Solution Supplied rate : About 0.7ml/min*</li> <li>• Carrier Gas: <math>N_2</math> 0.3L/min or  <math>O_2 + O_3</math> 0.3L/min (<math>O_3</math>:16vol%)</li> </ul>
$RuO_4$ decomposer	Temp. : $\sim 500^\circ C$ Estimated duration time** : 0.3~0.5s

\* If all solution vaped, gas volume is 0.8NL/min.

\*\* Estimated from solution supplied rate and carrier gas volume rate

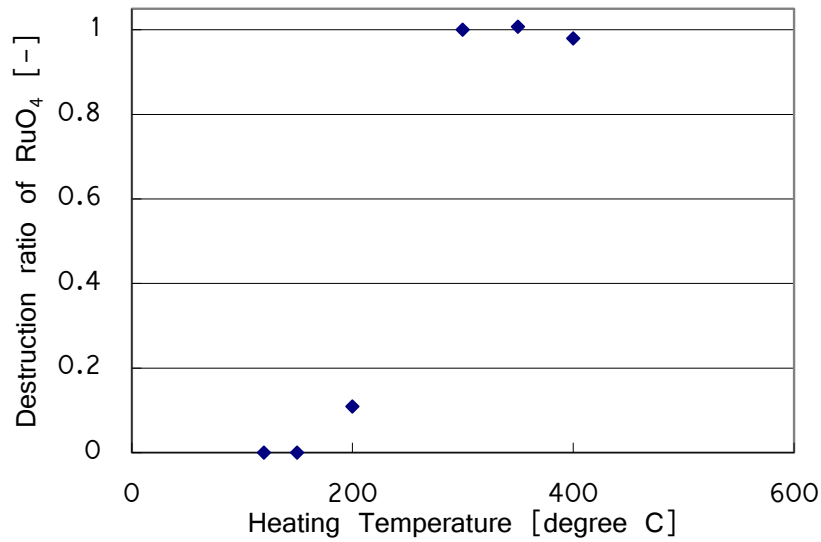


Fig. 6. Destruction ratio of RuO<sub>4</sub> to RuO<sub>2</sub> without O<sub>3</sub>

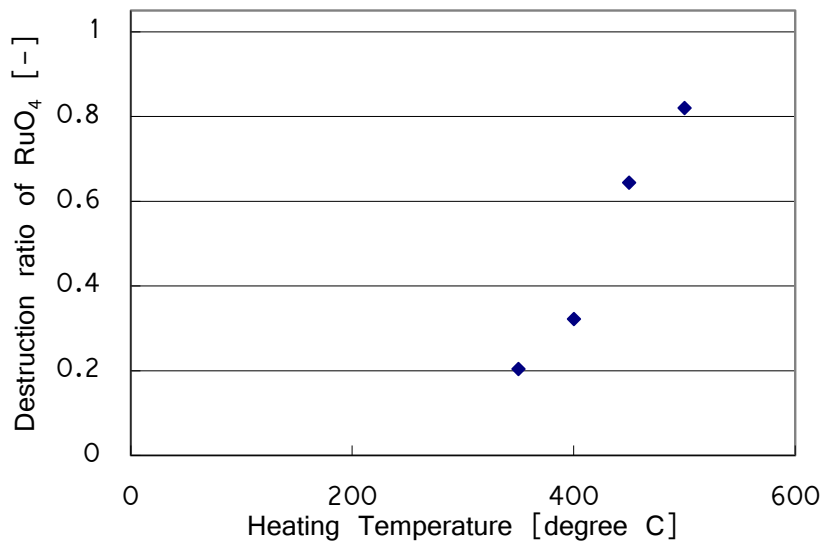


Fig. 7. Destruction ratio of RuO<sub>4</sub> to RuO<sub>2</sub> with O<sub>3</sub>

### Investigation of the way to decompose remaining O<sub>3</sub>

Experiments to decompose O<sub>3</sub> unused for oxidizing Ru were carried out using same experimental apparatus used in the experiment to decompose RuO<sub>4</sub>. Experimental conditions were also as same as TABLE III except for stopping supplying RuO<sub>4</sub>. Decomposition rate of O<sub>3</sub> was calculated from the measured value of O<sub>3</sub> in exhausted gas.

Fig. 8 shows the relation between destruction rate of O<sub>3</sub> and heating temperature. O<sub>3</sub> was destructed in 150 degree C, and the destruction rate reached 97% in 300 degree C in the residence time of 0.5 second. Half-value period of O<sub>3</sub> in about 300 degree C in the air

condition is 0.1 second [5]. From the value, 97% destruction rate of  $O_3$  in 300 degree C and in 0.5 second residence time is estimated. Therefore the results of these experiments are reasonable. Almost  $O_3$  can be destructed in over 300 degree C and in longer residence time than 0.5 second.

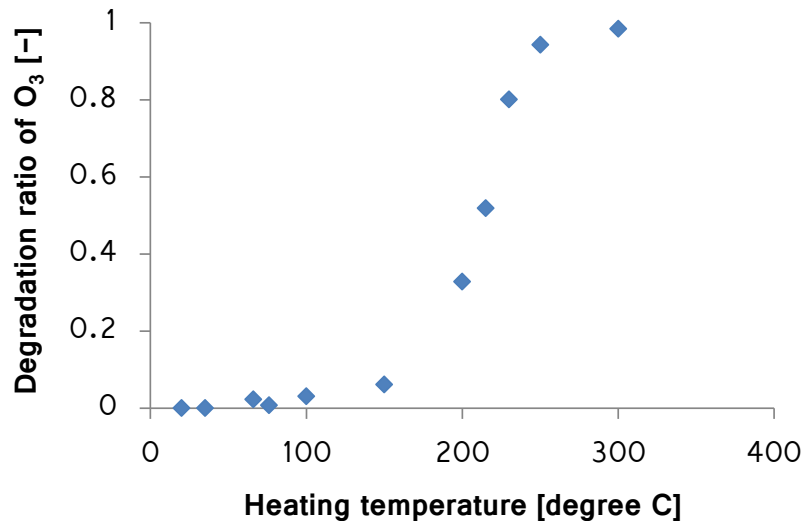


Fig. 8. Degradation ratio of  $O_3$

### Evaluation of the possibility of DBP decomposition in HLLW in the Ru removal process

A little amount of DBP (Di-Butyl Phosphate) is included in HLLW. It also negative affects the vitrification system, as same as the noble metal. And it has known that DBP can be decomposed by adding oxidant. Therefore, we had experiments to confirm if DBP decomposition and Ru removal can be accomplished in same process at the same time. The experiments were carried out in the experimental apparatus shown in Fig. 9. Generation of foam derived from DBP was expected, therefore two empty bottles were set to collect foam. Three experiments shown in TABLE IV were carried out. At first, DBP was added to SHLLW. And it was heated until the experimental condition temperature and ozone was supplied to SHLLW. Ru and DBP in collected foam/liquid in empty bottles, absorbing solution and SHLLW were analyzed. From analysis results, Ru removal rate and DBP decomposition rate were calculated.

TABLE V shows the results. From comparison with Run1 and Run2, it is found out that DBP can be decomposed adding ozone. And it is obvious that DBP decomposition is promoted by heating in comparing Run1 with Run3. In the condition of Run3, not only DBP was decomposed, but also Ru was removed. It shows that DBP decomposition and Ru removal



form at the same time.

However, foam shown in Fig. 10 was generated during addition of O<sub>3</sub>. Therefore, in a real system, treatment of foam is necessary in addition.

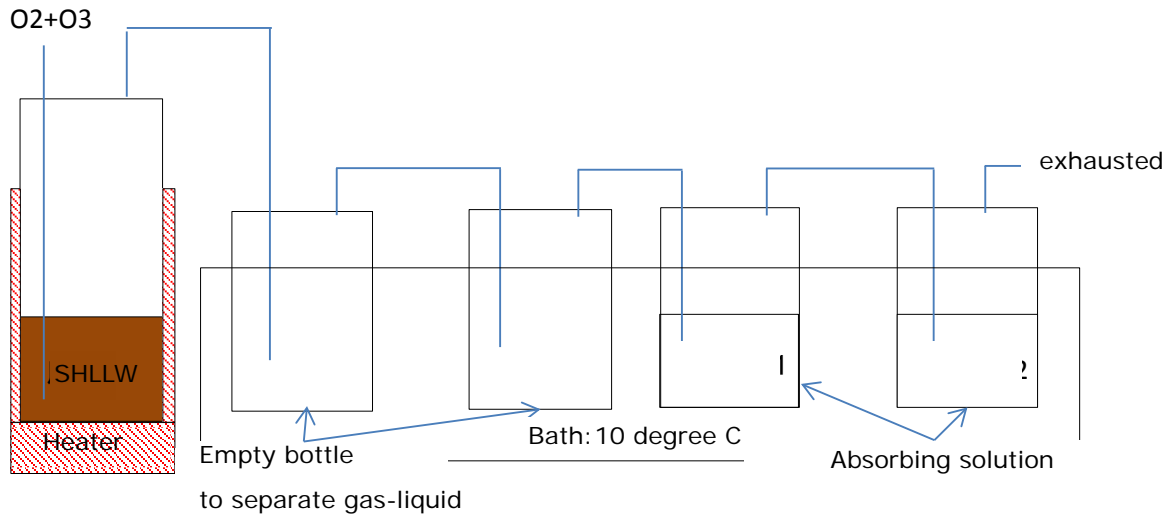


Fig. 9. Experimental apparatus to evaluate DBP decomposition and Ru removal adding O<sub>3</sub>

TABLE IV. Experimental conditions

	Run 1	Run 2	Run 3
Tested SHLLW	SHLLW: 90ml, DBP: 170 mg/l		
Gas Flow Rate	0.3 L/min	←	←
Concentration of O <sub>3</sub>	144 g/m <sup>3</sup>	0.0	144
Heating Temp.	30 °C	30 °C	80 °C
Kept time in Heating Time	1 hr	1 hr	1 hr

TABLE V. Removal ration of Ru and degradation ration of DBP in HLLW in each conditions

	Run 1	Run 2	Run 3
O <sub>3</sub> concentration [g/m <sup>3</sup> ]	144	0.0	144
Kept temperature of HLLW [°C]	30	30	80
Degradation ratio of DBP [%]	54.0	0.0	80.0
Removal ration of Ru [%]	26.8	4.5	84.6



Fig. 10. Foam generated from HLLW during supplying  $O_3$

### Transforming Rh-Pd-Oxide to lower-melting point alloy

Rh and Pd still remain in the HLLW after dealing with removal of Ru. Oxide of these elements which are high melting temperature and are not resolved into the glass, are formed in the melter. And it is expected that these precipitate on the bottom of the melter and prevent the melted glass from discharging from the melter. Therefore, we investigated about transforming these oxide to lower-melting alloy with tellurium dioxide ( $TeO_2$ ) to make their fluidity high.

In the experiment, two types of glass including 5%-PdO and 2% $-Rh_2O_3$  with/without  $TeO_2$  were prepared. These glasses were put into ceramic boats and those boats which were in tilted state in the furnace, like Fig.11, were heated up to 1150 degree C and were kept 2 hours in this temperature. After heating, they were cooled naturally and the fluidity of each glass was evaluated by the distance of flow.

Fig. 12 shows result. The glass with  $TeO_2$  flowed to the end of the boat. On the other hand, the glass without  $TeO_2$  flowed to the middle point of the boat. This means that adding  $TeO_2$  is effective to make the glass including Rh-Pd-Oxide easy to flow.

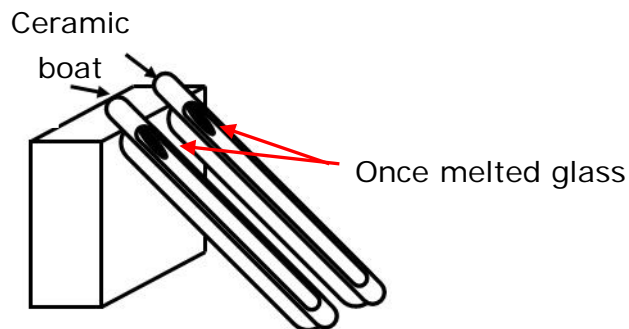


Fig. 11. The way to evaluate for glass fluidity



Fig. 12. The fluidity of the glass with/without  $\text{TeO}_2$

## DISCUSSION

To actualize the system to remove Ru from HLLW:

- $\text{O}_3$  generator must be installed to actualize the system. Consumed  $\text{O}_3$  should be minimized to downsize the  $\text{O}_3$  generator because of its high cost. In the experiment, mole of supplied  $\text{O}_3$  was 16 times of mole of oxidized Ru. In theory, one mole of Ru is oxidized to  $\text{RuO}_4$  by 4 moles of  $\text{O}_3$ . The difference of theoretical value and experimental value is caused by  $\text{O}_3$  consumption used for oxidizing other elements except for Ru and the less amount of  $\text{O}_3$  solved to SHLLW. To increase the amount of  $\text{O}_3$  dissolved to SHLLW, making contact area between  $\text{O}_3$  gas and SHLLW larger by installing  $\text{O}_3$  gas in small diameter bubble and making holding time of bubble in SHLLW longer by equipping with agitator are better.
- Heating systems are required to decompose  $\text{RuO}_4$  to  $\text{RuO}_2$  and  $\text{O}_3$  to  $\text{O}_2$ . Both decomposition can be done by setting operating temperature of the system over 500 degree C. And if gas including  $\text{RuO}_2$  particles after the heating system is treated with an off gas system different from the existed one, high purity  $\text{RuO}_2$  can be collected in dust collector. It can be reused after long time storage.
- As for the decomposition of DBP using  $\text{O}_3$ , the generated foam derived from DBP and the liquid entrained with foam included 10 % of DBP and Ru of the initially installed amounts. From this result, the foam and entrained liquid with foam are required to be returned to the reactor in which  $\text{O}_3$  is supplied. Therefore, a function to separate foam and gas including  $\text{O}_3$  is necessary for the system.

## CONCLUSION

We evaluated the feasibility of the system, shown in Fig.1, to remove Ru from HLLW by doing experiments using SHLLW. Approximately 100% of Ru could be removed from

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SHLLW as  $\text{RuO}_4$  by adding  $\text{O}_3$  to heated SHLLW in 80 degree C. And over 80% of gas  $\text{RuO}_4$

vaporized from SHLLW was destructed to  $\text{RuO}_2$  particle in over 500 degree C. And nearly 100 %  $\text{O}_3$  gas was also degraded in the same condition. Therefore, the system to remove Ru from HLLW before putting it into the glass melter must be realized by setting additional HLLW heating process with  $\text{O}_3$  supplying equipment and additional heating process of gas exhausted from the previous HLLW heating process. Moreover, degradation of DBP (di-butyl phosphate) in SHLLW by adding  $\text{O}_3$  was also confirmed in the experiment. The system for removing Ru from HLLW may also has capability to decompose DBP even though minor modification is required.

## **RERERENCE**

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