

VOLATILIZATION BEHAVIOR OF SEMIVOLATILE
ELEMENTS IN VITRIFICATION OF
HIGH-LEVEL LIQUID WASTE

-Research Report on Solidification of High-Level Liquid Waste-

Nov. 1 9 9 1

TOKAI WORKS
POWER REACTOR AND NUCLEAR FUEL DEVELOPMENT CORPORATION

複製又はこの資料の入手については、下記にお問い合わせ下さい。注)

〒319-11 茨城県那珂郡東海村大字村松 4 - 33

動力炉・核燃料開発事業団

東海事業所 (Tokai Works)

技術協力部 技術管理室

(Technology Management Section)

Inquiries about copyright and reproduction should be addressed to:
Technology Management Section, Tokai Works, Power Reactor and Nuclear Fuel
Development Corporation 4-33, Muramatu Ooaza, Tokai, Naka-gun, Ibaraki,
319-11, Japan)

動力炉・核燃料開発事業団 (Power Reactor and Nuclear Fuel Development
Corporation)1991

VOLATILIZATION BEHAVIOR OF SEMIVOLATILE ELEMENTS
IN VITRIFICATION OF HIGH-LEVEL LIQUID WASTE

—Research Report on Solidification of High-Level Liquid Waste—

Hiroshi Igarashi, Koh Kato and Takeshi Takahashi

Abstract

The effect of temperature on the volatilization of ruthenium, technetium, and selenium was observed in calcination experiments with simulated high-level liquid waste. Technetium and selenium were more volatile as calcining temperature increased. Ruthenium was less volatile when temperature exceeded 300°C. More than 80% of ruthenium that volatilized from room temperature to 500°C occurred between 200 and 300°C. A small amount of ruthenium volatilized above 300°C as well as below 135°C.

High-level waste technology section

Waste technology development division, Tokai-works

* The contents is based on the presentation at "'Volatilization Behavior of Semivolatile Elements During Vitrification of High-Level Liquid Waste', 1991 Joint International Waste Management Conference", Seoul, Korea Oct 21-24, 1991. (refer to the proceedings Vol.2 pp143-147)

VOLATILIZATION BEHAVIOR OF SEMIVOLATILE ELEMENTS
IN VITRIFICATION OF HIGH-LEVEL LIQUID WASTE

—Research Report on Solidification of High-Level Liquid Waste—

五十嵐 寛, 加藤 功, 高橋 武士

要 旨

高レベル廃液中の準揮発性元素であるRu, TcおよびSeに対し、ガラス固化プロセスでの挙動を把握するため、トレーサを添加した模擬廃液の連続仮焼試験を行い、各元素の揮発率について800℃までの温度依存性を評価した。さらに、Ruについては、バッチ仮焼試験を実施し、蒸発から仮焼が終了する500℃までの各温度領域に対する揮発率を評価することにより、温度依存性をより明確にするとともに、硝酸による影響について評価した。トレーサ試験では、TcおよびSeの揮発率は、温度の上昇とともに増加するが、Ruについては、温度が高くなるほど低下する結果が得られた。また、バッチ試験では、硝酸濃度にかかわらず、仮焼時のRuの揮発量の多くは、200～300℃の温度域における揮発によるもので、300℃以上での揮発量は僅かであることが判った。

東海事業所 環境技術開発部 環境技術第一開発室

*本文は「'Volatilization Behavior of Semivolatile Elements During Vitrification of High-Level Liquid Waste', 1991 Joint International Waste Management Conference, Seoul Korea, Oct 21-24, 1991」での発表に基づいてまとめたものである。(Proceedings Vol.2 pp143-147 参照)

Contents

1. INTRODUCTION	1
2. EXPERIMENTAL	1
2.1 Continuous Calcination for Ru, Tc and Se	1
2.2 Batch Calcination for Ru	3
2.3 Absorption of Semivolatile Elements	5
3. RESULTS	7
3.1 Entrainment in Continuous Calcination Test	7
3.2 Volatilization in a Continuous Calcination Test	7
3.3 Volatilization of Ruthenium in a Batch Calcination Test	7
3.4 Effect of Nitric Acid on Ru Volatilization	13
3.5 Effect of Glass Additives on Ru Volatilization	13
3.6 Absorption of Semivolatile Element in Continuous Calcination Test	13
4. DISCUSSION	15
5. CONCLUSION	16
ACKNOWLEDGEMENT	17
REFERENCES	18

1. INTRODUCTION

High-level liquid waste (HLLW) containing fission products is separated in reprocessing spent nuclear fuel and immobilized in stable form. Vitrification is used for immobilization of the HLLW in most reprocessing plants in the world.

We have developed liquid-fed Joule-heated ceramic melter (LFCM) at Power Reactor and Nuclear Fuel Development Corporation (PNC) that will be installed in the Tokai Vitrification Facility (TVF) now under construction^[1]. This equipment will also be used in the large-scale vitrification facility planned by Japan Nuclear Fuel Service Co., Ltd. ^[2].

In the LFCM process, the HLLW as nitric acid solution is directly fed, with glass additives, to the melter ^[3], where it is dried, calcined, and melted. In this process, a fraction of the HLLW elements is entrained in the off-gas from the melter. Semivolatile elements in the HLLW are generated in gaseous form by volatilization as well as in aerosol form together with other nonvolatile elements in the melting process. The off-gas treatment process is designed to minimize release of semivolatile and other elements. The elements entrained with air and nitrogen oxides from the melting process are removed by wet scrubbers and filters.

In this work, we studied the effect of temperature on the volatilization of ruthenium, technetium, and selenium during calcination as part of the vitrification process with continuous feeding. We also performed batchwise calcination of ruthenium to investigate details.

2. EXPERIMENTAL

2.1 Continuous Calcination for Ru, Tc and Se

Figure 1 is a diagram of the continuous calcination test apparatus, which consists of a stainless steel calciner, sintered metal filter, absorbing bottle, volumetric pump, and so on. The simulated HLLW with ^{103}Ru , $^{99\text{m}}\text{Tc}$, ^{75}Se and ^{85}Sr as radioactive tracers was fed continuously at about 19 ml h^{-1} and calcined in a 550 ml stainless steel calciner, which was heated at target temperature. The gas and entrained elements from the calciner were introduced into absorbing bottles after aerosols were removed by the sintered metal filter thermally insulated. Therefore, only gaseous components were captured in the absorbing bottles.

The sintered metal filter is made of SUS 316 stainless steel, and its

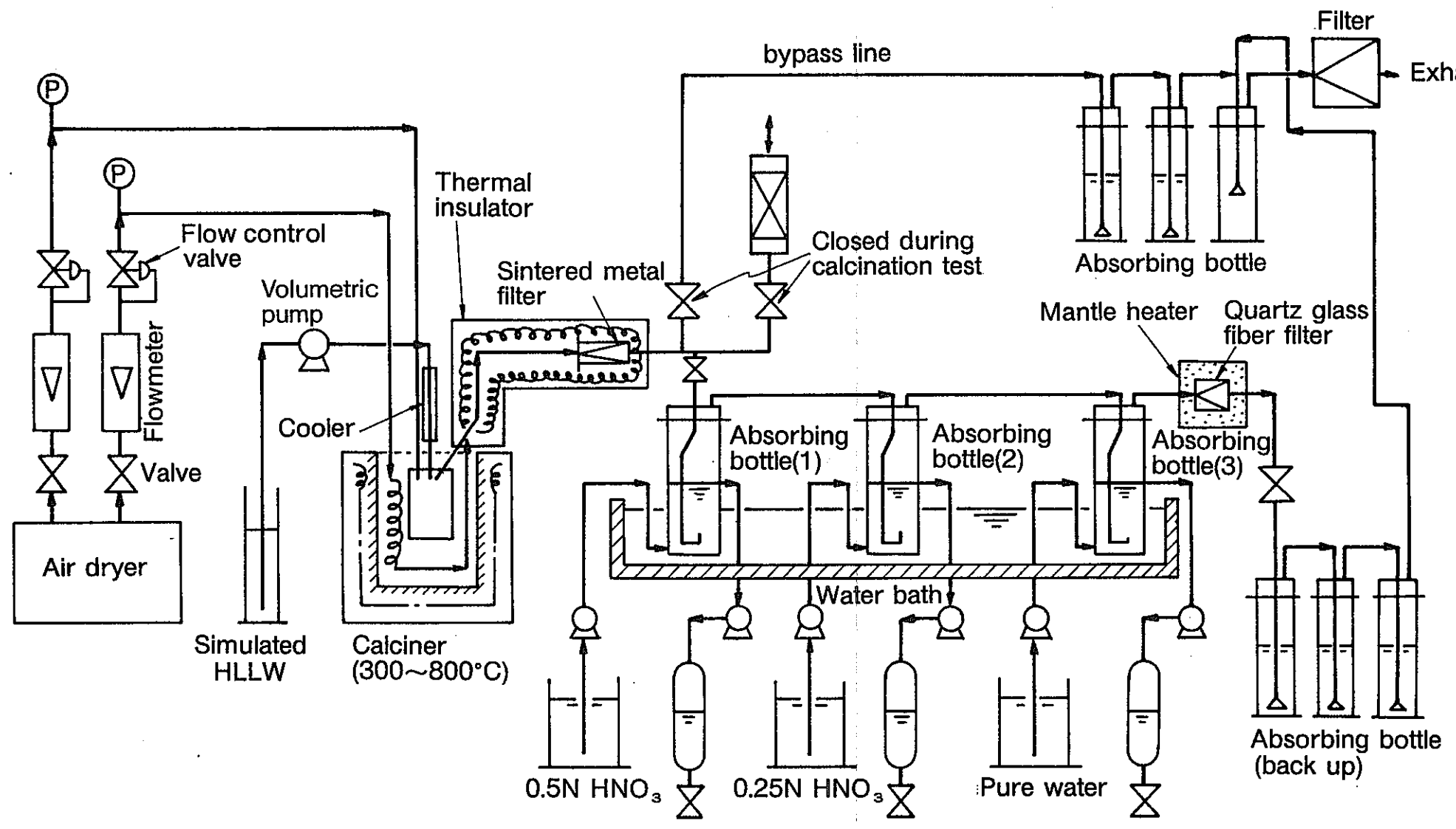


Fig. 1 Continuous calcination test apparatus

pore size is $0.5\mu\text{m}$. The measured collection efficiency of the filter was higher than 99.52%, which was comparable 99.75 to 99.92% attained with HEPA filters in preliminary tests. Absorbing bottles of Pyrex glass were kept at 40°C in the water bath. The gas purging pipe in the bottle is 3 mm in inner diameter and is immersed to 60 mm depth in 150 ml of liquid, which is 0.5 mol l^{-1} nitric acid, 0.25 mol l^{-1} nitric acid, and pure water for No.1,2 and 3 absorbing bottle, respectively. A quartz glass fiber filter has 99% of collection efficiency for $0.3\text{-}\mu\text{m}$ aerosol in a DOP (dioctyl phthalate) test. Other three absorbing bottles (after the fiber filter) were intended to collect gaseous elements passing the filter. The first bottle contained 3 mol l^{-1} sodium hydroxide solution, and the last two bottles contained a mixture of 0.095 mol l^{-1} sodium hydroxide solution and 1.5% hydrogen peroxide.

The activity of the radioactive tracers was measured with a germanium detector for 10 min, and counts lower than 1 cpm were judged to be below the detection limit.

The entrainment ratio was calculated from the ratio of the radioactivity of the tracer captured by the filters and all the components after the filter including the absorbing bottles to that of the tracer fed into the calciner. The volatilizing ratio was calculated from the ratio of the amount of captured tracer just after the filter to the amount of fed tracer. Volatilizing ratio was calibrated by the filter passing ratio which was assumed to be 0.5%.

Table 1 shows the composition of the nonradioactive simulated HLLW used in the test. The nitric acid concentration was 2 mol l^{-1} . The composition of the HLLW was estimated by ORIGEN-82 for pressurized water reactor (PWR) spent fuel of 45000Mwd/tU burn-up, 38MW/tU specific power and 4y cooling. The chemical forms of radioactive tracers used were ruthenium trichloride ($^{103}\text{RuCl}_3$), sodium pertechnetate ($\text{Na}^{99\text{m}}\text{TcO}_4$), sodium selenite ($\text{Na}_2^{75}\text{SeO}_3$) and strontium chloride ($^{85}\text{SrCl}_2$).

By measuring the entrainment and volatilizing ratio, the effects of temperature on the entrainment and volatilization of ruthenium, technetium and selenium from the calciner were evaluated for calcining temperatures from 300 to 800°C .

2.2 Batch Calcination for Ru

The volatilization of ruthenium showed a temperature-dependence different from that of technetium and selenium in the continuous calcination test. The temperature of the waste changes from ambient to the plenum temperature of the

Table 1 **Composition of simulated
High-Level Liquid Waste (HLLW)
(SW-30)**

Element	Oxide concentration ($g\ell^{-1}$)	Probable oxide	Reagent used in HLLW preparation
Na	0.197	Na_2O	$NaNO_3$
P	2.299	P_2O_3	$H_3PO_4(P_2O_5)$
Fe	21.558	Fe_2O_3	$Fe(NO_3)_3 \cdot 9H_2O$
Cr	4.043	Cr_2O_3	$Cr(NO_3)_3 \cdot 9H_2O$
Ni	3.518	NiO	$Ni(NO_3)_2 \cdot 6H_2O$
Rb	1.327	Rb_2O	$RbNO_3$
Cs	9.779	Cs_2O	$CsNO_3$
Sr	3.451	SrO	$Sr(NO_3)_2$
Ba	6.149	BaO	$Ba(NO_3)_2$
Zr	16.76	ZrO_2	$ZrO(NO_3)_2 \cdot 2H_2O$
Mo	14.06	MoO_3	MoO_3
Mn	3.408	MnO_2	$Mn(NO_3)_2 \cdot 6H_2O$
Ru	9.315	RuO_2	$RuNO(NO_3)_2$
Rh	1.345	Rh_2O_3	$Rh(NO_3)_3$
Pd	4.345	PdO	$Pd(NO_3)_2$
Ag	0.262	Ag_2O	$AgNO_3$
Cd	0.440	CdO	$Cd(NO_3)_2 \cdot 4H_2O$
Sn	0.366	SnO_2	$Sn(NO_3)_4$
Sb	0.092	Sb_2O_3	$Sb(NO_3)_3$
Se	0.273	SeO_2	SeO_2
Te	2.107	TeO_2	TeO_2
Y	2.032	Y_2O_3	$Y(NO_3)_3$
La	4.920	La_2O_3	$La(NO_3)_3$
Ce	14.77	CeO_2	$Ce(NO_3)_3$
Pr	4.627	Pr_6O_{11}	$Pr(NO_3)_3$
Nd	16.252	Nd_2O_3	$Nd(NO_3)_3$
Sm	2.912	Sm_2O_3	$Sm(NO_3)_3$
Eu	0.595	Eu_2O_3	$Eu(NO_3)_3$
Gd	29.362	Gd_2O_3	$Gd(NO_3)_3$

calciner in the continuous calcination test. Therefore we performed a batch calcination test of nonradioactive simulated HLLW to verify the temperature-dependence of ruthenium volatilization. The waste composition was the same as in the continuous test.

Figure 2 shows the batch calcination test apparatus. In this test, 2 ml of simulated HLLW (composition shown in Table 1) was heated in the calciner, and volatile ruthenium was generated. The heating process, from the beginning of evaporation to completion of calcination, was controlled stepwise at five temperatures from 135 to 500°C. Each temperature was maintained for 1h, and absorbing bottles were changed every calcining temperature.

The temperature-dependence of volatilization was evaluated in terms of the fraction of volatilized ruthenium for each temperature over the total volatilized amount : f_T . Volatilization was also studied for the overall temperature range tested. This volatilizing ratio was obtained from the mass ratio of the total volatilized amount of ruthenium for the overall temperature range to the initial amount in the sample.

The effect of nitric acid concentration in the simulated HLLW on the volatilization of ruthenium was studied for concentration of 2, 4 and 8 mol l⁻¹, respectively.

The formation of alkaline earth ruthenate may decrease the ruthenium volatilization⁽⁴⁾, and it is possible that this is formed during calcination along with the glass additives (wt%; 57.0 SiO₂, 17.4 B₂O₃, 8.4 Na₂O, 6.1 Al₂O₃, 3.7 Li₂O, 3.7 CaO, 3.7 ZnO). Therefore, calcination tests were performed for the simulated HLLW soaked into 1.5g of glass additives in the form of cylindrical shaped 10-μ m-dia. glass fibers used in the vitrification facility. The effect of reaction with glass additives at calcining temperature was studied.

2.3 Absorption of Semivolatile Elements

The absorption behavior of semivolatile elements was studied for gaseous ruthenium, technetium and selenium by measuring radioactivity in the absorbing bottles and subsequent filters. Absorption of the elements was evaluated in terms of the decontamination factor (DF), calculated by means of the following equation :

$$DF = \frac{\text{radioactivity at inlet of absorbing bottle}}{\text{radioactivity at outlet of absorbing bottle}}$$

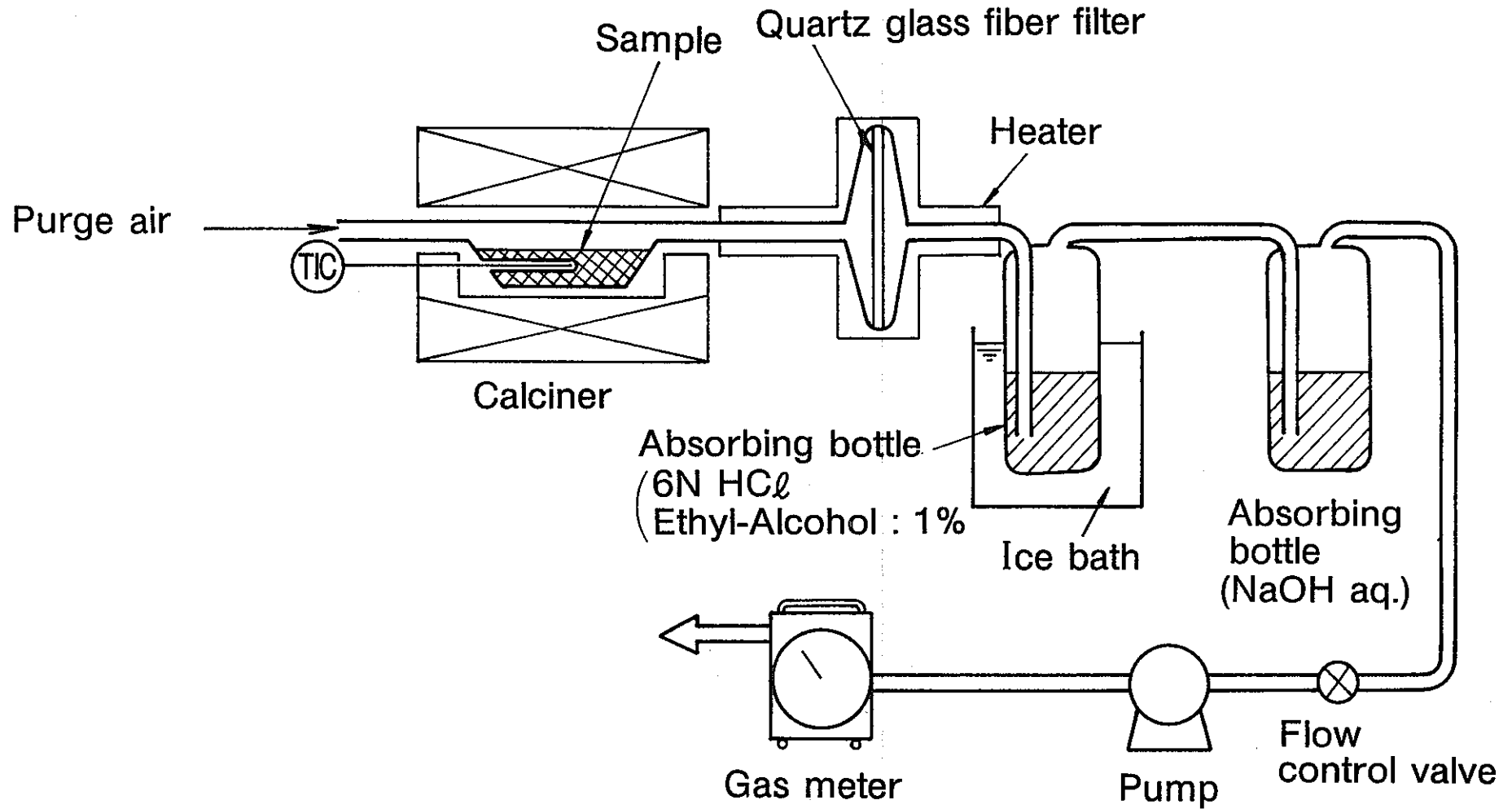


Fig.2 Batch calcination test apparatus

The radioactivity at the inlet is the sum of activity in the absorbing bottle of interest and in the downstream bottles and filters. Radioactivity at the outlet is the sum of activity only in the downstream bottles and filters. If activity in the downstream bottle is below the detection limit, the DF is calculated assuming that the radioactivity is equal to the detection limit.

3. RESULTS

3.1 Entrainment in Continuous Calcination Test

Table 2 shows the entrainment and volatilizing ratios for ruthenium, technetium, and selenium in the continuous calcination test. The temperature-dependence of the entrainment ratio is shown in Fig.3. The entrainment ratios for four elements are maximal at about 400°C and increase with calcining temperature above 500°C. The ratios are 0.27 to 23.2%, 0.71 to 35.1%, 1.4 to 21.2% and 0.22 to 13.3% for technetium, selenium, ruthenium and strontium, respectively. The maximized entrainment ratio around 400°C was confirmed by iterated tests made with one-element tracer. The reason for this is discussed later.

3.2 Volatilization in a Continuous Calcination Test

The effects of calcining temperature on volatilization of the three elements in a continuous calcination test are shown in Fig.4. Volatilization of technetium and selenium increased with calcining temperature. The ratios varied from 0.016% at 400°C to 1.43% at 800°C and from 0.016% at 500°C to 0.58% at 800°C for technetium and selenium, respectively. Figure 5 shows Arrhenius plots for volatilization ratio of technetium and selenium. Ruthenium, however, decreased in volatilization with temperature, from 16.9% at 300 °C down to 0.28% at 800°C, in contrast with technetium and selenium.

3.3 Volatilization of Ruthenium in a Batch Calcination Test

The simulated HLLW was calcined in the batch calcination test, and the volatilization of ruthenium was evaluated in terms of detailed dependence on temperature. Figure 6 shows the f_1 's for ruthenium volatilization with

Table 2 Entrainment and volatilizing ratio from calciner

Calcining temperature [°C]	Ru		Tc		Se		Sr
	Entrainment ratio [%]	Volatilizing ratio [%]	Entrainment ratio [%]	Volatilizing ratio [%]	Entrainment ratio [%]	Volatilizing ratio [%]	Entrainment ratio [%]
300	21.2	16.9	2.4	NA ^(b)	4.6	NA ^(b)	2.1
400	16.5	3.5	13.5	NA ^(b)	15.3	NA ^(b)	13.3
400 ^(a)	12.8	3.8	—	—	—	—	—
400 ^(a)	—	—	11.3	0.016	—	—	—
400 ^(a)	—	—	—	—	10.9	NA ^(b)	—
500	1.6	0.86	0.27	ND ^(b)	0.71	0.016	0.22
600	1.4	0.78	1.8	0.24	1.1	0.32	0.26
700	1.5	0.59	6.5	0.50	3.3	0.35	0.41
800	5.0	0.28	23.2	1.43	35.1	0.58	2.5

* note : (a) Only one radioactive tracer element was added to simulated HLLW ; four radioactive tracers were added in other calcining runs

: (b) NA and ND denote not available data and under detection limit, respectively.

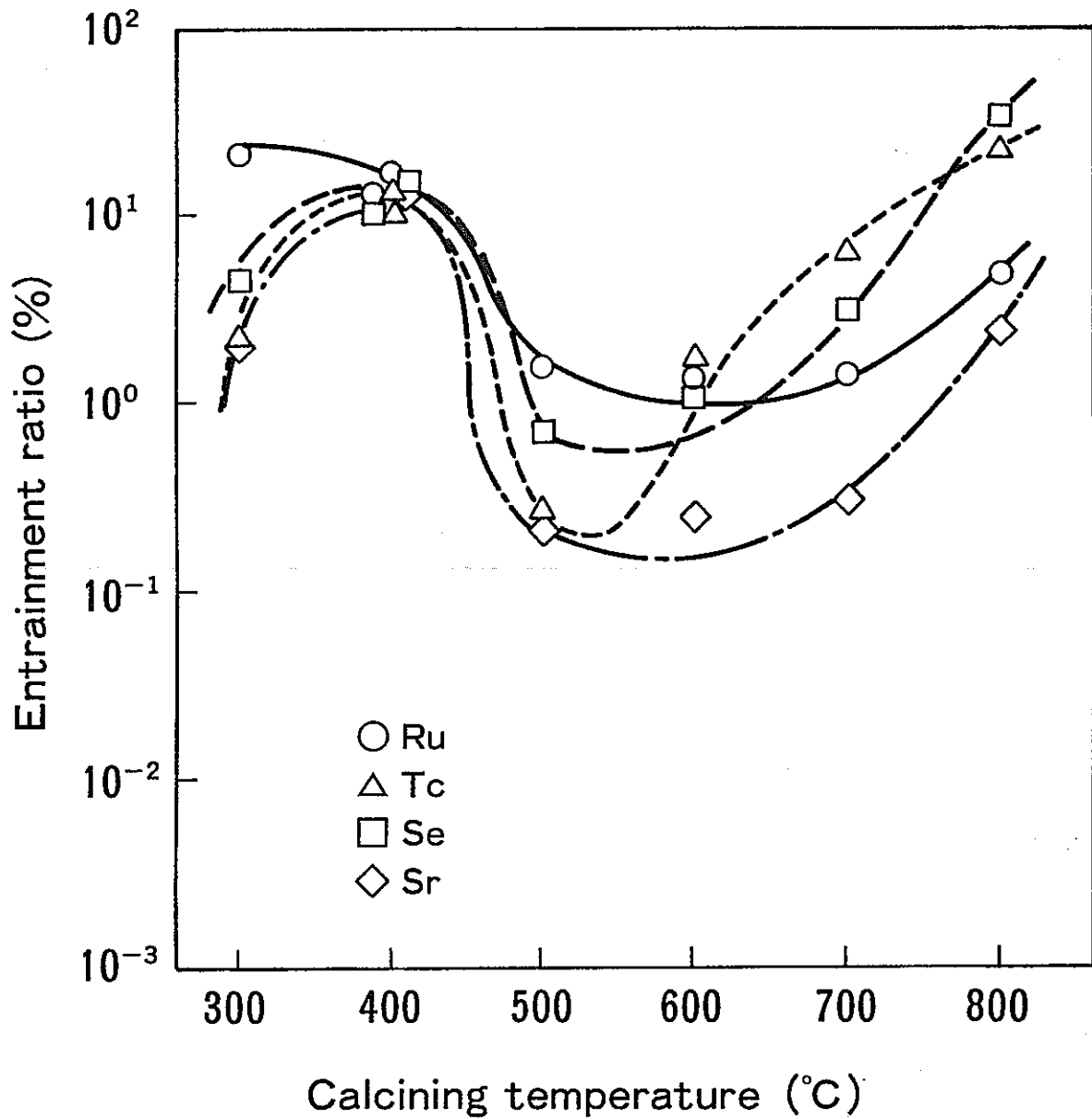


Fig. 3 Entrainment ratio of Ru, Tc, Se, and Sr versus calcining temperature during continuous calcination test

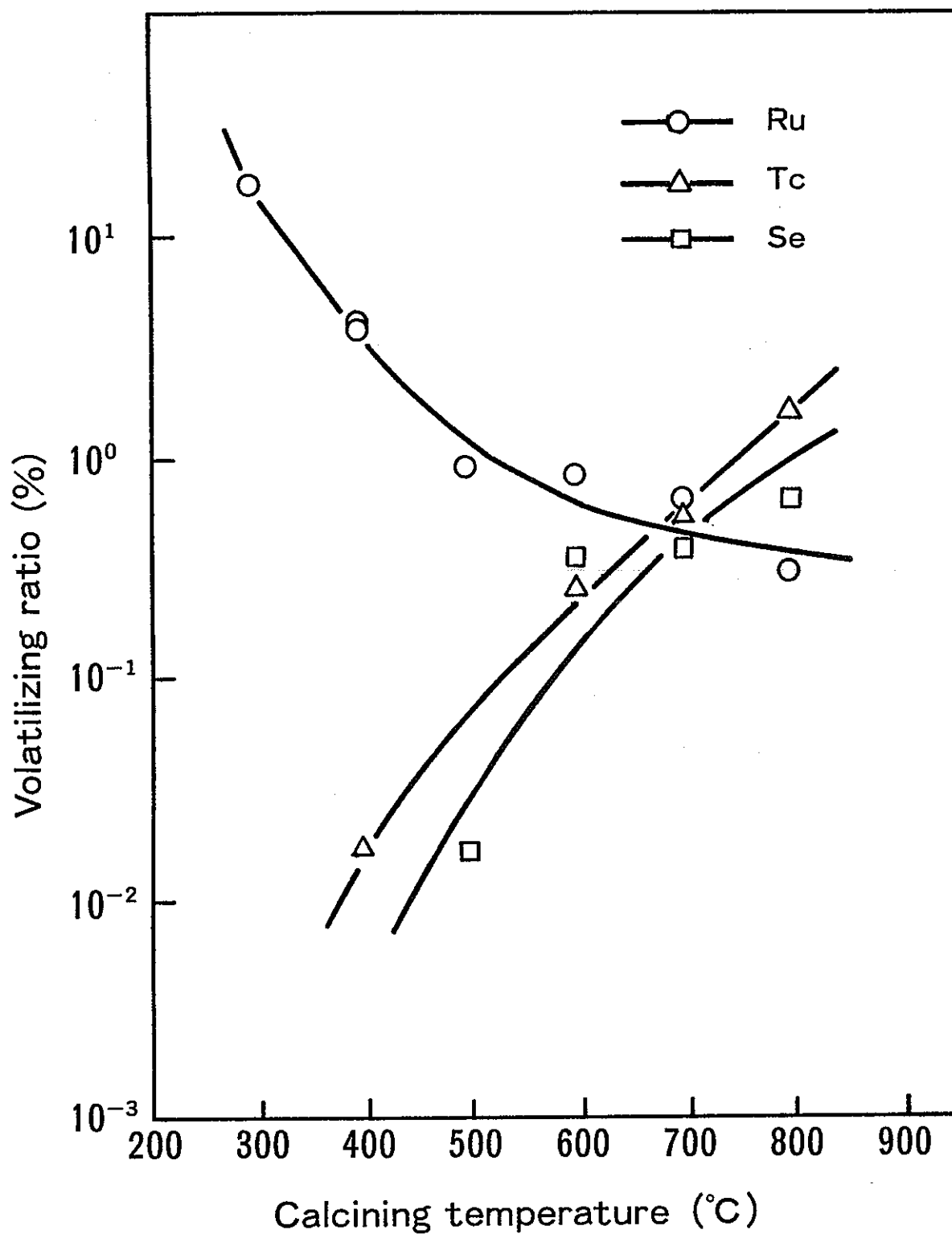


Fig. 4 Volatilizing ratio of Ru, Tc and Se versus calcining temperature

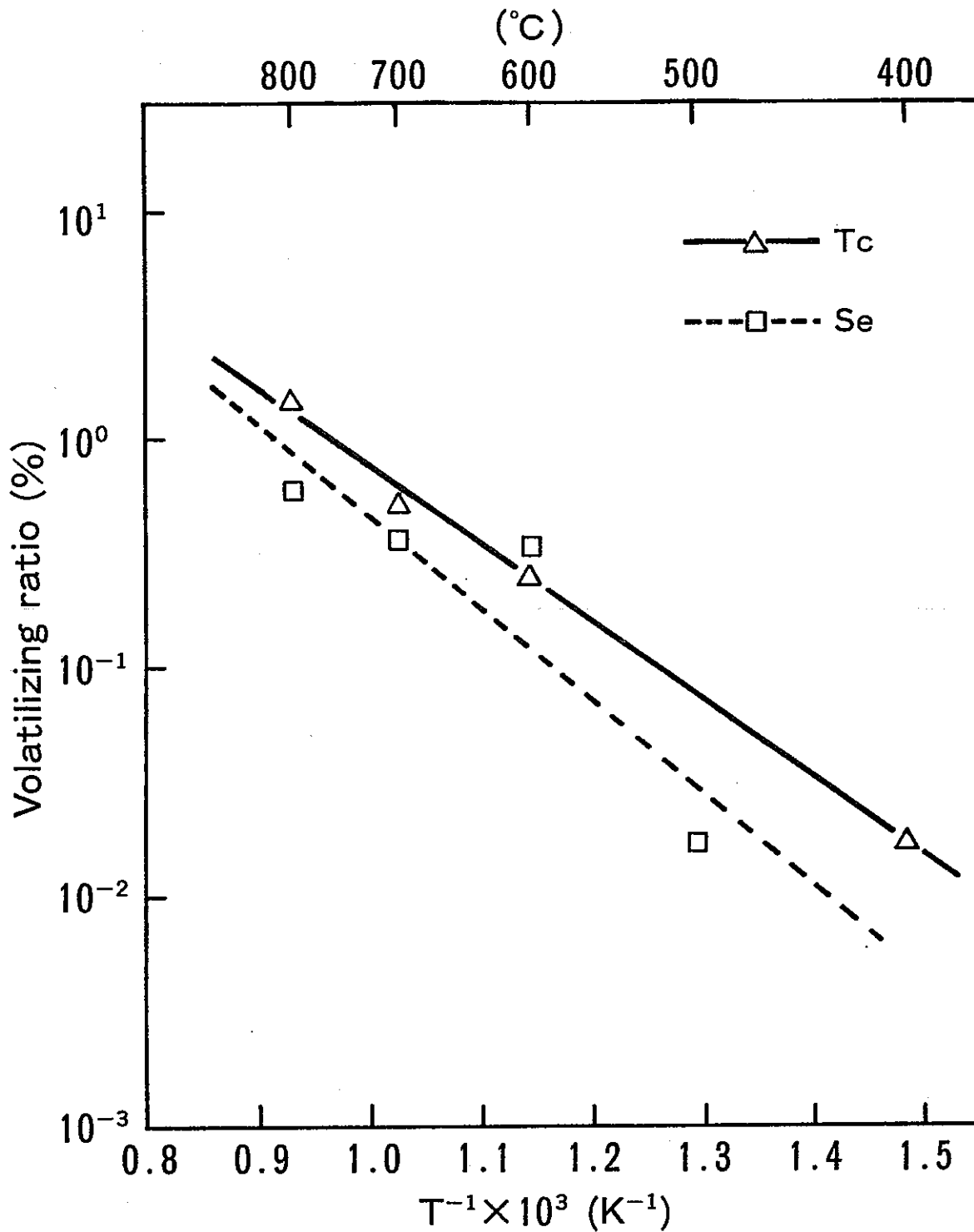


Fig. 5 Volatilizing ratio of Tc and Se versus calcining temperature

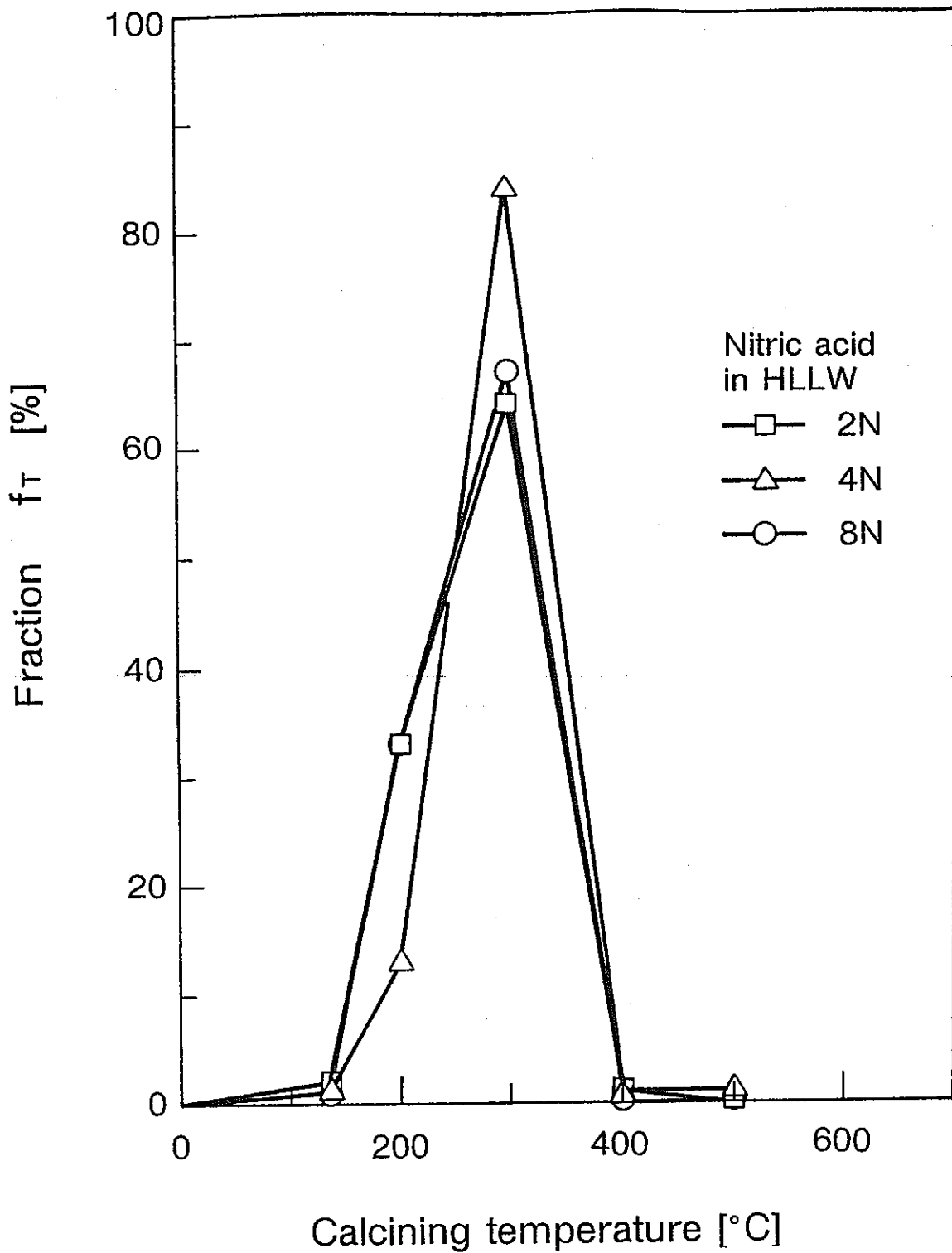


Fig.6 Fraction of volatilized Ru versus temperature for calcination of the simulated HLLW without glass additives

calcining temperature, showing where volatilization was most significant. This behavior was in contrast to the volatilizing ratio in the continuous calcination test, where volatilization occurred from room temperature through the plenum temperature of the calciner.

For a concentration of $4 \text{ mol } \ell^{-1}$ nitric acid in the simulated HLLW, the f_{r} s were 1%, 13%, 84%, 1% and 1% at 135°C , 200°C , 300°C , 400°C and 500°C , respectively. Ruthenium volatilization was insignificant from room temperature to 135°C , maximized at 200 to 300°C , and was again suppressed at temperatures higher than 300°C . This implies that the greatest volatilization of ruthenium occurred during calcination as part of the melting process.

3.4 Effect of Nitric Acid on Ru Volatilization

For ruthenium, the volatilizing ratio for the overall temperature range increased with nitric acid concentration. The ratio was 9.7%, 14.9% and 21.2% for 2, 4 and $8 \text{ mol } \ell^{-1}$ concentration of nitric acid, respectively.

The effect of nitric acid on f_{r} was small.

3.5 Effect of Glass Additives on Ru Volatilization

The overall volatilizing ratios were 10.3, 11.8 and 13.3% for the simulated HLLW with 2, 4 and $8 \text{ mol } \ell^{-1}$ nitric acid concentration, respectively when the HLLW soaked in the glass additives was calcined. The addition of glass additives suppressed the effect of nitric acid concentration on the ruthenium volatilization.

When simulated HLLW with $4 \text{ mol } \ell^{-1}$ nitric acid concentration soaked into the glass additives was calcined, the f_{r} s were 3%, 11%, 87%, 0% and 0%, at 135°C , 200°C , 300°C , 400°C and 500°C , respectively. The f_{r} s are shown in Fig.7. The f_{r} s were similar for calcination of simulated HLLW with 2 and $8 \text{ mol } \ell^{-1}$ nitric acid concentrations when the HLLW was soaked into glass additives.

3.6 Absorption of Semivolatile Element in Continuous Calcination Test

In most runs, the radioactivity was below the detection limits for the second absorbing bottle and the downstream bottles. For ruthenium, calcination runs at 300 and 400°C resulted in activity above the detection

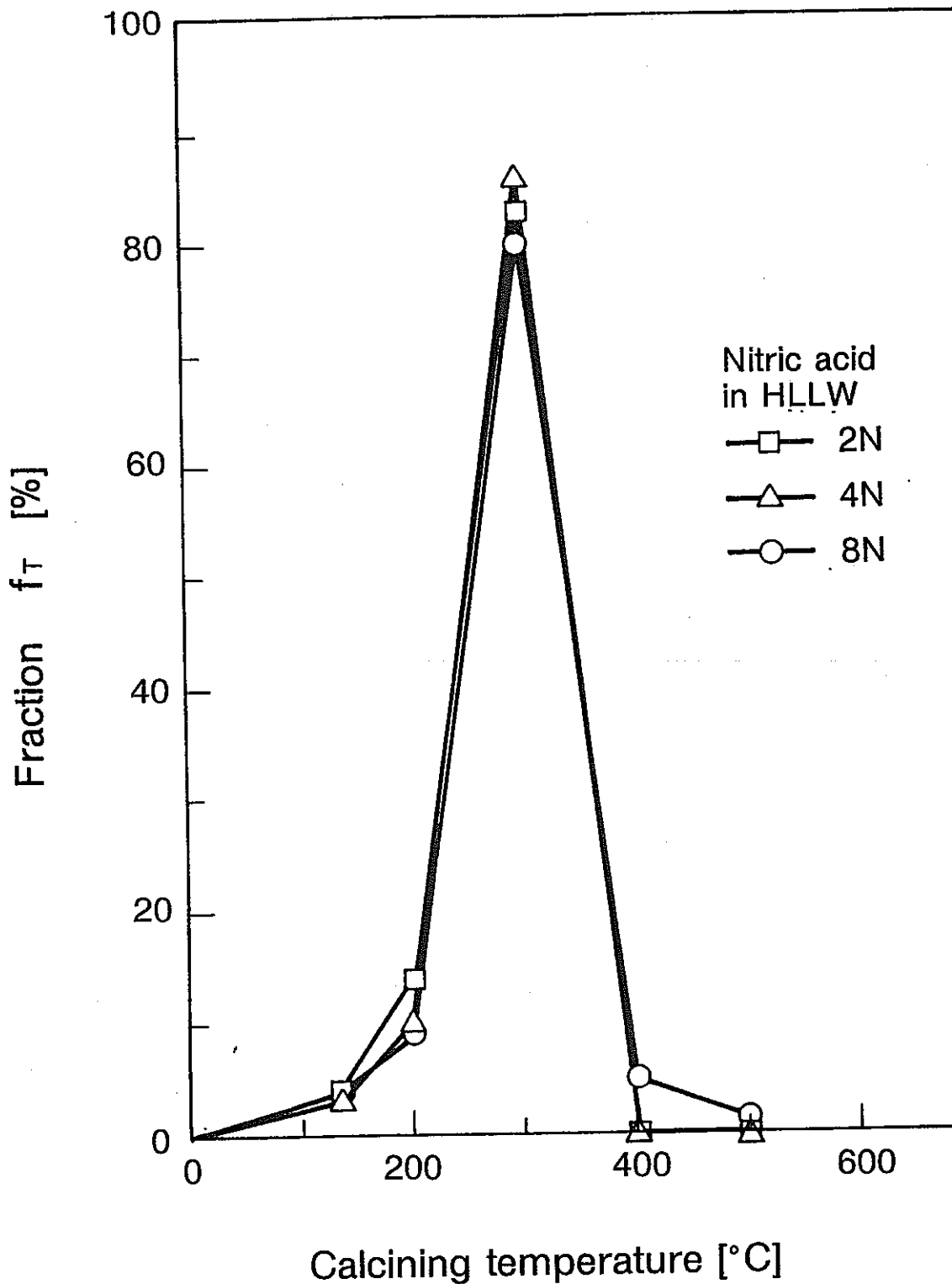


Fig.7 Fraction of volatilized Ru versus temperature for calcination of the simulated HLLW soaked into glass additives

limit in the second absorbing bottle only. The decontamination factors (DFs) of 70 and 210 were obtained for ruthenium during calcination at 300 and 400°C, respectively. The DFs for ruthenium at other calcining temperatures were estimated to be higher than 10^2 , and for technetium and selenium, 10 to 10^3 .

Radioactivity in the quartz glass fiber filter was quite low: 10^{-6} of volatilized technetium in calcination runs at 300, 600 and 700°C, and 10^{-5} of volatilized selenium at 800°C. Values in other runs were below the detection limit.

4. DISCUSSION

Entrainment ratios in the continuous calcination tests were maximal around 400°C and increased with temperature above 500°C. The reason for the increase with temperature is the greater vaporization of the HLLW with higher temperature. The higher entrainment ratio at about 400°C is, however, complicating. It is not merely characteristic of a volatile element; strontium, a nonvolatile element, also shows a similar trend. These values were confirmed in iterated tests, therefore they are probably not experimental errors. The most likely reason is for the excursion that the nitrates of HLLW elements decompose more vigorously with generation of NO_x at around 400°C for longer time since most nitrates of HLLW decompose below 500°C.

The volatilizing ratio of technetium and selenium increased with temperature, because the vapor pressure of both elements rises with increasing temperature.

The volatilization of ruthenium decreased with rising temperature. This temperature-dependence below about 400°C can be explained by the results from the batch calcination test, which indicated that ruthenium volatilization was enhanced at 300°C. It means that the continuous calcination test conducted at higher temperature suppresses the volatilization process that occurs around 300°C in the stepwise calcination process. The decrease in volatilization of ruthenium with temperature above 400°C was due to the transformation of gaseous ruthenium into solid material at high temperature, as reported by other investigators^[5]. Results suggest that little ruthenium volatilized at plenum temperatures above 400°C in the glass melter operation.

Ruthenium volatilization increased with higher nitric acid concentration in the HLLW. This was because higher nitric acid concentration generated more gaseous ruthenium, which was probably a nitrosylruthenium complex^[6].

The results on the effect of glass additives suggest that the reaction of the HLLW with the glass additives suppresses the ruthenium volatilization for the HLLW with higher nitric acid concentration, but not show any significant effect on the temperature-dependence.

5. CONCLUSION

The effect of temperature on the volatilization of ruthenium, technetium and selenium was observed from calcination experiments with simulated HLLW. The volatilization of technetium and selenium increased with elevation in calcining temperature. Ruthenium volatilization decreased with temperatures higher than 300°C. More than 80% of ruthenium that volatilized from room temperature to 500°C occurred between 200 and 300°C. A small amount of ruthenium volatilized at temperature higher than 300°C and below 135°C. Our results will be useful in the operation of the vitrification process and will contribute the safety evaluation in designing the vitrification plant to be built.

ACKNOWLEDGEMENT

The authors acknowledge the contribution of Mr. R.Tatsugae of Ishikawajima-Harima Heavy Industries Co.,Ltd. in the continuous calcination test and the contribution of Messrs.H.Maekawa and H.Kanesawa in the batch calcination test. The authors also thank the Process and Analysis Development Section of PNC Tokai-Works for the analytical work on ruthenium.

REFERENCES

- [1] Tsuboya,T.,Masuda,S.,Saito,S. and Asakura,Y., "Overview of High-Level Radioactive Wastes Management in Japan", The 1989 Joint International Waste Management Conference, Vol.2, High Level Radioactive Waste And Spent Fuel Management, Kyoto, October 22-28 (1989), pp105-110
- [2] Fushiya,K. and Yukawa,Y., "Nuclear Fuel Cycle Projects at Rokkasho Village, Aomori Prefecture", Proceedings of the Seventh Pacific Basin Nuclear Conference, March 4-8, 1990, Sandiego, California.
- [3] Yoshioka,M.,Igarashi,H.,Torata,S.,Takahashi,T. and Horie,M., "Glass Melter and Process Development for the PNC Tokai Vitrification Facility", The 1989 Joint International Waste Management Conference, Vol.2, High Level Radioactive Waste And Spent Fuel Management, Kyoto, 22-28, October (1989), pp13-19
- [4] International Atomic Energy Agency, Control of Semivolatile Radionuclides in Gaseous Effluents at Nuclear Facilities, Technical Reports Series No.220 Vienna (1982), p10
- [5] Christian,J.D., "Process Behavior and Control of Ruthenium and Cerium", ANS-AIChE Topical Meeting on Controlling Air-Borne Effluents from Fuel Cycle Plants, Sun Valley, Idaho, August 5-6 (1976)
- [6] Klein,M.,Weyers,C. and Goossens,W.R.A., "The behavior of Ruthenium, Cesium and Antimony during Simulated HLLW Vitrification", the 18th DOE Nuclear Airborne Waste Management and Air Cleaning Conference, Baltimore, 12-16, August (1984), pp702-731