

IAEA-SR-72/03

VOLATILIZATION AND TRAPPING OF
RUTHENIUM DURING CALCINATION OF
NITRIC ACID SOLUTIONS

M. KLEIN, C. WEYERS, W.R.A. GOOSSENS
TECHNICAL ASSISTANCE : M. DE SMET, J. TRINE

*Work performed in the framework of a
contract between CEN/SCK and DWK*

INTRODUCTION

Solid radioactive aerosols and semi-volatile fission products e.g. Ru, Cs, Sb are generated during high level liquid waste calcination and vitrification processes. The retention of Ruthenium has first been studied because of its strong tendency to form volatile compounds in oxidative media.

Since RuO_4 was the suspected form for high temperature processes, the study has started with the behaviour of RuO_4 and its retention on adsorbants and catalysts for various gas compositions.

The behaviour of volatilized Ru species obtained by calcination of nitrosyl Ru compounds has then be compared to the RuO_4 case.

1. BEHAVIOUR AND RETENTION OF RuO₄

The influence of various carrier gases on the behaviour of volatile RuO₄ has been studied for different gas compositions :

- RuO₄ mixed with dry air (I)
- RuO₄ mixed with moist air with a maximum dew point temperature of 85°C (II)
- RuO₄ mixed with NO_x and water vapour produced by high temperature calcination of 3.5 M nitric acid.
 - feed of RuO₄ at the outlet of the calciner (III)
 - feed of RuO₄ at the inlet of the calciner (IV)

1.1. Description of the experimental unit

The essential components of the system, described in figure 1, are :

- an RuO₄ generator;
- an Inconel calciner fed by a peristaltic pump;
- a sampling system for the determination of the Ru coming out of the calciner (Washing bottle + absolute filter);
- a Ru retention bed loaded with 15 to 30 g of material;
- a condensor;
- a caustic wash bottle and a final absolute filter.

Traced quantities of the isotopes Ru103 or Ru106 were added to the 50 mg/l Ru solutions.

The activities level were chosen in order to be able to measure DF's of 10⁴ for a sampling time of one hour.

With the Ru106, measured by Cerenkov Effect, the generation chosen was in the range 1 to 3 10³ Bq/h. With the Ru103, measured by γ counting in an Na I (Tl) detector, the generation chosen was in the range 4 10³ to 10⁴ Bq/h.

1.2. Behaviour of RuO₄ in the system

The RuO₄, produced by oxydation of a chloride with K10₄ in sulphuric acid, deposit partly on the outlet tube when its temperature is lower

than the generator temperature.

This yellow deposit, then slowly reduces to a black oxide deposit (unstability of the RuO_4). To avoid these losses the generator is operated at room temperature so that no condensation can occur. This deposit can be washed out easily and dissolved in a NaOH-NaOCl mixture.

When the gaseous mixture of RuO_4 and dry or moist air is heated up to 200 or 300°C for the retention experiments, a great fraction of RuO_4 (from 60 to 75 %) is reduced in RuO_2 on the walls of the tubing. This deposit is strongly chemically fixed on the glass tubing and is very difficult to remove.

When RuO_4 is fed at the outlet of the calciner (III) and mixed with NO_x vapours, there occur a reaction in the gaseous phase between RuO_4 and NO_x and a less volatile compound (probably a Ru nitrosyl complex) is formed; from 70 to 80 % of the Ru deposits then on the walls of the glass tubing and reduces to lower valencies.

When the RuO_4 is fed at the inlet of the calciner (IV), the losses on the glass tubing are higher and reach 85 to 90 % of the Ru fed. Nearly no deposit of ruthenium is observed inside the calciner, the deposit occurs at the outlet of the calciner during cooling of the gases; the maximum in the deposit is observed in the temperature range 550-450°C. This deposit is strongly fixed to the glass tubing.

Table I : Losses of Ru in the glass tubing (%) in function of temperature and gas composition.

Temperature (°C)	RuO_4 dry and wet air (I and II)	$\text{RuO}_4 + \text{NO}_x$ outlet (III)	$\text{RuO}_4 + \text{NO}_x$ inlet (IV)
100	0	75	85
200	60	80	85
300	75	75	90

1.3. Adsorption of RuO₄ on Silica-gel

Case I : RuO₄ + dry air.

A DF greater than 1.000 is obtained for a bed temperature of 20°C (5). The adsorption capacity increases linearly with the gaseous RuO₄ concentration and decreases with the adsorption temperature following the Arrhenius model (Heat of adsorption of 29 kJ/mole).

Table II : Adsorption capacity calculated for a 10 % break through (mg.g⁻¹)

	T_F (°C)	20	100
C mg.m ⁻³			
100		1	0.08
450		5	0.4

The adsorbed RuO₄ (yellow colour of the silica-gel pellets) can be swept out by air sparging quantitatively if the desorption is carried out immediately after saturation; if the desorption is carried out 1 day after saturation, about 25 to 40 % of the adsorbed RuO₄ has been reduced into solid RuO₂ which is then irreversibly fixed on the bed (gray-black deposit).

Case II : RuO₄ + moist carrier air

When the carrier gas contains water vapour, the adsorbant bed must work at a temperature higher than the dew point of the gas to avoid condensation problems.

The adsorption capacity is very small (Table II) and decreases rapidly with the bed temperature so that the adsorbant is very rapidly saturated and the DF falls to 1. The adsorption capacity decreases with an increase of the water vapour concentration for a given bed temperature.

TABLE II : Adsorption capacity of silica-gel for RuO₄ in function of bed temperature (T_F) and dew point (T_R)

T _F	T _R	(H ₂ O)	C _{RuO₄}	Q _{0.1}	A
°C	°C	z. v/v	mg/m ³ wet gas basis	mg/g	m ³ /g
20	15	1.6	100	1	10 ⁻²
48	47	10.4	108	1.9 10 ⁻¹	1.7 10 ⁻³
50	15	1.6	260	1.16	4.5 10 ⁻³
50	38	6.5	120	9 10 ⁻²	7.5 10 ⁻⁴
62	43	8.5	117	< 6 10 ⁻²	< 5 10 ⁻⁴
65	65	24.6	86	1.4 10 ⁻³	1.6 10 ⁻⁵
67	35	5.5	94	1.4 10 ⁻²	1.5 10 ⁻⁴
70	15	1.6	190	3.2 10 ⁻²	1.7 10 ⁻³
70	47	10.5	110	2.2 10 ⁻²	2 10 ⁻⁴
86	47	10.5	82	1.7 10 ⁻³	2 10 ⁻⁵
89	69	29.5	83	< 10 ⁻³	< 1.2 10 ⁻⁵
95	80	47	68	1.4 10 ⁻³	2 10 ⁻⁵
100	15	1.6	168	1.3 10 ⁻¹	7.7 10 ⁻⁴
100	77	41.0	46	< 10 ⁻³	< 2 10 ⁻⁵
120	80	47	64	< 10 ⁻³	< 1.6 10 ⁻⁵
150	80	47	63	< 10 ⁻³	< 1.6 10 ⁻⁵

For a wet gas, there is a competition for the adsorption sites between the low concentration of RuO_4 (20 to 50 Vpm) and the high concentration of water vapour (from 1.6 to 47 %) so that the water presence has a negative effect on the adsorption capacity for RuO_4 . The adsorbed water vapour doesn't significantly increase the reduction rate of RuO_4 into ruthenium dioxide so that the desorption sweeps out all the adsorbed ruthenium when immediately performed after saturation.

Case III : RuO_4 fed at outlet of calciner and mixed with NO_x

At 100°C , DF's higher than 100 are obtained and the bed efficiency increases with time; no saturation of the bed could be observed so that bed capacities were not determined.

The adsorbed species are more strongly fixed on the bed so that only a small quantity could be swept out of the bed.

At 200°C , the DF decreases of 1 to 2 orders of magnitudes; the retention on the bed being determined by the decomposition of the volatile species and not by the physical adsorption which has strongly decreased.

Case IV : RuO_4 fed at inlet of calciner

At 100°C , DF's higher than 10 but lower than in case III were obtained; no saturation of the bed could be observed and the DF increased with time. At 200°C , no high DF were obtained and the DF decreased with time revealing a saturation of the bed by the volatile species and the limitation of the efficiency by the decomposition rate of the adsorbed species.

1.4. Catalytic decomposition of volatile Ru on a ferric-oxide/chromium oxide catalyst.

For the retention of RuO_4 on a ferric-oxide/chromium oxide catalyst operating at 300°C , in all the 4 cases, the capture mechanism is a catalytic decomposition of the volatile species which is transformed into a more stable lower valency (4+).

Table III : Performance of Silica-gel for the trapping of gaseous Ru in presence of NO_x

T _C °C	T _F °C	η _F %	C _{RuO₄} mg/m ³	Q _{0.1} mg/g	losses line %	η _D %
Case III RuO₄ fed at outlet of calciner						
600	100	99.88 → 99.9	5	> 0.32	75 - 80	1.9
800	100	99.6 → 99.9	5	> 0.3	75 - 80	0.4
600	200	55.1 → 80.0	5	< 0.1	75 - 80	-
800	200	92.4 → 98.1	5	> 0.3	75 - 80	0.2
Case IV RuO₄ fed at inlet of calciner						
600	100	93.1 → 99.6	5	> 0.3	85	3.6
800	100	95.4 → 99.5	5	> 0.35	85	5.2
600	200	83.5 → 46.2	7	< 0.1	87	26.1
800	200	98.8 → 97.3	12	> 0.7	85	21.6

The ruthenium oxides deposit on the catalyst pellets enhances the reaction rate so that the DF increases with time.

The fixation is irreversible since only very small quantities of ruthenium could be swept out of the bed.

Table IV : Performance of a catalyst (Ferric-oxide/chromium oxide) operating at 300°C for the trapping of the RuO₄ in different gas compositions.

		Cases I/II	Case III		Case IV	
		RuO ₄	NO _x + RuO ₄ outlet		RuO ₄ inlet + NO _x	
T _C			600	800	600	800
η _F	%	99.6-99.7	24 → 46	88 → 99	12.6 → 85.1	86.6 → 96.6
C	mg/m ³	5	5	5	4	2
Qo.l	mg/g	> 0.3	-	> 0.3	> 0.2	>>0.1
losses	%	75	75	75	85	90
line						
η _D	%	0.1	0.5	0.6	0.4	0.5

The axial activity profile in the bed is in each case an exponential decrease so that no adsorption capacities could be determined.

The DF obtained with RuO_4 in dry or wet air is one order of magnitude greater than for the cases III and IV where RuO_4 is in presence of NO_x . For the cases III and IV there is also an order of magnitude of difference for the two different calcination temperatures. From these observations, it can be concluded that in presence of nitrous oxides gases, the volatile species is more stable and the decomposition rate into ruthenium oxide is slower; the reaction rate seem also to depend on the calcination temperature.

1.4. Conclusion of the intercomparison study

In presence of nitrous oxides, the concept of a stable RuO_4 compound is not any more valid and the volatile species which must be trapped is probably a nitrosyl ruthenium compound of lower valency (6 or 7), more stable than RuO_4 , more easily condensable (lower vapour pressure) and more easily adsorbable on silica-gel. As a consequence, the RuO_4 generator was abandoned and replaced by a high temperature calciner as volatile Ru source.

2. CALCINATION OF NITRIC ACID SOLUTIONS CONTAINING Ru NITROSYLNITRATE.

Two laboratory units called CALCILAB 1 and 2 and described in figure 2 and 3 have been used for the study of the behaviour of traced ruthenium nitrosyl nitrate $[\text{RuNO}(\text{NO}_3)_x(\text{OH})_3 - x]$ 50 mg/l in 3.5 M nitric acid during high temperature calcination in an Inconel calciner.

In the CALCILAB 1, the specific Ru filter is placed just at the exit of the calciner whereas in the CALCILAB 2, the specific Ru filter is placed after a condenser.

2.1. Behaviour of Ru during high temperature calcination.

The volatility of Ru in an Inconel calciner depends on the calcination temperature (Table V). At 600°C , the volatility varies between 50 and 80 % and decreases rapidly with calcination temperature to reach 30 % at 1100°C .

The deposit of ruthenium are mainly found at the exit of the calciner were the gases are cooled down, a maximum is observed in the 500°C region. A second increase is observed when the gases are again heated up till 300°C. This deposit is strongly fixed to the glass tubing and can only be removed by strong chemical attack of the glass.

The volatile Ru remaining in the off-gases is partly condensed in a glass condensor placed directly at the exit of the calciner. The condensed Ru is soluble in the acidic condensate giving a pink-purple colour but slowly reduces to an insoluble precipitate of ruthenium oxides.

The rest of Ru in the carrier gas is filtered by an absolute glass fiber sampling filter placed at the outlet of the condensor.

No activity higher than the back ground could be detected in a wash bottle following the sampling filter so that it can be deduced that only aerosols of ruthenium are still present at the outlet of the condensor which condenses all the volatile species.

The distribution of Ru between volatile and aerosol forms depends on the calcination temperature (table V)

The condensor DF decreases exponentially with the calcination temperature and the aerosol fraction increases exponentially (Fig. 4).

Table V : Distribution of Ru in the off-gas line of an Inconel Calciner.

T _C (°C)	600	800	1 000	1 100
VOLATILITY %	50 - 80	30 - 50	30	30
CALCINER DF	2 - 1.3	3.3 - 2	3.4	3.4
CONDENSOR DF	360	80	20	13
AEROSOL FRACTION %	0.2	1.0	4.6	7.7

2.2. Adsorption of volatile Ruthenium.

An adsorbant, such as silica-gel, installed at the exit of a condenser where only aerosols are present, can not work satisfactorily and only a minute fraction of the aerosol form of ruthenium is trapped by a classical filtration mechanism (efficiencies of 10 to 20 %).

In order to give satisfactorily results, the adsorbant bed must be placed directly at the exit of the calciner where volatile species are present.

In table VI, are reported the results of the tests performed with two types of silica-gel, two types of molecular sieves and one type of $\text{SiO}_2/\text{Al}_2\text{O}_3$ pellets with ferric-oxide/chromium oxide deposit of own fabrication.

The DF's obtained with silica-gel are qualitatively similar to the DF's obtained when feeding RuO_4 at the inlet of the calciner which indicate that the trapping mechanism could be similar.

For all the adsorbants tested similar DF's of 10 to 50 are obtained so that the choice could be made on basis of attrition resistance and resistance to condensed water.

From that point of view, ZEOLON 900 H molecular sieves or UC13X are better than the silica-gels which resist very poorly to water condensation. The choice can not be made on the adsorption capacity since no saturation of the beds were observed (exponential activity decrease with the length of the bed).

2.3. Catalysts for the retentions of volatile Ruthenium

Three types of catalysts were tried for the irreversible capture of the volatile ruthenium species :

Type I : Metal oxides on a Si/Al support

For these catalysts, the basic matrix is a mixture of clay, kaolin and cristobalite. To this matrix are added various quantities of powdered metal oxides and SiO_2 powder. After extrusion and drying, the pellets are fixed at 800 - 900°C.

Type II : Molecular sieves ZEOLON 900 H impregnated with RuO_2 , Fe_2O_3 or Cr_2O_3 .

Table VI : Adsorption of volatile Ru on various adsorbants.

	T _C °C	T _F °C	\bar{n}_F %	C _{RuO₄} mg/m ³	Q _{0.1} mg/g	\bar{n}_D %
SILICA GEL	600	100	96.5 - 97.8	14	> 0.3	19
GRACE F 125			91.7 - 99.4	14	> 0.3	-
			94.3 - 96.7	18	> 1	5
			96.6 - 97.5	18	> 1.2	96.0
	600	200	28.1 - 22.1	18	-	5.7
	800	200	80 - 95.2	9	-	-
	800	100	79.4 - 99	13	> 0.9	7.0
		100	97.6 - 99	36	> 1	8.0
	1000	100	94.1 - 96.7	10	> 0.3	5.0
KIESELGEL	1000	100	87.1 - 95.2	16	-	6.3
MERCK	1000	100	86.1 - 95.8	8	> 1	1.8
MOLECULAR SIEVES						
ZEOLON 900 H	800	100	96.3 - 99.0	8	> 0.2	5.0
	800	100	96.0 - 98.0	8	> 0.2	3.0
	1000	100	93.4 - 96.8	8	> 1	0.9
UC 13 X	800	100	98.3 - 97.0	10	> 0.3	2.7
FERRICOXIDE- CHROMIUM OXIDE ON SiO ₂ /Al ₂ O ₃	600	100	98.8 - 97.4	8	> 4.5	1.9
PELLETS						

Type III : Commercial catalysts

The results of the screening study are given in tabel VII

For all the catalysts tested, the same qualitative observations could be made :

- the efficiency of the bed increases with ruthenium oxides deposit;
- no saturation of the bed is observed, the activity decreases exponentially with the length of the bed;
- the efficiency is better at calcination temperature of 800°C than at 600°C;
- At 800°C, a loose deposit of ruthenium oxides is observed so that the use of a glass wool filter increases the efficiency.

From the screening study, it appears that type I catalysts with a mixture of various oxides is the best choise for the retention of Ru.

The two best catalysts are :

Cr₂O₃ 7 %, SiO₂ 20 %, SnO₂ 1 %

Fe₂O₃ 13 %, Cr₂O₃ 3 %, SiO₂ 17 %

The study of the influence of the bed temperature on the trapping efficiency has shown that 300°C is the optimum temperature.

At temperatures lower than 300°C, the volatile species are adsorbed physically and only partly reduced to lower valencies.

At temperatures above 300°C, the volatile species are only partly reduced on the catalyst.

The DF's obtained with the reference catalyst (Fe/Cr catalyst) are qualitatively comparable with the results obtained in the intercomparaison study with the case IV i.e. RuO₄ fed at inlet of calciner.

2.4. Conclusion of the calcination experiments

The volatile species obtained by high temperature calcination behaves qualitatively of the same manner as the species obtained by reaction between RuO₄ and NO_x when the RuO₄ is fed at the inlet of the calciner.

The volatile species is probably a Ru NC complex of lower valency than RuO₄, more stable, more easily condensable and adsorbable.

Table VII : Retention of volatile Ru on catalysts

	T _C	T _F	η _F	η _D	C
	°C	°C	%	%	mg/m ³
Fe ₂ O ₃ 33 % SiO ₂ 10 %	600	300	20.7 - 26.2	-	5
Fe ₂ O ₃ 15 % SiO ₂ 17 %	800	300	48 - 77	1	6
	800	300	87 - 93	1	5
Cr ₂ O ₃ 6 % SiO ₂ 20 %	800	300	80 - 94	3	6
SnO ₂ 2 % SiO ₂ 25 %	800	300	80 - 90	0.5	8
	1000	300	93 - 97	-	6
Cr ₂ O ₃ 7 % SiO ₂ 20 % SnO ₂ 1 %	800	300	87 - 99	-	5
ZEOLON 900 H	800	300	80 - 88	-	5
+ RuO ₂ 2 %	800	300	76 - 85	-	5
+ Fe ₂ O ₃ 2 %	800	300	70 - 81	-	5
+ Cr ₂ O ₃ 2 %	800	300	84 - 92	-	5
BASFK610 Fe ₂ O ₃ /Cr ₂ O ₃	800	300	89 - 90	-	6
Fe ₂ O ₃ 30 % Cr ₂ O ₃ 7 % SiO ₂ 40 %	800	300	99.0 - 99.8	-	8
+ glasswool filter					
Fe ₂ O ₃ 13 % Cr ₂ O ₃ 3 % SiO ₂ 17 %	800	300	93.0 - 99.9	0.03	5
+ glasswool filter					
Fe ₂ O ₃ 13 % Cr ₂ O ₃ 3 % SiO ₂ 17 %	600	300	80 - 96	1.4	5
	1000	300	90 - 95	2	5
	800	200	90	22.2	5
		300	92.5 - 97.1	1.0	5
		400	20 - 90.3	1.3	3
		500	10 - 50	-	2

3. BEHAVIOUR OF RUTHENIUM DURING VITRIFICATION IN A LIQUID FED MELTER

In the framework of the PAMELA programme on HLLW vitrification, experiments have been made on a laboratory scale to study, in simulating conditions, the behaviour of Ru during liquid feed on the glass pool.

The % of Ru present in the off-gases of the melter is lower (from 3 to 15 %) than during calcination (30 to 50 %) of Ru containing wastes. The chemical nature of the ruthenium seems also to be different since almost all the Ru in the off-gases of the melter can be trap on an aerosol filter and only a minor fraction is in volatile form.

The particle size distribution of the aerosol at the exit of the oven has been determined by cascade impactors. The distribution is quite large, the mass median aerodynamic diameter varies from 2 to 10 μm , and seems to be composed of two fractions; a fraction with "fly ash" dust of large diameters and a fraction with condensation aerosols of smaller diameters.

Detailed results on the experiments performed will be given at the Air Cleaning Conference.

SYMBOLS

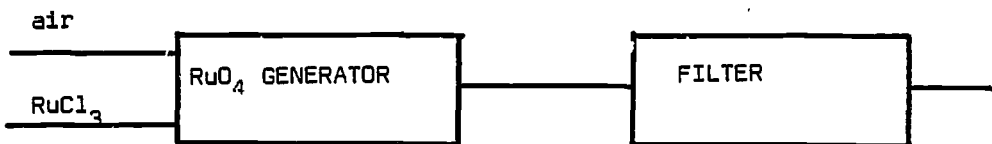
T_F	: Ru Filter temperature	(°C)
C	: Ru concentration in the gas phase	(mg/m ³)
T_R	: Dew point of the gas	(°C)
(H ₂ O)	: Water vapour concentration	(% v/v)
Q _{0.1}	: Capacity at 10 % break-through	(mg/g)
A	: Adsorption constant for linear adsorption model	(m ³ /g)
η_F	: Ru Filter efficiency	(%)
η_D	: Desorption by air sparging	(%)

REFERENCES

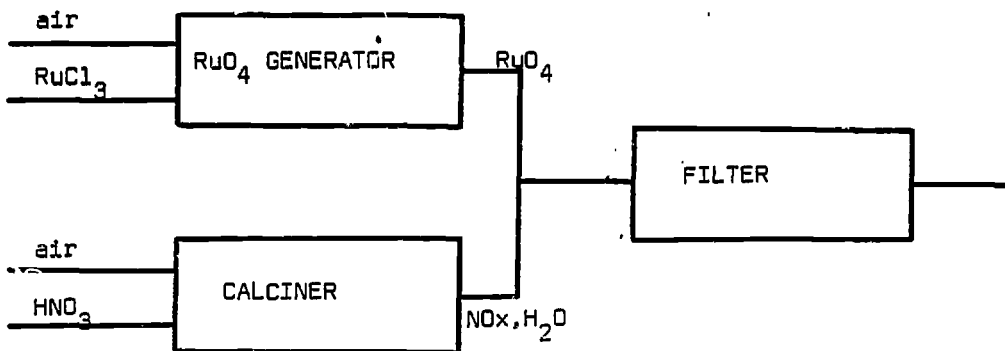
- [1] EICHHOLZ, G., "Hazards and control of ruthenium in the nuclear fuel cycle", Prog. Nucl. Energy 2 (1978) 29.
- [2] HANSON, M.S., Semi Volatile Fission Product Behaviour in High Level Waste Solidification, Battelle-Northwest, Richland, WA, Pacific Northwest Lab., Rep. BNWL-SA-6461 (1978).
- [3] NEWBY, B., et al., Volatile Ruthenium Removal from Calciner Off-Gas Using Solid Sorbents, Allied Chemical Corps, Idaho Falls, ID, Rep. ICP-1078 (July 1975).
- [4] CHRISTIAN, J.D., "Process behaviour and control of ruthenium and cesium", Controlling Airborne Effluents from Fuel Cycle Plants (Proc. ANS-AICHe Topical Meeting Sun Valley, 1976), American Nuclear Society, Hinsdale (1976).
- [5] KLEIN, M., "Filtration and capture of semi-volatile nuclides". IAEA-SM- 245/51 (1980).

Fig.1 DESCRIPTION OF THE EXPERIMENTAL SYSTEM

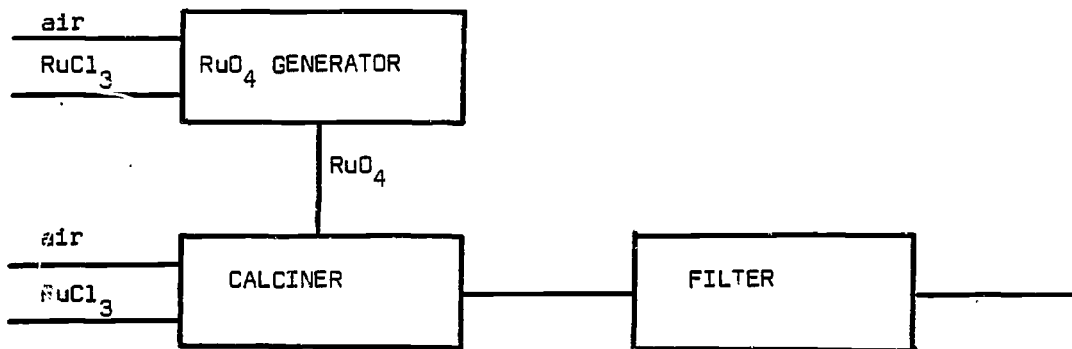
CASES I AND II RuO₄ with dry or moist air



CASE III RuO₄ FED AT OUTLET OF CALCINER AND MIXED WITH NO_x



CASE IV RuO₄ FED AT INLET OF CALCINER



CALCINATION OF NITRIC ACID SOLUTIONS CONTAINING RuNO₃_{3-x}(OH)_x

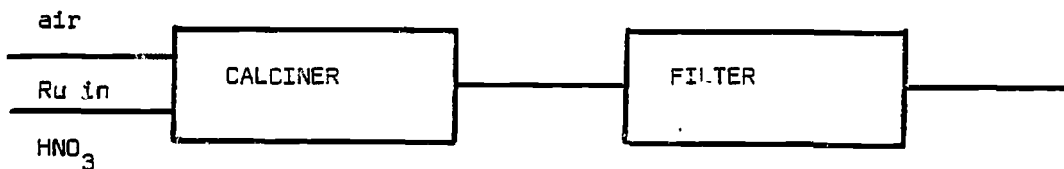


Fig 2.

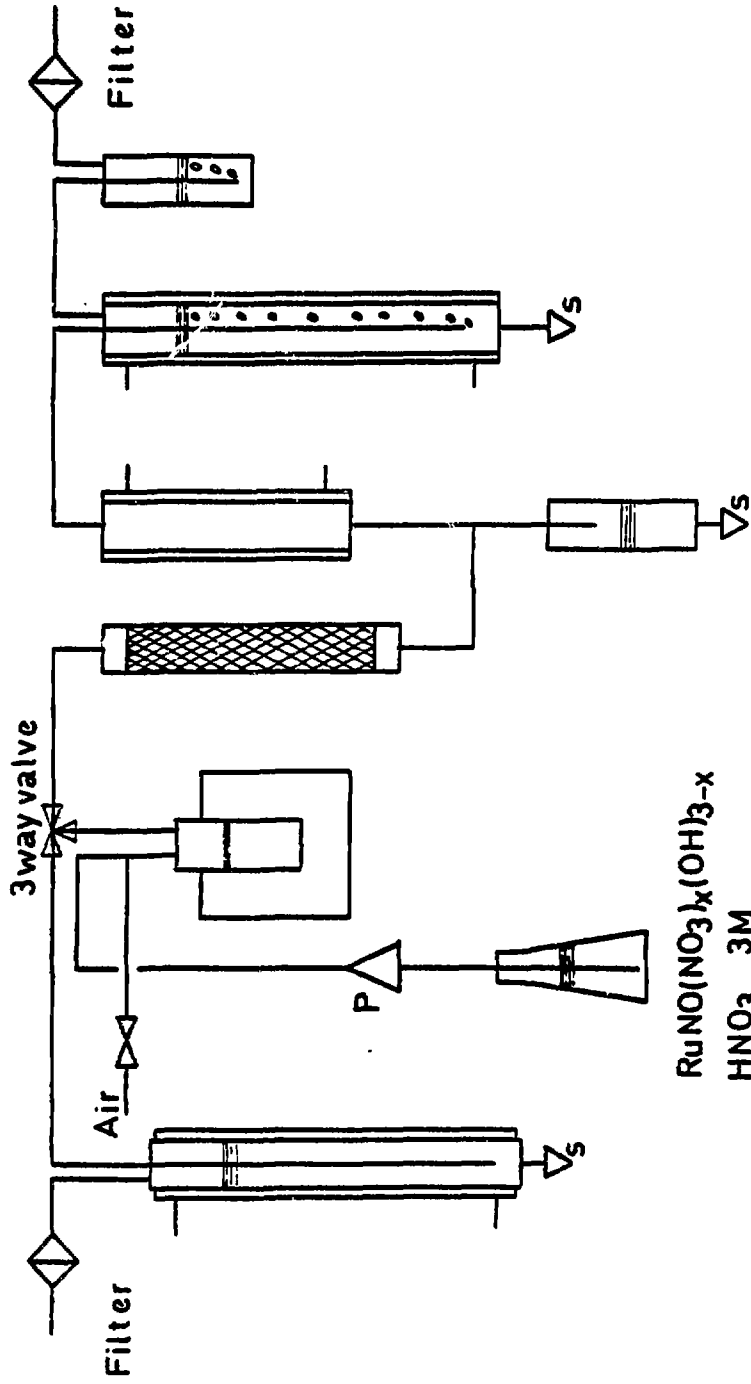
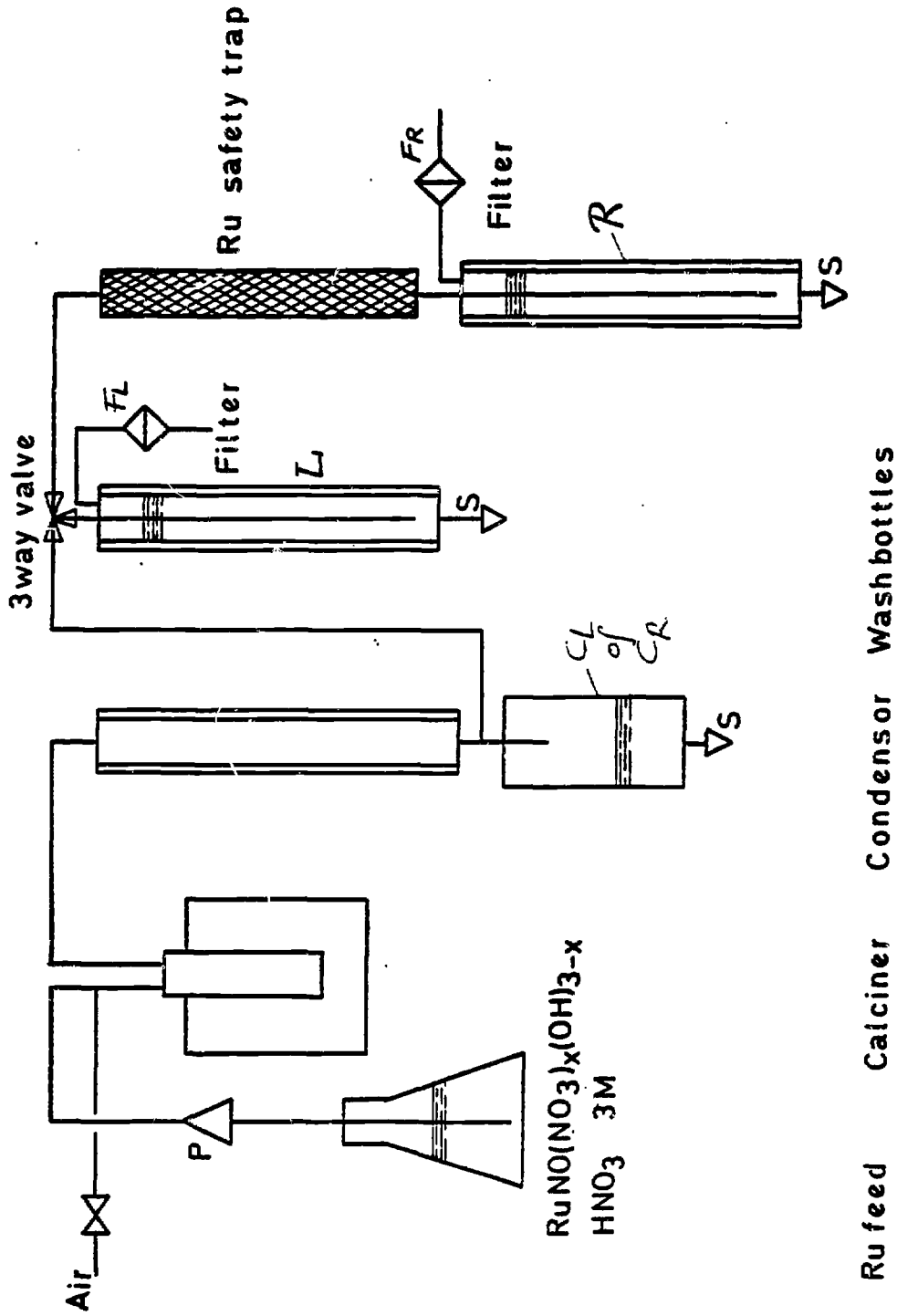


Fig 3.



Ru feed Calciner Condenser Wash bottles

