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THE BEHAVIOUR OF RUTHENIUM, CESIUM AND ANTIMONY DURING
SIMULATED HLLW VITRIFICATION

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Abstract

Work performed within a contract with DWK in Germany in the framework of the HAW technological programme for the vitrification of HLLW.

The behaviour of ruthenium, cesium and antimony during the vitrification of simulated HLLW in a liquid fed melter has been studied on a laboratory scale and on a semi-pilot scale. In the laboratory melter of a 2.5 kg capacity, a series of tests with the simulate traced with ^{103}Ru , ^{134}Cs and ^{124}Sb , has shown that the Ru and Cs losses to the melter effluent are generally higher than 10 % whereas the antimony losses remain lower than 0.4 %. A wet purification system comprising in series, a dust scrubber, a condenser, an ejector venturi and an NOx washing column retains most of the activity present in the off-gas so that the release fractions for Ru at the absolute filter inlet ranges between $5 \cdot 10^{-3}$ to $5 \cdot 10^{-5}$ % of the Ru fed, for Cs the corresponding release fraction ranges between $3 \cdot 10^{-3}$ to 10^{-4} % and for Sb the release fraction ranges between $1.7 \cdot 10^{-4}$ to $1.7 \cdot 10^{-5}$ %.

The same experiments have been performed at a throughput of 1 to 2 l h⁻¹ of simulated solution in the semi-pilot scale unit RUFUS. The RUFUS unit comprises a glass melter with a 50 kg molten glass capacity and the wet purification train comprises in series a dust scrubber, a condenser, an ejector venturi and an NOx washing column. The tracer tests were restricted to ^{103}Ru and ^{134}Cs since the laboratory tests had shown that the antimony losses were very low. The melter effluent losses occurring during LEWC feed and during the succeeding calcinate layer digestion ranges for ruthenium from 13 to 26 % and for cesium, from 8 to 48 %. The mean DF of the wet purification system amounts to $2 \cdot 10^3$ for ruthenium whereas a mean value of 400 is obtained for the cesium. In combination with the total melter losses, that means that the ruthenium release fraction at the HEPA filter inlet amounts to $1.3 \cdot 10^{-2}$ % of the ruthenium fed and the corresponding cesium release amounts to $8 \cdot 10^{-2}$ % of the cesium fed.

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I. Introduction

High Level radioactive liquid waste (HLLW) generated from LWR spent fuel reprocessing is considered to be treated by vitrification techniques in order to incorporate the fission products and the actinides into a glass matrix prior to disposal. In the framework of a contract between DWK in Germany and the CEN/SCK in Mol, a study has started in 1979 on the behaviour of so-called semi-volatile products which could be released during the vitrification process in the PAMELA plant.

The PAMELA plant, in construction on the Eurochemic site in Belgium, will treat 59 m³ of lewc (Low Enriched Waste Concentrate) solution. LEWC refers to the liquid waste solution from the first cycle extraction of low enriched (< 5 % U - 235) uranium fuel. LEWC is a waste solution evaporated to a concentration of about 0.5 m³ LEWC per ton of U reprocessed.

The experiments were performed on laboratory scale and on semi pilot scale using simulated LEWC solutions tagged with radio isotopes of the suspected volatile fission products. The composition of the simulated LEWC solution is given in table I.

The choice of the three elements Ruthenium, Cesium and Antimony is based on the assumption that those elements in a high temperature oxydative medium can form volatile compounds. The aim of this study is to determine on one hand the melter losses to the off-gas (i.e. the fraction of these elements not incorporated into the molten glass) and on the other hand the behaviour of these elements in the off gas purification system.

Due to its strong tendency to form volatile compounds, the behaviour of Ruthenium has first been studied. The main observations drawn from these studies are reported here after. In order to simulate the Pamela concept, laboratory units called VITRILAB I, II, III are then used to study the behaviour of Ru, Cs and Sb. Finally, the Pamela concept has been tested on a semi-pilot scale (1/10 of the real scale) in a unit called RUFUS.

Table I : Composition of the LEWC feed

Element	Element g/l	Nitrate salt	Oxide formed g/l	
Na	46.5	NaNO_3	Na_2O	62.7
Fe	15.7	$\text{Fe}(\text{NO}_3)_3$	Fe_2O_3	22.5
Cr	1.7	$\text{Cr}(\text{NO}_3)_3$	Cr_2O_3	2.5
Al	8	$\text{Al}(\text{NO}_3)_3$	Al_2O_3	15.0
Mn	4	$\text{Mn}(\text{NO}_3)_2$	MnO_2	6.3
Cs	1.5	CsNO_3	Cs_2O	1.6
Sr	0.5	$\text{Sr}(\text{NO}_3)_2$	SrO	0.6
Ba	0.1	$\text{Ba}(\text{NO}_3)_2$	BaO	0.11
Ce	1.8	$\text{Ce}(\text{NO}_3)_3$	Ce_2O_3	2.1
Zr	0.2	$\text{Zr}(\text{NO}_3)_4$	ZrO_2	0.27
Mo	1.3	Na_2MoO_4	MoO_3	1.95
Rb	0.25	RbNO_3	Rb_2O	0.27
Y	0.3	$\text{Y}(\text{NO}_3)_3$	Y_2O_3	0.38
La	1.6	$\text{La}(\text{NO}_3)_3$	La_2O_3	0.25
Ru	1	$\text{RuNO}(\text{NO}_3)_x$	RuO_2	1.32

II. Behaviour of Ruthenium in high temperature processes

A detailed description of these studies is given in (1), (2), (3). The main observations drawn from these studies are :

1. Gaseous Ruthenium tetraoxide

- RuO_4 is a strong oxidant which can rapidly be reduced to solid oxides of valencies 4 or 3 by reaction at room temperature with organic compounds.
- RuO_4 is unstable at temperatures higher than 100°C and decomposes into oxides of lower valencies. The rate of reaction is enhanced by the presence of metallic surfaces on which the ruthenium oxide deposit is strongly bounded.

- RuO_4 is physically adsorbed on Silica-gel at temperatures lower than 80°C ; above this temperature the adsorption capacity is negligible.
- RuO_4 is catalytically reduced to solid oxides on Fe/Cr catalyst operating at 300°C and the ruthenium oxide deposit enhances the reaction rate.

2. Volatile Ruthenium nitrosyl species

- Volatile RuNO species are formed either by reactions of RuO_4 with NO_x , either by calcination of Ru nitrosyl nitrate solutions in nitric acid.
- RuNO is more stable than RuO_4 , more easily adsorbable on Silica gel (tenfold increase of the capacity) and is adsorbed at temperatures as high as 120°C .
- RuNO is also catalytically reduced on Fe/Cr catalyst at 300°C but with a lower reaction rate and the RuO_2 deposit also enhances the reaction rate.
- The RuNO species has a lower vapor pressure than the RuO_4 species; at 20°C the partial pressure of RuNO is lower than $2 \cdot 10^{-3}$ atm so that almost the Ru is condensed whereas the corresponding RuO_4 partial pressure amounts to 10^{-2} atm.
- During calcination of Ru nitrosyl compounds dissolved in nitric acid, a fraction of Ru is plated out on the calciner walls, another fraction is volatile (RuNO species) and a last fraction is present in the off gases as submicronic aerosols. The distribution of Ru between these different states depends largely on the calcination temperature. At 600°C , the Ru release is mainly under the RuNO gaseous form (less than 0.2 % aerosol form), whereas at 1100°C , 8 % of the Ru release is in aerosol form.

Experiments were performed with the aim of comparing the volatilities of different Ru species fed simultaneously with a simulated high level liquid waste solution on a glass pool of an Inconel melter operated at 1100°C . The Ruthenium release in the melter off-gas depends on the nature of the Ru species fed.

- For a solution of $\text{RuNO}(\text{NO}_3)_x (\text{OH})_{3-x}$ dissolved in the waste simulate (LEWC), the melter losses to the off gas amounts to 7 % of the quantity fed. A fraction deposits on the crucible walls but the major part is incorporated into the glass.
- For a suspension of solid RuO_2 in LEWC, the melter losses amounts to only 2.5 %.
- When gaseous RuO_4 is simultaneously fed with liquid LEWC on the glass pool, the gaseous RuO_4 is partly decomposed on the hot

walls of the crucible and only 12 to 30 % of the Ru fed is lost to the melter off-gas; only a minor fraction is incorporated into the molten glass.

III. Laboratory vitrilab unit

3.1. Description of the laboratory units VITRILAB I, II and III

In the three vitrilab units, the liquid fed melter concept is used, but three slightly different purification schemes are tested.

The glass melter is an Incoloy 825 crucible with a 2.5 kg capacity molten glass externally heated by a resistance furnace. The simulated liquid waste solution (LEWC) traced with Ruthenium-103, Cesium 134 and Antimony 124 is directly fed by a membrane pump on the molten glass surface. The liquid through put on the melting surface area of 57 cm² varied between 20 and 40 l/h m². The off gas purification line of the three vitrilab units is different (Fig. 1).

In Vitrilab I, it comprises in series a packed bed dust scrubber, a specific Ru filter, an ejector venturi, a condensor and finally a washing bottle and an absolute filter.

In Vitrilab II, the specific ruthenium filter is removed and the condensor is installed between the dust scrubber and the ejector venturi.

In Vitrilab III, the specific ruthenium filter is removed and the positions of the condensor and of the ejector venturi can be interchanged by a by-pass valve system.

Liquid and gas samplings performed at various locations in these units allow to follow the evolution of the melter losses to the off-gas and to determine the efficiency of the off-gas cleaning system.

The particle size distribution of the aerosol present in the off-gas is determined by sampling with a cascade impactor followed by a condensor, a wash bottle and a final filter. The distribution between aerosol form and volatile form is determined with the same system where the impactor is replaced by a sampling filter.

3.2. Melter releases to the off-gas

3.2.1. Ruthenium. The melter DF for Ru lies between 3.3 and 67 with a mean value of 10.8 corresponding to a 9.3 %

entrainment. Generally, the entrainment by the off-gas in maximum at the start of a run and decreases as soon as a molten salt layer covers the molten glass surface. The particle size distributions, determined with a cascade impactor, appear all to be bimodal in nature. The large diameter component is deposited mainly on the first stage of the cascade impactor with a cut-off diameter of $14\mu\text{m}$. The small diameter component is deposited on the last stages of the cascade impactor with cut offs of 2, 1 and $0.6\mu\text{m}$. The rest is retained on the back-up absolute filter. The fraction of Ru found after the impactor represents the gaseous ruthenium release of the melter. The major part of this volatile component is found in the condensate. A low melter DF is always observed when volatile Ru species are formed. For two runs, with melter DF's of only 4.4 and 3.3 the volatile fraction of the ruthenium in the off-gas reached respectively 18 and 50 % of the total Ru loss to the off-gas.

Ru losses during melter idling. If the melter, containing the glass-waste oxides mixture kept at high temperatures (1000°C), is sparged with air volatilization of certain glass components may occur during that period and so lower the global melter DF. (This situation is called "idling melter"). For Ru, after glass refining during some hours, air sparging leads to a loss of $5 \cdot 10^{-3}$ % to $2 \cdot 10^{-2}$ % pro hour of the Ru activity present in the molten mixture. The particle size distribution of the aerosol during melter idling is shifted towards small values; all the activity is found on the last stage (cut-off of $0.3\mu\text{m}$) and on the back-up filter of the cascade impactor.

3.2.2. Cesium. The entrainment of Cesium in the off-gas varies widely between runs. The minimum and maximum entrainment observed are 0.3 % and 20 % respectively and the mean values for all the tests is 4 % corresponding to a DF of 25. The Cesium behaviour is quite different from the ruthenium behaviour. The fraction of Cesium in the entrained dust trapped on the first stage of the cascade impactor is also high (30 to 70 %), but the fraction of Cesium present on the last stage is always higher than the ruthenium or antimony fraction. That means that the melter release in the micron and submicron range is enriched in Cesium vs ruthenium and antimony. The fraction of Cesium still present after the cascade impactor is very low (from 0.1 to max 2 %) which means that cooling down of the gases to 120°C induces nearly total condensation of the volatile Cesium oxides to submicronic aerosols.

The Cesium release to the off-gas by air sparging during idling of the melter at 1000°C is one order of magnitude higher than the ruthenium loss. Off gas entrainments of 0.1 to 0.7 % pro hour of the cesium activity are measured during air sparging and this phenomenon can significantly lower the melter DF; for example after 15 hours of air sparging, the melter DF decreases from 24 to 9 for a mean hourly entrainment of 0.27 %.

3.2.3. Antimony. The melter DF for antimony lies between 58 and 2300 with a mean value of 260 corresponding to a 0.4% volatility which shows that antimony releases to the melter off gas are very low. The antimony entrainment during an "Idling test" is also very low; values from 4 to 6 10^{-4} % of antimony entrainment per hour from the glass melt were measured during 15 hours long sparging tests.

3.3. Packed bed dust scrubber

The characteristics of the dust scrubber and the values of the DF's are given in table I. In order to avoid an increase of the volume of the circulating solution of the dust scrubber, the scrubber operates at a temperature regulated in such a way that the water vapour content of the off gases does not condense out in this scrubber. The liquid flow is chosen to work below flooding conditions for the highest operating temperature.

3.3.1. Ruthenium. The Ruthenium trapped in the circulating solution is only partially soluble in this weak acidic medium and ruthenium dioxide deposits rapidly in the solution and also on the Raschig rings of the packing. The mean DF of the Vitrilab III scrubber is one order of magnitude higher than the corresponding DF of I and II vitrilab unit. The dust scrubber III is 30 % higher and has a free section 18 % greater which means that the residence time of the gas is higher, which allows to work with higher liquid to gas ratio. When the volatile fraction at the melter outlet is high (Low melter DF), then the dust scrubber DF is very high ($DF \sim 10^3$). In these cases, the colour of the washing solution is orange-yellow characteristic of the presence in the weak nitric acid of several Ru nitrosyl nitrates complexes. On the contrary, when the melter DF is high and when the volatile fraction is low than the dust scrubber DF is lowered to values around 25. The aerosol leaving the dust scrubber has a narrow size distribution and volatile species are not any more present in the off gas. The activity mass median aerodynamic diameter of the aerosol leaving the dust scrubber lies between 0.6 and 0.9 μm and the standard deviations varies between 1.25 and 1.4. This means, that when volatile ruthenium is present in the melter off gases, this species is completely washed out by the dust scrubber and the only species still present at the scrubber outlet is a sub-micronic aerosol.

Table I. Packed bed dust scrubber

GEOMETRIC CHARACTERISTICS			
	VITRILAB I	VITRILAB II	VITRILAB III
Diameter (cm)	5	5.8	6.4
Height (cm)	25	25	35
Packing	Raschig Rings		
	D = H = 7 mm		
	d = 4 mm		
OPERATING CHARACTERISTICS			
Liquid flow (l/h)	100	80 - 100	120
Temperature (°C)	90 - 95	90 - 95	90 - 95
DF FOR RUTHENIUM			
MIN	10	7	24
MEAN	20	22	305
MAX	50	230	2100
DF FOR CESIUM			
MIN	*	1.7	4.5
MEAN	*	2.3	19
MAX	*	3.3	160
DF FOR ANTIMONY			
MIN	*	*	20
MEAN	*	*	58
MAX	*	*	280

* The corresponding tracer is not used.

During an idling test, the DF of the dust scrubber decreases towards values of 3 to 5. This decrease is clearly bound to the aerosol particle size decrease which lies in the sub-micronic range (lower than 0.3 μm).

3.3.2. Cesium. As shown in the table, the efficiency for Cesium is lower than for Ruthenium due to the fact that the melter release in the micron and sub-micron range are enriched in Cesium v.s. Ruthenium and to the fact that there is no volatile Cesium species still present in this temperature range. The dust scrubber DF during idling test is not strongly reduced v.s. the LEWC feed period which shows that the release mechanisms are probably not significantly different.

3.3.3. Antimony. Due to the high value of the melter DF and to the low concentration of Sb in the feed, the concentration of antimony in the off gas is 1000 times lower than Cesium. Nevertheless, the dust scrubber DF for antimony is higher than the Cesium DF, probably due to the fact that antimony is evenly distributed on the aerosols leaving the melter.

3.4. Specific volatile ruthenium trapping bed

As described with more details in 3, the second barrier for Ru in the off gas line as initially foreseen in the Pamela project, was a Silica-gel bed operating at 120°C. Such a filter, which had given favourable results when placed at the exit of a calciner appeared useless in the Vitrilab off gas purification line after the dust scrubber. A ferric-oxide chromium oxide catalyst operating at 300°C gave also very low DF's. This can easily be explained by the fact that these filters were developed to trap gaseous ruthenium species whereas it has been shown that after the packed dust scrubber the only species still present is a stable, non reactive submicronic aerosol. Therefore, it was decided to remove this unit from the off-gas line for the further experiments (Vitrilab II and Vitrilab III) and also to discard it in the design of the active Pamela plant.

3.5. Condensor

Although, the condensers in vitrilab II and III have not the same dimensions, no significant differences are observed between their performances. The condensers, placed after the dust scrubber, have roughly the same DF of 5 for the three elements. This suggests a similar trapping mechanism for the aerosols leaving the dust scrubber. The still entrained solid submicronic aerosols work as condensation nuclei and are retainable in the condensor thanks to their size increase.

During Idling test, the condensor DF decreases to 1. This is expectable, since there is no water condensation and moreover the aerosol particle size is decreased to values down to 0.3 μm or less.

3.6. Ejector venturi

The ejector venturi operates at a nozzle pressure of 3 bars and a liquid flow rate of 300 l/h. The circulating solution is maintained at 30 to 48°C.

The ejector DF mean values (64 and 80) of vitrilab II and III do not differ significantly for ruthenium. (Table II) The DF variation is large since values ranging from 10 to 10^3 were measured. Generally, the DF of the ejector increases when the DF of the system melter-dust scrubber-condensor decreases and the DF decreases in the opposite case. The DF for antimony is similar to the Ru DF.

The DF's for Cesium are systematically higher than the Ru and the Sb DF's, this is perhaps due to the fact that Cesium species are soluble in the washing solution whereas ruthenium and antimony species are insoluble.

Table II. Ejector Venturi

	Ruthenium DF		
Unit	Vitrilab I	Vitrilab II	Vitrilab III
MIN	10	16	10
MEAN	25	64	80
MAX	50	1000	290
	Cesium DF		
Unit	Vitrilab I	Vitrilab II	Vitrilab III
MIN	*	1670	80
MEAN	*	4800	256
MAX	*	14000	5800
	Antimony DF		
Unit	Vitrilab I	Vitrilab II	Vitrilab III
MIN	*	*	18
MEAN	*	*	60
MAX	*	*	226

* Tracer not used in this unit

3.7. Global DF of the system

The global DF of the system is the product of the melter DF and of the wet gas purification system DF.

The wet gas purification system is different in vitrilab I, II and III as shown hereafter.

- Vitrilab I : Melter - dust scrubber I - ejector venturi - condensor - washing bottle
- Vitrilab II : Melter - dust scrubber II - condensor - ejector venturi - washing bottle
- Vitrilab III : Melter - dust scrubber III - ejector venturi - condensor - washing bottle.

The minimum, maximum and mean global DF values are given in table III.

Table III. Global DF's for the different Vitrilab Units

MIN GLOBAL DF			
	Ru	Cs	Sb
VITRILAB I	10 ⁴	-	-
VITRILAB II	1.1 10 ⁴	2.2 10 ⁵	-
VITRILAB III	2 10 ⁴	3.5 10 ⁴	6.8 10 ⁵
MEAN GLOBAL DF			
	Ru	Cs	Sb
VITRILAB I	3.2.10 ⁴	-	-
VITRILAB II	1.1 10 ⁵	4.7.10 ⁵	-
VITRILAB III	3.8 10 ⁵	1.7.10 ⁵	2.5.10 ⁶
MAX GLOBAL DF			
	Ru	Cs	Sb
VITRILAB I	10 ⁵	-	-
VITRILAB II	8.6 10 ⁵	10 ⁶	-
VITRILAB III	2 10 ⁶	1.2 10 ⁶	6 10 ⁶

3.8. Conclusion of the vitrilab tests

The series of tests performed in the various Vitrilab units has shown that the Ru and Cs losses to the melter effluent are generally higher than 10 % whereas the Sb losses remain lower than 0.2 %. For the vitrilab III unit, the release fractions for Ru at the absolute filter inlet ranges between $5 \cdot 10^{-3}$ % to $5 \cdot 10^{-5}$ % of the Ru fed, for Cs the corresponding release fraction ranges between $3 \cdot 10^{-3}$ to 10^{-4} % and for Sb the release fraction ranges between $1.7 \cdot 10^{-4}$ to $1.7 \cdot 10^{-5}$ %.

Antimony, due to its low volatility, will not be used in the RUFUS unit.

IV. Semi pilot scale unit RUFUS

4.1. Description of the RUFUS unit

The spatial projection of the Rufus installation (Retention Unit for the Filtration of Unidentified Species) is given in fig. 2.

The main characteristics of the RUFUS installation are given hereafter.

4.1.1. Vitrification unit

The vitrification unit comprises four elements.

- Vitrification oven : The crucible in Incoloy 825 has a molten glass capacity of 50 kg and the molten glass surface reaches 1328 cm^2 . The total available power delivered by external resistance heating elements can be varied between 8 and 9.6 kw.
- Molten glass feed : The glass frit from the dosing vessel is molten in an Incoloy crucible heated by a furnace of 2.2 kw and flows by gravity into the vitrification oven.
- LEWC liquid feed : The simulated LEWC solution is directly fed on the molten glass surface with a diaphragm dosing pump. The throughput during the tests was varied between 0.9 and 1.9 l/h corresponding to 6.3 to 14 l/h m^2 molten surface.
- Crucible emptying : The emptying of the crucible is performed via a freeze valve and the receiver is installed in a heated box to minimize the thermal stresses during glass cooling.

4.1.2. Dust Scrubber

The dust scrubber is a packed bed countercurrent dust scrubber with a glass spiral ring packing. The column has a diameter of 100 mm and a packing height of 880 mm.

4.1.3. Condensor

The condensor is a spiral type industrial glassware condensor with an exchange surface of 1.5 m^2 .

4.1.4. Ejector Venruri. The ejector Venturi is a SAPS stainless steel ejector operating at a nozzle pressure of 6 bars and a liquid flow of 500 l/h.

4.1.5. NO_x washing columns. The NO_x washing tower is a packed bed counter current column in industrial glassware with a packing of ceramic Raschig rings. The column has a diameter of 100 mm and two beds of 700 mm height.

4.1.6. Air Ejector. The installation is maintained in slight under pressure by a compressed air driven ejector placed at the end of the off gas purification after the final absolute filter. An under pressure of 10^3 to $1.5 \cdot 10^3$ Pa is maintained in the melter phenum by a guard siphon placed on the air inlet.

Two configuration can be chosen by a system of valves and by-pass :

- Configuration I
Dust-scrubber/Condensor/Ejector Venturi/NO_x Tower
- Configuration II
Dust-scrubber/Ejector Venturi/ Condensor/NO_x Tower

The dust scrubber operates always in a temperature range of 75-85°C so that the water vapour content of the off-gas remains nearly constant. The ejector venturi in configuration I operates always at low temperature (about 30°C) whereas in configuration II the ejector venturi can also be operated at 75-85°C so that the water vapour content of the off-gas remain nearly constant and so does also the ejector liquid volume.

4.2. Melter releases to the off-gas

The release of Ru and Cesium is determined by liquid sampling of the various scrub solutions and by gas sampling on absolute glass fiber filter. The activities of ^{103}Ru and ^{134}Cs are determined with a Ge (Li) detector

4.2.1. Description of the melter behaviour. During operation of the melter, three succeeding steps can be distinguished namely the LEWC feed period, the calcinate layer digestion period and the melter idling period.

- LEWC feed period

At the start of a run, the molten glass surface is at about 1050°C. The liquid feed on the molten glass surface induces a drop of temperature of the glass surface and a colder cap of dry solids is formed on the surface. If the liquid flow is sufficiently high, a liquid covered area will finally appear on the glass surface. The extend of the three zones (uncovered melt, dry solid layer, liquid covered area) depends mainly of the liquid flow rate, the heating power and the working time.

- Calcinate layer digestion period

When the liquid feed is stopped, after vaporization of the remaining liquid phase, the calcinate layer is progressively decomposed into oxides which are incorporated into the mass of the glass to finally form an homogeneous waste oxides-glass mixture.

- Idling period

When the calcinate layer digestion period is finished, the molten glass surface has reached again a temperature of about 1050°C and the uncovered glass mixture-waste oxides is exposed to the sparging air.

In fig. 3, the temperature evolution of the glass surface is given in function of working time for two liquid flowrates.

4.2.2. Presentation of the results. The Ruthenium and Cesium release to the off-gas are different for each period. The main observations drawn from the 7 runs are the following :

- LEWC feed period

The Ruthenium and Cesium losses to the off-gas decrease when the mean temperature of the calcinate layer formed during LEWC feed decreases. This is illustrated in fig. 4 and 5, which gives the Ru and Cs fraction volatilized in function of the mean glass surface temperature. However, for Cesium, it seems that the volatility depends not only of the quantity of Cesium in the liquid feed but it depends also of the quantity of Cesium already present in the molten glass. When this fact is taken into account, the relationship between cesium volatility and mean surface temperature appears, indeed, more clearly.

- Calcinate layer digestion

The Ru and Cs losses to the off-gas are generally high during the first four hours after the feed stop and level off to a very low value whereas for Cesium the release tends to a roughly constant value. This is illustrated in fig. 6 for the run 6/10.

- Melter idling

Air sparging of the melter leads to low Ru losses of about $3 \cdot 10^{-3}$ %/hour of the Ru activity in the molten glass whereas for Cesium 0.33 %/hour is released to the off-gas.

4.2.3. Release mechanisms of Ruthenium and Cesium. The particle size distribution of the dust leaving the melter has not been determined, because the use of a cascade impactor in a gas with a high dust loading appeared practically not feasible. The results obtained in the vitrilab where some impactor data were collected had lead to the following observations.

- The Ruthenium loss of the melter is partly under the form of a volatile species, partly under the form of entrained dust and the rest is a submicronic aerosol. The distribution between these forms vary widely and mainly depends on the temperature at the molten glass surface.
- The Cesium release is partly under the form of entrained dust and partly under the form of submicronic condensation aerosols. At the low outlet temperature of the melter, no volatile species are still present. In general the aerosol size distribution is bimodal in nature. This suggests that the overall size distribution is composed of two independent components, each having its own characteristic size distribution. The large component is certainly associated with a gross entrainment mechanism whereas the small diameter component of the overall distribution is probably a volatilization/condensation process that occurs within the melter plenum.

The different behaviour of ruthenium and Cesium during the LEWC feed and during the idling test can be explained by differences in the probable release mechanism.

The gross entrainment mechanism result in a dust emitted which has the same composition as the LEWC feed. For the small diameter component, generally, the submicronic loss fraction is enriched in Cesium vs ruthenium indicating a different mechanism.

Ruthenium loss mechanism

The formation of volatile species RuO_3 and RuO_4 by RuO_2 oxidation is very limited below 1200°C (Equilibrium constant $K = 10^{-3}$ at 1200°C). Even formed, these volatile species are highly unstable at the outlet melter temperature and are again decomposed into RuO_2 . This mechanism is probably responsible for the Ru release during idling test.

During LEWC feed, volatile RuO_4 can be formed by reaction between RuO_2 and NO_2 from 900°C ($K = 10^{-1}$ at 900°C). Again the gaseous RuO_4 is highly reactive and can at lower temperatures react with NO to give Ru nitrosylcomplexes or be decomposed again to solid RuO_2 .

Another way of volatile Ru formation and the most probable is the formation of a volatile Ru nitrosyl complex by partial decomposition of the nitrosyl nitrate.

Cesium loss mechanism

Solid Cs_2O , formed by CsNO_3 decomposition from 500°C onwards, can be transformed into volatile species in a temperature range of 750°C to 1200°C . Cooling of the gas induces condensation of these gaseous species to solid submicronic aerosols.

During LEWC feed, i.e. in the presence of great amounts of water vapour (till 50 %), volatile cesium hydroxides such as CsOH and $(\text{CsOH})_2$ can be formed. In the absence of water vapour, i.e. during calcinate layer digestion and idling melter, volatile species such as CsO and CsO_2 can be formed.

4.3. Dust scrubber

4.3.1. Operation of the dust scrubber.

- The liquid flow in the dust scrubber itself is fixed at 800 l/h corresponding to a liquid rate of $102 \text{ m}^3/\text{h}\cdot\text{m}^2$.
The nominal gas flow amounts to $7.2 \text{ m}^3/\text{h}$ when the dust scrubber operates at 82°C corresponding to a water vapour content of 50 %, the normalised gas rate equals to $904 \text{ m}^3/\text{m}^2 \text{ h}$.
- During idling test, the gas flow amounts to $3.3 \text{ m}^3/\text{h}$ when the dust scrubber is operating at 40°C corresponding to a water vapour content of 5 %.
- The by-pass liquid flow is kept at 300 l/h. The function of this flow is to clean the connecting tube between the melter and the dust scrubber.
- In practice, the temperature of the circulating liquid is kept between 75 and 92°C depending on the LEWC flow rate. The aim is to maintain the volume of the circulating liquid constant. In all the tests, the dust scrubber was operating at a higher temperature than the dew point of the gas so that a reduction of the circulating liquid volume was always observed - Generally the final volume was 70 to 80 % of the initial volume -
- In all the tests, an insoluble component appeared after some hours of operation. This insoluble component, essentially ruthenium dioxide, deposits in the circulating tank and on the packing.

4.3.2. Presentation of the results.

- Particle size distribution of the aerosol at the dust scrubber outlet

The particle size distribution of the aerosol leaving the dust scrubber has been determined by sampling with a low flow rate ($1 \mu^3/h$) 4 stages cascade impactor.

During LEWC feed and calcinate layer digestion, the major part of the aerosol leaving the dust scrubber is in the 0.3 to 0.5 μm range. When the calcinate layer is nearly completely digested, the distribution is shifted towards smaller values concentrated of around 0.4 μm . During idling test, the major part of the activity is found back on the back-up filter which means that the distribution is again shifted towards values smaller than 0.4 μm .

- Distribution between soluble and insoluble form

As shown in the table hereafter, the Cesium trapped in the dust scrubber is nearly completely soluble whereas for Ru about 14 % of the total Ru trapped is not soluble and forms black ruthenium dioxide which deposits in the tank, on the spiral rings of the packing and in the pipes. It is obvious that the insoluble fraction will increase with the Ru trapped concentration. Indeed in the vitrilab laboratory installation, insoluble fraction of about 50 % were found for Ru concentrations of 200 mg/l.

	^{103}Ru	^{134}Cs
insoluble %	14	0.4
concentration mg/l	90	150

- Dust scrubber DF

During normal operation i.e. during LEWC feed and calcinate layer incorporation, the mean DF for Ru reaches 5.5 and is always higher than the mean DF for Cs which only reaches 2.5. During idling test, the DF's for Ru and Cs decrease to respectively 1.9 and 2.1.

DF	^{103}Ru		^{134}Cs	
	Normal operation	Idling test	Normal operation	Idling test
MEAN	5.5	1.9	2.5	2.1
MIN	2.8		2	
MAX	9.5		4	

The lower efficiency of the dust scrubber observed for Cesium is probably bound to a difference in particle size distribution at the dust scrubber inlet.

Conclusion

The dust scrubber DF of the RUFUS unit is one order of magnitude lower than the dust scrubber of the vitrilab unit. Reasons for these differences can be :

- a lower dust concentration at the melter outlet due to a higher ratio inert air/l LEWC for the Rufus (1.8 m³ air/l LEWC for Rufus v.s. 0.6 m³ air/l LEWC for the vitrilab unit)
- a different particle size distribution at the Rufus melter outlet
- a higher L/G ratio for the vitrilab (370 l/m³) than for the Rufus (111 l/m³)
- a lower superficial gas velocity for the vitrilab (3 cm/s) than for the Rufus (25 cm/s).

4.4. Condensor and ejector venturi

4.4.1. Operation of the condensor and the ejector venturi

- 50 l of drinking water is used as washing solution in the ejector-venturi. The liquid flow of 0.5 m³/h obtained for a nozzle pressure of 6 bars induces a draft of 300 Pa on the gas flow.
- If the venturi solution is not directly removed, a deposit of ruthenium oxide can appear in the tank.
- Three different purification schemes have been tested :
 - I Condensor followed by ejector venturi operating at 30°C
 - II Ejector operating at 30°C followed by condensor
 - III Ejector at 70-85°C followed by condensor.

In the cases I and III, the ejector washing solution volume remains nearly constant whereas in the case II the volume in the ejector steadily increases because it in fact, acts as condensor.

4.4.2. Decontamination factor of the ejector venturi and the condensor

Ejector venturi

The mean DF's obtained during the various runs are given in table IV. The main observations drawn from these results are :

- The over-all DF is always lower than the DF obtained during the feeding period of a run, this is probably bound to a shift of

the particle size distribution towards the smaller values and to a decrease of concentration in the gas effluent.

- The DF for Cesium is always lower than the Ru DF when no significant difference in the particle size distribution were observed.
- In spite of the small number of experimental runs for each configuration, it seems that the ejector shows the highest efficiency when it is used at a low temperature and after the condenser.

Condensor

The values of the operating temperature and the DF's are given in table V. The main observation drawn from these tests are :

- the condensor DF is generally lower for Cs than for Ru;

Table IV : Ejector Venturi DF in function of the chosen purification shemes

Mean DF values	DF during feed		Global DF	
	Ru	Cs	Ru	Cs
DS-C-V (32°C)	670	109	240	122
DS-V (32°C)-C	99	65	66	43
DS-V (75°C)-C	30	22	30	29

* The operating temperature is given between brackets.

Table V : Condensor Df in function of the chosen purification scheme

MEAN GLOBAL DF	Ru	Cs
A) Condensor at 30°C Followed by E.V.	1.4	1.2
B) Condensor at 30°C After E.V. at 35°C	1.2	1.1
C) Condensor at 30°C After E.V. at 70-85°C	4.6	2.4

- It seems that the best Df's are obtained when the condenser is installed after the ejector operating at high temperature. The activity ratio condensate/feed is given here after for the three purification schemes.

$\frac{\text{activity in condensate}}{\text{activity in feed}}$	Ru	Cs
Scheme I C-V ³²	3.10^{-5}	$1.5.10^{-4}$
Scheme II V ³² -C	2.10^{-5}	8.10^{-5}
Scheme III V ¹⁵ -C	6.10^{-6}	8.10^{-6}

This table shows that the lowest activity level in condensate is found for the scheme III.

Comparison of the performance of the three purification schemes

The three purification schemes give total DF's which are of the same order of magnitude. Due to the small number of tests a choice can not be made on the basis of the total Df for condenser and Venturi-ejector together.

All the three schemes have their advantages and disadvantages which are summarized here after.

	ADVANTAGES	DISADVANTAGES
I C-V ³⁰	- Venturi operates at low temperature - Constant washing solution volume	- Highest activity level of the condensate - water cooling of the venturi
II V ³⁰ -C	Venturi operates at low temperature and can act as a condenser (which can be suppressed)	Increase of the washing solution volume
III V ⁷⁵ -C	Lowest activity level of the condensate/constant volume of the washing solution	Venturi works at high temperature

The choice between the different possibilities can then be governed by the recycling philosophy adopted in the process.

For the schemes I and III, the constancy of the washing solution volume, in the ejector, allows to recycle a small fraction of the solution to the melter feed without the need of an evaporator.

For the condensate recycling, which needs always an evaporator, the scheme III is the most advantageous since the activity levels handled are one order of magnitude lower than for scheme I.

For the scheme II, a volume equivalent to the waste volume fed must be removed and sent to an evaporator prior to go to the melter.

4.5. NO_x washing tower

4.5.1. Operation of the NO_x washing tower

20 l of drinking water solution are used as washing solution in the NO_x tower. The liquid flow varied during the tests between 300 and 500 l/h with a corresponding pressure drop of 800 to 2000 Pa.

4.5.2. Efficiency for the removal of Cs and Ru

The main operating parameters as well as the DF's values for Ru and Cs are given in table VI.

The DF and the gas pressure drop increase with the liquid flow rate. A reasonable DF is obtained when the NO_x scrubber operates near the flooding point of the column (Flooding point L = 600 l/h, G = 3 m³/hl).

Table VI NO_x washing tower

Date	Gas flow rate at 40°C	Liquid flow rate	Pressure drop	Global DF	
	m ³ /h	l/h	Pa	Ru	Cs
02/08	3.1	300	800	1	1.3
10/08	3.1	300	800	1.6	1.2
11/08	3.1	350	1000	2	1.4
27/09	3.1	400	1200-1500	1.4	1.4
29/09	1.7	450	1600-1700	2	1.8
06/10	3.1	500	1800-2000	3	3.4

V. Comparison with the Pamela design DF's

Table VII and table VIII give a comparison of the results obtained in RUFUS with the PAMELA design values. The DF obtained in the gas purification train RUFUS are lower than the PAMELA design values.

For Ru, it appears that the weak points in the purification systems are the dust scrubber and the condensor. The venturi ejector shows a better efficiency than expected. The NO_x dust scrubber has a DF which is of the same order of magnitude as the design value.

For Cs, it appears that the melter loss is greater than the design value (16 to 25 % instead of the expected 4 %). The weak points in the purification system are also the dust scrubber and the condensor whereas the ejector and the NO_x tower satisfy the requirements.

Several actions can be undertaken in order to improve the system DF for Ru and for Cs.

5.1. Reduction of the melter losses

- Long duration tests with a constant covering of the molten glass with a calcinate layer give generally lower losses for Ru and Cs due to the lower temperature at the top level of the melt. Ru release of 15 % and Cs release of 10 % can be achieved for a top level temperature of 700°C for example.
- Lower the surface temperature of the melt during idling in order to minimize the Cesium release mainly. This can be obtained by applying a water feed such as is foreseen in the Pamela design.

Table VII : Mean DF's values of the purification units in RUFUS compared to the PAMELA design values

	Ru			Aerosols	Cs	
	Pamela design	During LEWC feed	Global DF	Pamela design	During LEWC feed	Global DF
Melter	6.7	12.7	6.1	25	6	3.9
Dust scrubber	10	8.8	6.5	10	2.4	2.5
Condensor	10	2	2	5	1.5	1.5
Venturi	20	95	78	20	52	52
NO _x	2.5	1.9	1.8	2.5	2.1	1.6

Table VIII : Mean DF's values of the purification system RUFUS compared to the VITRILAB results and to the PAMELA design values

Mean DF of the wet purification system			
System DF	Pamela design	Vitrilab	Rufus
Ru	$5 \cdot 10^3$	$3.5 \cdot 10^4$	$2 \cdot 10^3$
Cs	$2.5 \cdot 10^3$	$6.8 \cdot 10^3$	400

5.2. Increase of the dust scrubber efficiency

The dust scrubber used was a low pressure drop counter-current bed dust scrubber. Test are foreseen to design a new type of more efficient dust scrubber. The idea is to use a co-current dust scrubber with impingement plate followed by a counter-current impingement plate dust scrubber. The two columns would be installed on the same circulating tank.

5.3. Increase of the condensor efficiency

A classical stainless steel tube and shell condensor will be tested in the future with the hope of a better efficiency due to more efficient contact between the condensate flow and the gas.

VI. Conclusion

The RUFUS experiments have shown that the vitrilab laboratory results could not directly be extrapolated to semi-pilot size units. The off-gas line consisting of a dust scrubber, a condensor, an ejector venturi and an NO_x tower is quite effective for trapping of semi-volatile species of ruthenium and Cesium whereas some improvements mainly in the dust scrubber should increase the overall system DF. For the two isotopes tested and in the context of the LEWC composition, Cesium, with accounts for about 73 % of the gamma radiation appears to be the reference isotope for the volatile elements released from the melter. Ru is not a problem on the point of view of gas purification but can cause local radiation problem due to its trend to deposit on metal and to form insoluble components.

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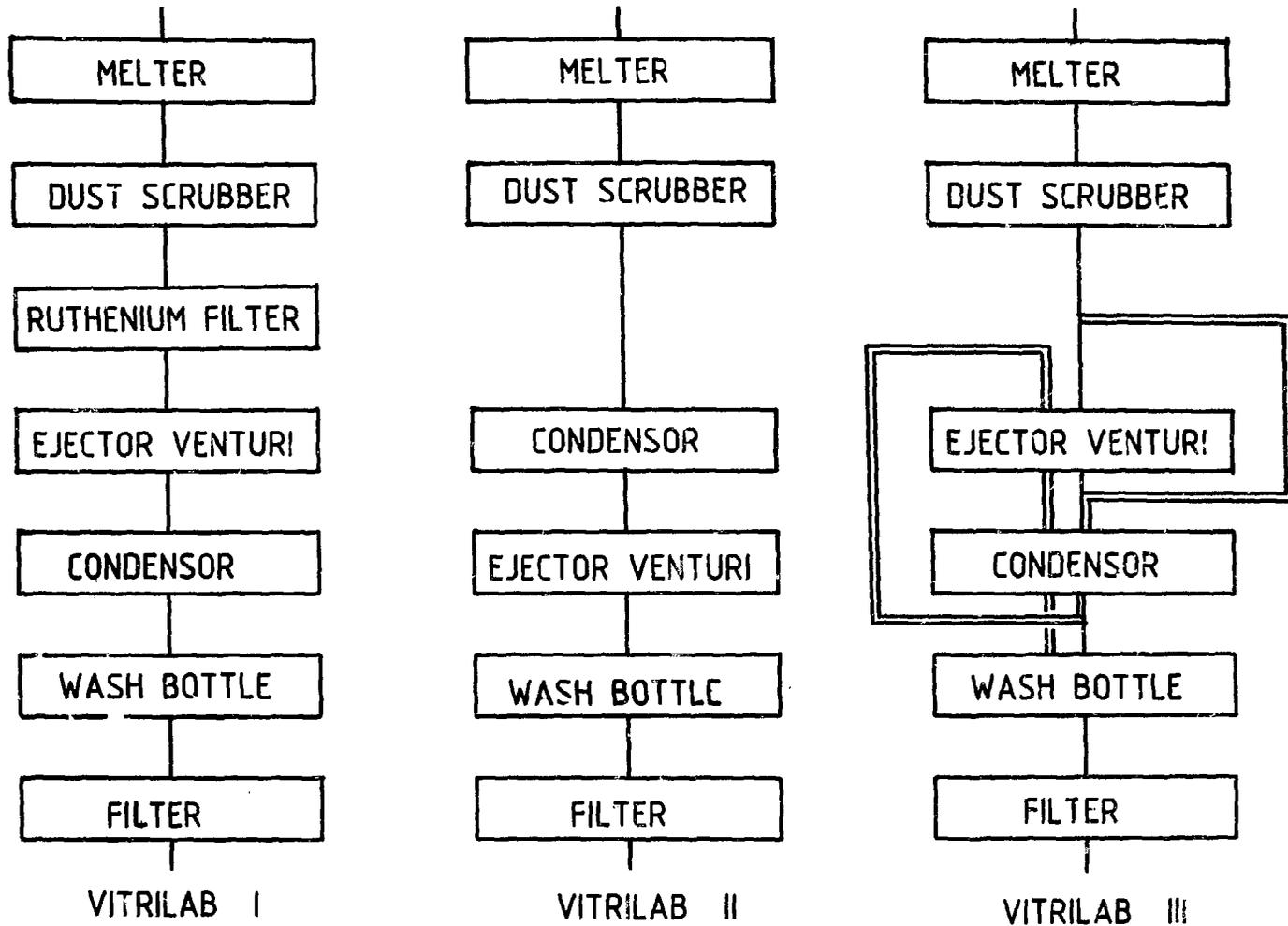
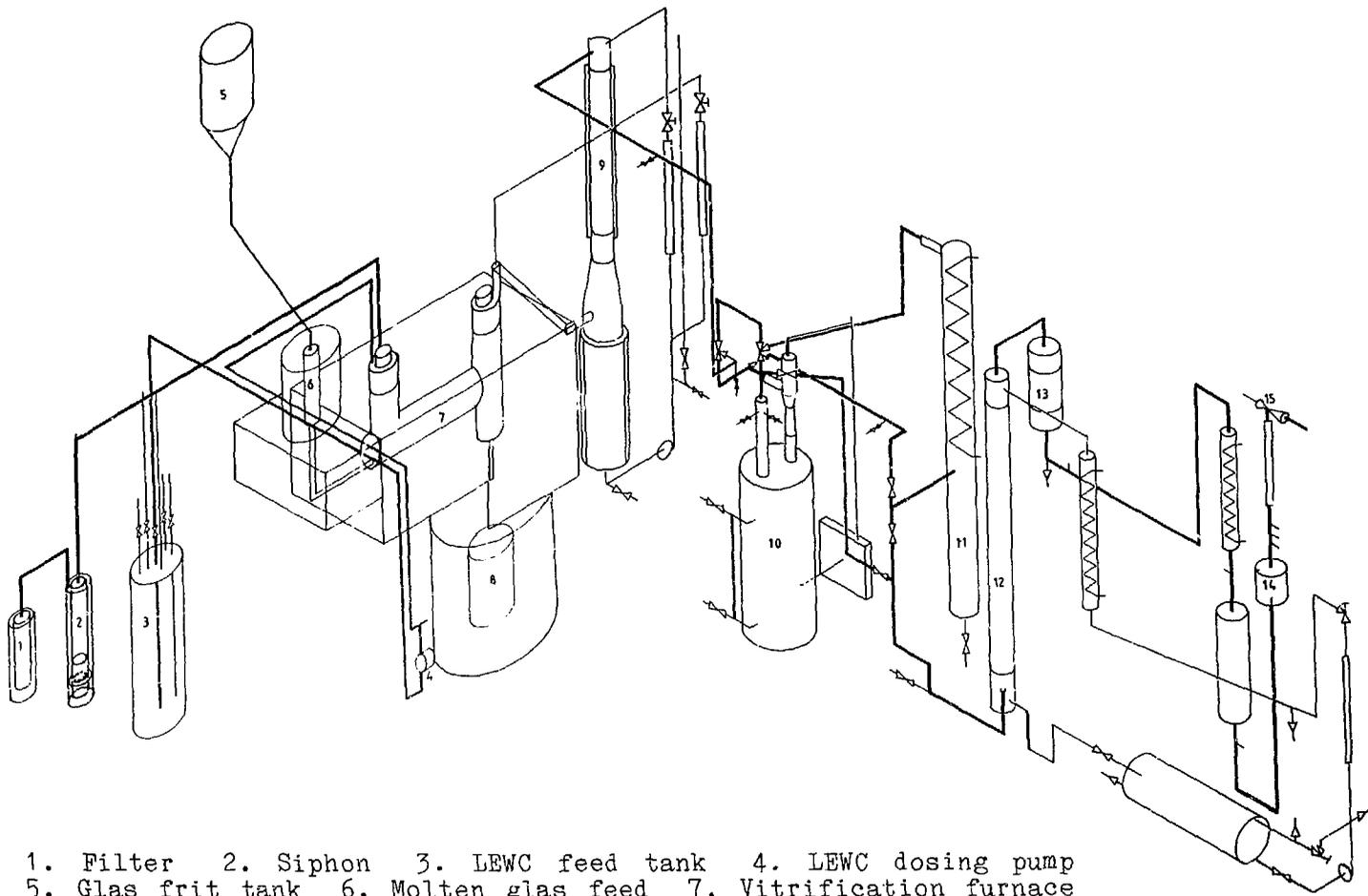


FIG. 1 BLOCK DIAGRAM ON THE VITRILAB UNITS



- 1. Filter
- 2. Siphon
- 3. LEWC feed tank
- 4. LEWC dosing pump
- 5. Glas frit tank
- 6. Molten glas feed
- 7. Vitrification furnace
- 8. Active glas container
- 9. Dust scrubber
- 10. Ejector venturi
- 11. Condensor
- 12. NOx washing tower
- 13. Demister
- 14. HEPA filter
- 15. Air ejector.

Fig. 2. : Vitrification unit "RUFUS" ---- treatment of LEWC type liquid waste.

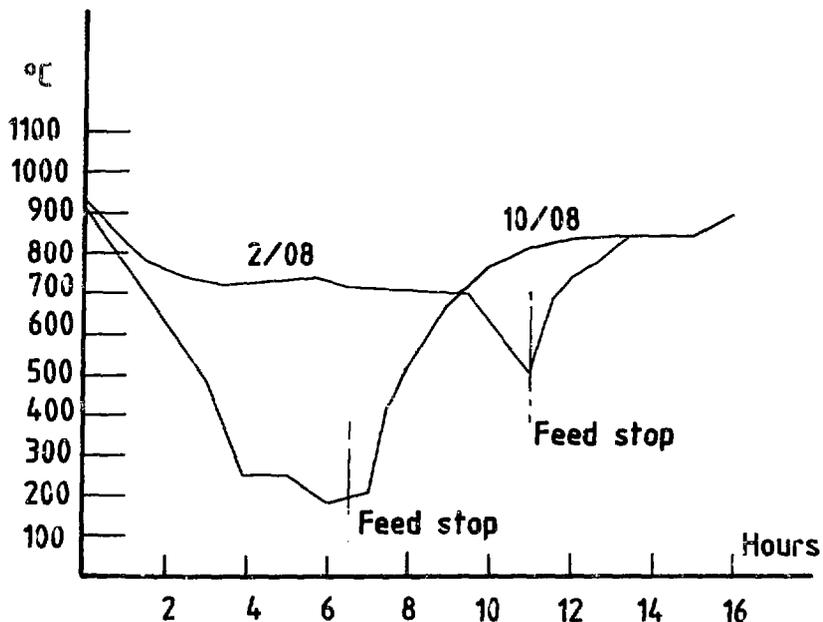


FIG. 3 GLASS SURFACE TEMPERATURE PROFILE

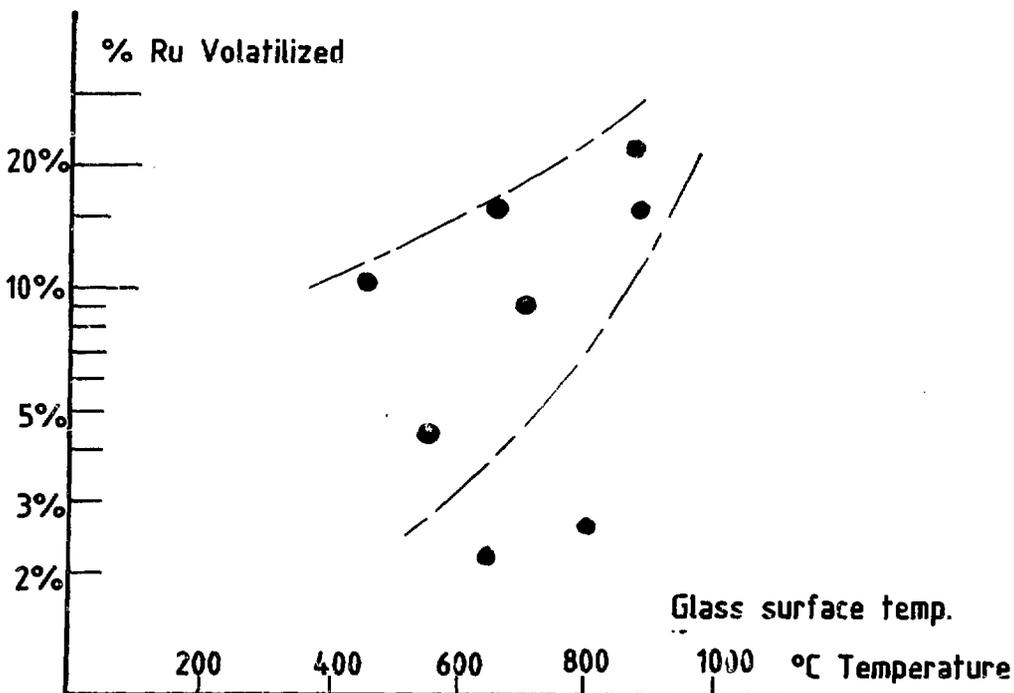


FIG. 4 VOLATILIZATION OF Ru DURING L.E.W.C. FEED

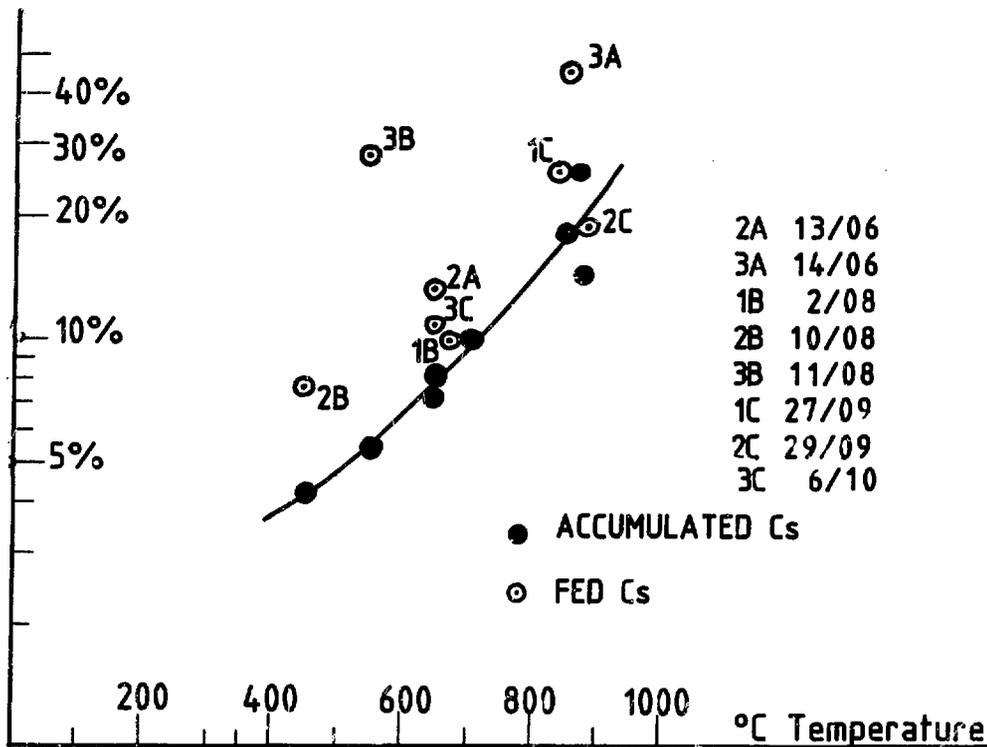


FIG. 5 CESIUM RELEASE IN FUNCTION OF THE GLASS SURFACE TEMP.

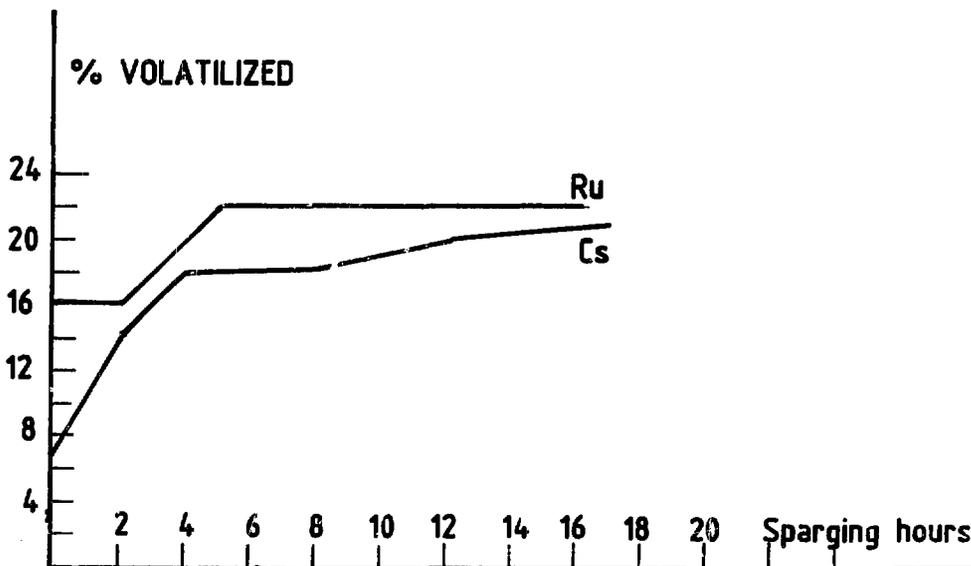


FIG. 6 RELEASE AFTER FEED STOP