

SESSION 10/11

PROCESSING AND FUEL REPROCESSING

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M. Kikuchi

A STUDY ON THE EXPULSION OF IODINE FROM SPENT-FUEL SOLUTIONS

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23rd DOE/NRC NUCLEAR AIR CLEANING AND TREATMENT CONFERENCE

A STUDY ON THE EXPULSION OF IODINE FROM SPENT-FUEL SOLUTIONS

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Abstract

During dissolution of spent nuclear fuels, some radioiodine remains in spent-fuel solutions. Its expulsion to dissolver off-gas is important to minimize iodine escape to the environment. In our current work, the iodine remaining in spent-fuel solutions varied from 0 to 10% after dissolution of spent PWR-fuel specimens (approximately 3 g each). The amount remaining probably was dependent upon the dissolution time required. The cause is ascribable to the increased nitrous acid concentration that results from NO_x generated during dissolution. The presence of nitrous acid was confirmed spectrophotometrically in an NO-HNO₃ system at 100°C. Experiments examining NO_x concentration versus the quantity of iodine in a simulated spent-fuel solution indicate that iodine (I⁻) in spent fuels is subjected to the following three reactions: (1) oxidation into I₂ by nitric acid, (2) oxidation into I₂ by nitrous acid arising from NO_x, and (3) formation of colloidal iodine (AgI, PdI₂), the major iodine species in a spent-fuel solution. Reaction (2) competes with reaction (3) to control the quantity of iodine remaining in solution. The following two-step expulsion process to remove iodine from a spent-fuel solution was derived from these experiments:

Step One - Heat spent-fuel solutions without NO_x sparging. When aged colloidal iodine is present, an excess amount of iodate should be added to the solution.

Step Two - Sparge the fuel solution with NO_x while heating.

Effect of this new method was confirmed by use of a spent PWR-fuel solution.

I. Introduction

Radioiodine (¹²⁹I) freed during dissolution of spent nuclear fuels in reprocessing is prone to escape to the environment. Its strict control is required for environmental safety. High-efficiency silver-impregnated adsorbents recently have been developed that provide sufficiently high decontamination factors for radioiodine in off-gas.⁽¹⁾ The next consideration is the treatment of iodine remaining in the fuel solution. Untreated, it distributes itself into the Purex process where it causes an increase of radioiodine released to the environment. Thus, as much iodine as possible must be expelled from the fuel solution to the dissolver off-gas where it will be fixed on the high-efficiency adsorbent. Our current work is concerned with this expulsion of iodine from fuel solutions.

Earlier workers postulated iodate (IO₃⁻) to be the main iodine species remaining in spent-fuel solutions. NO_x sparging of the solutions was proposed to change the iodate into volatile iodine (I₂).⁽²⁾ However, recent research provides a different understanding. Most remaining iodine may be colloids of insoluble iodides of silver

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and palladium⁽³⁾ or nonvolatile organic iodides.⁽⁴⁾ Moreover, our recent research has found that, although the amount of fission-product iodine increases with increasing burnup of nuclear fuels, its amount is not necessarily proportional to the burnup.⁽³⁾ Thus, there are ambiguities about the behavior and chemical form of iodine in the dissolution step. Our current research determined factors that influence the iodine species and their quantities in spent-fuel solutions. This allowed the derivation of a new method for effective expulsion of iodine from these solutions.

II. Experimental Method

Spent PWR-fuel specimens with burnups between 21 and 39 Gwd/t (approximately 3 g each) were dissolved in 30 ml of 4 M HNO₃ at 100°C. The volatilized iodine was carried onto an iodine filter by bubbling helium (40 ml/min) through the solution. Details of the experimental apparatus and procedure were described elsewhere.⁽⁵⁾ Dissolution progress was monitored by continuous measurement of ⁸⁵Kr radioactivity in the dissolver off-gas. After the insoluble residue had been removed by centrifugation, the expulsion of iodine from the solution was also performed using this experimental apparatus.

The simulated spent-fuel solution used had the same composition as that described previously,⁽⁶⁾ that is, uranium of 50 g-U/l and amounts of simulated fission-products corresponding to those in spent fuels with a burnup of 40 Gwd/t. A corresponding amount of iodine (as potassium iodide) labeled with ¹³¹I was added to 30 ml samples of the solution at 100°C with and without an NO or NO₂ supply. The iodine species in the solutions were analyzed by the carbon tetrachloride extraction method that determined the quantities of I₂, I⁻, IO₃⁻, organic iodide, and colloidal iodine present.⁽⁷⁾ Except the nitrogen dioxide, purified by flowing oxygen through its liquid, commercial grade reagents were used without purification.

III. Results and Discussion

1. Reactions of iodine in the dissolution step

Study of the dissolution of the spent-fuel specimens suggests the amount of iodine remaining in the fuel solutions is associated with the rates of dissolution. Figure 1 shows two typical ⁸⁵Kr concentrations in dissolver off-gas during dissolution. Table 1 provides specific details. In the case marked UO₂ in the figure, the ⁸⁵Kr concentration reached a maximum about 18 min after the start of the dissolution and then decreased rapidly. The dissolution was complete within about 1 h. Dissolution of most ordinary UO₂ fuel specimens provided similar ⁸⁵Kr concentration curves. Only small amounts of iodine (0 to 3.3% of the total iodine quantity) remained in solution, despite the high burnup of the fuels (Table 1).

In the other case, the ⁸⁵Kr concentration provided a long-tailed curve as shown by the Gd₂O₃-UO₂ curve in Fig. 1. This showed the dissolution continued for more than 2 h. Most of the Gd₂O₃-UO₂ fuel specimens used showed similar curves. Considerable amounts of iodine (4.5 to 9.7%) remained in solution, even for the fuel specimen having the lowest burnup (Table 1). Gadolinium does not form its insoluble iodide. A smaller dissolution rate causes a smaller NO_x generation

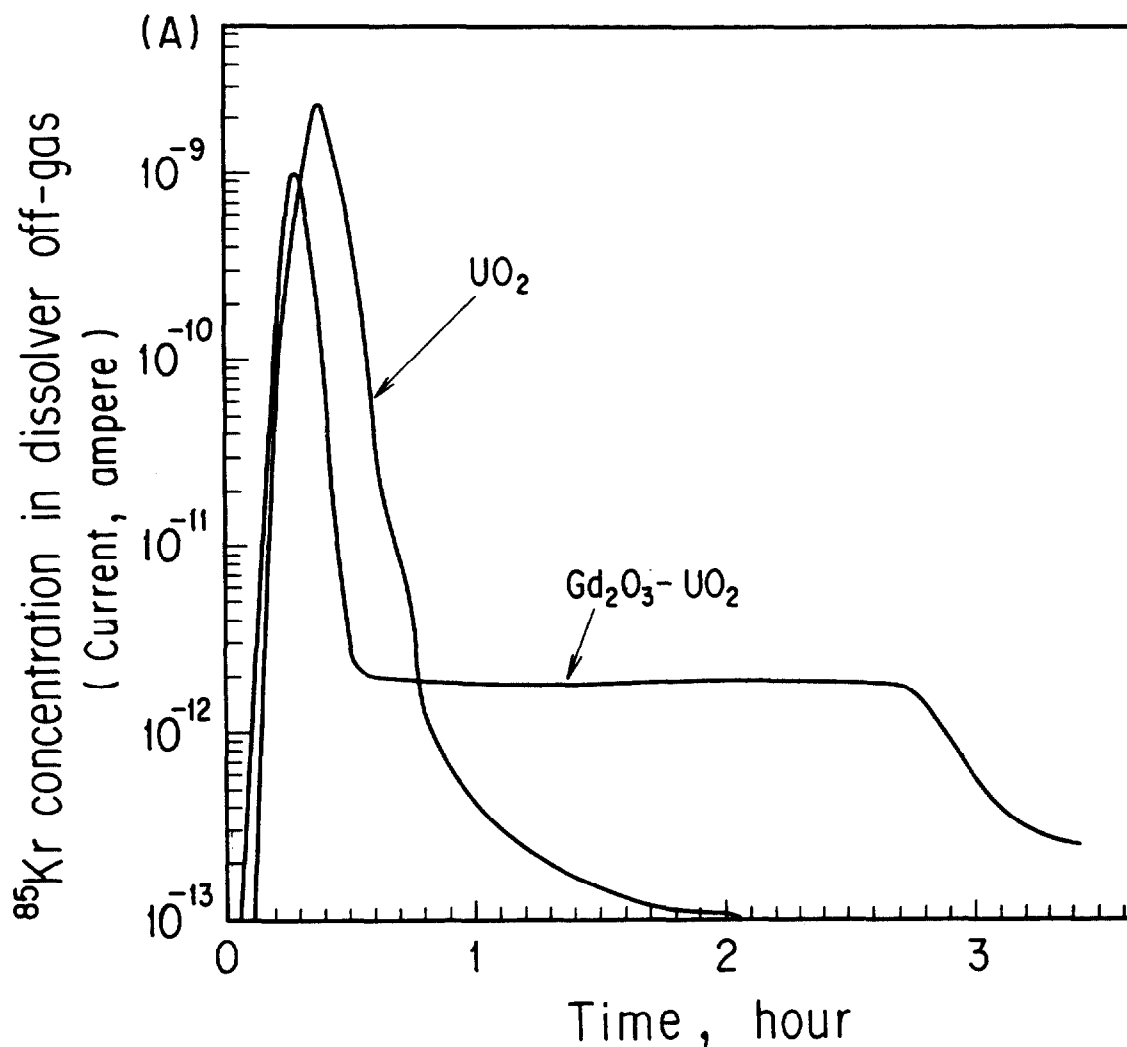


Figure 1 Two types of ^{85}Kr concentrations in dissolver off-gas during the dissolution of spent fuel specimens (approximately 3 g each).

Table 1 Details for the examples shown in Fig.1

Type of sample (No.)	Weight (g)	Burnup* (GWd/t)	Iodine quantity remaining in solution (%)**	Ratio of total iodine quantity to ORIGEN (%)***
UO_2 (89G09)	1.769	39.0	<0.1	85.2
$\text{Gd}_2\text{O}_3 - \text{UO}_2$ (89G06)	2.140	25.3	4.5	62.1

* The iodine quantities in the UO_2 and $\text{Gd}_2\text{O}_3 - \text{UO}_2$ samples, calculated from the ORIGEN-2 code, are 1400 and 860 Bq/g-U₀, respectively.

** Ratio of iodine quantity in the solution to total iodine quantity.

*** Ratio of the total iodine quantity to that calculated by the ORIGEN-2 code.

rate. Thus, the amount of iodine in solution was thought to be associated with the amount of NOx produced per unit time. Next, the relation between NOx concentration and the remaining quantity of iodine was examined using simulated spent-fuel solution.

2. Influence of NOx concentration on the quantity of colloidal iodine

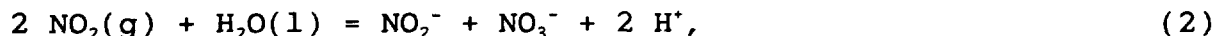
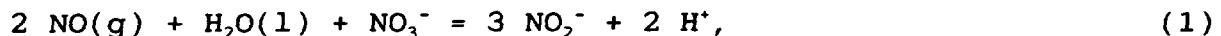
Figure 2 shows the quantities of iodine species remaining 30 min, and 2 h after the addition of 0.42 mg of iodine (I^-) to 30 ml of simulated spent-fuel solution at 100°C. NO_2 (24%) in N_2 (2.6×10^{-4} mol- NO_2 /min) was bubbled through the solution. The main iodine species was colloidal iodine, which only slightly decreased with time. The amount of iodate (IO_3^-) was small, as predicted from a thermochemical calculation.⁽⁸⁾

Figure 3 shows the dependence of colloidal iodine quantity on NOx concentration in 100°C fuel solutions 30 min after the addition of iodine (0.42 mg- I^-). Both NO and NO_2 suppress the formation of colloidal iodine in proportion to their concentration up to about 10%. However, the effect from NO was greater than from NO_2 and the data for NO_2 concentration varied considerably.

The weights of the spent PWR-fuel specimens (Table 1) and their dissolution rates (Fig. 1) were used to calculate the amounts of NO generated during dissolution. The average concentrations in dissolver off-gas are shown in Fig. 3. These averages are in the region where the colloidal iodine quantity is very sensitive to a change in NO concentration, a small change in NO concentration results in a considerable change in the quantity of colloidal iodine. Calculations suggested that the quantity of colloidal iodine would be greater for Gd_2O_3 - UO_2 than UO_2 shown in Fig. 1. This is consistent with the experimental results shown in Table 1. The quantity of iodine remaining in fuel solutions is less for spent-fuels with higher rates of dissolution than for fuel with lower rates, despite the amount of burnup.

3. Chemical reactions of iodine (I^-) during dissolution

Introducing (bubbling) NOx into nitric acid solution produces nitrous acid (HNO_2) in the solution according to the following reactions:



Combining (1) and (2):

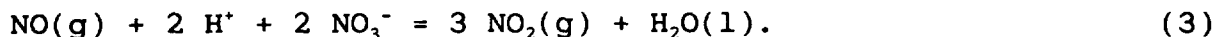


Figure 4 shows the absorption spectrum of HNO_2 detected in 3.5 M HNO_3 bubbled with an NO- N_2 flow at 100°C. This implies the influence of NOx on colloidal iodine quantity is ascribable to the influence of the nitrous acid formed. Iodine in spent fuel, postulated to be in the form of CsI, most probably is subjected to the following three reactions during dissolution:

(a) Oxidation into I_2 by nitric acid:

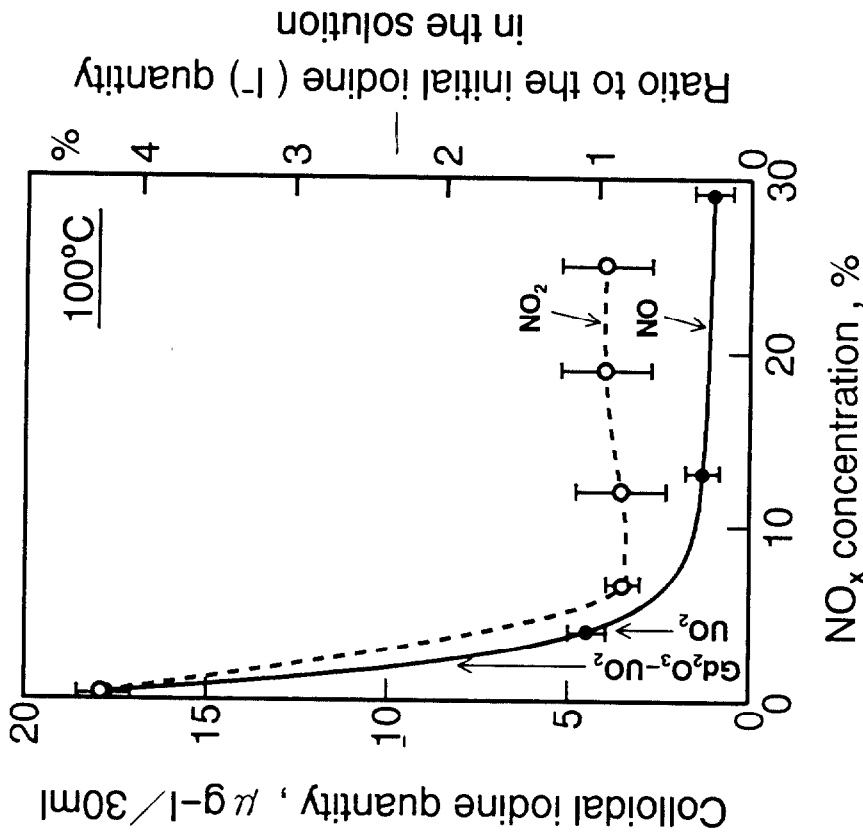


Figure 3. Dependence of colloidal iodine quantity on NOx concentration in simulated spent-fuel solutions at 100°C. Iodine (0.42 mg-I⁻¹) was added to the solutions having NOx in various concentrations. The iodine species in the solutions were measured 30 min after the addition of the iodine. UO₂ and Gd₂O₃-UO₂ denote the calculated values of the average concentration of NO in the dissolution of the two spent-fuel specimens described in Fig. 1 and Table 1.

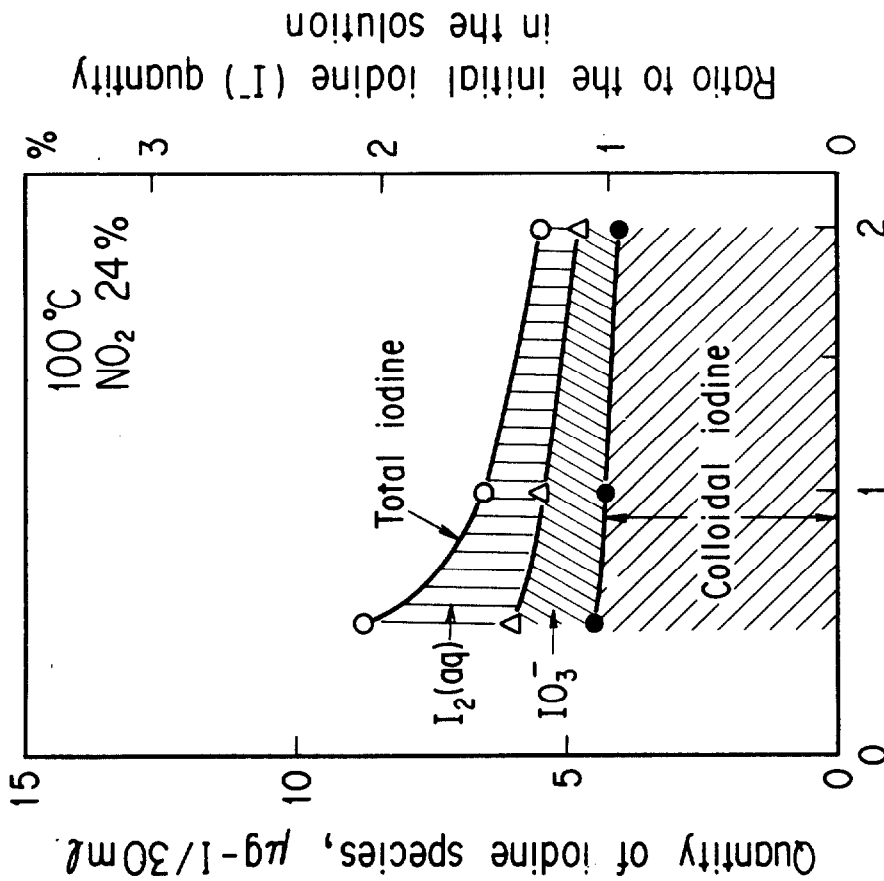


Figure 2. Iodine species produced by addition of iodine (I⁻) into the simulated spent-fuel solution and their change in quantity with time. 30 ml of simulated spent-fuel solution was heated to 100°C, 24% NO₂ in N₂ was bubbled through the solution, and then (5 min later) iodine (0.42 mg-I⁻¹) was added. 0.5 ml samples of the solution were analyzed 30 min, 1 h, and 2 h after the addition of the iodine.

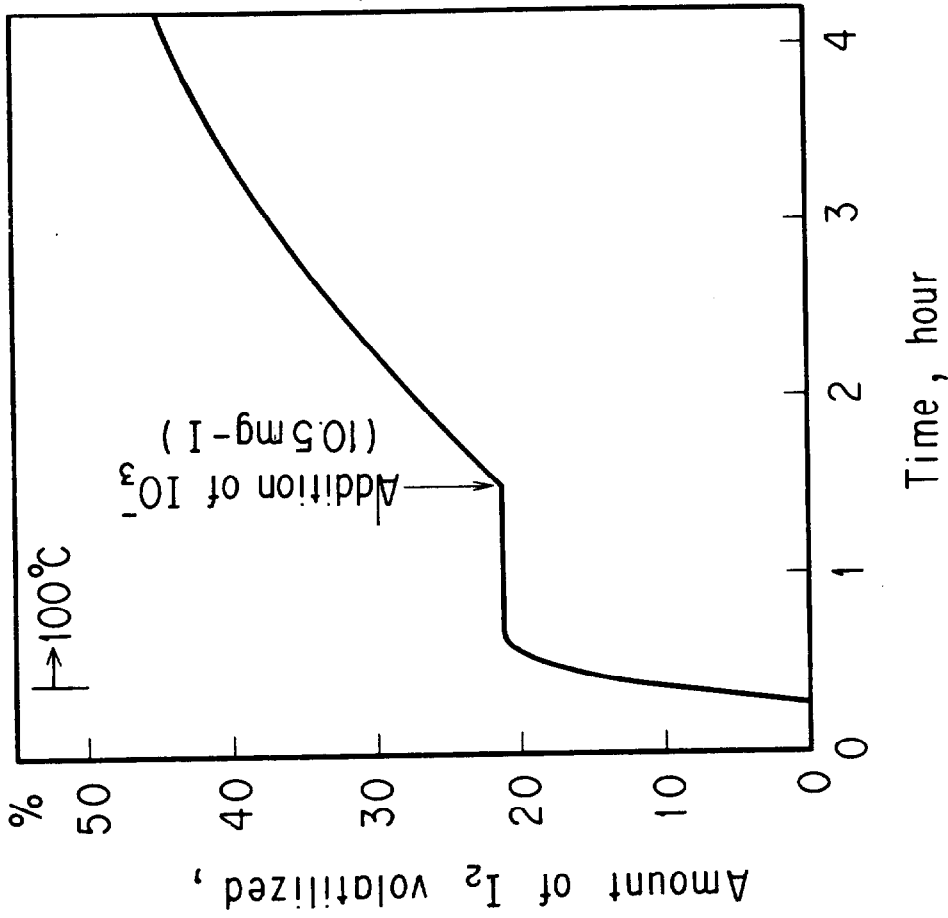


Figure 5. Effect of iodate (IO_3^-) on decomposition of silver iodide into I_2 in 3.4 M HNO_3 at 100°C . Heating of 30 ml of 3.4 M HNO_3 containing 19.3 mg of AgI volatilized a small amount of iodine (I_2). Addition of more iodate (10.5 mg-I) into the solution at 100°C caused a second volatilization of I_2 .

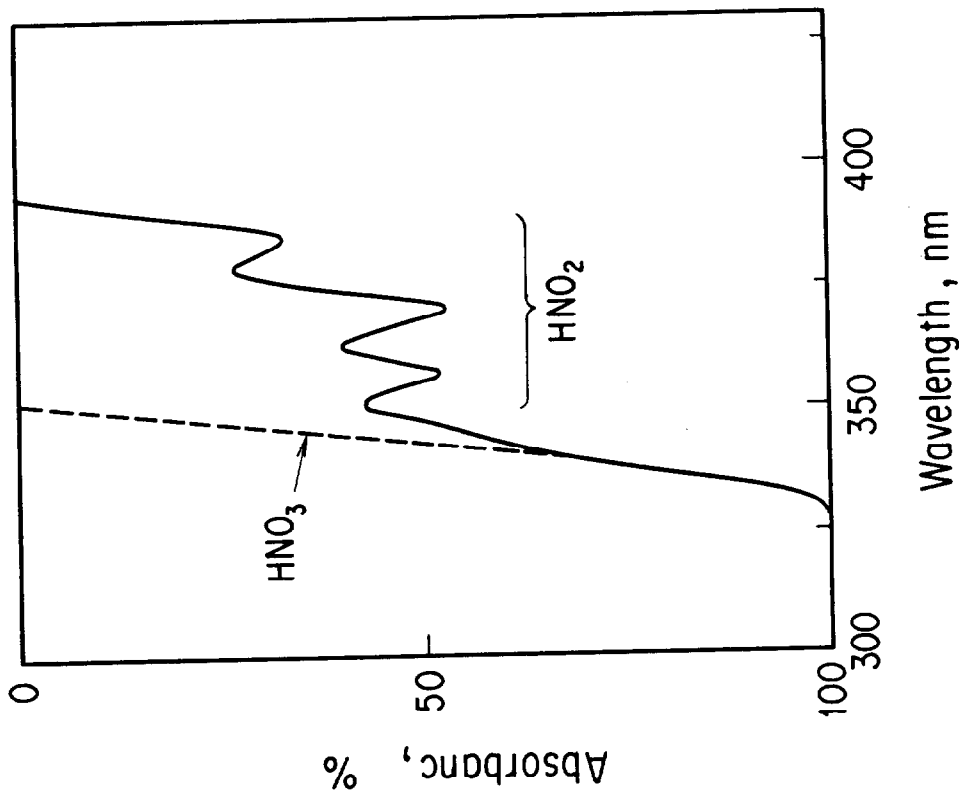
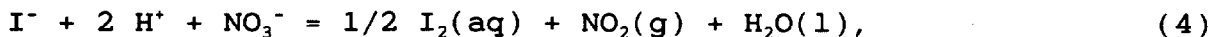
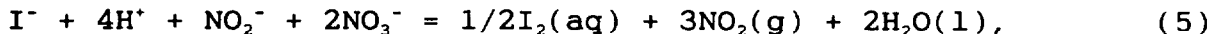


Figure 4. Absorption spectrum of HNO_2 produced when passing NO through 3.5 M HNO_3 at 100°C . While 14% NO in N_2 was bubbled into the solution, a 2 ml sample of the solution was cooled rapidly to 20°C for this measurement.

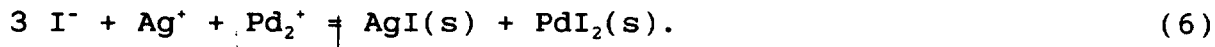
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(b) Oxidation into I_2 by nitrous acid formed from NO_x :



(c) Formation of colloidal iodine:



Of these, reaction (5) competes with reaction (6) in the presence of NO_x and controls the quantity of colloidal iodine produced during dissolution. At 100°C , the equilibrium of reaction (3) lies so far to the right, that is, 80% of NO_x is NO_2 and 20% is NO .⁽⁸⁾ Nitrous acid needed in reaction (5) is likely to be provided by reaction (1). Therefore, the colloidal iodine quantity is suppressed more by NO than by NO_2 , as already shown in Fig. 3.

4. Expulsion of iodine from spent-fuel solutions

Colloidal iodine is unstable immediately after its formation and is decomposed in a hot nitric acid solution by the following reaction:



Two factors retard this decomposition, the presence of NO_x and the aging of the colloidal iodine. While suppressing the formation of colloidal iodine, NO_x interferes with the decomposition of the already-formed colloid by reversing reaction (7).

The aging of the remaining colloidal iodine proceeds concurrently with its decomposition. To decompose the aged colloid, the addition of an excess amount of iodate (IO_3^-) is effective, as Figure 5 shows.⁽⁶⁾ In this procedure, a precipitate of AgI was prepared from potassium iodide solution (which had been labeled with ^{131}I) and silver nitrate solution. The precipitate was dried and the solid AgI (19.3 mg) was heated in 3.4 M HNO_3 . A small amount of I_2 was observed to volatilize at the beginning of heating; however, further volatilization needed the addition of iodate.

Effects of these two factors on the decomposition of colloidal iodine are shown in Figure 6 together with the experimental conditions. NO_x retards the decomposition (curves 2 and 3). Effect of iodate is more prominent when it was added at the later part of the process (curve 4) than when it was added at the beginning of the process (curve 1). This is because the aging proceeds rapidly with time. Based on these results, the following two-step process for the expulsion of iodine remaining in spent-fuel solutions is proposed:

Step One - Heat the fuel solution without supplying NO_x to decompose the colloidal iodine. When aging of colloidal iodine has proceeded after dissolution, an excess amount of iodate should be added.

Step Two - Supply (bubble) NO_x through the solution while heating to reduce the iodate ($^{129}\text{IO}_3^-$) to volatile I_2 .

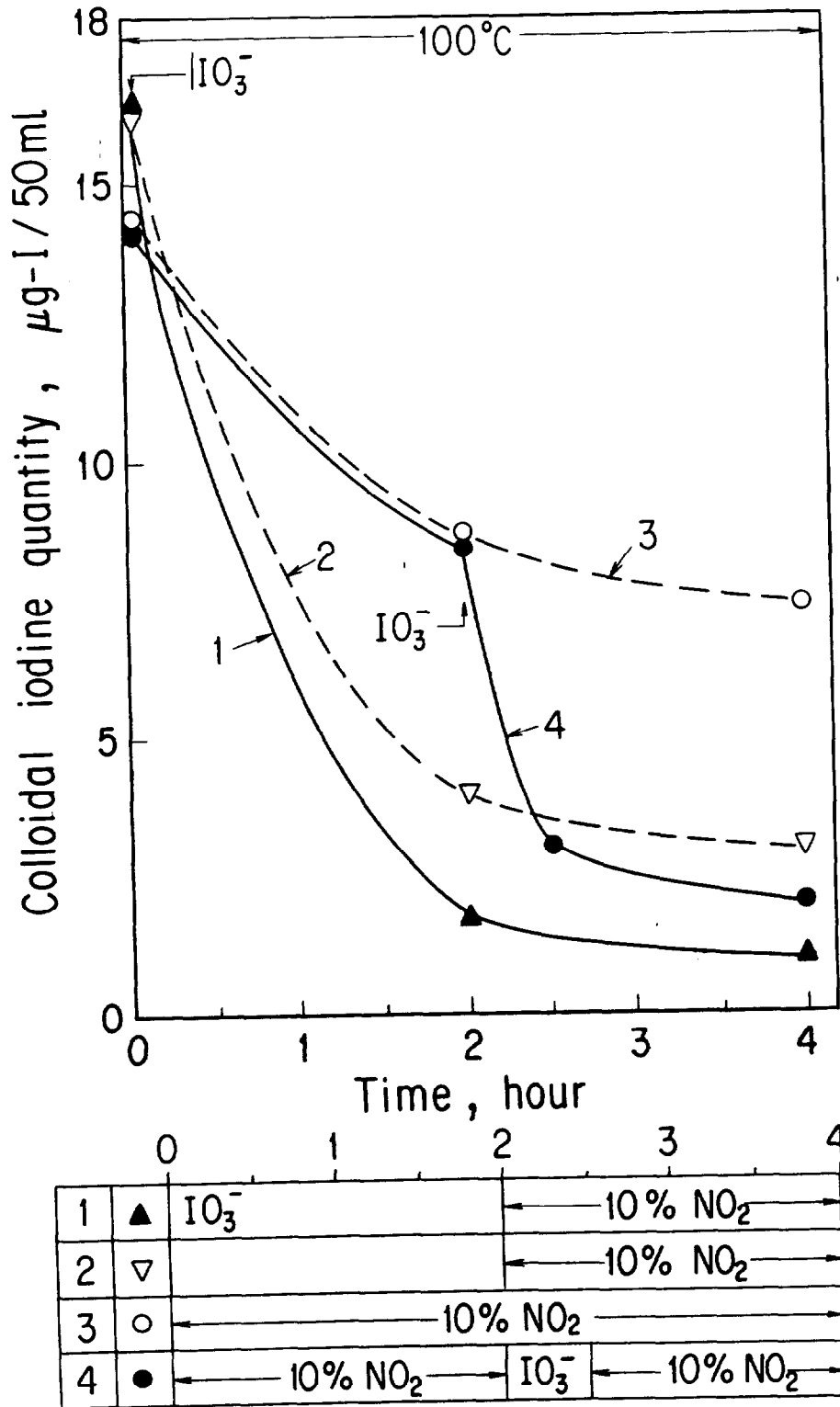


Figure 6. Effects of NO_x and iodate on decomposition of colloidal iodine. The simulated spent-fuel solution (50 mfℓ each) containing colloidal iodine was heated at 100°C with and without a NO₂ supply. An amount of iodate (2 mg-I) was added at the beginning of heating for the run marked 1 and 2 h later for the run marked 4.

Table 2 Comparison of conventional NO_x sparging method with the new process for expulsion of iodine from solution

Operation to expel iodine	Spent fuel specimens dissolved			Iodine quantity in the solution	
	Type (No)	Burnup (GWd/t)	Weight (g)	Before the expulsion process, Bq (%)*	After the expulsion process, Bq (%)**
Supply of NO (30% in N ₂) at 100°C for 2 h. (The conventional method)	UO ₂ (89G08)	30.8	1.302	23.6 (3.3)	7.9 (33.3)
	UO ₂ (87H02)	39.7	2.250	11.7 (1.2)	3.2 (27.4)
	G ₂ O ₃ - UO ₂ (89G01)	21.9	1.659	34.8 (6.6)	15.9 (45.7)
	G ₂ O ₃ - UO ₂ (89G05)	21.2	1.382	63.9 (9.7)	28.2 (44.1)
Addition of IO ₃ ⁻ (1 mg - I/30mL) and heating at 100°C for 2 h without NO _x supply (The new process)	UO ₂ (89G10)	39.3	1.746	9.6 (1.2)	N.D*** (0)
	UO ₂ (87C05)	~ 32.1	2.008	2.1 (0.3)	N.D (0)
	G ₂ O ₃ - UO ₂ (89G06)	25.3	2.140	24.0 (4.5)	N.D (0)

* Ratio of the initial iodine quantity in the solution to the total iodine quantity collected during dissolution and expulsion processes

** Ratio of the final iodine quantity to the initial iodine quantity in the solution

*** Not detected

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The efficiency of this process is compared with that of the conventional method (NO_x sparging) for spent PWR-fuel specimen solutions (30 ml each) in Table 2.⁽³⁾ After two hours of NO_x sparging (30% NO in N₂) at 100°C, 27 to 46% of the initial iodine quantity remained in solution. However, two hours (without NO_x supply) at 100°C after addition of iodate (1 mg-I⁻) removed all iodine from solution. For both ordinary UO₂ and Gd₂O₃-UO₂ specimens, the new process was much more effective. Here, Step Two was not necessary. However, there is a possibility that a small amount of iodate may remain in solution as shown in Fig. 2 and that a small portion of I₂ may be oxidized to iodate during Step One. So, NO_x feeding, viz. Step Two, is desirable for more effective expulsion. These findings show that the main iodine species remaining in actual spent-fuel solutions is colloidal. Thermochemical calculations have determined that the formation of iodate during dissolution was suppressed because of the generated NO_x.⁽⁸⁾

In our current work, the expulsion was performed on spent-fuel solution previously separated from insoluble residue. In actual reprocessing, the expulsion would be carried out in the presence of insoluble residue. Then, it is expected that part of iodine deposited on the insoluble residue will be expelled by the new expulsion process.⁽⁹⁾

Boukis and Henrich attributed the residual iodine to nonvolatile organic iodine that originated from organic impurities in nitric acid.⁽⁴⁾ They noticed that recycled acid that had not been carefully purified increased the residual iodine quantity. In our case, however, colloidal iodine was observed only in simulated spent-fuel solutions containing Ag⁺ and Pd₂⁺. When iodide (I⁻) was added into UO₂(NO₃)₂-HNO₃ and HNO₃ solutions, the amount of colloidal iodine was negligibly small. Thus, we understand the residual iodine cannot be nonvolatile organic iodine arising from organic impurities in nitric acid.

IV. Conclusion

1. In dissolution of spent nuclear fuels, iodine (I⁻) from CsI in the fuels is subjected to the following three reactions:

- (a) Oxidation into I₂ by nitric acid,
- (b) Oxidation into I₂ by nitrous acid (HNO₂) arising from NO_x generated in the dissolution, and
- (c) Formation of the colloid of insoluble iodides such as AgI and PdI₂. Depending upon the NO_x concentration, NO_x suppresses formation of colloidal iodine.

2. The main iodine species in spent-fuel solutions is colloidal iodine.

3. The following two-step process is more effective than the conventional process (NO_x sparging) for expulsion of the residual iodine from the fuel solution:

Step One - Heat the fuel solution without NO_x supply. When aged colloidal iodine is present after the dissolution step, an excess amount of iodate should be added into the solution.

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Step Two - Supply NO_x to the fuel solution while heating.

Acknowledgment

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DISCUSSION

WREN: Have you looked at the effect of the oxidation state of UO_2 (e.g. UO_{2+x}) on the rate and behavior of iodine repulsion? Depending on the oxidation state of UO_2 , I think the oxidation state of iodine and the release rate of iodine from fuel would change. Another question: what is the effect of radiation on AgI stability?

SAKURAI: The oxidation state is known to influence the dissolution rate of fuels. But I have not considered its effect on behavior of iodine. Your comment is very useful. Silver iodide was stable against Co-60 irradiation up to 10^3 C/kg.

KOVACH, L.: Have you considered that in this type of experiment, the actual sequence of dissolution is slightly different than in a continuous desorber in a fuel processing plant? Have you considered the differences in heat-up rates and contact temperatures in your experiment versus an actual reprocessing plant application? Do you consider that the experimental sequence described matches the thermal sequence in an actual reprocessing plant?

SAKURAI: I know the difference. Our experiment was on a very small scale. In the near future we have to do the same experiments on a larger scale, for certain actual data points. However, the behavior of iodine that I reported here is thermochemically reasonable; hence, it is expected to hold for actual reprocessing plants. The process we proposed can be incorporated with a reprocessing plant that adopts the continuous dissolution of spent nuclear-fuels. It is desirable to confirm its efficiency on a much larger scale.

KOVACH, L.: In these experiments you started out by placing the fuel into your container and then heating it up, which is slightly different from the actual desorber in a reprocessing plant.

SAKURAI: In actual reprocessing plants, the fuels are put into hot nitric acid solutions. The dissolution rate will be faster than in these experiments.

EVANS: Could you give us some more information on how you separated the iodide, iodate, and the colloidal forms of iodine using chloroform?

SAKURAI: In our analytical scheme, colloidal iodine is the final species remaining in the aqueous solution after ionic species, as iodide and iodate, were extracted in the CCl_4 phase.

Details of the analytical scheme are described in the literature cited in the text (Ref. 7).

**THE DEVELOPMENT AND DESIGN OF THE OFF-GAS TREATMENT SYSTEM FOR
THE THERMAL OXIDE REPROCESSING PLANT (THORP) AT SELLAFIELD**

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Abstract

British Nuclear Fuels plc (BNFL) completed construction of its Thermal Oxide Reprocessing Plant (THORP) at Sellafield in 1992, at a cost of £1,850M. After Government and Regulatory approval, active commissioning was initiated on 17 January 1994.

From the outset, the need to protect the workforce, the public and the environment in general from the plant's discharges was clearly recognised. The design intent was to limit radiation exposure of members of the general public to "As Low as Reasonably Practicable" (ALARP). Furthermore no member of the most highly exposed (critical) group should receive an annual dose exceeding 50 microsieverts from either the aerial or marine discharge routes.

This paper describes how the design intent has been met with respect to aerial discharges. It outlines the development programme which was undertaken to address the more demanding aspects of the performance specification. This ranged from small-scale experiments with irradiated fuel to inactive pilot plant trials and full-scale plant measurements. The resulting information was then used, with the aid of mathematical models, in the design of an off-gas treatment system which could achieve the overall goal.

The principal species requiring treatment in the THORP off-gas system are iodine-129, carbon-14, nitrogen oxides (NO_x), fuel dust particles and aerosols containing plutonium or mixed fission products. The paper describes the combination of abatement equipment used in different parts of the plant, including counter-current absorption columns, electrostatic precipitators, dehumidifiers and High Efficiency Particulate Air (HEPA) filters. Because a number of separate off-gas streams are combined before discharge, special depression control systems were developed which have already proved successful during plant commissioning.

BNFL is confident that the detailed attention given to the development and design phases of the THORP off-gas system will ensure good performance when the plant moves into fully radioactive operation.

I - Introduction

Brief History

THORP is the third reprocessing plant to be constructed on BNFL's Sellafield site in Cumbria, UK. The plant is designed to reprocess irradiated fuel from Advanced Gas-Cooled Reactors (AGR) in the UK and from Light Water Reactors (LWR) in Europe and Japan: virtually all of its first 10 years operation are committed with contracts for 7000t(U).

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Conceptual design of the plant started in 1974, supported by construction and operation of a number of major development facilities during the later 1970's and early 1980's. Design of the plant was delayed by the Government's decision to hold a public inquiry (the Windscale Inquiry) in 1977. Following the successful outcome of the inquiry, design recommenced in 1983, leading to the start of civil construction in 1984 and eventual handover of the completed plant in 1992. Plant commissioning then proceeded but the progression to active commissioning, planned for December 1992, was delayed by a protracted public consultation exercise to satisfy recent environmental legislation. Government and Regulatory approval to proceed was finally given, leading to the commencement of active commissioning on 17 January 1994.

Design Intent

All BNFL's operations on the Sellafield site are strictly controlled by Government Authorising Bodies. For the control of discharges to the environment, the relevant bodies are Her Majesty's Inspectorate of Pollution (HMIP) and the Ministry of Agriculture, Fisheries and Food (MAFF). Certificates of Authorisation issued by the Departments impose strict conditions on the discharge and disposal of radioactive waste. They also require BNFL to carry out detailed environmental radioactivity monitoring programmes (in addition to their own independent measurements) and to use "Best Practicable Means" to further limit the radioactivity in the waste discharged.

BNFL's strategy for the management of aerial and marine radioactive effluents arising from THORP operations were first formally stated at the Windscale Inquiry in 1977. In summary the design intent was that:

- (a) radiation exposure of members of the general public, arising from discharges from THORP and associated facilities, should be "As Low As is Reasonably Practicable" (ALARP);
- (b) in any case, no member of the most highly exposed (critical) group should receive an annual committed effective dose equivalent (CEDE) in excess of $50\mu\text{Sv}$ from either aerial or marine discharge routes.

In the context of exposure to the general public, it is important to consider both:

- (a) individual risk, as measured by doses to members of the critical group, and
- (b) societal risk, as measured by the collective dose to large populations over a long time period.

In addition to dose uptake constraints, HMIP has more recently set an Aerial Discharge Authorisation for THORP which limits the quantity of specific radionuclides which can be released from the THORP stack on a daily, quarterly or annual basis. The annual discharge limits for the most significant radionuclides are given in Table 1.

Scope of Paper

This paper describes how the design intent on aerial discharges has been met. It examines the different sources of off-gas arisings from the THORP process and describes how the different types of stream have been segregated for treatment prior to extraction and discharge from a common 125m stack. The development work associated with some of the key process equipment is described and key design features of the equipment are covered, including depression control in such a complex system. Finally the predicted discharges from the plant are compared with the latest Discharge Authorisation to illustrate how well the plant design is expected to meet its objectives.

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Table 1 - Comparison of Predicted THORP Discharges with Discharge Authorisation

Radionuclide	THORP Discharges (TBq/yr)	THORP Downstream Plant Discharges (TBq/yr)	THORP ⁽¹⁾ Total Discharges (TBq/yr)	THORP Authorisation (TBq/yr)
H-3	21.6	0.0007	21.6	43
C-14	0.434	~0	0.434	0.87
Kr-85	369,000	6.61	369,007	470,000
Sr-90	0.004	0.0036	0.0076	0.0078
Ru-106	0.0355	0.0016	0.0371	0.05
I-129	0.0218	0.0031	0.0249	0.044
Cs-137	0.0055	0.005	0.0105	0.011
Pu(Alpha)	0.00027	~0	0.00027	0.0005
Total Alpha	0.00048	~0	0.00048	0.001
Total Beta (β5)	0.152	0.017	0.169	0.28

Critical Group dose ⁽¹⁾ = 22μSv/yr

Target dose = 50μSv/yr

(1) Based on 1200t(U)/yr of reference fuel

II Gaseous Arisings

THORP is an integrated reprocessing plant with all the major process steps being carried out in a single building (See Fig 1). Only where use could be made of waste and effluent treatment facilities serving existing process plants on the Sellafield site are certain operations performed outside the THORP building. The THORP process breaks down principally into a shear/leach "Head End" section with clarification of the dissolver solution, followed by chemical separation of the uranium, plutonium and fission products by solvent extraction in pulsed column contactors. The uranium and plutonium products are purified by further solvent extraction prior to conversion to solid forms suitable for storage or return to customers.

Within the plant as a whole, a variety of different off-gases arise.

Dissolver Off-gas

Leaching of the sheared fuel in boiling nitric acid releases virtually all the volatile components of the irradiated fuel assemblies, principally I-129, C-14 and Kr-85. Also Nitrogen oxides (NO_x) are generated by dissolution of the fuel. The dissolver off-gas (DOG) stream consists of the ventilation air from the shear machine and the off-gases from each of three dissolvers, amounting to a flow of about 400m³/hour. The stream also contains very fine particles of fuel dust which are not captured in the dissolver and, in total, represents by far the biggest off-gas challenge in THORP.

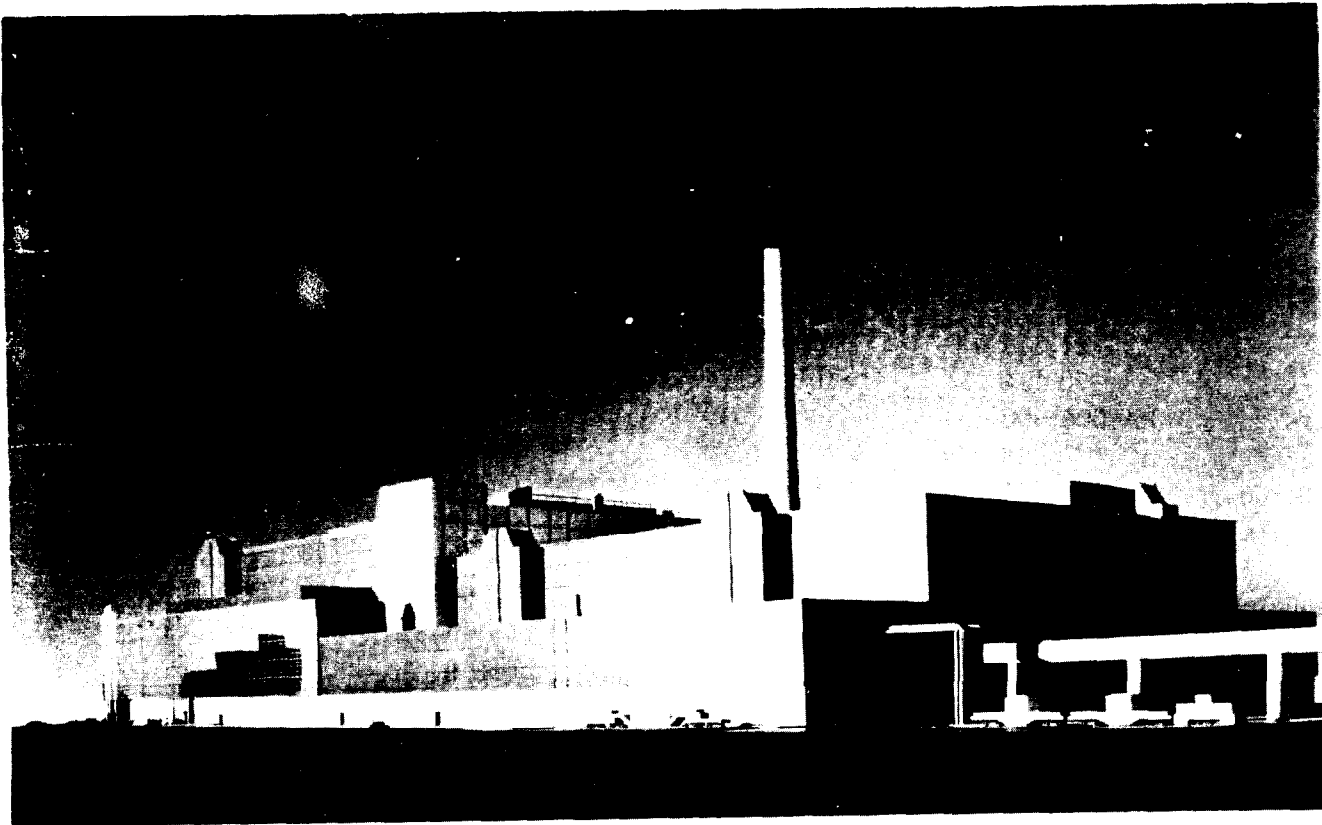


Figure 1 THORP building

Central Off-gas

Apart from the dissolvers, most of the other vessels and process equipment within the Head End and Chemical Separation Plant are vented via a separate Central Off-gas (COG) system. This has to accept a large number of streams with widely differing flows and compositions.

The most environmentally significant component of the COG arisings is I-129. Although the vast majority is volatilised into the DOG system, any residual amount is assumed to be released from downstream vessels into the COG system. In addition, aerosols created in the chemical treatment and liquor transfer processes throughout the plant carry particles of non-volatile actinides and fission products into the ventilation stream. The nuclides that contribute significantly to the aerial activity levels are Ru-106, Pu, Sr-90 and Cs-137.

There are certain non-active arisings which have to be considered in the design of the COG system. The only one subject to regulatory discharge limits is NO_x.

Cell Ventilation

THORP is designed on the principle of cascading depressions between areas to provide barriers against spread of contamination. Cells and caves which contain the most highly active processes in the plant are therefore maintained under a depression with reference to the adjoining access areas. Generally inleakage at cell depression is adequate to provide the air flow required in a cell with little or no heat emitting equipment. In cells with large heat sources, additional air is

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provided to dissipate the heat by purpose-built engineered inlets comprising HEPA filters and control/fire dampers.

Air extracted from cells and caves exhibits the same distribution of radionuclides (footprint) as is present in the process equipment in the cell. Arisings from mechanical operations of fuel shearing in head end caves has been assessed on empirical data from similar operations on other plants. On cells where operations should be clean under normal operating conditions (washdown provisions are installed to clean-up spillages and leaks), the arisings have been based on potential re-suspension of liquors from sprays or pools on the bunded floors.

Building Ventilation

Building ventilation and heat systems provide a comfortable working environment in 'normal' and 'limited' access areas of the plant.

Normally accessible (unrestricted access) areas, despite having no definitive arisings (except under abnormal circumstances), are allocated a mean airborne contamination which, if inhaled over a 2000 hour year, would result in 1% of the whole body dose target being received by inhalation.

Limited (restricted) access areas normally have very low arisings but have the potential for activity being present for short periods or in abnormal circumstances. Such areas are allocated a mean airborne contamination of ten times that allocated to the normal access areas. During such circumstances personnel would wear respiratory protection. In each instance the nuclides present are in proportion to the 'footprint' of the active material being processed.

Total Ventilation System

A schematic diagram showing the inter-relationship of the various components of the THORP ventilation system is given in Figure 2. It illustrates that main ventilation streams are kept separate until they enter the 125m stack from which they are discharged.

III Flowsheet and Equipment Development

Dissolver Off-gas

The prime task of the DOG system is to remove nitrogen oxides generated by the dissolution of the UO₂ fuel, together with the major volatile radioactive species released as the fuel is dissolved. The DOG challenge is illustrated in Table 2, together with the flowsheeted Decontamination Factors (DFs) for each item of equipment.

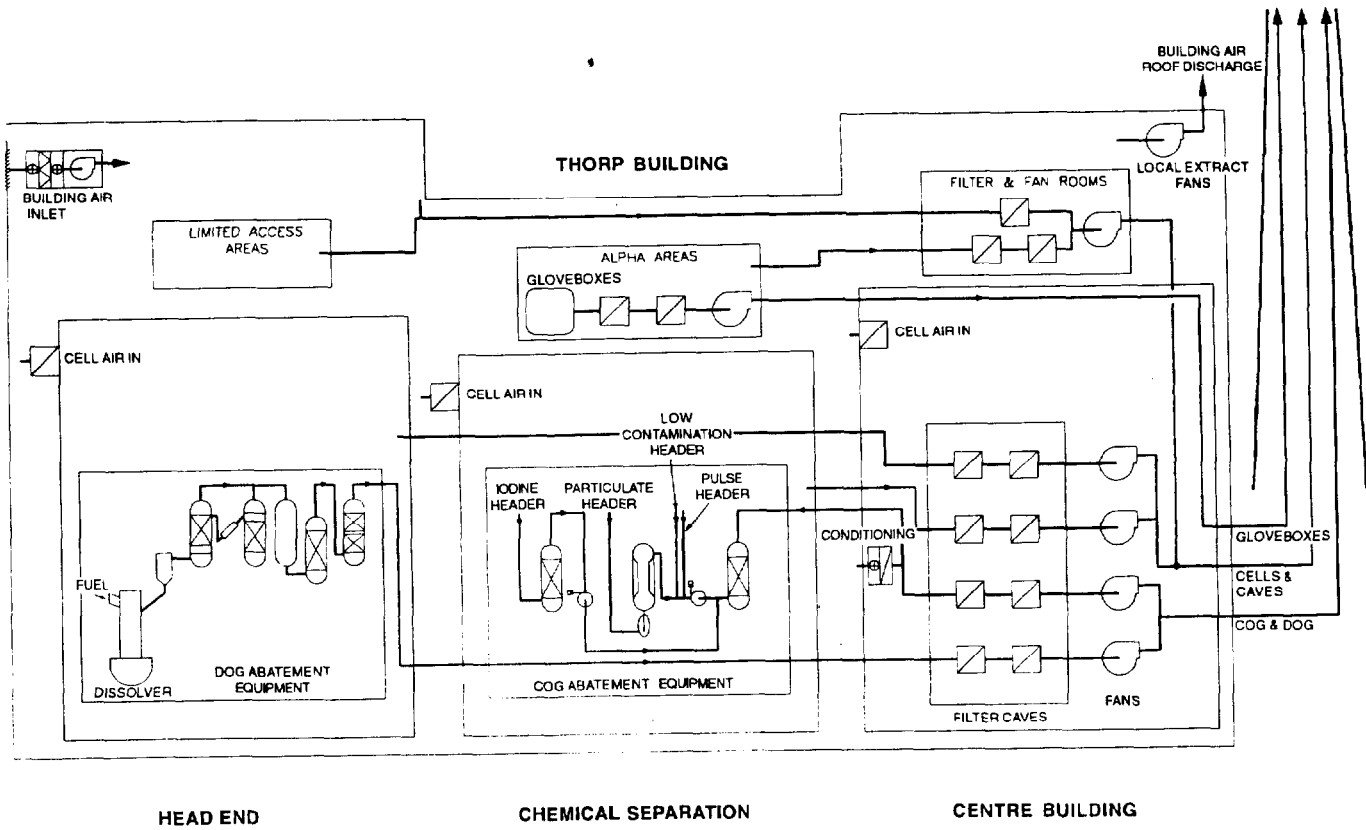


Figure 2 Schematic of THORP active ventilation systems

Table 2 DOG System Performance

Radionuclide or species	Arising ⁽¹⁾ (TBq/yr)	Flowsheet Decontamination Factor (DF)				
		Condenser	Acid Scrubber	Caustic Scrubber	Weak Acid Scrubber	HEPA
H-3	97.2	1	3	1.5	1	1
C-14	28.9	1	1	70	1	1
Kr-85	3.69E5	1	1	1	1	1
Ru-106(gas)	37.5*		20	100	1	1
Ru-106 (solid)	37.5*		1	1	1	10E4
I-129	1.41	1	1.05	100	1	1
NOx	8.1E4 m ³	1.5	3	100	1	1
Fuel Dust	2.6E3 kg	25	70	1.2	1.4	10E4

* post condenser

(i) Based on 1200t(U)/yr of reference fuel

Recognizing the need for highly efficient I-129 removal in THORP, the first requirement is to volatilise as much as possible at the dissolver stage. Once converted to organic forms by contact with solvent (TBP/OK) further down the process, iodine capture is much more difficult. Experimental work has demonstrated that the NO_x evolved during dissolution of the fuel is effective in maintaining the I-129 in its volatile molecular form, which renders it easier to remove from the off-gas system.

Treatment of the DOG stream is performed principally by acid and caustic scrubbing in packed columns. The full train of DOG equipment is shown in Fig 3

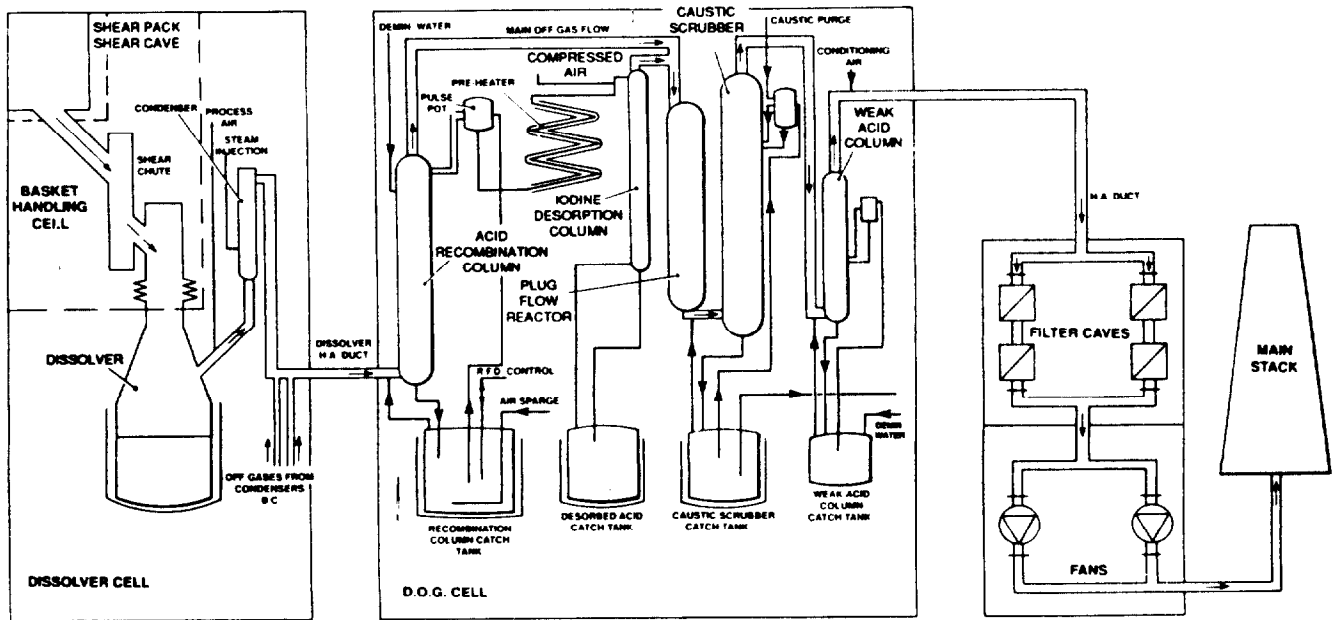


Figure 3 Dissolver off gas (DOG) extract system

The off-gases from each dissolver pass through their own dedicated reflux condenser and are then combined to be fed to the recombined acid column. Here, scrubbing with 6M nitric acid serves to remove the bulk of the oxides of nitrogen and two impingement plates at the base of the column assist removal of the entrained fuel dust.

A small amount of the iodine is also absorbed in the acidic scrubber liquor and this has to be removed before the liquor is fed back into the main process stream. This iodine desorption is achieved by heating a bleed of scrubber liquor and passing it through a small diameter packed column, counter current to a flow of air, which then joins the main off-gas flow carrying the desorbed iodine.

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Following the recombined acid column is a large empty vessel, termed the "noxidiser", which provides a residence time of about two minutes in which the nitric oxide present is substantially oxidised to nitrogen dioxide by the oxygen in the air (which makes up the major proportion of the off-gas flow).

Increasing the proportion of nitrogen dioxide in this way improves the absorption of the nitrogen oxides in the caustic scrubber immediately downstream. The caustic scrubber will achieve a reduction in the nitrogen oxide concentration to below 1000ppm and a reduction in the I-129 and C-14 by factors of 100 and 70 respectively. Following the caustic scrubber the gas stream will be scrubbed with chilled recirculating water to remove entrained caustic soda droplets and dehumidify the gas. Finally the DOG stream undergoes two stages of HEPA filtration for final particulate removal before discharge to atmosphere.

DOG Supporting Development

In view of the dependence of the off-gas system upon aqueous scrubbing, the major facility in the development programme was a pilot scale rig - the dissolver off-gas pilot plant - to enable study of each of the scrubbing processes in the DOG system.

The rig, depicted in Fig 4, consisted of a small packed column, 100 mm diameter, with a packed height of 3m. Equipment was provided to generate a suitable mixture of oxides of nitrogen in air to which gaseous iodine could be added as appropriate. The scrub liquor could either be nitric acid or caustic soda solution and the liquor recirculated continuously through the column or treated in a single pass.

Sampling of the gases by means of heated sample lines enabled gas phase analysis by UV or IR spectrometers for nitrogen oxides and carbon dioxide respectively. Sampling for iodine was achieved by selective absorption on heated beds of silver nitrate impregnated absorbers.

As originally conceived the pilot plant was to have handled iodine traced with I-131 in order to facilitate analysis to the low levels required. This increased significantly the complexity of the rig and would have made experimental work much more unwieldy. However,

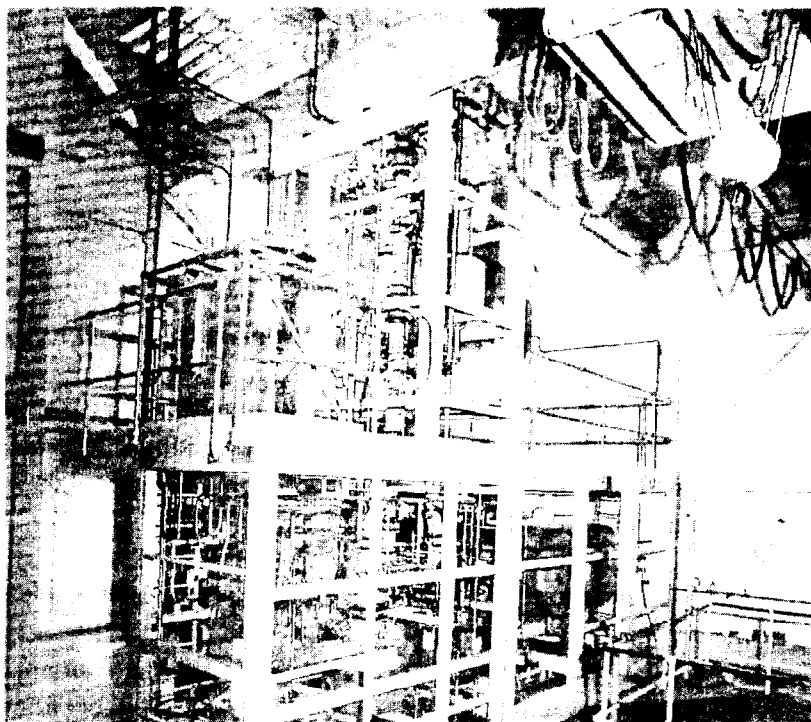


Figure 4 Dissolver off gas pilot plant

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satisfactory development of ion selective electrode techniques sensitive to iodine concentrations as low as 1×10^{-7} M removed the need for trace active work and considerably simplified the experimental programme. The outstanding analytical difficulty was the determination of inactive iodine on the silver nitrate absorbers used for sampling the gas streams but this was readily overcome by the use of neutron activation analysis.

Experimental investigation of acid and alkaline scrubbing of nitrogen oxides was supported by work on computer simulation of the processes in a package developed by BNFL. This package, NOXSIM, was thoroughly validated against the pilot plant experimental results and thus could be used with confidence in the design of the THORP off-gas columns. NOXSIM is discussed further in Section IV.

Apart from the development work on the DOG pilot plant, other supplementary development was undertaken to address specific issues within DOG system. For example, experiments were performed to investigate iodine behaviour during dissolution of irradiated fuel and the subsequent treatment of dissolver off-gases. These investigations were part of the experimental work carried out on the THORP miniature pilot plant, a highly active 1:6500 scale pilot plant built primarily to study solvent extraction flowsheets. The dissolution of irradiated fuel served to show that the I-129 was present as molecular iodine and hence the simulation in the DOG pilot plant was valid.

Carbon-14 behaviour was less of a problem than I-129 since the bulk of it would be present as carbon dioxide and this would mix with the much larger quantities of CO_2 in air. There is abundant information on caustic scrubbing of CO_2 in air but a number of confirmatory experiments were necessary on the DOG pilot plant to ensure that the presence of 1 to 2 per cent NO_x would not affect the CO_2 removal.

Not all the C-14 released from the dissolver is in the form of CO_2 : a small amount is present as CO. Measurements performed during dissolution of irradiated fuel on the THORP miniature pilot plant confirmed literature information that the CO component was less than 1% and would not compromise the ability of the caustic scrubber to reduce C-14 levels by a factor of 70.

Measurement of CO_2 absorption has also proved important in the detection of potential maloperation. Experiments with the DOG pilot plant have shown that monitoring for increased CO_2 in the off-gases downstream of the scrubber provides adequate warning of approaching loss of alkalinity.

One issue raised well into the design phase of the THORP DOG system was a suggestion that troublesome quantities of volatile Ru-106 might penetrate into and even through the off-gas system. At first this question was explored by means of dissolution of irradiated fuel in a highly active cell and then in greater depth using trace active laboratory experiments. These two pieces of work were sufficient to indicate that only relatively small amounts of volatile Ru-106 would be generated and that the off-gas system as designed would ensure adequate removal. Subsequent studies with irradiated fuel dissolution in the THORP miniature pilot plant have indicated that the removal efficiency in the THORP dissolver off-gas system will be ten times greater than initially estimated and thus the impact of volatile Ru-106 has proved to be of little significance.

Central Off-Gas

As already described, the COG system serves most of the vessels and equipment downstream of the dissolvers. The full train of COG equipment is shown in Fig 5. The off-gas arisings from different parts of the plant or from different types of equipment are combined into a series of "headers", which feed into the COG system at an appropriate point according to the type of decontamination required. The arising of key components in the COG feed is shown in Table 3, together with the flowsheeted DFs for each item of equipment.

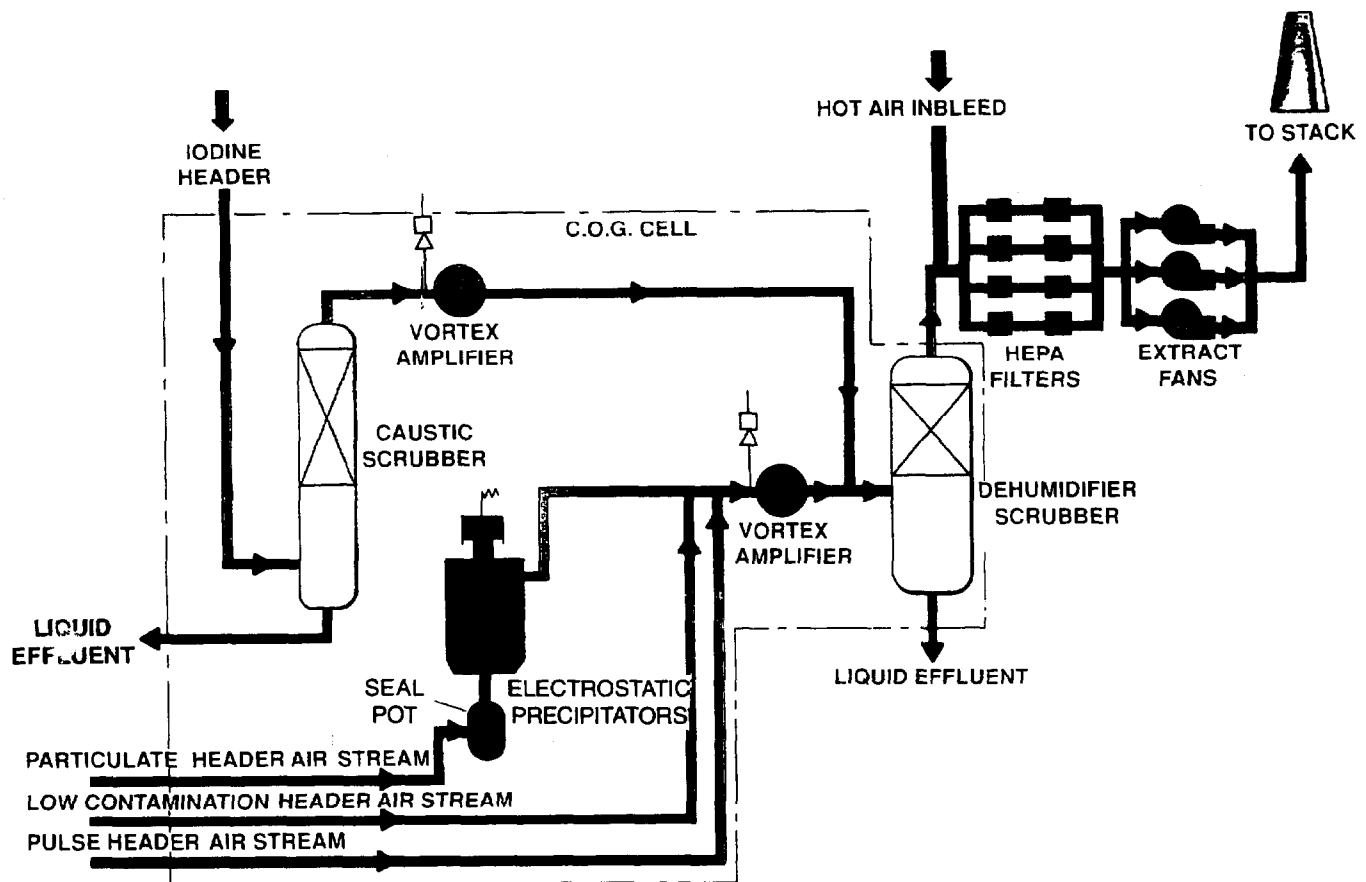


Figure 5 Central off gas (COG) extract system

First in the COG system is a 1.8m diameter caustic scrubber which serves the iodine header. This is primarily for iodine removal though it removes NO_x and some particulate as well. A conservative Decontamination Factor (DF) of 2 has been assessed for iodine removal because the residual iodine from these downstream operations will be substantially organic. The scrubber performs a secondary function as an iodine trap in the event of accidental neutralisation of iodine-bearing streams in the Low Active Effluent Treatment Plant.

Table 3 COG System Performance

Radionuclide or species	Arising ⁽¹⁾ (TBq/yr)	Flowsheet Decontamination Factor (DF)			
		Caustic Scrubber	ESP	Dehumidifier	HEPA
Sr-90	56.4	10	100	10	10E4
Ru-106(gas)	0.15	1	1	5	1
Ru-106(solid)	14.4	10	100	10	10E4
I-129	0.009	2	1	1	1
Cs-137	79.9	10	100	10	10E4
Pu(alpha)	6.19	10	100	10	10E4
NOx	84.9 m ³	43	1	1.6	1

⁽¹⁾ Based on 1200 t (U)/yr of reference fuel

The next equipment in the train is a pair of 680 m³/hr Electrostatic Precipitators (ESPs) whose purpose is the removal of entrained droplets and aerosols from the particulate header. These devices have proved to be very reliable and effective in other applications in highly active plant at Sellafield and only generate a low volume of liquid waste for treatment. Furthermore, by reducing the load on the HEPA filters at the end of the train, they reduce filter change frequencies and waste disposal costs. However care has to be taken to ensure that any solvent vapour in the feed stream is well below its lower flammability limit because the high voltage across the electrodes represents a potential ignition source.

The dehumidifier scrubber downstream of the ESPs is primarily aimed at removing moisture from the gas stream prior to HEPA filtration. This would cause deterioration of the filter elements, leading to their eventual collapse and hence increased solid waste arisings. In order to prevent this the vent gas has to be cooled below its dew point, using a chiller unit to cool the dehumidifier scrubber liquor.

In addition, the dehumidifier acts as the primary disentrainment device for streams for which treatment in the ESPs is unnecessary. These include the low contamination vent header and the pulse header from the pulsed column drive legs in the highly active and plutonium purification cycles. With a large number of pulse systems operating independently the header could, theoretically, receive a very high flowrate if all the pulse systems discharged simultaneously. A Monte Carlo approach was used to predict the highest realistic flow likely to arise, thereby minimising the degree of over- design.

The final equipment in the train are banks of primary and secondary remote-change HEPA filters, which act as a final polishing step for particulates and as a back-up in the event of equipment maloperation upstream. Hot air is bled into the vent before the filters to ensure that the feed is well above its dew point.

The COG stream is finally discharged from a 125m stack, together with other THORP off-gases.

COG Supporting Development

In comparison with the DOG system, very little specific development work was necessary to support the COG system design. In relation to scrubber design, data generated from the DOG pilot plant were used, with the help of the NOXSIM computer model, to assist design of the COG unit.

One area which did require special attention was the characterization of the aerosols generated by pulsing systems, agitation systems and various liquor transfer devices within the plant. Information on quantity and droplet size distribution was generated by development trials on replica equipment. This work showed that treatment of many of these streams in the ESPs was unnecessary; scrubbing in the dehumidifier gave sufficient decontamination.

Some development was performed on the ESP units during the design phase. Experience on earlier plants and collaboration with the manufacturer enabled a simpler and more compact design to be used on THORP without losing any efficiency. The simplification of the central electrode design within the collection tubes was demonstrated on a test rig.

Glovebox Ventilation

The finishing processes on the purified plutonium stream are largely conducted in glovebox containments. As gloveboxes with their high alpha inventories have to be protected against both overpressure and excessive depression under fault conditions, they are separately vented from the COG system.

The glovebox extracts are fitted with vortex amplifier (VXA) control devices operating under ambient pressure control to provide a controlled normal operating depression with small gas purge flows. VXAs and other fluidic devices are used extensively in THORP because their maintenance-free operation is invaluable in a highly radioactive environment. If a glovebox containment develops a leak or is breached the VXA device automatically opens to provide enhanced containment flow through the breach. These devices have proved highly reliable on both plutonium glovebox and alpha laboratory analytical suites in existing Sellafield facilities.

The glovebox extracts are collected together and pulled through primary and secondary HEPA filters prior to discharge up the 125m stack in a dedicated flue.

Cell and Cave Ventilation

The plant is designed on the principle of segregation of ventilation streams of different activity levels to restrict the spread of contamination and minimise the amount of highly active waste materials.

Cell and cave air is extracted through fully shielded ducting to two active filter caves located in the centre building where the streams are filtered through 2-stages of HEPA filtration prior to discharge through the main stack. Several cells with minimal contamination potential have local manual-bag-change, circular filters, as do cells with predominantly alpha-bearing streams.

To prove the concept of the filter cave, prototype filter modules were constructed to minimise the pressure drop and improve the isolation damper maintenance problems. The grab assembly, which is essential for reliable filter change operations, underwent several revisions which were

extensively tested to ensure the action was positive and reliable over a long period in a hazardous environment.

Building Ventilation

The largest proportion of THORP building is devoted to normally accessible work-areas and interconnecting corridors. The air required for ventilation purposes is supplied filtered at a constant temperature of 19°C in winter. Overall air change rates are inappropriate for use on large plants and would have resulted in an expensive and uneconomic installation. Each ventilated space within the THORP building has had its requirement for fresh air assessed on the need for heat, fume or humidity removal, occupation level and function. This approach has resulted in a smaller, more economic ventilation plant able to meet the large variations in individual room requirements.

To maintain the principles of containment, air is transferred from zones of low contamination potential to zones of higher contamination potential, thus minimising the spread of activity. Air extracted from the various zones is collected in separate dedicated ducting systems. In the case of the building air from beta-gamma areas, this is discharged unfiltered from short ducts terminating above the building parapet height. Air from alpha areas where there is normal access is passed through single stage HEPA filters before discharge from the main stack.

Air from limited access areas is extracted through single-stage HEPA filters in manually changed (bagged out) housings and discharged to atmosphere from the main stack. Limited access alpha areas are filtered through two stages of HEPA filters before stack discharge.

IV Specific Design Issues

The Role of Mathematical Modelling

A number of computer-based mathematical models were used in the design of the THORP ventilation systems. Some were commercial computer programmes such as PIPENET and others bespoke programmes such as HYPO which was used for analysing the effects of pulsed air flows on depression control. One of the most useful bespoke programmes was a suite of computer codes called NOXSIM to model the complex behaviour of NO_x used in various process stages in THORP.

The NO_x chemistry and absorption mechanisms are complex involving up to 10 reacting species with 7 reversible reactions. The NOXSIM model was validated against experimental data obtained both from the DOG pilot plant and from a caustic scrubber on a nitric acid recovery plant at Sellafield. The validation confirmed accuracy to within 330 ppm at ambient temperatures and normal flow rates.

As indicated previously the design of the caustic scrubbers in both DOG and COG and the acid recombination column in DOG was largely based on NOXSIM performance predictions. The most dramatic benefit was a reduction in the packed height of the DOG columns by a factor of nearly two compared with earlier design predictions. The impact of this was a marked reduction in both the cell height and the overall THORP building height. Other benefits have been the recognition of the importance of controlling the nitrous acid concentration in the recombined acid column (to improve its performance) and increasing the NO₂ : NO ratio before caustic scrubbing, by means of the noxidiser, to achieve high scrubbing efficiency for nitrogen oxides.

COG System Depression Control

The pressure in the ullage spaces of the process vessels and the interconnecting transfer routes is controlled at around 10mbarg below atmospheric, which is below the pressure of the surrounding cells so that any air or gas leakage is into the primary containments. The control system has to maintain this depression in a system of over 7000 m³, with air inputs varying from 900 m³/hr under plant shut down conditions to 8000 m³/hr under peak operating conditions, with air inputs from fluidic pumps, agitators and pulsed column drive legs.

The control system employs a transducer-controlled VXA (TC-VXA). This is a device based on the glovebox control VXAs with the ventilation duct depression measured by a transducer which controls a valve in a compressed air line routed to the VXA control ports. The attached line diagram (Figure 6) illustrates the control links. The control air flow is up to 2000 m³/hr at plant shut down which is added to the plant arisings of 900 m³/hr. As the plant flow increases the control flow reduces.

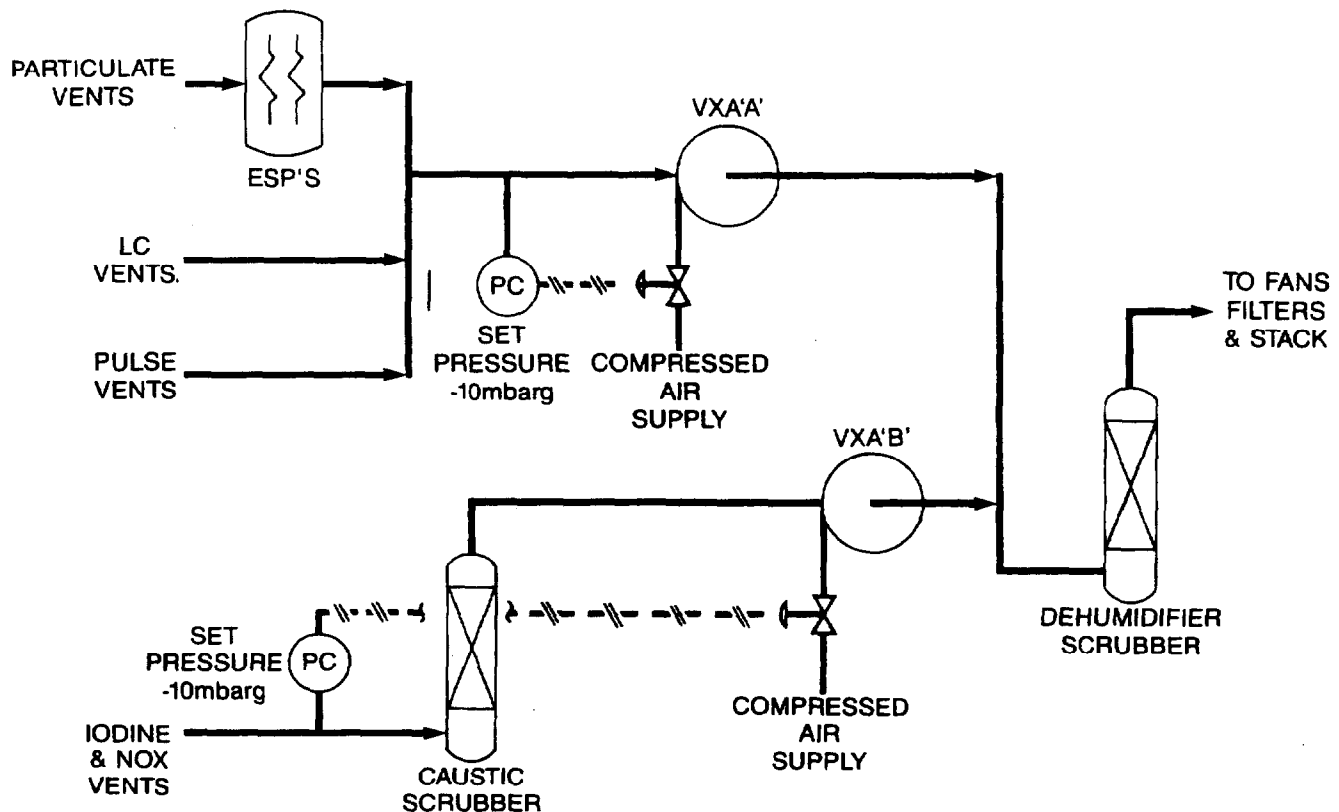


Figure 6 Vessel vent depression control system

The pressure drop through the caustic scrubber is significantly higher than through the other treatment devices and hence this stream is separately controlled with its own TC-VXA. The remaining streams with similar pressure drops are controlled by a single TC-VXA device.

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The TC-VXA was developed and tested on an inactive laboratory test rig which demonstrated that close control could be maintained on ventilation system depression over the large flow ranges required with short response times. The transducer control circuit and control valve are duplicated and the air supply is reinforced to provide a high degree of reliability. The failure mode leads to high depression which is considered preferable to loss of depression.

HEPA filtration

Circular HEPA filters are used extensively on THORP to clean up contaminated airflows. For low contamination air streams, unshielded manually changed canister-type units are employed which allow filters to be changed off-line whilst maintaining containment by the use of fully sealed bagging-out techniques. Single or two-stage filtration may be required, depending on the DF requirement. A typical canister-type safe change unit is shown in Figure 7.

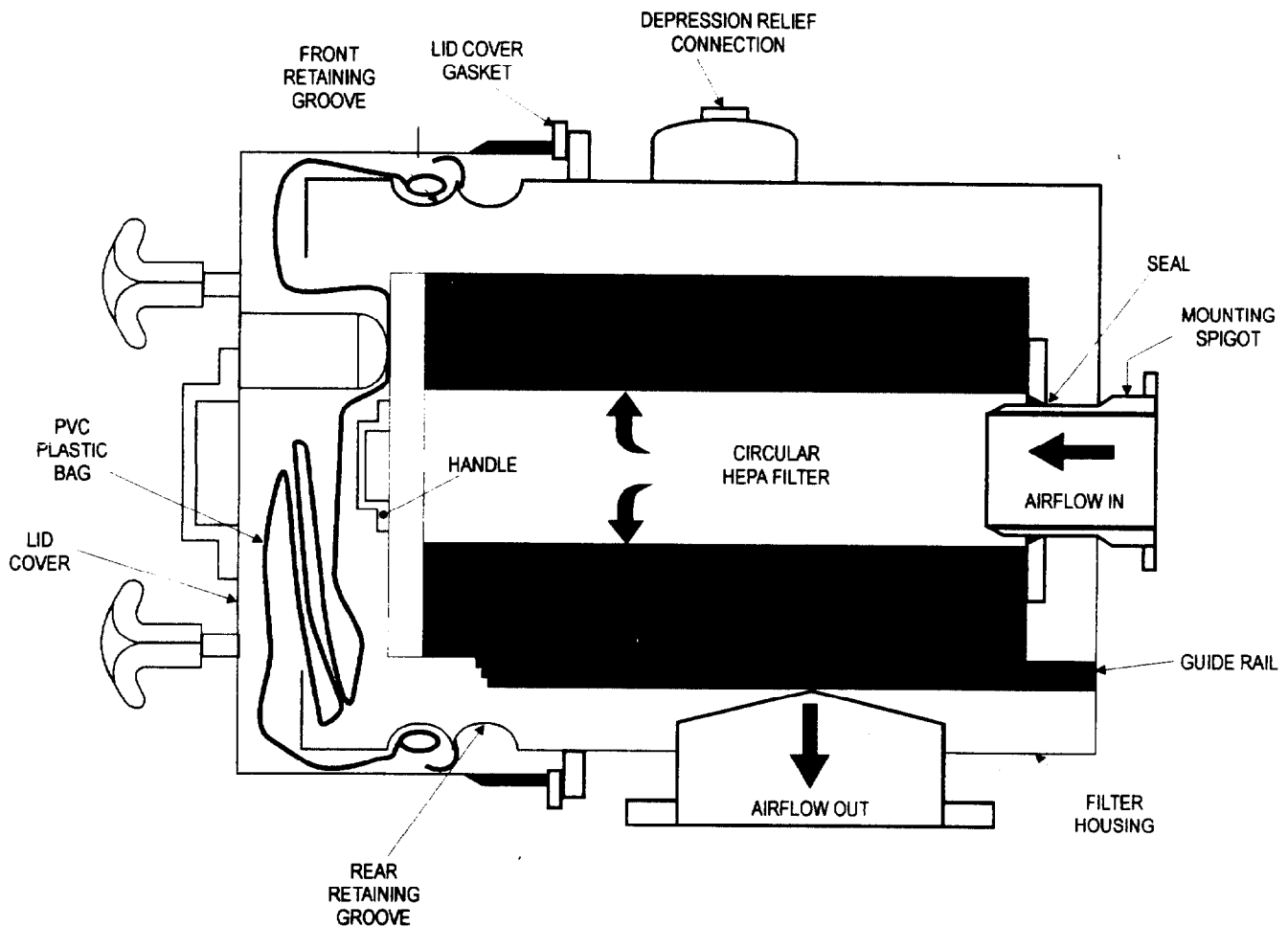


Figure 7 Typical HEPA filter

On remote shielded installations, multiple filter units are installed in purpose-built filter modules located in dedicated filter caves (shown in Fig 8), serviced by an overhead crane-mounted, power manipulator/hoist assembly.

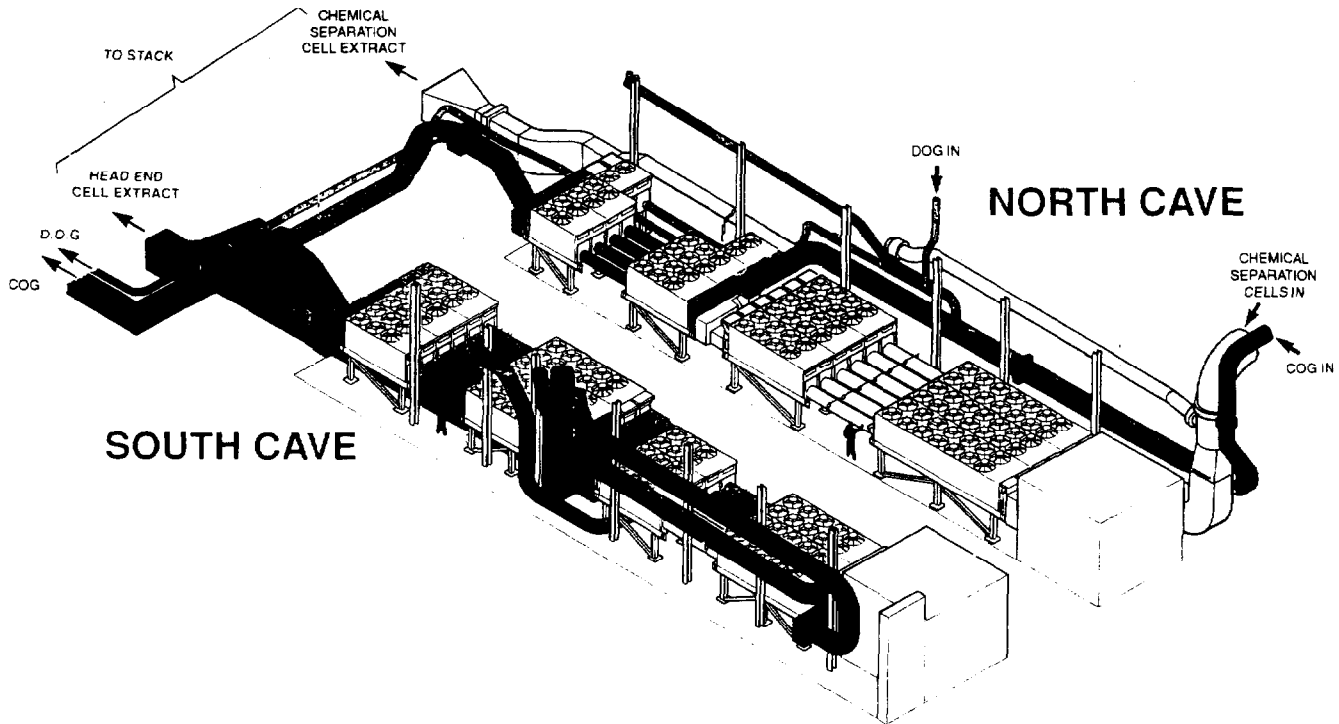


Figure 8 Filter cave isometric

The filters are changed after the removal of the filter access lid (using the hoist and auto-latching grab assembly), allowing the filter element to be removed from the module by use of the same grab. Refitting of the clean element and replacement of the lid is a reversal of this procedure. Dirty filters are posted out of the facility through a gamma-gate and into a flask, having first monitored the spent element for activity level before ultimate disposal. Clean filters are posted into the facility utilising the shielded and protected crane maintenance/decontamination facility. The central control room supervises all operations within the filter caves, the filter-change operation being remote-controlled from local stations situated adjacent to the caves themselves. Operations within the caves are normally overviewed from the window stations with remote CCTV enhancement for such operations as filter seat cleaning.

Stack Dispersion Modelling

The first detailed flowsheets identified a requirement for a stack capable of discharging 485,000 m³/hour of effluent at a discharge height of between 80m and 120m based on a building height of 35m. A multi-flue connected to the main plant (centre building) was proposed, the main ducts being contained within a bridge section which would be used for flow measurement and sampling/monitoring.

Wind tunnel tests were carried out to assess the performance of both stacks (80m and 120m) on a 1:200 scale site model, with varying windspeeds and directions and a range of discharge flue

velocities. Due to the lack of sufficiently accurate gas concentration measurement equipment at this time, much of the work was done using high speed camera techniques with a neutral buoyancy smoke tracer in the flue discharge. The 120m high stack, employing a discharge velocity in excess of 30m/sec gave an effective height of 120m based on the visual appearance of the plume.

Further wind tunnel tests were carried out in 1988 to verify the performance of the stack based on final flowsheet values and using modern Flame Ionisation Detector systems which can detect levels an order of magnitude smaller than the earlier technology. In the interim period, the stack design had been simplified to one central flue of 3m dia housing the major ventilation streams but incorporating COG and DOG streams at 108m level. The glovebox discharge joined the main flue at 108m level but continued inside the flue in its own discharge pipe to prevent back-pressure.

The later tests were used as a basis for quantitative effective height assessment, and demonstrated an effective height of only 85m for a 120m stack when buildings are present and in the most limiting weather conditions. Further tests with the model were able to show that an additional flue extension of 5m to give a height of 125m would produce an effective discharge height of 92m, which was sufficient to keep the critical group dose impact well below the target value and ensure the plume clears all site buildings. Thus the final design has a flue discharge height of 125m, a windshield roof level of 115m and a flue velocity of 34m/s.

Reverse Flow Protection

The use of a common flue provided the potential for pressure reversals on any failed fan system where isolation dampers did not close. This could result in a back-flow of contaminated air down the affected system. To minimise this potential, duplicate (inlet/outlet) actuated isolation dampers were fitted on some fan systems, spring closure was included on actuators serving critical isolation dampers and diverse failure detection systems were incorporated.

To protect manned areas against pressurisation from adjacent containment areas of higher contamination potential, filters are included on engineered inlet connections to cells and caves. Provisions are also incorporated to check DFs of filters in situ in these installations.

V Commissioning/Testing Experience

At the time of writing, only inactive equipment commissioning experience was available.

The building ventilation systems were commissioned during 1991 and early 1992. The main air flow balances were within the design target and equipment performed to specification. The accessible area systems could not be finally commissioned and balanced until the non-access area systems had completed their initial stage of setting to work and inleakage measurement. This process was accelerated by using temporary fan rigs to exhaust cells and caves to enable constructional deficiencies to be made good. It proved to be a lengthy process to achieve the desired degree of sealing but the integrity of the cell containment eventually established was excellent - typically ≤ 0.5 air changes/hour at 2mbars depression in a cell. The variable-speed fan drives enabled the systems to be adjusted to keep within volumetric and depression control tolerances whilst compensating for filter dirtying characteristics.

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The final balanced airflow requirements for the Head End caves and cells was 68% of the design figure and 73% on the Chemical Separation cells. This gave a substantial reduction on design discharges which increased the usable margin on filter/fan capacity.

The DOG system was originally intended to function under depression control from the two 100% fans linked to a pressure controller situated in the common duct downstream of the dissolvers. This, however, proved to be difficult to control due to inleakages in the shear chute and dissolver lid areas. Increasing the fan speed increased the airflow which caused flooding of the reflux condensers without increasing the depression at the shear. The inleakage problem was solved by improving the mechanical joints on the articulated shear chute and fitting dissolver lids with closer tolerances.

Within the COG system, VXAs on the pulsed and non-pulsed headers have proved to be reliable and effective. The system was commissioned with few problems and although minor control changes have been incorporated into the fan start/stop sequences, the overall system has performed as designed. The successful use of fluidic controls in this application has confirmed the advantages to be gained by having non-maintainable equipment in a highly active environment.

On filter testing, DFs across both types of filter module have exceeded expectation. On canister-type (unshielded) units, DFs in excess of 10^3 have been achieved, and 10^4 has been the norm. In remote change, fully-shielded installations, $10^3 - 10^4$ per stage has been measured and on two stages, DFs have exceeded 10^6 generally.

VI Conclusions

- 1 BNFL's Thermal Oxide Reprocessing Plant provides a major off-gas treatment challenge.
- 2 This challenge has been met by subdivision of the arisings into discrete treatment trains, viz: dissolver off-gas, central off-gas, gloveboxes, cells and caves, and building ventilation.
- 3 Each stream is treated by a combination of process steps appropriate to its composition and the required degree of decontamination.
- 4 Development work on key parts of the off-gas treatment system, supported by theoretical modelling, has ensured that plant design has a firm foundation.
- 5 All active streams are discharged, after treatment, from a 125m stack whose effective height has been demonstrated to be 92m.
- 6 Modelling work has demonstrated that the maximum critical group dose from THORP aerial discharges will be $22\mu\text{Sv}$ compared with a design target of $50\mu\text{Sv}$.
- 7 As illustrated in Table 1, all the discharge targets on individual radionuclides specified in HMIP's Discharge Authorisation will be met.
- 8 Although commissioning experience is limited, early indications are that confidence in the design of the THORP off-gas system is well founded.

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DISCUSSION

EVANS: I am curious as to what is limiting the decontamination factor of iodine in your caustic scrubber. Can you give me an idea what the residence time was and what sort of bubble size you had in there?

HUDSON: When you say what is limiting it, did you expect a higher DF than a hundred?

EVANS: I have no idea what sort of flows you are dealing with and what the bubble size is. I am just curious.

HUDSON: The gas residence time in the THORP caustic scrubber is 2 minutes. Since iodine absorption is gas-phase controlled, the gas residence time is an important factor in determining the DF. The flowsheeted DF of 100 is thought to be conservative because measured DFs of several hundred were achieved during pilot plant trials. Provided organics are excluded, the flowsheet DF should be exceeded during plant operation. There will be a limit caused by a small proportion of organic iodine being present, which will not be removed very readily.

MYERS: I was surprised to learn that the government allows you to not treat noble gases. Is this typical, or is it that you just do not have enough to be concerned about?

HUDSON: There are various aspects of this question. The impact of noble gases on the critical group is very small, it is less than five percent of the total impact on the critical group. We are already less than a half of the discharge target so there was no concern there. What is perhaps more difficult is the societal risk caused by noble gas release. There is no proven full-scale method of removing noble gases. Lots of people have done development work on it and there are prototypes in operation but there is no full-scale operating plant. We did estimate what it would cost to build and operate such a plant based on German technology, and the cost came out to about a hundred million pounds. Based on that figure, the dose detriment saved did not justify spending the money. As a precaution, the plant is designed to enable the backfitting of a krypton removal process, should suitable technology be developed in time.

DEVELOPMENT OF SILVER IMPREGNATED ALUMINA FOR IODINE SEPARATION
FROM OFF-GAS STREAMS

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Abstract

An inorganic iodine adsorbent, silver impregnated alumina (AgA), has been developed to separate iodine effectively from off-gas streams of nuclear facilities and to decrease the volume of waste (spent adsorbent). Iodine removal efficiency was improved at relatively high humidity by using alumina carrier with two different pore diameters. Waste volume reduction was achieved by impregnating relatively large amounts of silver into the alumina pores. The developed adsorbent was tested first with simulated off-gas streams under various experimental conditions and finally with actual off-gas streams of the Karlsruhe reprocessing plant. The decontamination factor (DF) was about 100 with the AgA bed depth of 2cm at 70% relative humidity, which was a DF one order higher than that when AgA with one pore size was used. Iodine adsorption capacity was checked by passing excess iodine into the AgA bed. Values were about 0.12 and 0.35 g-I/cm³-AgA bed for 10 and 24wt% silver impregnated AgA, respectively. The results obtained in this study demonstrated the applicability of the developed AgA to the off-gas treatment system of nuclear facilities.

I. Introduction

Nuclear facilities, such as nuclear power plants and reprocessing plants, separate radioactive iodine from off-gas streams and then release the off-gas to the environment.[1-3] Nuclear fission reactions of reactor fuel material produce several iodine isotopes. Most iodine isotopes have short half lives and/or low fission yields, except for ¹²⁹I and ¹³¹I. ¹²⁹I is the more important because of its long half life. But ¹³¹I should be radiochemically considered when dealing with short decay times and/or in the presence of spontaneous fission nuclides such as ²⁴⁴Cm.[4] Account must also be taken of the chemical amount of a stable isotope, ¹²⁷I, which has a fission yield about

one third that of ^{129}I . [1]

A number of iodine separation methods from off-gas streams are known and have been summarized in the literature. [1,5-6] Scrubbing the off-gas streams with acid or alkaline solution can absorb iodine into the solution. These liquid scrubbing methods need large amounts of solution, so beginning about 15 years ago the authors started to develop an adsorption method with iodine adsorbent. Although several solid adsorbents were known at that time, such as activated carbon and silver zeolite, [5-6] much room remained for improvement. The authors finally developed a silver impregnated alumina adsorbent (AgA) after various experimental studies. [7-15] This paper reviews the development process for the adsorbent and the demonstration of its suitable characteristics for iodine separation in off-gas treatment systems of nuclear facilities.

The adsorbent development placed an emphasis on effective iodine separation at high relative humidity. Water vapor was found to clog the small pores of the adsorbent carrier, activated alumina, and to interfere with the reaction of iodine and impregnated silver. So mainly, the pore distribution was considered to avoid clogging of pores with impurities. In this case, effectiveness of the iodine separation was evaluated with a parameter, decontamination factor (DF), which is defined as the iodine concentration at the inlet of the adsorbent column divided by that at the outlet.

After developing the optimum adsorbent, laboratory tests were carried out to check the effects on DF of various conditions, namely iodine form, concentrations of iodine and impurities, and linear velocity of iodine gas. A plant test was finally carried out in the dissolver off-gas treatment line of the Karlsruhe reprocessing facility in Germany.

Iodine adsorption capacity was investigated by passing simulated off-gas with a relatively high iodine concentration through the adsorbent column under various conditions. Adsorption capacity should strongly relate to the waste (spent adsorbent) volume. Iodine release property was also studied from the adsorbent with a saturated amount of iodine, considering the interim storage of spent adsorbent.

II. Experimental

Activated alumina was used as a carrier (base material) of the adsorbent. Industrially obtained aluminium sulphate was the starting material for the activated alumina. Addition of ammonium hydroxide solution into aluminium sulphate solution produced aluminium hydroxide precipitate. The precipitate was filtered and washed by demineralized water to remove ammonium and sulphate ions. The dried precipitate was calcinated at 600-800°C to get aluminium oxide (alumina) and, if necessary, crushed to smaller particles and calcinated again. Crushing and second calcination processes provided alumina with different pore diameters (distribution). Then, the alumina was put into the silver nitrate

solution, discharged from the solution and dried in air to get the final product of silver impregnated alumina (AgA) adsorbent. Repeating the impregnation of silver nitrate yielded AgA with different silver contents. The AgA tested here had pore diameters of 10 to 100nm, silver contents of 3 to 30wt%, particle diameter of about 2mm, specific surface area of about 10m²/g and bulk density of about 1.5g/cm³.

The test apparatus is schematically shown in Fig. 1. The iodine species were methyl iodide and elementary mainly labelled with ¹³¹I. Iodine, air, steam-air and nitrogen oxides were mixed to provide various conditions of simulated off-gas. The gas temperature was kept constant at 150°C before making contact with AgA in an adsorption column. The column was divided into several beds to get the decontamination factor (DF) and iodine distribution (adsorption profile) in a column. Iodine concentrations at the inlet and outlet of the column were measured with an NaI(Tl) scintillation counter or spectrophotometer after absorbing the iodine in an alkaline solution. ¹³¹I in each bed was measured with an NaI counter after removing the bed from the column. The DF value was determined by equation (1),

$$DF = [I]_o/[I]_x \quad (1),$$

where [I]_o and [I]_x are iodine concentrations at the inlet and outlet of the column (bed) of x cm length, respectively. As the iodine concentration was constant during the test and the iodine amount introduced into the column was quite low compared with the adsorption capacity of the adsorbent, adsorbed iodine amount in all beds and in beds after x cm should be proportional to [I]_o and [I]_x, respectively. Then, DF value could also be obtained by measuring iodine amount in each bed.

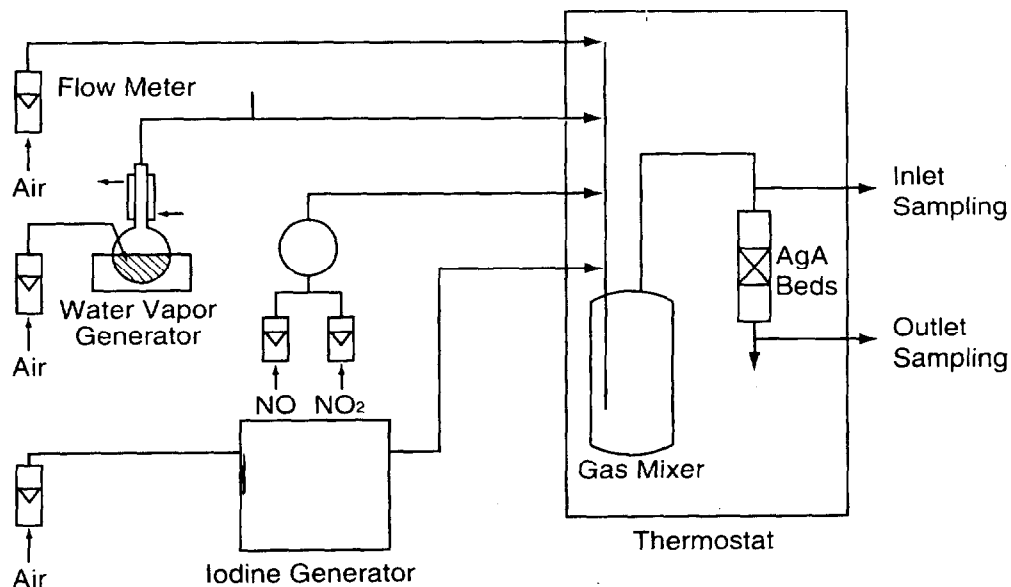


Fig.1 Outline of the Test Apparatus

The DF value was finally checked by putting AgA in a column of the dissolver off-gas sampling line of the Karlsruhe reprocessing plant. Average iodine concentration, relative humidity and NO_x concentration of the actual off-gas were 0.1volppm, 5vol% and 4vol% at the column, respectively. Radioactivity of ¹²⁹I was measured in each bed with a pure Ge detector.

Adsorption capacity for AgA was determined from the adsorption profile after passing simulated off-gas with sufficient iodine quantity into the column. Stability of adsorbed iodine was checked by blowing air onto AgA with a saturated amount of iodine. The temperature of the air was held constant at 28°C and 50°C during the desorption test. Desorbed iodine was trapped in two stages, containing alkaline solution. Iodine in the solution was measured by an ordinary photospectrometric method using ferric thiocyanate. Desorption ratio, which is defined by the amount ratio of desorbed iodine to initial adsorbed iodine, was calculated to evaluate the stability of adsorbed iodine.

Tests conditions were set to cover the range actually encountered in iodine removal operations at nuclear power and reprocessing plants. Severer conditions, such as high impurity concentrations, were also included. A severe desorption test was carried out at higher temperature than usually considered for adsorbed (spent) iodine adsorbent.

III. Development of Silver Impregnated Alumina Adsorbent

The optimum pore diameter (distribution) was first determined for activated alumina carrier with constant silver content of 10wt%. From preliminary experiment results, three kinds of AgA were prepared with main pore diametes of ~15nm, ~60nm, and both ~15nm and ~60nm. These AgA's were tested to compare the DF values at different relative humidities. The results are shown in Fig. 2. AgA with ~15nm pores was efficient at low relative humidity, but showed a low DF value at higher relative humidity. By contrast, AgA with ~60nm pores was not so efficient at low relative humidity, and it did not show such an abrupt DF decrease at higher relative humidity. This could be explained by clogging of small (~15nm) pores by water molecules at high relative humidity. Iodine reacts with silver impregnated in small pores and is effectively adsorbed onto AgA with small pores. But at high humidity, small pores are occupied by water, which disturbs the reaction of iodine with silver. Large (~60nm) pores do not promote iodine reaction with impregnated silver at low humidity and they can avoid occupation by water, which mean there are relatively constant DF values for different humidities. Thus, the combination of small and large pores was predicted to be suitable for iodine separation over a wide humidity range. The results confirmed this prediction as shown in Fig. 2.

The DF value dependency on silver content was next examined at higher relative humidity. The results are shown in Fig. 3, which shows DF increased from 3 to 10 wt% and decreased from 24 to 30wt% of the AgA. This could be

explained by an effective surface area change for the reaction of iodine with silver. Small pores should be covered by water under this condition. AgA with lower silver content provides an insufficient reaction surface area for a small silver amount. AgA with higher silver content also has a small surface area because large pores are covered with a large amount of silver nitrate. Thus, the optimum silver content for AgA was found to be in the region between 10wt% and 24wt%.

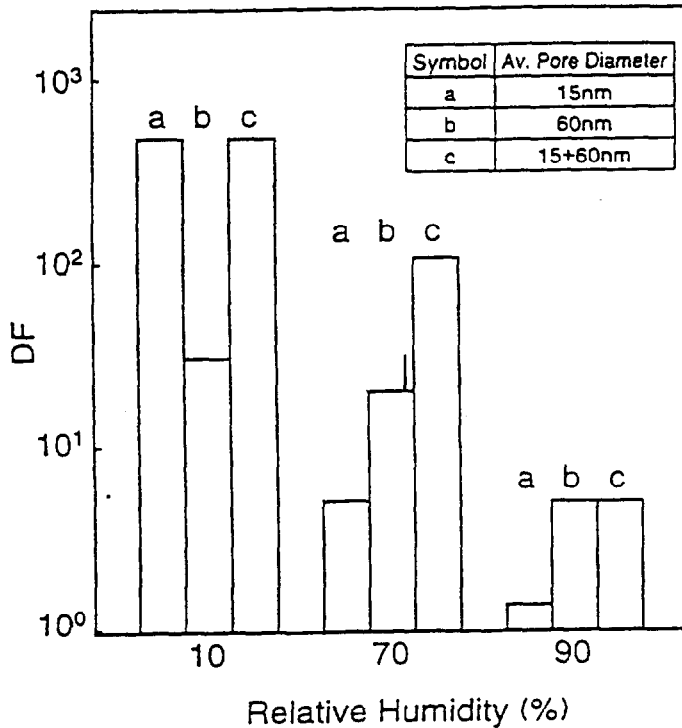


Fig.2 DF of AgA with Different Pore Diameters at Different Relative Humidities

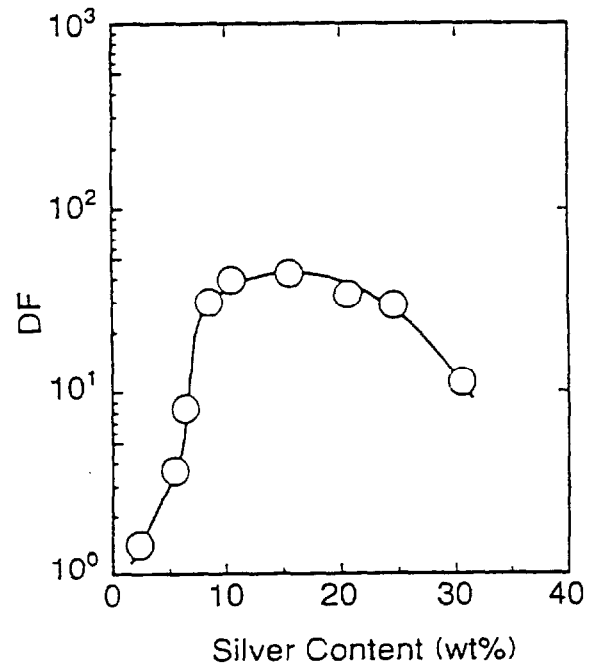


Fig.3 Dependency of AgA DF for CH₃I on Silver Content at 90% RH and 30°C.

IV. Decontamination Factors at Various Conditions

Typical iodine forms selected here were methyl iodide (CH₃I) and molecular iodine (I₂). CH₃I is known to be the most difficult species to separate from simulated off-gas among the major organic iodines, and I₂ is the main form in the dissolver off-gas of spent fuel reprocessing[1,13]. The DF values for both iodines with AgA are shown in Fig. 4 as a function of gas temperature. I₂ showed a higher DF because the reactivity of CH₃I with silver would be low. DF values of over 100 could be obtained for both iodines at 100°C and 150°C with AgA of 3cm bed depth. Temperatures below 100°C lowered the DF values for both CH₃I and I₂, but NO_x of 1.5vol% did not lower the DF values in this experiment.

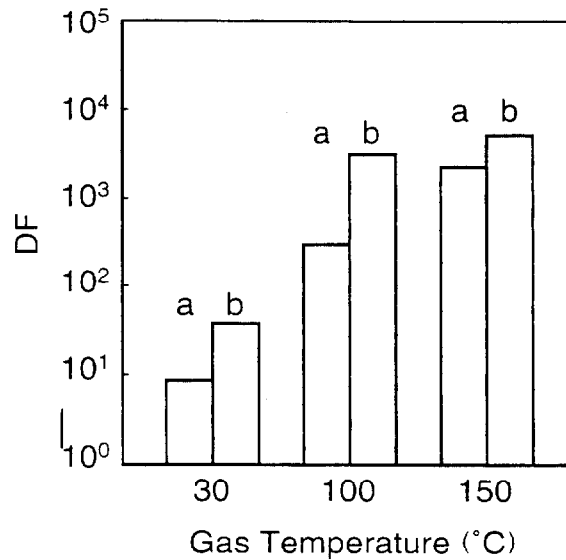


Fig.4 DF for CH₃I (a) and I₂ (b) as a Function of Gas Temperature

The DF dependencies for CH₃I and I₂ were also investigated for several conditions of simulated off-gas other than temperature. The results are shown in Figs. 5 to 9 which were obtained by changing parameters of iodine concentration (standard condition: ~20volppm), linear gas velocity (20cm/s), AgA bed depth (3cm), NO_x concentration (0vol%), and H₂O concentration (0vol%), respectively. The parameters were widely changed for I₂ compared with CH₃I. When the iodine concentration at the column outlet was under the detection limit, a DF value was calculated by substituting the detection limit for [I]_x in equation (1); these values are indicated with an upward pointing arrow in the figures. Although most DF values were the minimum ones, no apparent dependencies were observed for any parameters except AgA bed depth. CH₃I seemed to show relatively lower DF values than I₂, which was also observed in Fig. 4. DF values of over 10³ were obtained for both iodine forms for any combination of conditions in Figs. 5 to 9 if the AgA bed depth was larger than 3cm. Thus it was concluded that DF for CH₃I and I₂ with AgA was independent of various parameters, except bed depth and temperature.

Finally the plant test was carried out to check the properties of AgA and to demonstrate its applicability to an actual reprocessing plant. The results are shown in Fig. 10 after loading dissolver off-gas of the Karlsruhe reprocessing plant into a column of AgA beds. DF values were measured for different bed depths and operation times. The DF values depended on bed depth and were independent of operation time up to 118 days. DF values of over 10², 10³ and 10⁴ were obtained for bed depths of 2.5, 5 and 10cm, respectively. DF values obtained here were almost the same as those obtained in laboratory tests. Little DF change during 118 days operation confirmed the stable separation characteristics of AgA. In all cases, DF of the 10cm AgA bed depth was more

than 10^3 in the presence of NO_x and water vapor in off-gas of the actual reprocessing plant, which revealed that AgA could be applied in an actual off-gas treatment system.

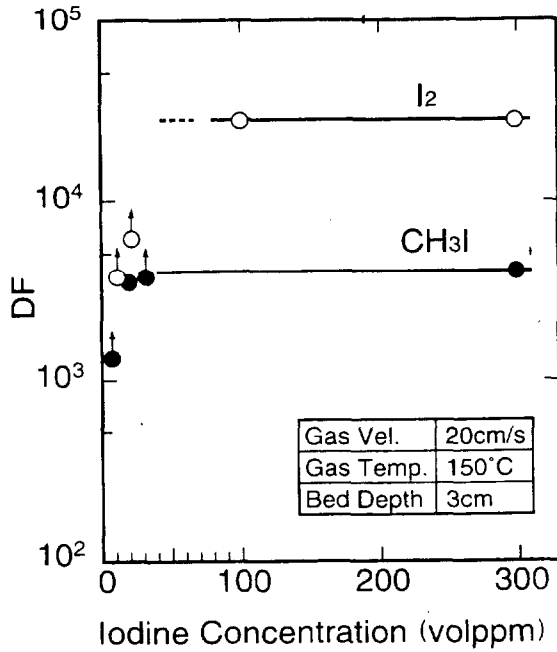


Fig.5 DF Dependency on Iodine Concentration

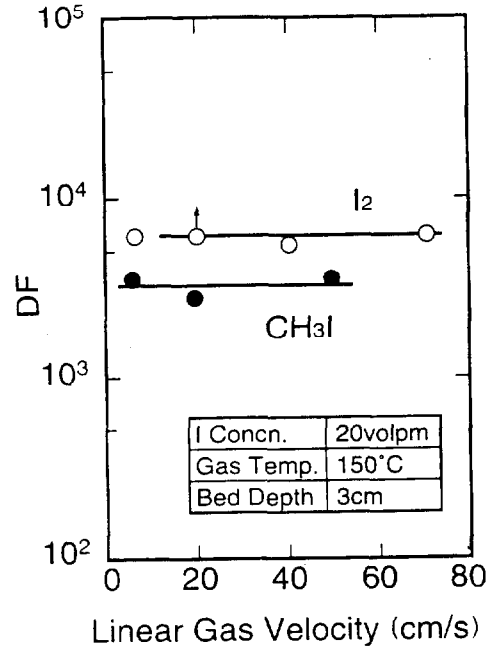


Fig.6 DF Dependency on Linear Gas Velocity

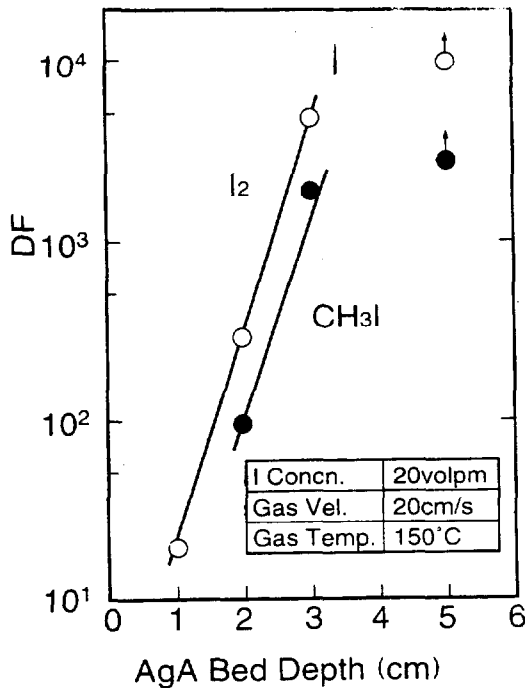


Fig.7 DF Dependency on Bed Depth

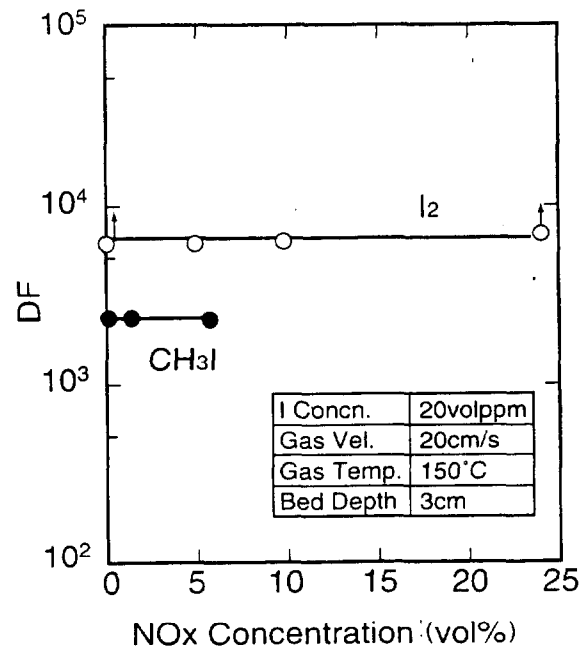


Fig.8 DF Dependency on NO_x Concentration

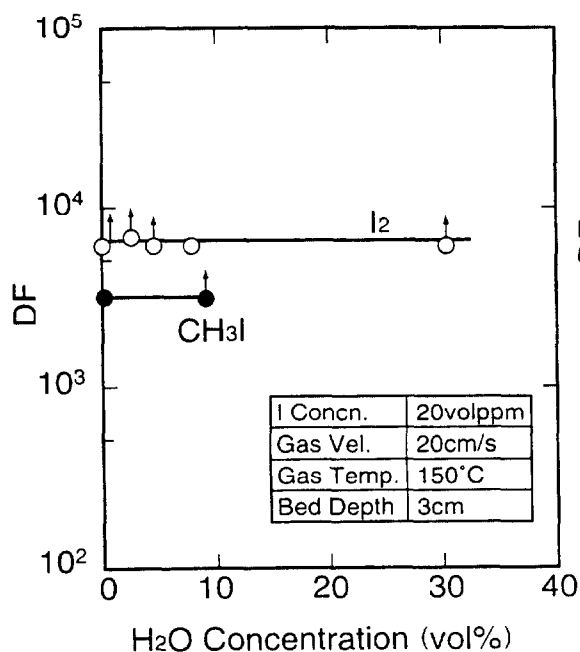


Fig.9 DF Dependency on H₂O Concentration

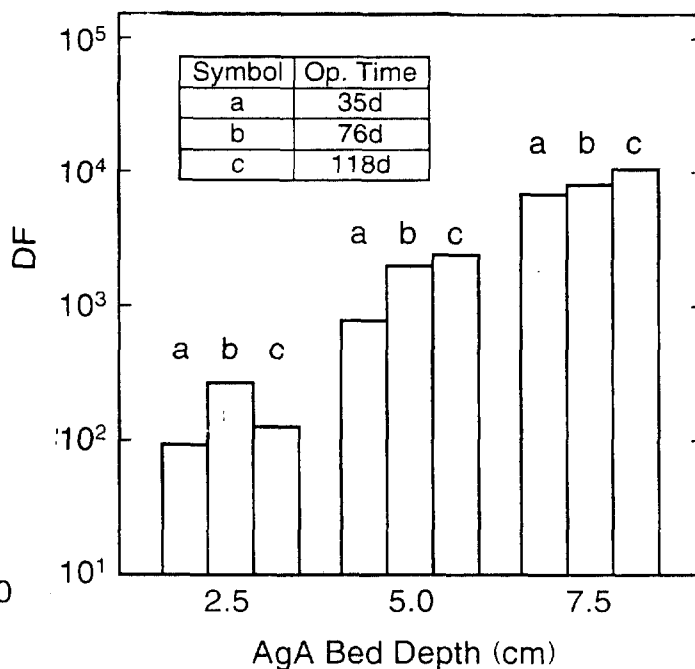


Fig.10 DF Dependency on Bed Depth and Operation Time Obtained in the Karlsruhe Plant Test

V. Iodine Adsorption Capacity of AgA

In order to estimate the volume of waste (spent AgA), iodine adsorption capacity of AgA was checked by adsorbing iodide onto AgA. The results are shown in Fig. 11 for AgA's with silver contents of 10wt% and 24wt%. Both CH₃I and I₂ adsorptions showed the same results. The vertical axis of Fig. 11 is the adsorbed weight of iodine per unit bulk volume (1cm³) of AgA adsorbent. The shape of the AgA particles is a sphere with a diameter of 1-2mm and their bulk volume is important for estimation of waste volume. Iodine adsorption capacity of AgA depended on its silver content and was about 0.12 g-I/cm³-AgA(10wt%) and 0.35 g-I/cm³-AgA(24wt%). Iodine reacts with the same number of moles of silver in AgA and capacity data obtained indicated about 80% silver utilization.

Iodine adsorption capacities could also be calculated for other iodine adsorbents from the published data.[12,16] The capacities were in the region of 0.07 to 0.17 g-I/cm³-adsorbent for previously developed adsorbents, silver zeolite, silver mordenite and silver silca gel. Thus AgA with 24wt% silver content had a higher iodine adsorption capacity than other adsorbents and it could reduce the waste volume to 1/5 - 1/2. Such a reduction would cut the volume of waste treatment, and size of storage and disposal facilities.

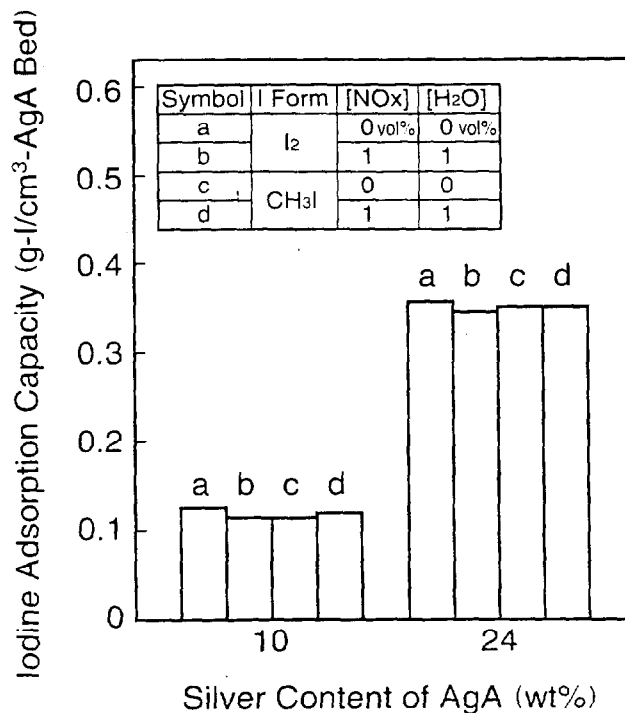


Fig. 11 Iodine Adsorption Capacity of AgA

VI. Desorption of Adsorbed Iodine from AgA

Iodine holding capability for AgA after adsorption was evaluated by desorption tests. Desorbed amount of iodine from AgA was measured by blowing air through the AgA (24wt% silver) with a saturated amount of iodine (I₂) in a column. The temperature was 28°C and 50°C, and the relative humidity was 100%. The absolute humidity was then 2.4% and 8.6% for 28°C and 50°C, respectively. The amount of desorbed iodine absorbed in the two series for a 0.05mol/l sodium hydroxide solution was below the detection limit (5ppb) after 144 hours of air blowing. This meant that the desorption ratio was below 0.00011% and 0.00019% at the desorption air temperature of 28°C and 50°C, respectively. The difference between the two series was caused by the water vapor content difference, that is, much water was absorbed in the alkaline solution at 50°C.

The annual iodine desorption ratio were calculated from these data to be below 0.007%/y and 0.012%/y at 28°C and 50°C, respectively. This desorption test was carried out under a severe condition such as high humidity and large amount of blowing gas. The flow rate of the humid air was 60cm³/s. As the air volume for this test in a column was about 3cm³, the air was replaced by new air at a frequency of 20 times per second. No iodine desorption was detected even under such severe conditions, which demonstrated the stability of adsorbed iodine in AgA.

VII. Conclusions

An iodine separation adsorbent, silver impregnated activated alumina (AgA), was developed and its characteristics were investigated to get an effective iodine separation technology for off-gas treatment systems of nuclear facilities. The studies consisted of AgA development and AgA property investigations for iodine separation, iodine adsorption capacity, and iodine desorption. Various tests were conducted and the following conclusions were obtained, which confirmed the applicability of the iodine separation technology with AgA to the off-gas treatment systems.

1. Silver alumina adsorbent with pores of two different diameters had excellent iodine separation capability at both low and high humidities. Silver in smaller and larger pores reacted with iodine at relatively low and high humidities, respectively. Silver content of AgA was also optimized to be in the region of 10-24wt%.
2. Test conditions such as iodine concentration, linear gas velocity, nitrogen oxides concentration and humidity had no effect on iodine separation efficiency of AgA, whereas iodine form, gas temperature and AgA bed depth did. DF values for elemental iodine were higher than those for methyl iodide probably because of the higher reactivity of I_2 with silver. DF values increased with temperature and bed depth because of the increase of reactivity and adsorption site number, respectively. DF values of over 10^3 were obtained in the actual plant test as well as in laboratory tests.
3. Iodine adsorption capacities were ~ 0.12 and ~ 0.35 g/cm³-AgA bed for AgA with 10 and 24 wt% silver contents. These values did not affected by iodine form and impurities. AgA with 24wt% silver content could reduce the waste volume to 1/5 -1/2 compared with previously developed adsorbents.
4. No iodine desorption was observed from AgA saturated with iodine after about 6 days blowing air (60cm³/s) with 100% relative humidity at 28 and 50°C, which demonstrated the stable iodine holding capability of AgA.

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DISCUSSION

WREN: I have a few questions. Did you look at the temperature effect on adsorption capacity? I know you looked at the DF, but what about the adsorption capacity at a high temperature?

KIKUCHI: Adsorption capacity was measured up to 150° C. Adsorption capacity is almost the same in the temperature range of our experiments (30°-150° C).

WREN: I understand that it does not have any temperature dependence. When you looked at the effect of NO_x, did you look at it at various relative humidities? What was the combined effect of relative humidity and NO_x? The adsorption behavior of NO_x on surfaces is likely to change depending on humidity. Thus the combined effect could be quite different from what one would expect from just simple addition of two effects. Could NO_x under dry conditions be more detrimental than NO_x under humid condition, depending on how NO_x is adsorbed?

KIKUCHI: Your question is about the combination of relative humidity and NO_x concentration. I have done the experiments, and the most severe condition is high relative humidity and high NO_x concentration. We have evaluated the combination of factors at about 90% RH and the highest NO_x concentrations. Addition of NO₂ under humid condition lowers more the adsorption capacity than simple addition of two effects, that is, NO₂ under humid condition is more detrimental than NO₂ under dry condition. This might be due to the fact that the formation of NO₃ in the micropores by NO₂ dissolution to capillary water increases the apparent relative humidity.

WREN: Do you have any idea how NO_x was adsorbed? Was it completely saturated?

KIKUCHI: It is really hard to measure because of the impregnated material, silver nitrate. Unless you have a labelled compound of NO_x, you cannot measure the profile of the

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adsorbed NO_x .

WREN: Was there any effect from radiation exposure?

KIKUCHI: No radiation effect was observed on iodine adsorption.

WILHELM: Experiments are not needed for reprocessing plants at 90% RH, because at 150° C it would give several bars pressure in the offgas.

KIKUCHI: We have two problems. One is the reprocessing plant (150° C, ~1% RH). In that case, we don't have to worry about relative humidity, only about NO_x . Eventually we plan to install this adsorbent in gas treatment systems in nuclear power plants, which have a running temperature of about 30°-40° C and 50-90% RH. Therefore we have done experiments at high relative humidity conditions.

**TREATMENT OF TRITIATED EXHAUST GASES AT THE
TRITIUM LABORATORY KARLSRUHE**

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Abstract

The Tritium Laboratory Karlsruhe (TLK) accomplished commissioning; tritium involving activities will start this year. The laboratory is destined mainly to investigating processing of fusion reactor fuel and to developing analytic devices for determination of tritium and tritiated species in view of control and accountancy requirements.

The area for experimental work in the laboratory is about 800 m². The tritium infrastructure including systems for tritium storage, transfer within the laboratory and processing by cleanup and isotope separation methods has been installed on an additional 400 m² area. All tritium processing systems (= primary systems), either of the tritium infrastructure or of the experiments, are enclosed in secondary containments which consist of gloveboxes, each of them connected to the central depressurization system, a part integrated in the central detritiation system. The atmosphere of each glovebox is cleaned in a closed cycle by local detritiation units controlled by two tritium monitors.

Additionally, the TLK is equipped with a central detritiation system in which all gases discharged from the primary systems and the secondary systems are processed.

All detritiation units consist of a catalyst for oxidizing gaseous tritium or tritiated hydrocarbons to water, a heat exchanger for cooling the catalyst reactor exhaust gas to room temperature, and a molecular sieve bed for adsorbing the water. Experiments with tracer amounts of tritium have shown that decontamination factors >3000 can be achieved with the TLK detritiation units.

The central detritiation system was carefully tested and adjusted under normal and abnormal operation conditions. Test results and the behavior of the tritium barrier preventing tritiated exhaust gases from escaping into the atmosphere will be reported.

I. Introduction

The Tritium Laboratory Karlsruhe (TLK) provides the technical means for R&D work on the fuel cycle and components of the next fusion machine within the framework of the European Technology Program (NET/ITER). Work at TLK will concentrate on the development of advanced processes of plasma exhaust fuel cleanup.⁽¹⁾ In experiments performed on a technical scale up to 10 g of tritium will be handled.

The government license in accordance with Sec. 3 of the Radiation Protection Ordinance, being part of the German Atomic Energy Act, was granted in April 1993 by the State Ministry for the Environment of Baden-Württemberg.

II. Treatment of Tritiated Exhaust Gases

Description of the Multi-barrier Concept of Depressurization and of the Tritium Retention Concept

According to a multi-barrier concept (Figure 1), tritium is prevented from escaping into the ambient atmosphere. Most of the tritium carrying primary systems of the TLK infrastructure and of the experiments have been designed as metal-made standard UHV components. The specified leak tightness is $< 1 \times 10^{-9}$ mbarl/s for the single leak and $< 1 \times 10^{-8}$ mbarl/s for the entire primary system (integral leak).

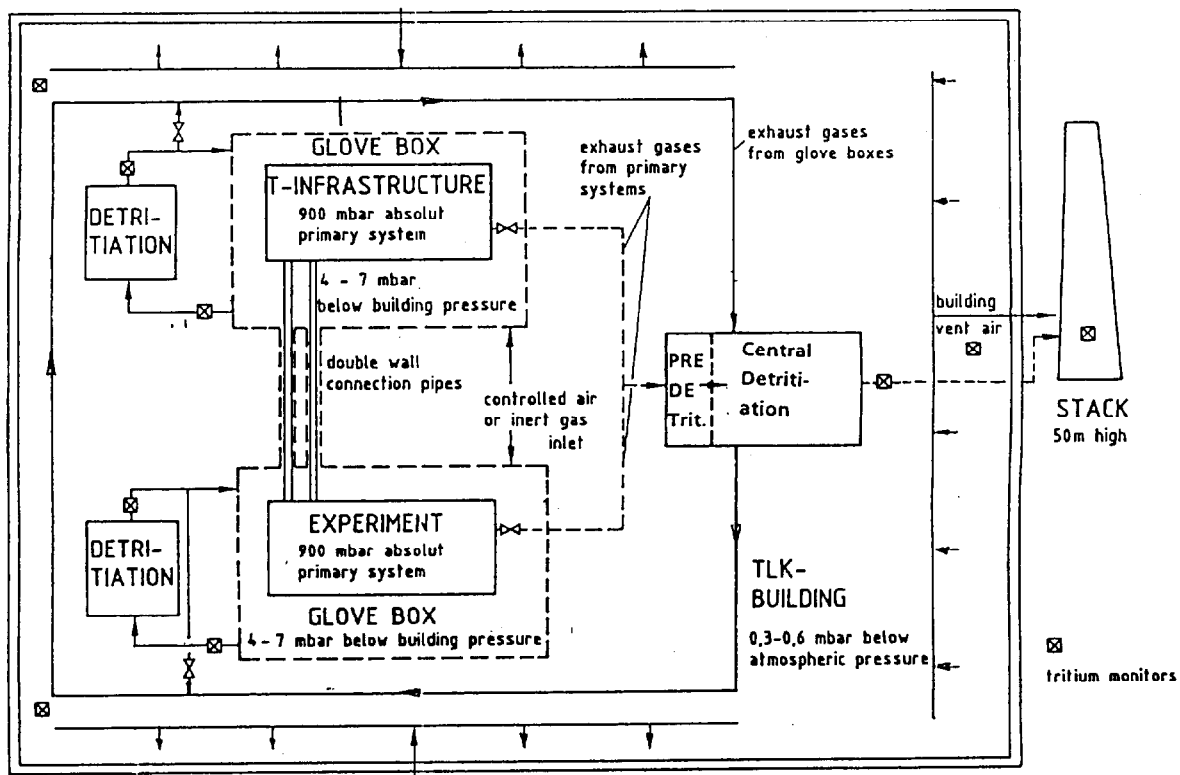


Figure 1 Containment and exhaust gas concept at TLK.

Each of these primary systems is enclosed in a secondary containment (most frequently a glovebox) filled with either air or an inert gas. Typical features of the gloveboxes are stricter requirements on tightness, namely < 0.1 vol.%/h leak rate compared to the DIN standard of 0.25 vol.%/h. The gloveboxes are kept at 4 - 7 mbar negative pressure rela-

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tive to the laboratory atmosphere, which, in turn, is kept at a negative pressure of 0.3 to 0.6 mbar relative to atmospheric pressure.

The secondary containments are equipped with individual Tritium Retention Systems (TRS) the exhaust gases of which are passed for safety reasons through a Central Tritium Retention System (ZTS) - likewise responsible for depressurization in the gloveboxes - before they are discharged via the vent air stack. Both systems will be described in more detail below.

Depressurization

The secondary containments are the gloveboxes, which are connected to a central depressurization system (Figure 2). A closed circular pipeline installed in the tritium infrastructure rooms and in the experimental rooms generates through blowers a negative pressure of 11 - 18 mbar relative to the laboratory atmosphere. The gloveboxes release their leaking air via a pressure control valve into the closed circular pipeline (4 - 7 mbar operating range below laboratory atmosphere). Most of the boxes previously installed have a volume of 6 - 12 m³. About 10 boxes have already been installed. The only exception is the 32 m³ box of the Hydrogen Isotope Separation System. This means that the amount of air to be exhausted per box is small. However, should a glove be torn off, up to 50 m³ /h of air would have to flow through the glovebox hole into the interior of the box in order to prevent tritium from diffusing out of the box again. In this case, the higher rate flow is fed into the depressurization system through a safety valve, which opens when the negative pressure in the glovebox has attained approx. - 1 mbar. The leaking air exhausted by the depressurization system from the gloveboxes and from other suppliers is discharged as vent air via the stack.

The safety-related components of the depressurization system - blowers, control valves - are made redundant.

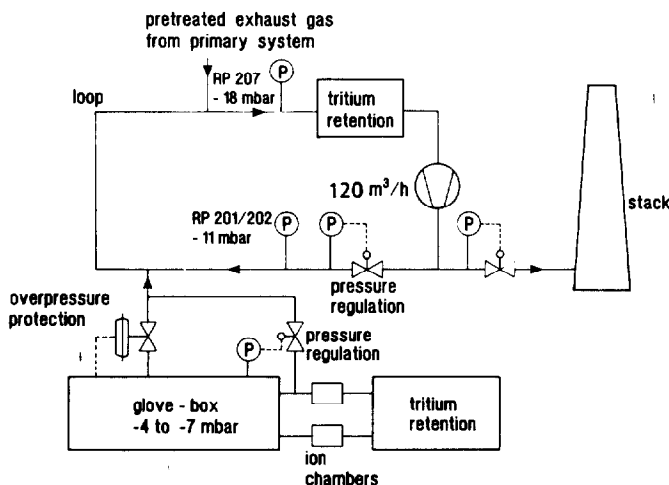


Figure 2 Flow sheet of the Central Tritium Retention System (ZTS).

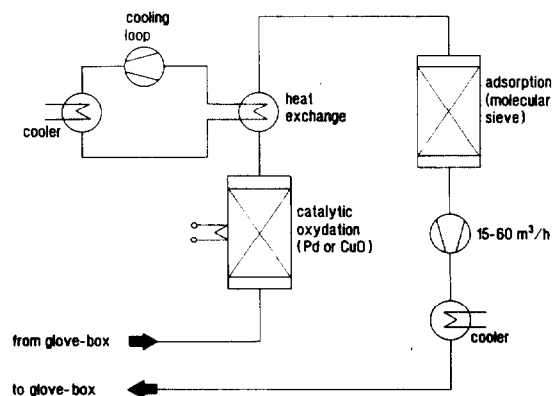


Figure 3 Flow sheet of glove box Tritium Retention System (TRS).

Tritium Retention System (TRS)

Each glovebox is equipped with a separate Tritium Retention System (Figure 3) based on conventional technology and consisting of a catalyst bed for hydrogen and hydrocarbon oxidation (0.5% Pd on alumina carrier or CuO) and a molecular sieve adsorber connected in series.

Depending on the size of the box, the dimensions selected for the Tritium Retention Systems are such that during normal operation the air is changed five times per hour. Should an elevated tritium level be measured in the box atmosphere, the TRSs are switched over to 10 times air change and the operating temperature of the catalysts is raised. The construction sizes (Table 1) are defined by the modular parallel connected expansion of the catalyst and molecular sieve units.

Table 1 TRS construction sizes.

Size	Gasflow	Catalyst	Molecular sieve	Heat exchanger	Refrigerator	Blower
I	15/30 m ³ h ⁻¹	1	1	1	1	1
II	30/60 m ³ h ⁻¹	2	2	2	1	1
III ¹⁾	60/120 m ³ h ⁻¹	4	4	4	2	2

1) Size III consists of two parallel connected units size II

Dependent on the nature of the processes and experiments, the primary systems do not only contain pure hydrogen species (H₂, HD; D₂, HT, DT, T₂) but also hydrogen compounds such as ammonia and methane. In order to be able to retain these substances too, which escape into the box during malfunctions, the catalysts of TRSs are operated at different temperatures (Table 2):

- Boxes filled with air and processes without hydrocarbons (L) are operated at 100 °C. If tritium escapes, the temperature is raised to 180 °C.
- Boxes filled with air and processes with hydrocarbons (L/CH) are operated at 300 °C. If tritium escapes, the temperature is raised to 450 °C.

Besides, gloveboxes with inert gas (IG) atmosphere are used for experimental reasons. The TRSs connected to this type of box need an oxygen donator for oxidation of any tritium which might escape. In these boxes the Pd catalyst has been replaced by CuO operated at 250 °C. The latter substance must be regenerated periodically with air.

Table 2 Types of catalyst and modes of operation of TRS.

Application	Internal indication	Catalyst material	Regeneration necessary	Operation temperature
TRS for air without hydrocarbons	L	Pd	no	100 °C - 180 °C
TRS for air with hydrocarbons	LCH	Pd	no	300 °C - 450 °C
TRS for inert gas without hydrocarbons	IG	Cu O	yes	200 °C
TRS for inert gas with hydrocarbons	IGCH	Cu O	yes	250 °C

The exhaust gas removed from the secondary containments for depressurization is extracted from the return flow from the TRS to the gloveboxes. Thus, two-stage tritium retention is ensured during normal operation (but not if gloves have been torn off) (Figure 2).

The specified activity of the glovebox atmosphere during normal operation is $< 4 \times 10^6$ Bq/m³. It is monitored by one tritium monitor each (ionization chamber) in the feed and return flows to and from the TRS. In case of alarm due to rise in activity the gas flow rate is doubled, as stated before.

Central Tritium Retention System (ZTS)

In the Central Tritium Retention System (Figure 2) all exhaust gases of the secondary containment, the pretreated exhaust gases of the primary systems, and all other exhaust gases which might have been contaminated are processed in a single loop. This loop generates the negative pressure for all gloveboxes in the laboratory. A constant gas flow rate of 110 - 120 m³/h circulates in the loop at a negative pressure (see III). The constant operating conditions are achieved by controlled release of the vent air into the stack.

In the main stage (RHH) of the ZTS (Figure 4) all the gas circulating in the loop is processed in the once-through mode. This is achieved by two redundant cleanup units of the same make and fulfilling the same function as the TRS, construction size III (L/CH) described before. An activity monitor placed at the outlet of these units monitors the clean gas and hence the partial gas stream released to the atmosphere.

When a limit is attained (5×10^6 Bq/m³), the catalyst temperature is automatically increased from 300 °C to 450 °C. In case the result is unsatisfactory, the second standby main stage of the retention system is connected in parallel. At the same time, operations in the laboratory are restricted by administrative measures which means that all ongoing work in the gloveboxes is temporarily discontinued. Should other malfunctions occur (e.g. failure of the catalyst heating system) switching over takes place to the redundant system.

Different from the TRSs, the two main stages of the retention system are equipped with emergency cooling sets. These are switched on and maintain cooling of the process gas between the catalysts and the molecular sieves in cases where the laboratory coolant water system fails. In this way, the danger is eliminated that the non-cooled gas stream warms up the molecular sieves and releases already adsorbed tritiated water.

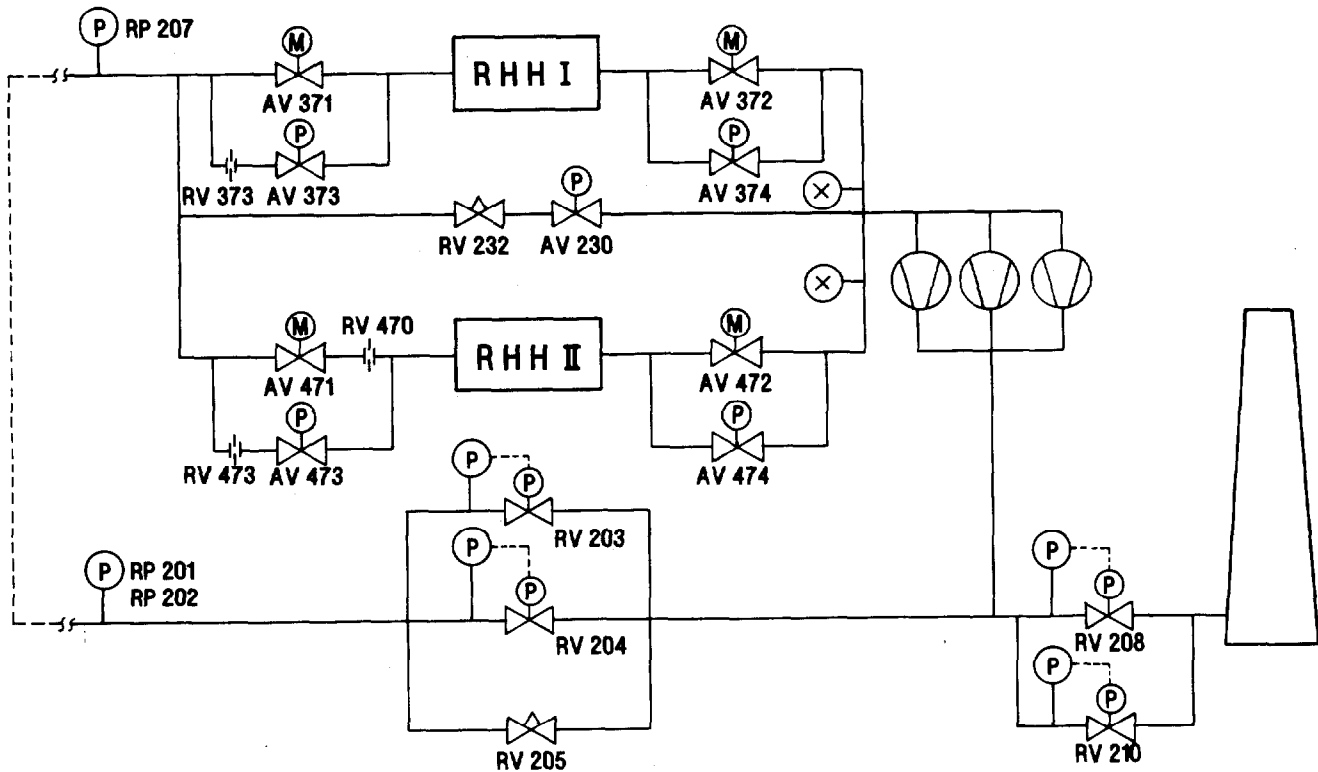


Figure 4 Improved concept of control valves of the closed circular pipeline.

At the preliminary stage (RHV) of the ZTS all exhaust gases originating in the primary systems of the tritium-carrying units at TLK are precleaned, i.e. mainly the exhaust gases from the vacuum pumps. All these exhaust gases are collected in buffer tanks (three units). Following an analysis and in case of necessity, these gases are treated, in the way already described, in a separate Tritium Retention System (TRS construction size I for inert gas). After a residual activity of about 10^{10} Bq/m³ has been achieved, this gas can be discharged into the closed circular pipeline and into RHH.

These are the alternating modes of operation of the three buffer tanks:

- reception,
- inspection and treatment, if necessary,
- delivery and conditioning for reception of new batches.

As it cannot be excluded that considerable amounts of hydrogen from the primary systems are misrouted, the buffer tanks, before being switched to the gas reception mode, are flushed with nitrogen (700 mbar) in order to exclude the formation of an explosive gas mixture.

Like all systems of the TLK infrastructure, this system is program controlled and monitored by the Siemens Teleperm M process control system (PLS). The switches of the components made redundant for safety reasons (blowers and control valves) are hard wired and released by relays.

III. Difficulties Encountered during the Commissioning Phase

During commissioning of the ZTS weak points were detected. These, together with the solutions found, will be described below.

Negative Pressure in the Closed Circular Pipeline at Different Throughputs of Gas Delivery

Independent of the throughput of external gas deliveries (between 0 and 77 m³/h according to specification), the negative pressure in the closed circular pipeline must be kept within a tolerable narrow band. The minimum negative pressure ($p_e = -10$ mbar) is necessary to guarantee the performance of the safety valves of the gloveboxes. The maximum negative pressure ($p_e = -20$ mbar) must not be underrated to ensure that the mechanical integrity of the glovebox is not put at risk upon failure of the regular depressurization system of a glovebox. On account of the preciseness of the measuring instruments (approx. ± 0.5 mbar) and to obtain a normal range of responses, the tolerable range at the end of the closed circular pipeline (in direction of flow) is defined as follows: RP207: $p_e = -11.5$ mbar at the minimum; $p_e = -18.5$ mbar at the maximum. Taking into account a maximum pressure drop of 2.5 mbar in the closed circular pipeline, about 100 m in length, nominal width DN 100, the tolerable range at the beginning of the closed circular pipeline (RP201, RP202) is defined as follows: $p_e = -11.5$ mbar at the minimum; $p_e = -16$ mbar at the maximum (Figure 4).

Keeping the pressure level in the range mentioned before is to be ensured by one of the redundant negative pressure-controlling valves installed (RV203 or RV204). These mechanical spring actuated and diaphragm controlled valves control the back pressure in direction of flow.

It was not possible during the first tests to maintain the values specified for the negative pressure because the admission pressure at the control valve and at the bypass valve (RV205) underwent excessive variations as a result of the different throughputs of external gas deliveries.

This is the reason why the exhaust gas pipe leading to the stack was retrofitted with admission pressure control valves, likewise two in number (RV208 and RV210). These mechanical spring actuated and diaphragm controlled valves serve to maintain between 8 and 12 mbar the admission pressure at the negative pressure control valves (RV203 and RV204) and at the bypass valve (RV205), independent of the throughput of the exhaust gases given off to the stack.

The rate of exhaust gas removal may vary between 7 and 84 m³/h. Besides the external gas deliveries (0 to 77 m³/h), the closed circular pipeline within the ZTS is permanently flushed at a rate of 7 m³/h. This flushing gas serves to change the air in the sampling and valve cabinet of the system where gas samples are collected from the RHV tanks while the necessary protective measures are taken as in a hood.

The modified system has since produced satisfactory results. Some measured values have been entered in Figure 5 and in Table 3.

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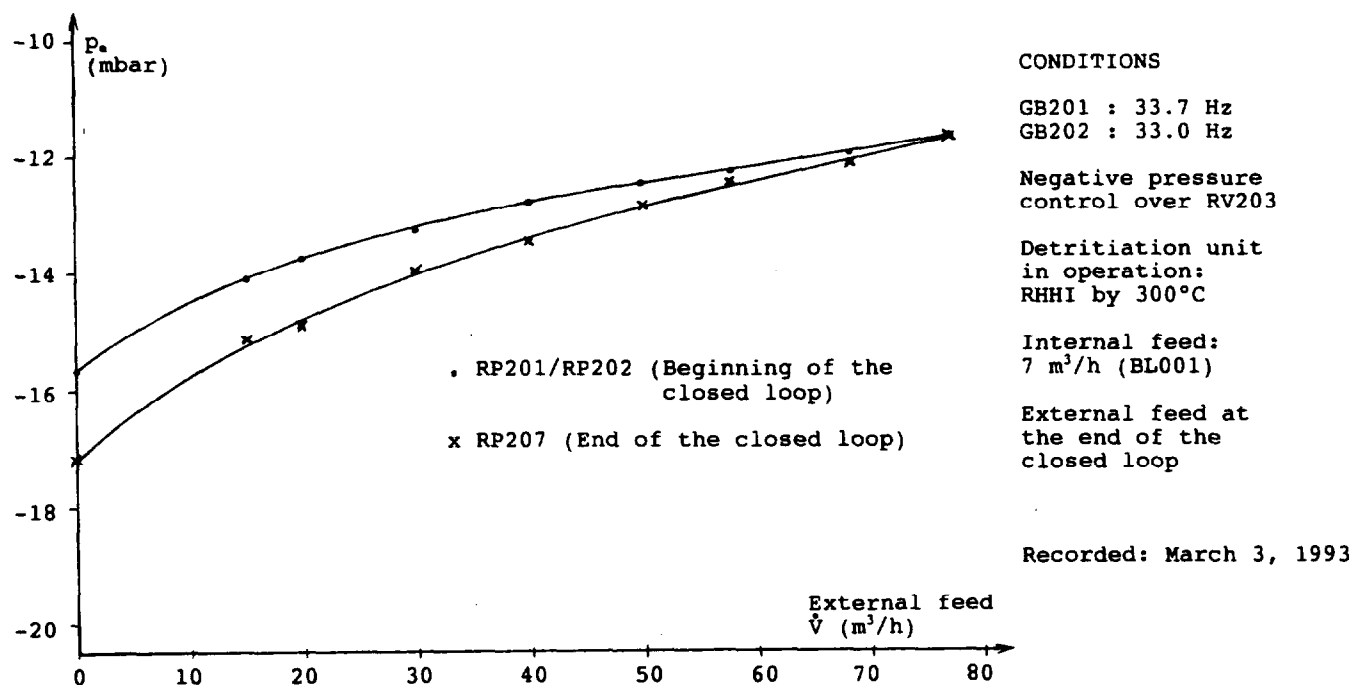


Figure 5 Variation of the negative pressure in the closed circular pipeline in function of the volume flowrate of external feed.

Table 3 Data related to figure 5.

\dot{V}	0 m ³ /h	15 m ³ /h	20 m ³ /h	30 m ³ /h	40 m ³ /h	50 m ³ /h	58 m ³ /h	68.5m ³ /h	77.5m ³ /h
RF201 (m ³ /h)	51/52	51/52	51/52	51/52	51/53	52/53	52/53	52/53	52/53
RF202 (m ³ /h)	54/55	55	55	55/56	55/56	55/56	55/56	55/56	56
RF211 (m ³ /h)	103/104	103/104	103/104	103/104	104/105	103/105	104/105	104/105	104/105
RP201 (mbar)	-15.8/ -15.6	-14.2/ -13.9	-13.8/ -13.7	-13.4/ -13.2	-12.9/ -12.7	-12.6/ -12.4	-12.3/ -12.2	-12.1/ -11.9	-11.7/ -11.6
RP202 (mbar)	-15.8/ -15.5	-14.2/ -14.0	-13.9/ -13.8	-13.4/ -13.2	-12.9/ -12.8	-12.6/ -12.4	-12.4/ -12.3	-12.1/ -12.0	-11.8/ -11.7
RP207 (mbar)	-17.3/ -17.1	-15.3/ -15.1	-15.0/ -14.8	-14.1/ -13.9	-13.6/ -13.4	-13.0/ -12.8	-12.6/ -12.4	-12.3/ -12.1	-11.8/ -11.7
RF213 (m ³ /h)	20.2	20.2	20.2	20.2	20.2	20.2	20.3	20.3	20.3

Negative Pressure in the Closed Circular Pipeline as a Function of the Tritium Retention Systems in Operation

The tritium retention function can be fulfilled either by RHH I or by RHH II or by both stages connected in parallel. During this operation the negative pressure in the closed circular pipeline must obviously remain unchanged, independent of the passage through one RHH or the combined RHH I/RHH II.

As had been expected, this condition was not fulfilled in the first tests.

The pressure drop at 300 °C of RHH I together with its connecting pipework and the related motor driven valves was taken as a reference value and assumed to apply to RHH II as well, by installation of a diaphragm (RV 470) downstream of the motor driven valve AV471.

The same pressure drop was generated for the two parallel connected RHHs by installation of diaphragms into the inlet nozzles of the pneumatic valves AV373 and AV473.

Operation of the Central Depressurization System without Tritium Retention Function

Regular operation of the ZTS is characterized by passage of flow through one RHH (RHH I or RHH II). In case of a defect of the RHH in operation, automatic switchover to the standby system is effected via a program controlled by the process control system (PLS). During the tests concerning takeover of the retention function by the standby system difficulties occasionally emerged in the performance of the refrigerators of the RHH just connected. This deficiency could cause in future operation excessive heating of components and, maybe, the release of HTO from partially laden molecular sieves. As a countermeasure, the process of takeover is now monitored more precisely by the process control system and, in case of failure of the refrigerator taking over, the RHH just connected would no longer be passed by gas. However, the central depressurization function of the closed circular pipeline is maintained by the flow of permanently circulated gases via a bypass valve (AV230). The pressure drop characteristic of the bypass section was compensated by means of the valve RV232 with that of RHH I. During this emergency mode of operation any tritium involving activities in the laboratory are interrupted.

IV. Tests on Hydrogen Retention at the Tritium Retention Systems with Palladium as the Catalyst

The Tritium Retention Systems with palladium as the catalyst used in the main cleaning stages (RHH) of ZTS were examined in a test series for their capability of hydrogen retention.

The retention capability tested related to hydrogen in the range of concentrations from 10,000 ppm (= 1%) down to 1 ppm, as a function of the catalyst temperature (100 °C, 180 °C, 300 °C, 450 °C) and the air flow.

Test Setup

A Tritium Retention System (TRS), construction size II, with palladium as the catalyst, was connected to a glovebox of approx. 5 m³ volume. At the operating stage I of the blower (= 30 m³/h) this corresponds to six air changes per hour; at the operating stage II (= 60 m³/h) this is equivalent to twelve air changes per hour.

The test configuration was such that the TRS can be operated either within the loop via the glovebox or in the bypass mode outside the glovebox. Hydrogen can be introduced

into the glovebox at a defined flow rate. The atmosphere of the glovebox can be homogenized in the bypass mode by means of a separate blower mounted outside the TRS.

The hydrogen concentration of the processed gas was measured downstream of the Tritium Retention System and in the box.

Hydrogen Measuring Technology

Two leak detectors UL 100 Plus, supplied by Leybold AG, were used for continuous measurement of the hydrogen concentration downstream of the TRS and in the glovebox. These instruments (quadrupole mass spectrometers) have been designed above all for use with helium; however, they can be switched over to the mass 2 (H_2). The detectors were sniffing detectors which means that a gas stream of constant flow rate is analyzed for its H_2 fraction.

The instruments were calibrated using eleven calibrating gas mixtures of different concentrations, between 5 ppm and 2% hydrogen in air.

Experimental

At the beginning of a test TRS operated via the glovebox was brought to the respective operating temperature corresponding to a specified gas flow rate (30 or 60 m³/h). When steady-state conditions had established, TRS was switched over to the bypass mode and the blower was connected to circulate the atmosphere in the glovebox. Then hydrogen was fed into the glovebox until the readout at the point of hydrogen measurement showed the desired concentration.

When steady-state conditions and the desired hydrogen concentration, respectively, had established in the glovebox, the test could be started. For this, the recirculating blower of the glovebox was disconnected and TRS operated via the glovebox. During the test the hydrogen concentrations at the gas outlet of TRS and in the glovebox were measured continuously.

When the hydrogen concentration in the glovebox approached the limit of detection of 1 ppm, the test was terminated. To do this, the glovebox was flushed with laboratory atmosphere while TRS was operated in the bypass mode and the recirculating blower was running. Flushing was done by opening one nozzle of the glovebox and by exhausting the gas at the opposite end of the glovebox using the mobile exhaust system of TLK.

Results Obtained

The dependence of the reduction of hydrogen concentration in the glovebox on the temperature of the catalyst and the gas flow rate has been plotted in Figure 6. The following results can be derived from that figure:

- The reduction of hydrogen concentration in the glovebox is nearly independent of the catalyst temperature.
- The reduction of hydrogen concentration in the glovebox is heavily dependent on the gas flow rate and hence on the number of air changes.

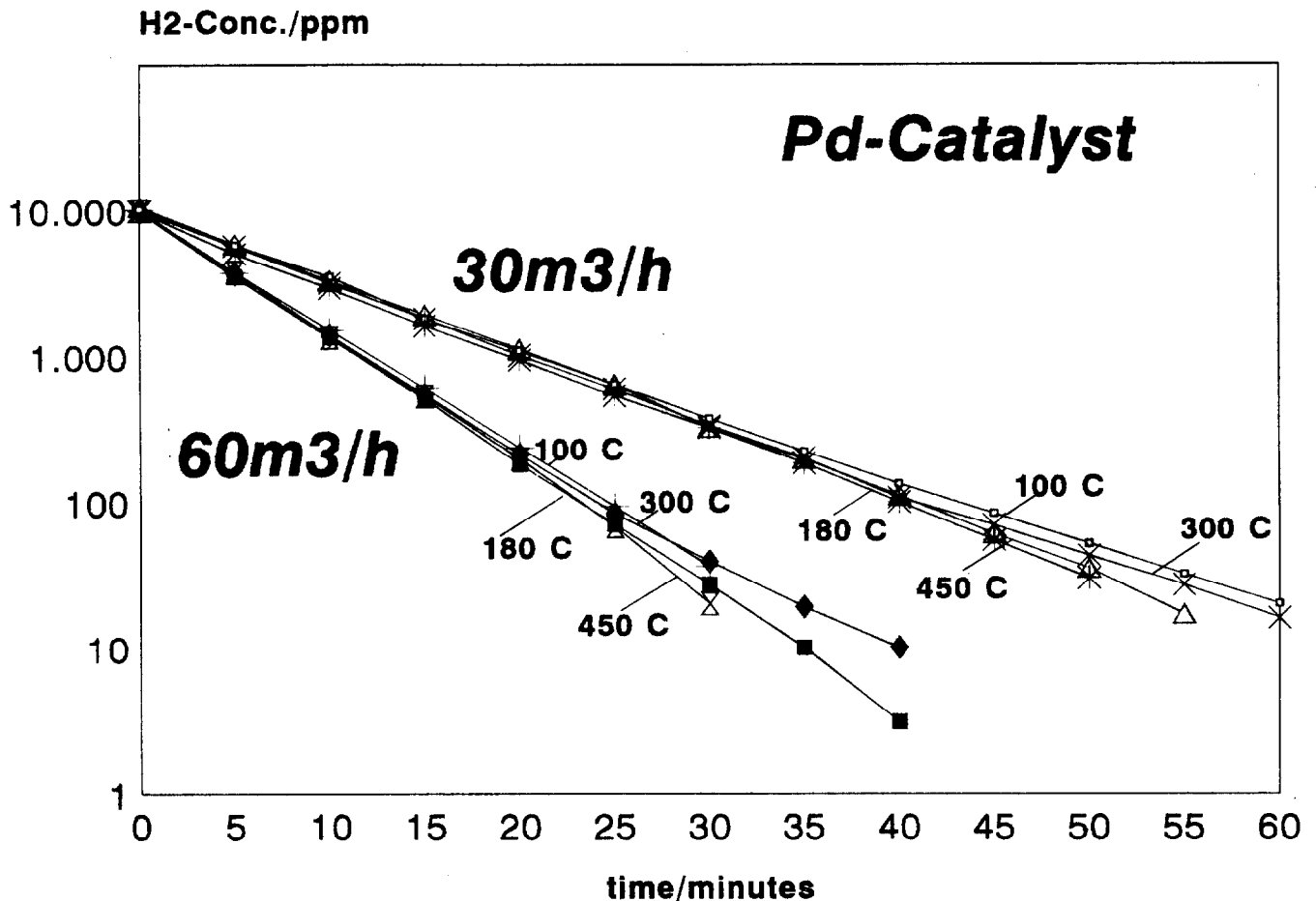


Figure 6 Dependence of decrease of concentration in the glovebox on catalyst temperature and gasflowrate.

Also Table 4 makes evident these results. It has been entered in the table after which time interval the hydrogen concentration in the glovebox has dropped to half its former value, i.e. from approximately 10,000 ppm to approximately 5000 ppm (half-life) and after which time interval a concentration of 100 ppm has been attained starting from an initial concentration of 10,000 ppm, both as a function of the gas flow rate and the catalyst temperature.

In order to be able to determine the anticipated cleaning effect in once-through gas flow - the operating mode of RHH - experiments were performed at the Radiochemistry Institute of KfK regarding the determination of the decontamination factor (DF), prior to conceiving the Central Tritium Retention System. The desired low residual concentrations of hydrogen (tritium) could be measured only with tracer amounts of tritium used. A DF >3000 was measured which is deemed adequate considering the anticipated tritium concentrations in the TLK exhaust gases (10^{11} Bq/m³ at the maximum).

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Table 4 Reduction of hydrogen concentration in the glovebox.

Gas Flow Rate	Catalyst Temperature	Half-life	Duration of Concentration Drop from 10,000 to 100 ppm
30 m ³ /h	100 °C	6 min	43 min
	180 °C	6 min	40 min
	300 °C	6 min	40 min
	450 °C	6 min	41 min
60 m ³ /h	100 °C	4 min	25 min
	180 °C	4 min	24 min
	300 °C	4 min	24 min
	450 °C	4 min	23 min

Reference

- (1) H.J. Ache, M. Glugla, E. Hutter, G. Jourdan, R.-D. Penzhorn, D. Röhrig, K. Schubert, H. Sebening and J.E. Vetter, "The Tritium Laboratory Karlsruhe: R&D Work and Laboratory Layout", Fusion Engineering and Design 12 (1990) 331-341, North Holland

DISCUSSION

GOOSSENS: I would like to ask about peak releases of tritium from the primary equipment into the glove boxes. How do you handle a peak release by accident of a relatively large quantity, including the explosion hazard?

HUTTER: I pointed out that we have multi-barriers, and if you have an escape of tritium out of the primary system into the glove box, you always have your glove box sealed. If you want to discuss a broken primary systems and a broken glove box, in the first case, the glove box is always tight, there is a glove box atmosphere treatment system that takes out the hydrogen escaping to the glove box within about two hours. I must say, for the moment, we have limited the amount of tritium per glove box to 25,000 ci, about 2.5 g of tritium. That gives in the smallest existing box of 3 m³ volume a maximum tritium concentration (homogenized) of 0.3 v%. Taking into account the continuous air flow through the box by the glove box Tritium Retention System (TRS), we don't expect a tritium concentration higher than 1% even in the vicinity of the leak (explosion limit is 4 v%). Systems with a high content of hydrogen isotope mixtures (H, D, T) are equipped with an inerted box atmosphere. Remember there are two stages of tritium retention, the glove box clean-up system and the offgas out of the box that is given to the large loop under negative pressure. This gas flow is small and is treated with the TRS-like system. In the case of a glove box disintegration, there must be a large hole to discharge tritium into the laboratory atmosphere. That is, however, the reason we have restricted the tritium amount per box. A specialist calculated that this is far from the activity accidentally allowed in the environment.

MYERS: I am not sure I understand the process, but it looks like you are taking hydrogen in the tritium state and, by treating it with a catalyst, converting it into a liquid state, to water. Is this correct? How is the tritiated water treated, removed, or retained?

HUTTER: This is correct. The water is retained on molecular sieve beds, 30 kg each by weight. These are taken out of the cleanup system and regenerated in a special unit by heating the molecular sieve to 300° C in a nitrogen stream as carrier gas. The desorbed tritiated water is condensed in a heat exchange (25° C) followed by a freezer (-196° C) to dry the nitrogen stream. The water separated and collected in this way in a vessel is transported to the KfK Decontamination Department where it is prepared for storage.

Cracking of water (hot metal bed or electrolysis) to recover the tritium is actually not foreseen in TLK because of the low tritium content expected in the waste water.

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CLOSING COMMENTS OF SESSION CO-CHAIRMAN WILHELM

I would like to give a short summary of the first three papers. The first paper handles a very important issue, how much iodine will be transferred into the dissolver offgas when a desorption process is used to prevent iodine from remaining in the spent fuel solution. Iodine may remain in small amounts in the solutions in all of the vessels of the final process of separating uranium and plutonium and may be in the vessel offgas. To take it out of this large volume of offgas is very expensive, and the decontamination factors for the vessel offgas are much lower than for the dissolver offgas, the volume of which is much smaller. So, it is very important to come down with the rest of the iodine in the dissolver dissolution of the spent fuel. I found it very interesting to get figures for these operations. The question is whether they are figures that refer to a big reprocessing plant. Still, there is a question: what form is the iodine which does not come out from the dissolver solution? The colloidal form may be only a part. It may be an important part, or it could be that it is not, as we may expect with a recycled acid solution in the dissolver. Then we will have more problems.

I was happy to hear that the THORP is finished, and I hope very much that it goes into operation. It will be quite interesting to learn what the real decontamination factor will be with this offgas system design. There is a difference in the philosophy of the units used to retain iodine. At the moment, there are two processes discussed and used. One is a dry process. People expect the decontamination factor to be a little higher than in the wet process, the target being 10^3 compared to 10^2 for the wet process. The dry process was developed to get rid of all the problems of disposing of iodine in solution; after you trap it in an alkaline solution, you have to do something with it. We have seen a lot of work in the United States to transfer iodine into a dry form for storage. It is just hard work, and I do not think it will pay out because the English can release it as an alkaline solution to the sea where long-lived iodine-129 will be diluted. In some countries, this would not be allowed, so they have to use the dry process, where they will have the material ready for final disposal in one step.

The last paper covered work done on solid material to trap iodine in the form of silver iodide. A very important point was brought out in the paper that this process is very insensitive to changes of operating parameters in the reprocessing plant, and especially in the dissolving process. That means that even when there is a huge range of operating parameters, or parameters which will change by some small accident, one can still expect high decontamination factors. I think that is very much in favor of this process and of the material used.

CLOSING COMMENTS OF SESSION CO-CHAIRMAN KIKUCHI

I want to comment on the last paper. I think development of a tritium gas treatment system will become a very important technique for nuclear fusion research. Of course, nuclear fusion is far from commercial operation, but several places are doing research using tritium. The technology discussed in the paper uses a catalytic reaction which oxidizes tritium gas to water. The second paper on the program (that was not given today) uses the same technology. These technologies could become even more important, not only in fusion research but also for fuel reprocessing plants, when environmental standards become more severe. Therefore this research should be continued.