Session 6

ADSORPTION

WEDNESDAY: August 4, 1982
Co-CHAIRMEN: C.A. Burchsted, Oak Ridge National Laboratory
V.R. Deitz, Naval Research Laboratory

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NEW ADSORBENT, SILVER-ALUMINA FOR RADIOACTIVE IODINE FILTER

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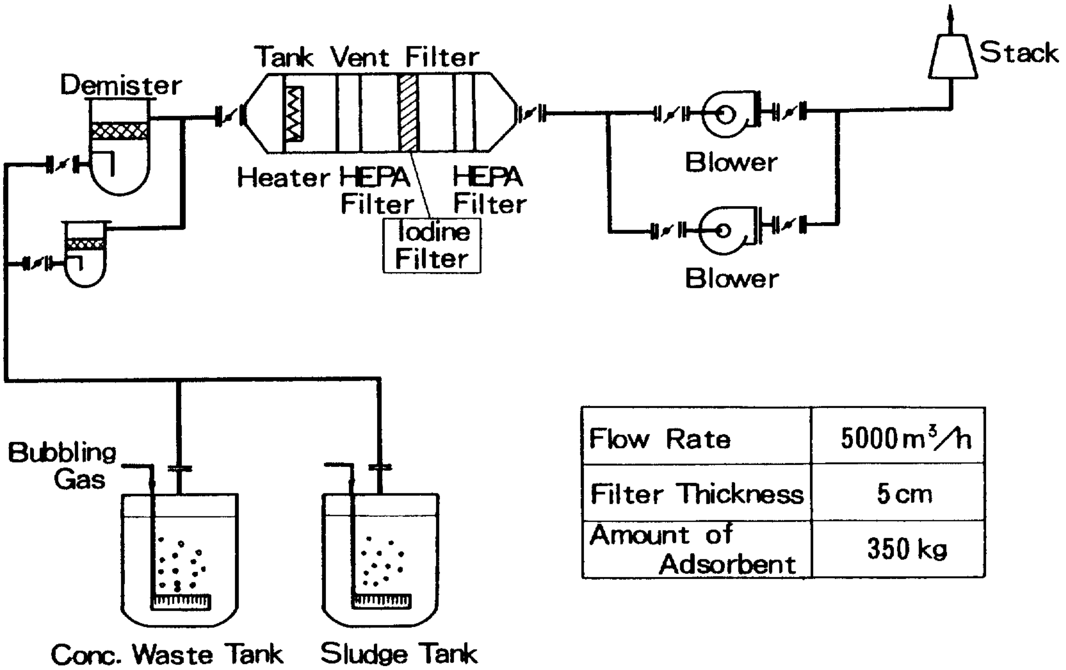
Abstract

Silver-alumina adsorbent has been developed for the iodine filter installed in the off-gas treatment system of a radioactive waste tank vent. In order to improve the removal efficiency under a highly humid atmosphere and to reduce susceptibility to contaminants in the air, the optimum average pore size of alumina was determined to be about 600 Å when the impregnated silver compound was silver nitrate. The holding capability of impregnated silver was also improved by developing a double pore structure alumina. The effects of chemical forms and contaminants on the removal efficiency were explained by an ionic reaction mechanism at high relative humidity, which involves water vapor adsorption in micro-pores by capillary condensation followed by formation of a silver iodide compound.

I. Introduction

For the past several years, emphasis has been placed on the reduction of radioactive gaseous waste released from nuclear facilities to the "as low as reasonably achievable" level. It is known that, among the radioactive gases encountered at nuclear facilities, fission produced iodine and its compounds are the primary species.

One source of such iodine in light water reactors(LWR) is the off-gas of the radioactive waste tanks. Figure 1 presents an outline of a typical tank vent off-gas system. Usually bubbling gas is introduced to the tanks, containing concentrated liquid waste (main composition: 20 wt% Na_2SO_4) and sludge, to stir the wastes and prevent the solid waste from sedimemtation. Consequently the off-gas contains moisture and contaminant gases such as NO_2 and SO_2. The iodine adsorbent utilized in the tank vent filter must be resistant to deterioration from these two factors.



Flow Rate	5000 m³/h
Filter Thickness	5 cm
Amount of Adsorbent	350 kg

Fig.1 Outline of Tank Vent Off-Gas System

Recently, Ag impregnated adsorbents, such as Ag-zeolite and Ag-silica gel, have been developed for application under similar gas conditions.(1)-(3)

Table I compares the specifications of these adsorbents with newly developed, Ag-alumina, as well as listing the gas conditions to be treated. Silver-zeolite and Ag-silica gel were developed primarily for the treatment of reprocessing plant off-gas. The main differences between tank vent gas and reprocessing plant off-gas are in the chemical forms of radioactive iodine (mainly CH_3I), concentration (10^{-3}- 10^{-2} ppm), relative humidity (50 - 90 %) and NO_2 concentration (10^{-2} ppm). Therefore, good removal efficiency for low concentration CH_3I is a basic requirement for the tank vent iodine adsorbent, while adsorption capacity is more important for the reprocessing filter since iodine concentration is high (∼100 ppm).

Thus research objectives are development of a new adsorbent that:

(1) has high removal efficiency for CH_3I;
(2) maintains high performance under a highly humid atmosphere;
(3) is not susceptible to contaminants in the air; and
(4) contains a smaller amount of impregnated Ag.

The fourth point is important particularly for large filters, which requires large amounts of adsorbent.

Table I Comparison of Iodine Adsorbents

			Silver Zeolite	Silver Silica Gel	Silver Alumina
Adsorbent Spec.	Carrier		Molecular Sieves 13X	Silica Gel	Activated Alumina
	Impregnated Material		Ag^+	$AgNO_3$	$AgNO_3$
	Content (wt%)		37	12	10−20
	Particle Size (mm)		1−2	1−2	1−2
	Maker		CTI (U.S.A)	Süd Chem (W. Germany)	Hitachi
Gas Conditions	System		Reprocessing Plant Off Gas		LWR Tank Vent
	Iodine	Species	I_2 (>90%)		CH_3I (∼90%)
		Conc. (ppm)	100		$10^{-3}-10^{-2}$
		Isotope	^{129}I ($T_{1/2}$: 2×10^7 y)		^{131}I (8d)
	Temp. (℃)		150	150	10−50
	Rel. Humidity (%)		<1	<1	50−90
	NO_2 Conc. (ppm)		10^4	10^4	10^{-2}

II. Experimental

The experimental conditions and specifications of Ag-alumina are given in Table II. The test facility for the dynamic adsorption is shown in Fig. 2. Details of the facility and experimental procedures are described in a previous report.(4) Air or air mixed with SO_2 and NO_2 was used as flow gas. The ^{131}I labelled CH_3I was prepared by the conventional method using sodium iodide and dimethyl sulfate. The specific activity was about 1 mCi/gCH_3I. After the adsorbents were preconditioned by passing an air stream with the desired humidity through the adsorbent for at least 16 hours, air containing CH_3I was passed through for 0.5 hours, followed by clean air for at least another 0.5 hours to remove unreacted CH_3I from the column. In the regular experiments, a 10 cm thick column (2.5 cm for each section x 4 sections) was used and the CH_3I removal efficiency was determined by measuring the gamma rays emitted from ^{131}I. The radioactivity of ^{131}I on adsorbents in each column section was measured by a 3 in x 3 in NaI(Tl) detector, and the removel efficiency E (%) for 5 cm thick adsorbent was calculated using the following equation.

$$E\ (\%) = \frac{A + B}{A + B + C + D} \qquad \text{..........(1)}$$

where A, B, C, D = radioactivity adsorbed in the column sections.

The impregnation of Ag compound was performed by dipping alumina into silver nitrate ($AgNO_3$) solution under reduced pressure. The chemical form was transformed by exposing the $AgNO_3$ impregnated alumina to a solution of sodium salt of the desired compound, i.e. $NaClO_3$ and Na_2SO_4 for $AgClO_3$ and Ag_2SO_4, respectively. For Ag_2O, $AgNO_3$ was hydrolyzed by exposing it to a NaOH solution, then drying the adsorbents.

Table II Experimental Conditions

Test Conditions	Temp.		10 − 50°C
	Rel. Humid.		0 − 90%
	Lin. Velocity		20 cm/s
	Iodine	Species	CH_3I
		Conc.	10^{-3} − 1 ppm
	SO_2 Conc.		200 ppm
	NO_2 Conc.		200 ppm
	Pre−Blow		≧ 16h
	CH_3I Injection Time		0.5 h
	After−Blow		≧ 0.5 h
Adsorbent	Ag Content		2 − 20 wt%
	Chemical Forms		Ag_2O , Ag_2SO_4 , $AgNO_3$ etc.
	Pore Diameter		100 − 1000 Å
	Surface Area		20 − 300 m²/g

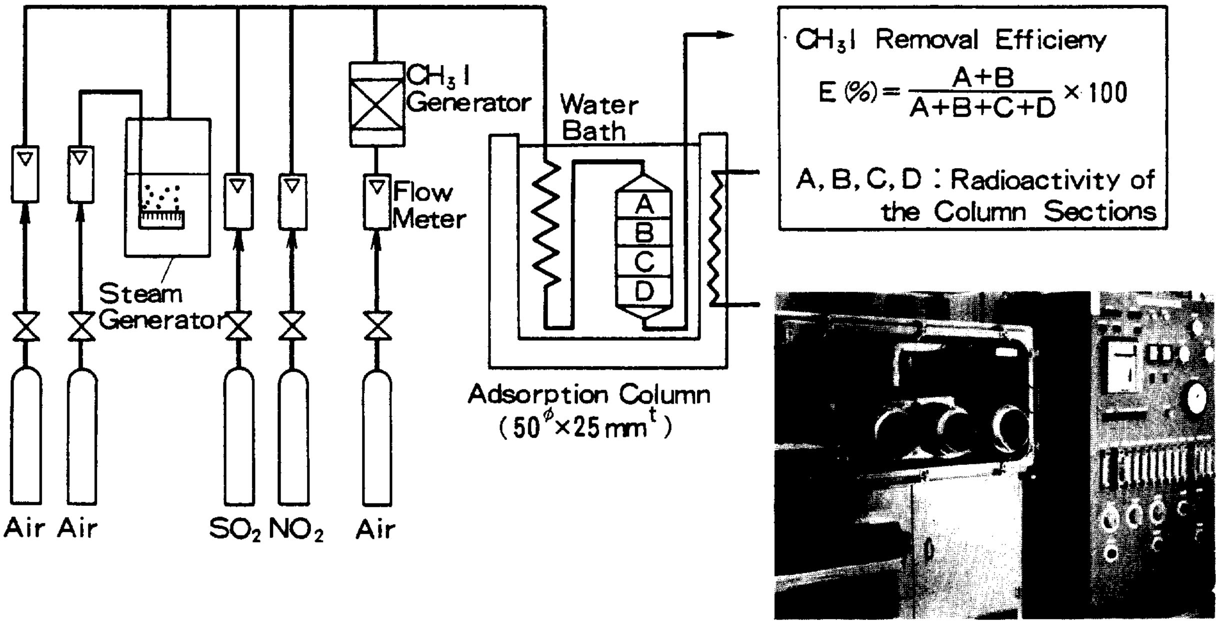


Fig.2 Flow Diagram of Experimental Apparatus

III. Results and Discussion

Selection of Impregnated Silver Compounds

Figure 3 compares the CH_3I removal efficiency of Ag-alumina impregnated by Ag_2O or $AgNO_3$, as a function of relative humidity. In the case of Ag_2O (solubility: $\sim 10^{-4}$ mol/l), the CH_3I removal efficiency decreases sharply at low relative humidity, while $AgNO_3$ (solubility: $\sim 10^{1}$ mol/l) retains its efficiency even at high relative humidity. The amount of water vapor adsorbed is also shown in Fig. 3, and no difference was observed for the two adsorbents. Qualitatively speaking, the water vapor is adsorbed into the micro-pore by a capillary condensation process, resulting in the formation of a water layer on the impregnated Ag compound. These results suggest the CH_3I removal efficiency is strongly dependent on the chemical forms at high relative humidity, i. e. higher efficiency is obtained with Ag compounds of larger solubility.

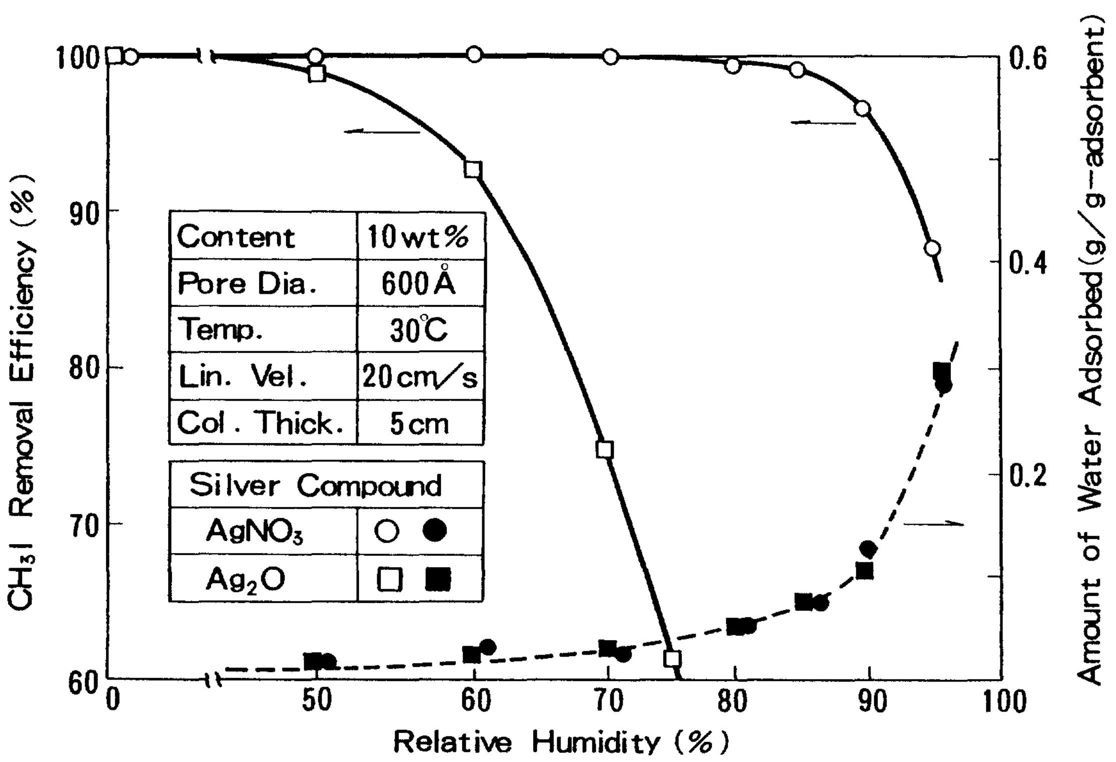


Fig.3 Effect of Relative Humidity on CH_3I Removal Efficiency

To examine the effect of relative humidity and the chemical forms in more detail, CH_3I removal efficiencies for five different Ag compounds (Ag content: 10 wt%) were measured. Figure 4 summarizes the efficiencies at different relative humidities as a function of solubility. More than a 99 % removal efficiency was obtained at 0 % relative humidity for all compounds. However, at higher relative humidity, a higher efficiency was obtained with compounds of larger solubility. The $AgNO_3$ demonstrated the highest removal efficiency among the compounds we examined. The effect of chemical form and relative humidity can be explained by the following reaction mechanism. The water adsorbed into the micro-pore forms a water layer on the impregnated Ag compound (cf. Fig. 4). In the case of low solubility Ag compounds such as Ag_2SO_4 and Ag_2O, this water layer interferes with the reaction between CH_3I and Ag. In the case of high solubility Ag compounds such as $AgNO_3$, Ag^+ ions in the water layer contribute to the CH_3I adsorption by a water surface ionic reaction. However, the Ag^+ ion concentration decreases slightly due to excess water adsorption at high relative humidity which reflects the lowered CH_3I removal efficiency even for $AgNO_3$. At low relative humidity, since CH_3I reacts directly with the Ag compound through a gas-solid reaction, differences in removal efficiency between the impregnated Ag compounds cannot be observed.

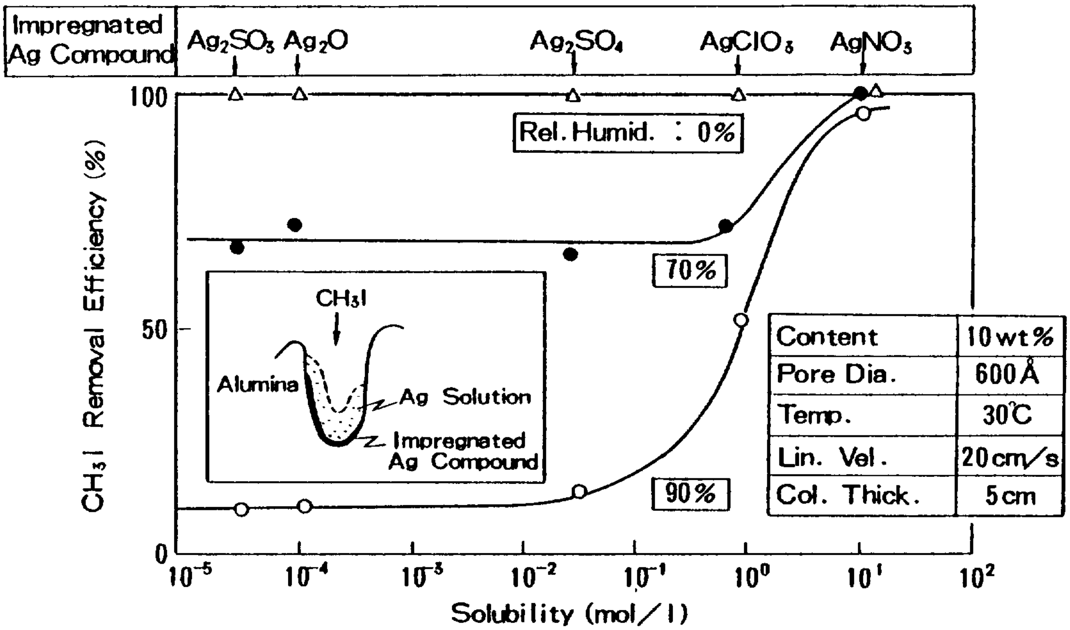
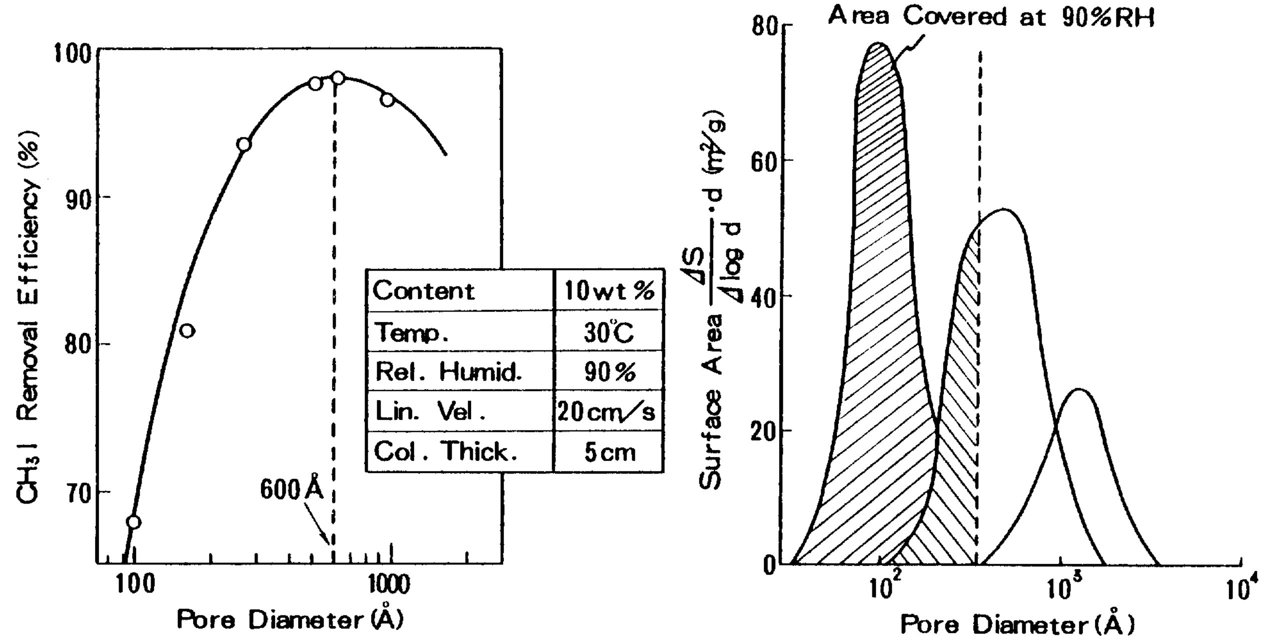


Fig.4 CH_3I Removal Efficiency and Solubility of Silver Compounds

Determination of Pore Diameter

The effect of pore diameter on the removal efficiency was examined using alumina impregnated with 10 wt% $AgNO_3$. The results are shown in Fig. 5(a). The maximum efficiency was obtained at a pore diameter of 600 Å. The diameter dependence can be discussed in two ways; capillary condensation and effective reactive surface area.(4) In the capillary condensation process, the micro-pore is filled with water vapor from a smaller size pore as the relative humidity increases. The relationships between the pore diameter, amount of condensated water and the relative humidity can be quantitatively expressed by Kelvin's equation.(6) Figure 5(b) shows the pore diameter distribution of three samples having average pore diameters of 100, 600 and 1000 Å. The area covered with water vapor at a relative humidity of 90 %, calculated using Kelvin's equation, is also indicated. Since the ionic reaction process is less efficient than the direct reaction process, as described in Fig. 4, the adsorbent with a pore diameter of 600 Å has a higher removal efficiency than the 100 Å sample. The efficiency decrease for 1000 Å is due to the decrease of surface area. Thus the optimum average pore diameter for alumina was determined to be 600 Å.



(a) CH_3I Removal Efficiency

(b) Pore Distribution

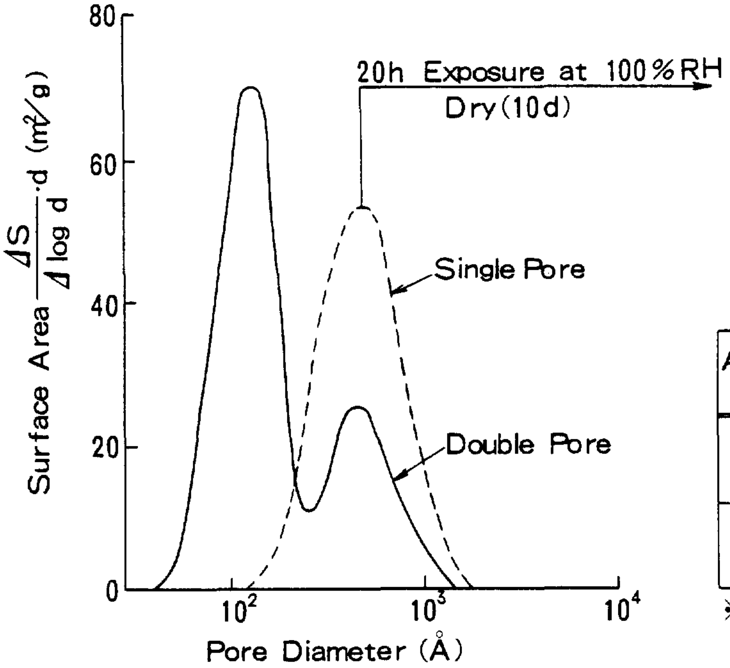
Fig.5 Determination of Pore Diameter

Improvement of Silver Holding Capability

One problem was found for the Ag-alumina with 600 Å pore diameter. When the adsorbent was exposed to high relative humidity for a long time (e.g. 100 % for 20 hours) and then gradually dried for 10 days, horn-like crystals growing out of the pore were observed. A microscopic photo of the crystal growth is shown in Fig. 6. X-ray crystallography showed these crystals to be $AgNO_3$. This phenomenon can be explained by deliquescence and recrystallization of $AgNO_3$ in the micro-pore. Since the deliquescence humidity for $AgNO_3$ at 20 °C is about 83 %, impregnated $AgNO_3$ is completely dissolved in the water condensed in the micro-pore. When the adsorbent is dried very slowly, $AgNO_3$ recrystallizes and grows out, if the pore is a simple structure. This phenomenon was not observed when the adsorbent was dried quickly, e.g. within 5 hours, probably due to the formation of fine crystals.

In order to prevent this problem, alumina having a complex pore structure of two sizes (150 and 600 Å), or double pore alumina, was developed. The wearing test using ball mill was conducted to evaluate Ag loss due to this crystal growing. A 100 g sample was put into the ceramic ball mill (15 cm x 15 cm) along with 10 ceramic balls and Ag content was measured after 10 minutes rotation at 50 r.p.m.. The samples were both single and double pore alumina which had been exposed to a 100 % relative humidity atomosphere. The results show that Ag content loss from 10 to 8.3 wt% was observed for single pore alumina, while little loss (10 to 9.7 wt%) was observed for the double pore sample.

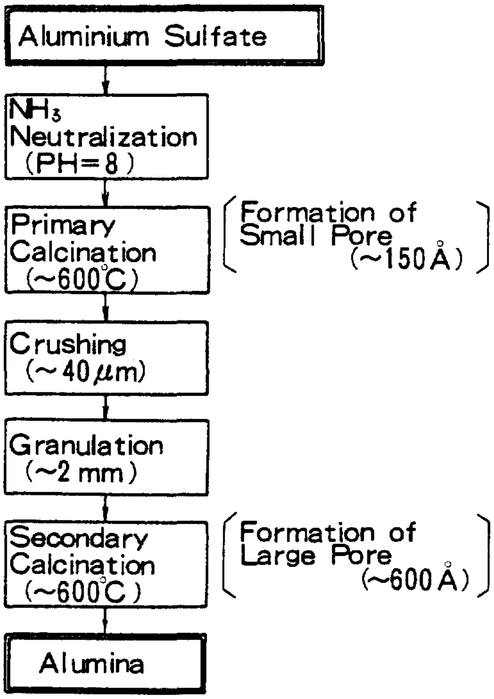
The preparation method for double pore alumina is outlined in Fig. 7(a). The starting material, aluminium sulfate ($Al_2(SO_4)_3$), was neutralized by NH_3 followed by primary calcination, which forms small pores of 150 Å. Then the product was crushed into a 40 μm powder followed by granulation to 2 mm particles. The granular particles were then calcinated again at 600 °C with large pores of 600 Å being formed. Figure 7(b) shows the CH_3I removal efficiency as a function of Ag content at 90 % relative humidity. Optimum Ag content to maintain a removal efficency about 95 % is 10 wt%. At higher Ag content, no significant increase in efficiency was observed.

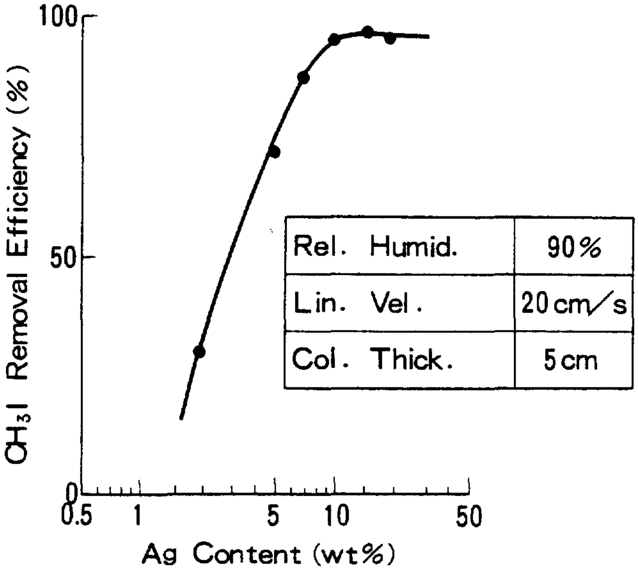


Ag Content after Wearing Test※ (Initial Ag Content : 10wt%)	
Single Pore	8.3wt%
Double Pore	>9.7wt%

※ Wearing Test :
Ball Mill (50 r.p.m , 10 min)

Fig.6 Improvement of Silver Alumina





Rel. Humid.	90%
Lin. Vel.	20cm/s
Col. Thick.	5cm

(a) Preparation of Double Pore Alumina (b) Silver Content

Fig.7 Preparation of Double Pore Alumina and Silver Content

The Effects of Contaminant Gases

The CH_3I removal efficiency was measured after adsorbent exposure to a number of possible contaminant gases (Table III). Data for Ag^+ impregnated adsorbent (Ag-zeolite) is also shown as a reference.(7) The effect of NO_2 would be serious particularly in the reprocessing plant, since its concentration is about 10000ppm.(8) The NO_2 does not have a large effect on either adsorbent. However the removal efficiency of Ag^+ is greatly reduced by SO_2, while only slightly changed for $AgNO_3$. This difference can be qualitatively attributed to the chemical form of Ag impregnated, i.e. Ag^+ for Ag-zeolite and $AgNO_3$ for Ag-alumina, which undergo different chemical reactions with SO_2.

Table III Effect of Contaminant Gases on Removal Efficiency

Chemical Form	Ag^+ (ref.7)		$AgNO_3$	
Contaminant Gas	Contaminant Conc. (Vol%)	CH_3I Removal Efficiency (%)	Contaminant Conc. (Vol%)	CH_3I Removal Efficiency (%)
NO_2	10	99.8	2.0	99
SO_2	1.9	31.5	1.0	97
H_2S	0.06	42.2	—	—
Test Conditions	Temp. : 90℃ Rel. Humid. : 90% Lin. Vel. : 23 cm/s		Temp. : 20℃ Rel. Humid. : 70% Lin. Vel. : 20 cm/s	

When SO_2 gas dissolves into the water condensed in the micro-pore, sulfite ion, SO_3^{2-} is formed.(9)

$$SO_2 + H_2O \longrightarrow SO_3^{2-} + 2H^+ \quad \text{.......................} (2)$$

For Ag-zeolite, the Ag is impregnated by an ion exchange method, thus Ag ionizes easily and reacts with SO_3^{2-} forming insoluble silver bisulfite, Ag_2SO_3.

$$2Ag^+ + SO_3^{2-} \longrightarrow Ag_2SO_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Thus the amount of Ag^+ ions available to react with CH_3I is depleted, resulting in a sharp decrease of CH_3I removal efficiency. For Ag-alumina, impregnated $AgNO_3$ reacts with SO_3^{2-} in the following equation.

$$2Ag^+ + 2NO_3^- + SO_3^{2-} \rightleftarrows Ag_2SO_3 + 2NO_3^{2-} \quad \ldots\ldots(4)$$

Since the strongly acidic ion NO_3^{2-} exists in the solution, the Ag_2SO_3 redissolves and the depletion of Ag^+ ion is not as much, which results in the higher removal efficiency.

The small effect of NO_2 can be explained by the formation of very soluble $AgNO_3$ which does not deplete Ag^+ ion available for the CH_3I removal reaction. This analysis of effects by contaminant gases further supports the adsorption reaction mechanism at high relative humidity.

Pence et al.(10) studied the CH_3I adsorption mechanism on Ag-zeolite and found silver iodide (AgI) in the zeolite structure and methyl alcohol (CH_3OH) in the gas. Wilhelm et at.(11) investigated the reaction products of several alky halides R-I with $AgNO_3$ impregnated silica gel and proposed the following.

$$AgNO_3 + R\text{-}I \longrightarrow \left[NO_3RIAg\right] \longrightarrow RNO_3 + AgI \quad \ldots\ldots(5)$$

A similar sequence might occur in Ag-alumina at low relative humidity. However, the reaction mechanism must be more complicated at high relative humidity since our data indicate the Ag^+ ion contributes to the reaction process in some steps. Further efforts must be directed towards elucidating this.

IV. Conclusion

Silver impregnated alumina was developed for the tank vent filter. In order to maintain high CH_3I removal efficiency in highly humid air with contaminant gases, the chemical form of the impregnated silver compound ($AgNO_3$), its content (10 wt%) and pore diameter were experimentally determened. Double pore alumina (150 Å and 600 Å average diameters) was developed to improve Ag holding capability and prevent loss of impregnated Ag.

The effects of relative humidity, chemical form and contaminant gases suggest that a gas-solid direct reaction is the predominant mechanism while an ionic reaction involving Ag^+ ion occurs in the micro pore at higher relative humidity.

V. Acknowledgments

The authors wish to thank Messrs. K. Kamiya and M. Kitamura of Energy Research Laboratory for their valuable discussion. The authors also express their appreciation to Messrs. H. Irokawa and M. Ichimura of Japan Engelhard Co. for supplying the samples used in these experiments.

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DISCUSSION

DEITZ: What was the total Me^{127} during the test with 1 millicurie $^{131}I\text{-}CH_3$?

YUSA: Total concentration of iodine, mainly ^{127}I, was between 10^{-3} and 1 ppm during the test.

ROUYER: What is the influence of NO and what is the initial efficiency?

YUSA: When $AgNO_3$ is used as the chemical form of impregnated Ag, there is no difference betwen NO_2 and NO because of the large solubility of $AgNO_3$. Initial CH_3I removal efficiency is more than 99% under a condition of 70% R.H.

PORREY: Is the 10% silver content on the basis of silver or $AgNO_3$, and does the $AgNO_3$ come off the substrate if excess water is present?

YUSA: It is on the basis of silver. Silver does not come off the substrate unless the adsorbent is washed out by water.

BURCHSTED: Are you concerned about the situation were sprays come on, or something like that?

PORREY: Condensation might take place when a high relative humidity stream reaches the bed before the bed is preheated.

HAAG: Your talk indicated that at 90% R.H., capillary condensation of H_2O in the 150 Å pores is crucial to the overall process. In the literature, it has been reported that 2 or 3 layers of surface water (corresponding to a relative humidity, or P/P_o, about 50%) will behave as a liquid film. Such a condition, in your case, should result in greater available surface areas as the pores (150 Å) would not be filled at these conditions. How does your double-pore material behave under such conditions and is the length of the mass transfer zone decreased, or the bed efficiency increased?

YUSA: At 90% R.H., the impregnated $AgNO_3$ on the surface of 600 Å pores, which are the larger pores of the double pore alumina, can retain high CH_3I removal efficiency.

WILHELM: In your flow sheet you showed a heater in front of your filter system. At what relative humidity is your filter working?

YUSA: Less than 90% relative humidity.

WILHELM: With the heat on, you lower the temperature by only 7° and you will be down to 70% relative humidity in the range between normal room temperature and 90°, so I think it will be much lower. My next question is, did you try carbons under these same conditions? We have never seen an LWR reactor problem we couldn't solve with impregnated carbons. Did you try impregnated carbon under the same conditions and did they work?

YUSA: No.

PORREY: Why was it necessary to develop a new adsorbent? Carbon is very low in price compared to silver impregnated materials.

BURCHSTED: I believe there are applications where fire could be a consideration and fire-resistant inorganic material might be preferrable.

WILHELM: We would like to know if this was a special purpose application because it has a certain impact on design with respect to safety. I don't know that silver substituted inorganic adsorbents are really necessary.

CHARCOAL PERFORMANCE UNDER SIMULATED ACCIDENT CONDITIONS

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Abstract

Regulatory Guide 1.52 stipulates a radiation level for iodine buildup of the adsorber of 10^9 rads as one of typical accident conditions for atmospheric clean up systems. The research in progress at the Naval Research Laboratory involves the interaction of the following parameters: (1) in-service weathering, (2) exposures to atmospheric contaminants, and (3) radiation exposure. Both service and weathered carbons have been exposed to the gamma-radiation from the NRL cobalt-60 source (about 1 MeV) and to the radiation from the NRL Linac facility (about 45 MeV). Total radiation levels of 10^7, 10^8, and 10^9 rads were used and the carbons evaluated before and after radiation by the methyliodide-131 penetration test (30°C, ASTM 3803-79). Unexpected improvements in the efficiency of the carbons for methyliodide trapping were observed after static (and with air flow) exposures of the carbons to the irradiation. These will be reported as a function of the radiation level, service age of the carbon, and the original impregnation of the carbons.

I. Introduction

At any stage in the service life of an activated carbon adsorber that is used in air cleaning applications, the carbon must have the capability to retain airborne contaminants that may be liberated under accident conditions. During normal operations there is a slow and continuous degradation in the efficiency of a service carbon (1,2) and, when accident conditions are superimposed, additional problems can be expected.

It is not possible, of course, to expose carbons in the laboratory to a radioactive gas at the high Curie level of an accident. However, the carbons can be exposed to equivalent radiation levels (γ and β sources) and at the same time be subjected to gas flows of non-radioactive species.

In a nuclear accident mode, the concentration of $^{131}I_2$ can increase manyfold above background levels, thus increasing the rates of chemical reaction with both the base carbon and the impregnated chemicals. The iodine trapped within the carbon networks can then slowly form the more volatile methyliodide and ''bleed'' (3) into the effluent air at a rate that will be dependent on the accumulated carbon weathering, the impregnation chemicals, and the magnitude of the radiation dose. Several accident scenarios were postulated and the subsequent carbon behavior was studied. Service and weathered carbons have been exposed to γ-radiation (^{60}Co, approximately 1 MeV) and to the radiation from the NRL LINAC (linear accelerator, approximately 45 MeV) for total radiation levels of 10^7, 10^8 and 10^9 rads (4).

II. Radiation Exposures of Carbons to the γ-Source ^{60}CO

The samples are positioned around the Cobalt-60 A-source at NRL as shown in Figure 1. The static exposures of the carbons to date have made use of the positions A-1, A-3, A-5, and A-7. The A-1 position is located within the cylindrical array of eight Co-60 rods and the remaining positions are outside of this array, as shown. The half-life of Co-60 is 5.2 years and the activity was essentially constant over the duration of each exposure. The calibrated intensities at the three positions are:

A-1	7.5×10^5 rads per hour
A-2 to A-7	1.4×10^4 rads per hour
A-8 to A-19	2.5×10^3 rads per hour

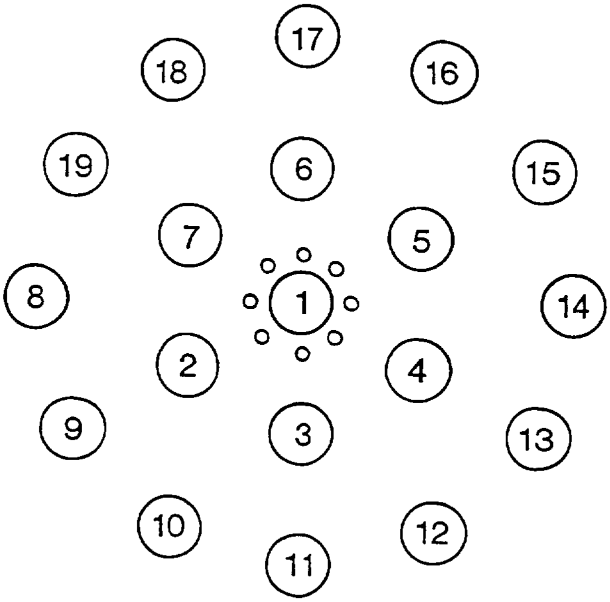

Figure 1: The A-1 position is located within the cylindrical array of eight Cobalt-60 rods as shown above.

The sample container is of stainless steel, 3 in. (7.62 cm) i.d., and the useful height in the radiation field was 2.5 in., (6.35 cm), measured from the center. This permits a sample volume of 580 cm^3. The closure at the top is made with a new 3 in. (7.62 cm) O-ring (synthetic rubber) and the assembly lowered through a depth of 12 ft. (3.66 meters) water (22°C) to the desired location.

Results

New Impregnated Carbons. In earlier studies (1,2), it was found that water vapor retained by new, impregnated carbons had a degrading influence on subsequent tests for methyliodide-131 penetration. It was considered worthwhile, therefore, to irradiate several new carbons for about 100 hrs, with and without the added moisture and without air flow and to determine the subsequent penetration of methyliodide-131.

The results are given in Table 1. Tests 1, 2, and 3 were made with dried carbons in the period 20-24 November 1981. The carbons, prehumidified in an air flow of 90% relative humidity (21-24 November), were then irradiated in tests 4, 5, and 6 for the period 24-28 November. The total radiation flux was approximately the same in both cases, namely 1.4 x 10^7 rads. The subsequent penetration test with methyliodide-131 was made by procedure for all samples: The air flow at 95% RH was maintained for two hours; the insult of methyliodide-131 in 95% RH was then added for two hours, and finally, the air purge at 95% RH was conducted for four hours.

The radiation damage to the above new carbons, as measured by methyliodide penetration, was not significant. In two of the three carbons, prehumidification before radiation gave the same behavior as previously observed for prehumidified and non-prehumidified penetration tests.

Table 1: Penetrations of methyliodide-131 through three new carbons after exposure to γ-radiation from A-source of Cobalt-60.

Position in ^{60}Co Source		Carbon	NRL Test	Exposure Time	Total Rads	Penetration %	
1	A-3	615	5217	98 hours	1.46x10^7	0.27	.02
2	A-5	727	5218	98 hours	1.39x10^7	0.30	.11
3	A-7	S and S	5219	98 hours	1.49x10^7	0.08	.06
			Prehumidified Carbon				
4	A-3	615	5221	96 hours	1.38x10^7	0.10 0.16	.08 .08
5	A-5	727	5222	96 hours	1.32x10^7	1.40	.84
6	A-7	S and S	5223	96 hours	1.42x10^7	1.51	.84
			13 Jan. - 6 March (1981)				
7	A-1	G-615 new, as received	5228	52.15 days	9.03x10^8	0.07	.05

A total exposure of 9 x 10^8 rads was completed with a sample of G-615 (KI and TEDA impregnation) placed in the A-1 position (see Table 1). The required time was estimated to be 56 days. The exposure was interrupted in short intervals for which an accurate log was maintained. The integrated intensity for the 52.15 days in the A-1 position (7.22 x 10^5 rads/hr, av.) was 9.03 x 10^8 rads. The penetration of methyliodide-131 after the long exposure was 0.07 ± .05%. This value is of the same order of magnitude previously observed for G-615 (see Table 1) without radiation. One may conclude at this point in time that a new carbon that passes the ASTM qualification test is not subject to significant degradation under the above conditions of radiation exposure.

Radiolysis of Used Carbons

Since all carbons accumulate atmospheric contaminants during the time in service, the ionization of some of these contaminants in the radiation field and the retention of the products was considered as an influence on the retention of iodine compounds by activated carbons. Two used carbons were first irradiated, each at 10^7 and 10^8 rads, in the Co-60 facility. The penetration of methyliodide-131 was determined before and after the irradiation. The results are given in Table 2.

The NRL sample 5143 was a discard carbon removed from a utility operation where it had been in place for four years. The moisture content was 19.7% and the pH of the water extract was 7.3. It was installed as a KI_x-impregnated coconut carbon.

The NRL sample 5233 had been used for two years in a glove box operation in which iodine-125 was used to prepare organic preparations for medical treatments. The pH of water extract was 6.9 and there was no significant change in the pH after exposure to Co-60 radiation. The material when new was a co-impregnation of TEDA (triethylenediamine) and KI (potassium iodide) on coconut shell carbon.

Table 2: Penetration of Methyliodide-131 before and after ^{60}Co irradiation.

NRL sample	% Penetration of Methlyliodide-131*		
	Orignal	10^7rads	10^8rads
	Static Environment		
5143	31.0	16.4	6.31
5233	30.1	11.7	7.25
	Continuous Air Flow		
5143	31.0	-	4.45 3.84

*Standard Test Procedure ASTM/ANSI D3803-79

The exposure of the above two samples to the γ-radiation of ^{60}Co decreased the penetration of methyliodide-131. In other words, the efficiency for the removal of methyliodide-131 was increased. This is a remarkable observation and will be further supplemented by the results obtained after exposures of the same carbons to the LINAC radiation.

III. Linac Irradiation of Carbon Samples At NRL

Since the times required to reach 10^9 rads in the available positions of the ^{60}Co facility proved to be excessive, the use of the NRL LINAC (linear accelerator) facility was explored with the cooperation of Dr. K.M. Murray (Code 6654). A cylindrical aluminum sample container (11 cm. diameter and 11 cm. high) was used to expose the activated carbons. The total volume of approximately one liter was divided into four equal sections (to accommodate four different samples) by inserting thin aluminum partitions having a snug fit with the inside diameter and with the inside height. Each section could hold about 200 cc of carbon. The container was mounted on a rotating base operating at about 5 rpm.

In order to determine the dose rate, three short tests were made by Dr. Murray and the LINAC staff on 7 January 1981. In the first two tests, an array of nine TLD's (thermoluminescent dosimeter) was placed at first 50 cm and then at 75 cm for about three seconds at each location. The 75 cm location resulted in a more uniform dose distribution than did the 50 cm and was chosen as the final distance. The dose count distribution as a function of distance was determined.

Choosing a dose of 20 x 10^3 rads as representative of most of the sample, the value of 5.5 x 10^3 rads per count was obtained with the VFC (voltage to frequency converter) set at 1 HZ/VOLT. The following counts correspond to the designated total rads that are desired:

1.8 x 10^5 counts	10^9 rads
1.8 x 10^4 counts	10^8 rads
1.8 x 10^3 counts	10^7 rads
1.8 x 10^2 counts	10^6 rads

Induced Activity After LINAC Irradiation

The first samples were irradiated continuously at NRL on 10-11 August 1981, resulting in 191,000 counts on the beam monitor. This corresponded to a total dose of 1.05 x 10^9 rads.

The irradiated samples were found to be radioactive. The presence of this activity raised a problem of interference in subsequent penetration tests with iodine-131 when crystal counting is employed. Using a weight of 1g from each of the four samples, Dr. K.M. Murray made an analysis for the induced activity. The spectrum of each sample was found to be dominated by the gamma rays of I-126, as shown below:

1.	KI + TEDA (G-615)	0.25μCi/g	50.9μCi/sample
2.	KI + TEDA (G-615)	0.25μCi/g	46.7μCi/sample
3.	KI + TEDA (BC-787)	0.27μCi/g	43.1μCi/sample
4.	KI + TEDA (KITEG II)	0.14μCi/g	23.4μCi/sample

Linac exposures have since been made at 10^8 and 10^7 rads. Table 3 summarizes the results for the formation of radioiodine-126 which decreased about tenfold for each tenfold decrease in the total rads of exposure.

The iodine-126 activty is attributed to a γ,n nuclear reaction with ^{127}I. In addition to I-126, other minor reactions were detected: I-127 $(\gamma, 3n)\rightarrow$I-124 and C-12 $(\gamma, n)\rightarrow$C-11. The half-life of the above radioactive species are:

I-126	13.2d	C-11	20.5m
I-124	4.2d		

Table 3: Formation of Iodine-126 in Linac Exposures.

Irradiation		Measured		Calculated to t = 0
Date	NRL	μC I	Date	μC I
10-11 Aug 81 at 10^9 rads	5242	21.71	27 Aug.	50.9
	5243	20.99	26 Aug	46.7
	5244	18.39	27 Aug	43.1
	5245	10.52	26 Aug	23.4
20 Oct 81 at 10^8 rads	5251	2.02	3 Nov	4.26
	5252	1.73	5 Nov	4.06
	5253	1.99	2 Nov	3.98
	5254	2.00	3 Nov	4.22
20 Oct 81 at 10^7 rads	5255	0.174	12 Nov	0.593
	5256	0.314	2 Nov	0.628
	5257	0.166	12 Nov	0.566
	5258	0.242	5 Nov	0.567

The initial intensity of iodine-126 A(o) was calculated from the measured value A(t) at time t as follows: $A(t) = A(o)e^{-kt} = A(o)e^{-0.693\ t/t_{1/2}}$, where $t_{1/2}$ is the half-life. Sufficient iodine-126 activity was found to invalidate a penetration measurement based on a sodium iodide crystal counting procedure. This is due to the interference of the Compton Scattering from ^{126}I into the channel used for the ^{131}I measurement.

Gamma-ray analyses were then carried out utilizing 10% efficient Ge-Li detectors and a Canberra Series 80 multichannel analyzer system used in conjunction with a PDP 11/34 computer (Nuclear Environmental Services, 3 Choke Cherry Road, Rockville, MD 20850).

Exposure of Used Carbons

A number of carbons withdrawn from service were exposed on the LINAC facility to an accumulated value of 10^9 rads (32 hours). The penetrations of methyliodide-131 were determined using the Ge-Li detector and the results are given in Table 4.

Table 4: Penetration of Methyliodide-131 before and after LINAC exposure of 10^9 rads (10-11 Aug 1981)

NRL sample	Weight (g)	Penetration, % Initial	Penetration, % Radiated	Ratio
5233	160	30.1	0.039	1000
5234	147	10.5	0.033	320
5214	143	9.99	0.03	330
5251	141	38.9	0.002	1900

The NRL sample 5233 has been described above. NRL sample 5234 had been used for one year in a glove-box operation in which I-125 was used to prepare organic-iodine preparations for medical treatments. The original material was NACAR-G615, having a co-impregnation of TEDA (triethylenediamine) and KI (potassium iodide) on coconut shell carbon.

NRL sample 5214 had been weathered at NRL by passing outdoor air (1.05 x 10^6 cubic feet) from 17 Sept 1980 to 25 June 1981 (0.77 year). The pH of the inlet layer was 4.2 and that for the exit layer was 9.5. The original material was BC 787 which had been impregnated with TEDA and KI on a coconut shell carbon.

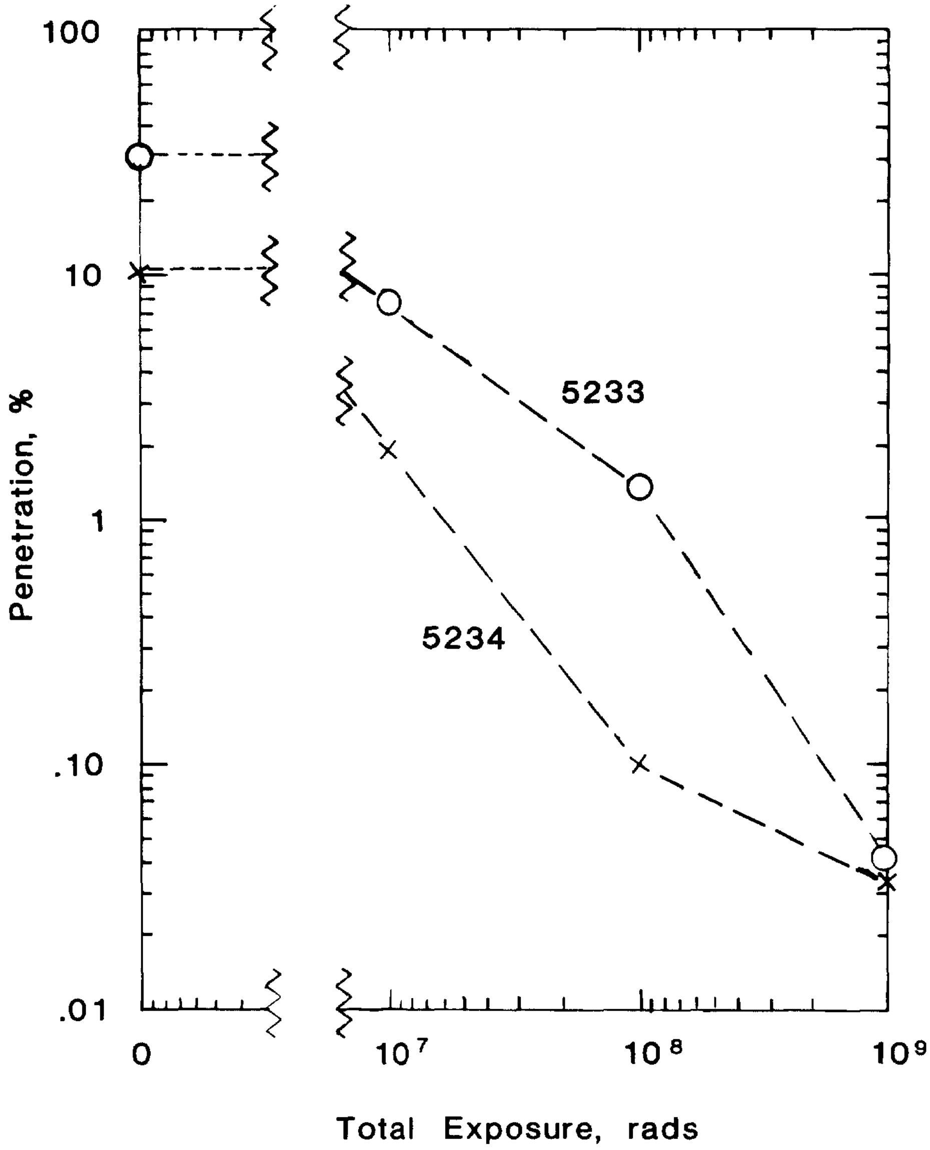

Figure 2: Decrease in Penetration of methyliodide-131 with increase total exposure on the NRL LINAC.

NRL sample 5151 had been weathered at NRL by passing outdoor air (2.79×10^6 cubic feet) from 30 May 1979 to 25 June 1981 (2.07 years). The pH of the inlet layer was 2.1 and that for the exit layer was 8.0. The original material was designated by the manufacturer as Nucon KITEG II, Lot 024.

The improvement realized for two of the used carbons (5233 and 5234) are shown in Figure 2. The initial penetrations are indicated by the horizontal lines marked on the Y-coordinate axis. The penetrations decreased approximately two decades for the increase of total exposure of two decades.

The recovery of carbon efficiency for trapping methyliodide-131 is outstanding. Since all carbons accumulate a considerable amount of contaminants during the time in service, the ionization of some of these contaminants in the radiation field and the retention of the products could influence the retention of iodine compounds by activated carbons. The recovery of carbon efficiency appears to increase with the quantity of contaminants directed to the carbon adsorber during service. The ratio of the penetration of the initial carbon to that observed after irradiation is plotted in Figure 3 as a function of time in service. There is definite trend relating the improvement of the carbon with the service time.

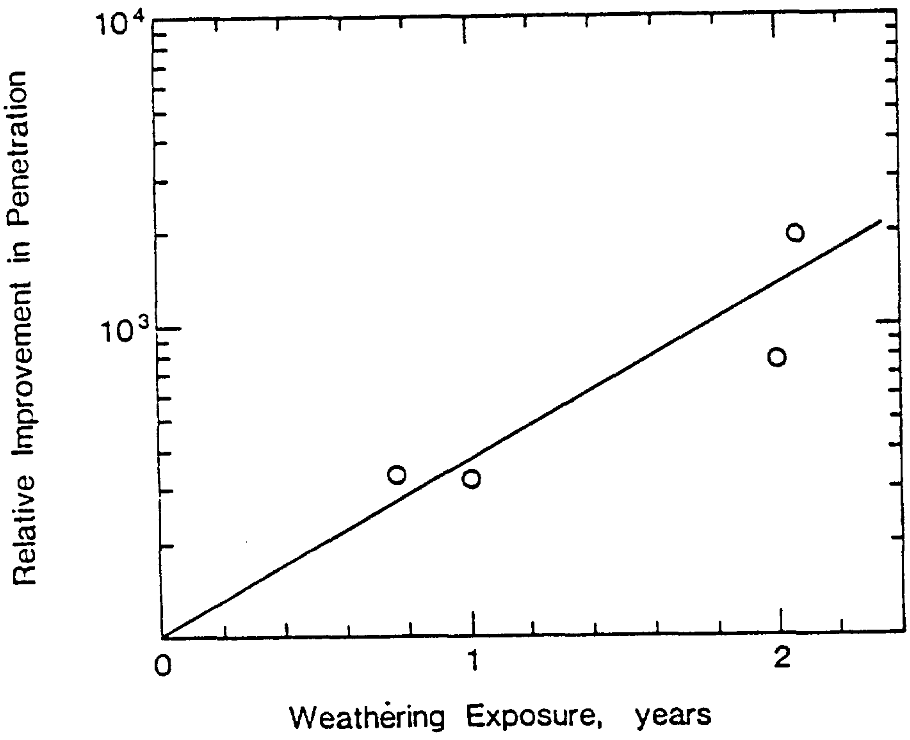

Figure 3: Ratio of the Penetration of the Initial Carbon to that Observed After Irradiation as a Function of Time in Service.

During the methyliodide-131 penetration measurements (ASTM D-3803, 79), it was found that some of the induced I-126 was detected in the two back-up beds. The amounts (see Table 5) are small, but it is evidence of isotope ''scrambling'' among the species ^{126}I, ^{127}I, ^{131}I present on the carbons during the test procedure. The mechanism is quite complex and involves exchange among both gaseous and adsorbed species. However, it is possible to calculate the penetration of ^{126}I from the post-test counts of the test samples and back-up beds. The results given in the last column of Table 5 compare favorably with the observed penetration of ^{131}I, of Table 4.

Table 5: Migration of Induced ^{126}I during the Test Procedure (ASTM D-3803) for Trapping Methyliodide-131 at 30°C.

NRL Sample No.	Post-test Count for ^{126}I (μC_i)			^{126}I Penetration %
	Test Sample	Back-up A	Back-up B	
5233	16.13	8.89(-3)	3.29(-5)	0.005
5234	18.14	1.98(-3)	<5.6(-5)	0.011
5214	13.45	4.89(-3)	2.54(-5)	0.036
5251	9.38	2.48(-3)	2.67(-5)	0.026

Measurements made by Nuclear Environmental Services,
3 Choke Cherry Road, Rockville, MD 20850

The exposures of carbons to gamma-radiation of Cobalt-60 in wet and dry air flows are in progress using exposure times sufficient to accumulate radiation levels of 10^6, 10^7 and 10^8 rads. Changes in methyliodide-127 penetration are followed daily by monitoring with gas chromatography using the electron capture detector for a 2-hour dose period and a 4-hour purge period. The penetration of methyliodide-131 increases with the duration of the humidified air flow (5) and decreases with the time of exposure to the radiation. The observed results may be interpreted in terms of the degree of balance of these two opposing tendencies.

Tests will be conducted to determine the effect of non-radioactive argon and/or krypton in contact with the carbon during irradiation. The ionized noble gas may interact with the contaminants of a used carbon as indicated by a subsequent measurement of penetration using methyliodide-131.

The above study has been made with KI and KI + TEDA impregnations in which I-126 is generated on exposure to radiation of 10^7 rads and above. It has yet to be reported how TEDA impregnations alone behave.

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1. ''Effects of Weathering on Impregnated Charcoal Performance,'' Victor R. Deitz, NUREG/CR-2112, NRL Memo Report 4516 (1981).

2. ''Effects of Weathering on Impregnated Charcoal Performance,'' Victor R. Deitz, NRL Memo Report 4006, NUREG/CR-0771 RQ (1979).

3. ''Testing Iodized Activated Carbon Filters with Non-Radioactive Methyl Iodide,'' Victor R. Deitz and James B. Romans, NRL Memo Report 4240 (1980).

4. ''Charcoal Performance under Simulated Accident Conditions,'' Victor R. Deitz, NRL Memo Report 4760 (1982).

5. ''The Effect of Exposure Times in the Prehumidification of Impregnated Charcoals,'' by Victor R. Deitz and Charles Blachly, Proc. 14th ERDA Air Cleaning Conf. <u>1976,</u> Volume 2, 836-843.

DISCUSSION

KOVACH, J.L.: You have reported using the ASTM D3803, 30°C test but later in the paper you mentioned using two hours of prehumidification. Does not ASTM D3803 specify sixteen hours? Would you have steady state after only two hours?

DEITZ: The used carbons, either before or after irradiation, were not prehumidified sixteen hours before the $^{131}ICH_3$ test. We have found little effect of prehumidification when testing the used carbons such as those used in the present investigation.

KOVACH: Do you daily expose the samples being irradiated to two hours of stable CH_3I loading and four hours of purging? Does this process result in any "regeneration" of the used carbons?

DEITZ: The used carbons were irradiated either with static air or in air flows. The latter were exposed for 100 hours, and during that period, the tests with ^{127}I Me were made daily with two hours dose and four hours post-dose measurements.

EVANS: In defense of what he has done here, we did an extensive series of tests under dynamic flow conditions at Savannah River in a fairly high intensity radiation field. With extended irradiation, we could follow progress on the same sample as it was being irradiated. It was a cumulating exposure. We saw an ever-decreasing penetration of the organic iodide species that were generated in the radiation field. This would seem to confirm Dr. Dietz's data, indicating an improvement in carbon performance with increasing radiation exposure.

DEITZ: I want to take this opportunity to thank Gary Evans for his advice and numerous discussions during the conduct of our researches at the Naval Research Laboratory on our radiolysis experiments.

JOLLEY: Dr. Deitz, do you have some ideas why carbon performance in terms of penetration is improved with radiation?

DEITZ: The program committee in its great wisdom limited me to one paper. In the second paper we were going to discuss that point. We will present it in two years.

TEDA VS. QUINUCLIDINE: EVALUATION AND COMPARISON OF TWO TERTIARY AMINE IMPREGNANTS FOR METHYL IODIDE REMOVAL FROM FLOW AIR STREAM

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ABSTRACT

The use of tertiary amine impregnants on activated carbon for removal of alkyl halide fission products has gained acceptance in the United States since the early 1970's. This industry wide acceptance has encouraged a search for compounds capable of complexing with alkyl halides as strongly as the industry-accepted TEDA (triethylenediamine). One such compound is the tertiary amine quinuclidine.

Tests were performed at Nuclear Consulting Services, Inc., the results of which have enabled a comparison between TEDA and quinuclidine. Samples of activated carbon, impregnated with 2% TEDA and quinuclidine were tested in accordance with test Method A, ASTM D3803, 1979, "Standard Test Methods For Radioiodine Testing of Nuclear Grade Gas-Phase Adsorbents". Further tests were performed to detail the adsorption process. Mass transfer zone length and rate of movement were determined for Methyl Iodide-127 on both TEDA and quinuclidine impregnated carbons at relatively high concentrations at both 70% and 90% relative humidities. Using carbon beds saturated with MeI-127 from the previous tests, an investigation into isotopic exchange between ^{131}I and ^{127}I was also conducted. From the results of the test series performed, TEDA and quinuclidine were compared based on the known process for adsorption of Methyl Iodide on impregnated activated carbon: 1) diffusion to the carbon grain surface, 2) transfer from the adsorbent surface to the pore structure, 3) adsorption, 4) chemical reaction (complex formation) and 5) isotopic exchange. The results of these tests have indicated quinuclidine to be superior for removal of methyl iodide from flowing air streams.

I. INTRODUCTION

Tertiary amine impregnated carbons have been originally developed for the control of various halide type war gases by the formation of stable quaternary salts on the surface of activated carbon, (1) (2) (3). Their use for the control of organic radioactive halides specifically $CH_3\,^{131}I$ has been introduced by British researchers (4) (5). The original optimum halide complexing amines were reported to be Piperidine, Morpholine, Piperazine, 4-Amino Pyridine and Triethylenediame (TEDA) (6), the latter being the most popular. In the last few years other amines were reported to be as good or superior to TEDA (7) (8). The use of these tertiary amine impregnated carbons is currently very extensive in the US both for air sampling and nuclear facility air cleaning application (9).

However very limited test data was available to analyze the actual working behavior of the tertiary amine impregnated carbons and only such basic information was available that the $CH_3\,^{131}I$ removal efficiency is higher than that of stable iodine impregnated carbons and that their weathering properties are superior also when compared with stable iodine impregnated carbons. In general it was presumed that their superority lies in the complex forming ability of the tertiary salt. This investigation was initiated to evaluate the $CH_3\,^{127}I$ and $CH_3\,^{131}I$ adsorption and removal properties of a base carbon and the same base carbon impregnated with two tertiary amines TEDA and Quinuclidine in the temperature and humidity range of common use.

II. EXPERIMENTAL METHODS AND PROCEDURES

Radioiodine efficiency tests were performed using test Method A of ASTM D3803. Counting of radioiodine was performed at the 0.364 MeV gamma level using a 4 inch Thallium Activated Sodium iodide well crystal.

Additional radioiodine efficiency tests were performed using the above method but with modifications:

1. Various weight percent TEDA and Quinuclidine impregnants on carbon. These tests were performed on 0.5 inch segmented beds.

2. Me ^{131}I penetration of 2% TEDA impregnated carbon as a function of relative humidity.

3. Removal efficiency of KI/TEDA impregnated carbon as a function of bed depth (eight inches, one inch segments).

4. Radioiodine removal efficiency of 2% TEDA impregnated carbon and 2% Quinuclidine impregnated carbon saturated with methyl iodide-127 from an air stream containing 161 mg/m^3 of methyl iodide-127 at 95% RH and 30°C.

5. Mass Transfer Zone Length (MTZ) and rate of travel were performed on the 2% TEDA and 2% Quinuclidine impregnated carbons at relatively high (compared to D3803) inlet concentrations of methyl iodide-127 (161-178 mg/m^3) using essentially the same test apparatus as described in ASTM D3803. Inlet concentration was generated by diffusion tubes and detection of breakthrough was performed using either a continuous FID or an ECD in conjunction with a G.C. and sampling valve. The temperature was 30°C at 95 and 70% RH. In addition, the same tests were performed on the substrate carbon (10X16 mesh 60 CTC coconut shell carbon).

III. RESULTS

A. Methyl Iodide-131 Removal Efficiencies

In Table I are the results of removal efficiency of carbon impregnated with different amounts of TEDA and Quinuclidine and tested at 95% RH and 30°C according to Method A ASTM D3803. It should be noted that each layer is 1/2 inch deep and the carbon used here was 8X16 mesh 60CTC coconut shell.

TABLE I

$CH_3{}^{131}I$

		Removal Efficiency/Layer (%)			
SAMPLE	WT%	0.5 inch	1.0 inch	1.5 inch	2 inch
Quinuclidine	0.5	79.89	96.14	99.22	99.79
	1.0	80.67	96.44	99.28	99.89
	1.5	82.45	96.90	99.49	99.92
	2.0	85.51	97.58	99.68	99.95
TEDA	0.5	24.72	46.49	67.06	83.16
	1.0	28.62	57.66	74.39	87.40
	1.5	38.36	63.34	83.22	93.62
	2.0	61.51	90.21	97.01	99.16

In Table II are the radioiodine removal efficiencies of the two impregnated carbons (10X16 mesh) performed according to Method A, ASTM D3803 both as is and after saturation with 161 mg/m^3 of Methyl Iodide-127 at 95% RH and 30°C.

TABLE II

SAMPLE	$CH_3{}^{131}I$ REMOVAL EFFICIENCY (%)
2% Quinuclidine (As Is)	99.98
2% Quinuclidine (After Saturation With $CH_3{}^{127}I$)	98.46
2% TEDA (As Is)	99.83
2% TEDA (After Saturation with $CH_3{}^{127}I$)	84.15

Shown in Table III are the results of radioiodine penetration for 2% TEDA impregnated 8X16 mesh carbon at various humidities at 30°C. These results are shown graphically on Figure 1.

TABLE III

RH%	$Me^{131}I$ PENETRATION (%)
95	0.96
90	0.90
85	0.76
80	0.52
75	0.15
70	0.02
65	0.01
55	0.007
45	0.006
40	0.004
30	0.002

In Table IV the removal efficiency for methyl iodide-131 is shown as a function of bed depth. Each section was one inch deep. The carbon was 8X16 mesh 60CTC coconut shell impregnated with KI/TEDA.

TABLE IV

SECTION	REMOVAL EFFICIENCY (%)
1	92.73
2	99.52
3	99.88
4	99.98
5	99.984
6	99.986
7	99.993
8	99.998

Figure 1

Me^{131}I Penetration Vs Relative Humidity

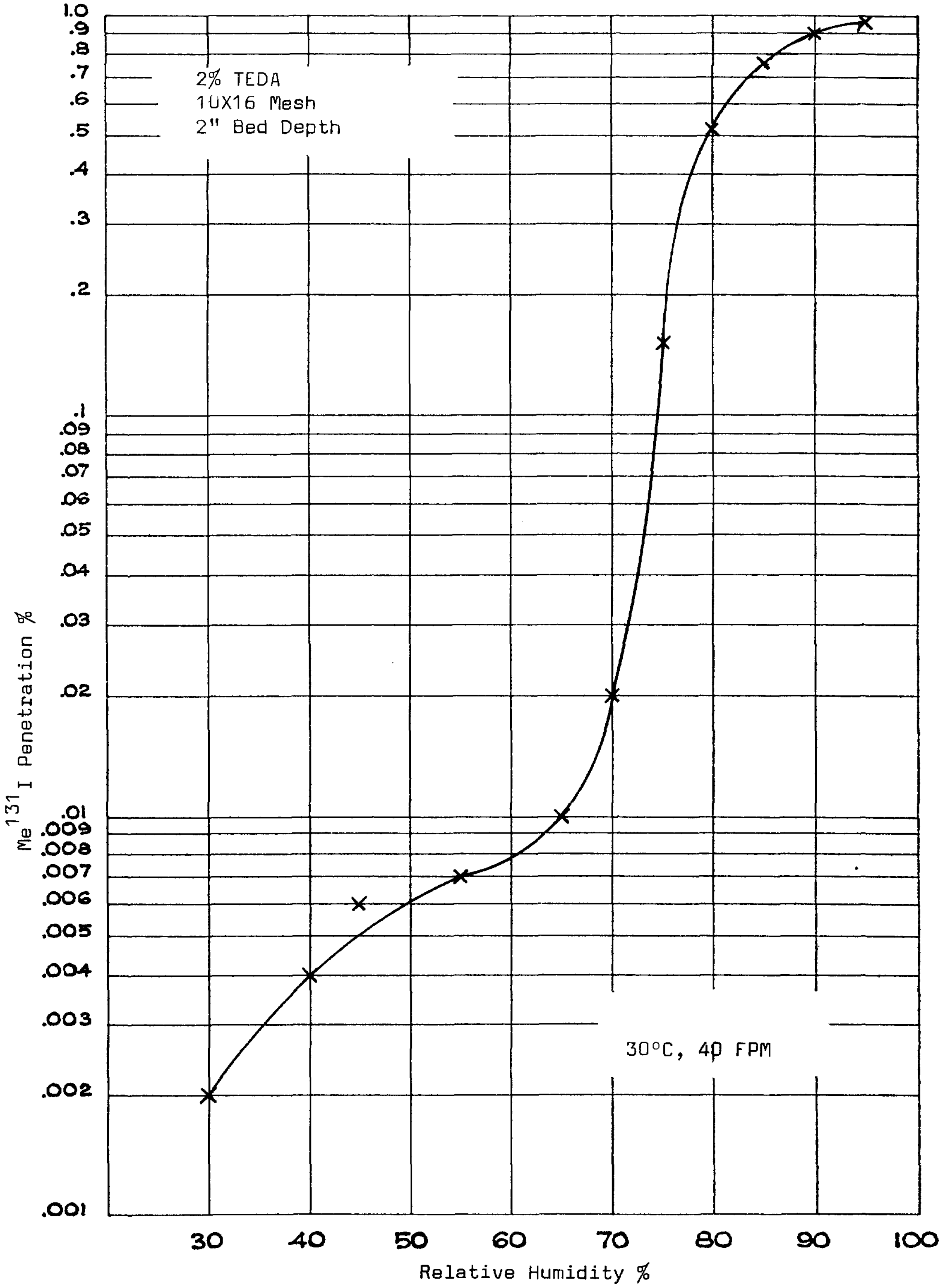


Figure 2
PERCENT BREAKTHROUGH VS TIME

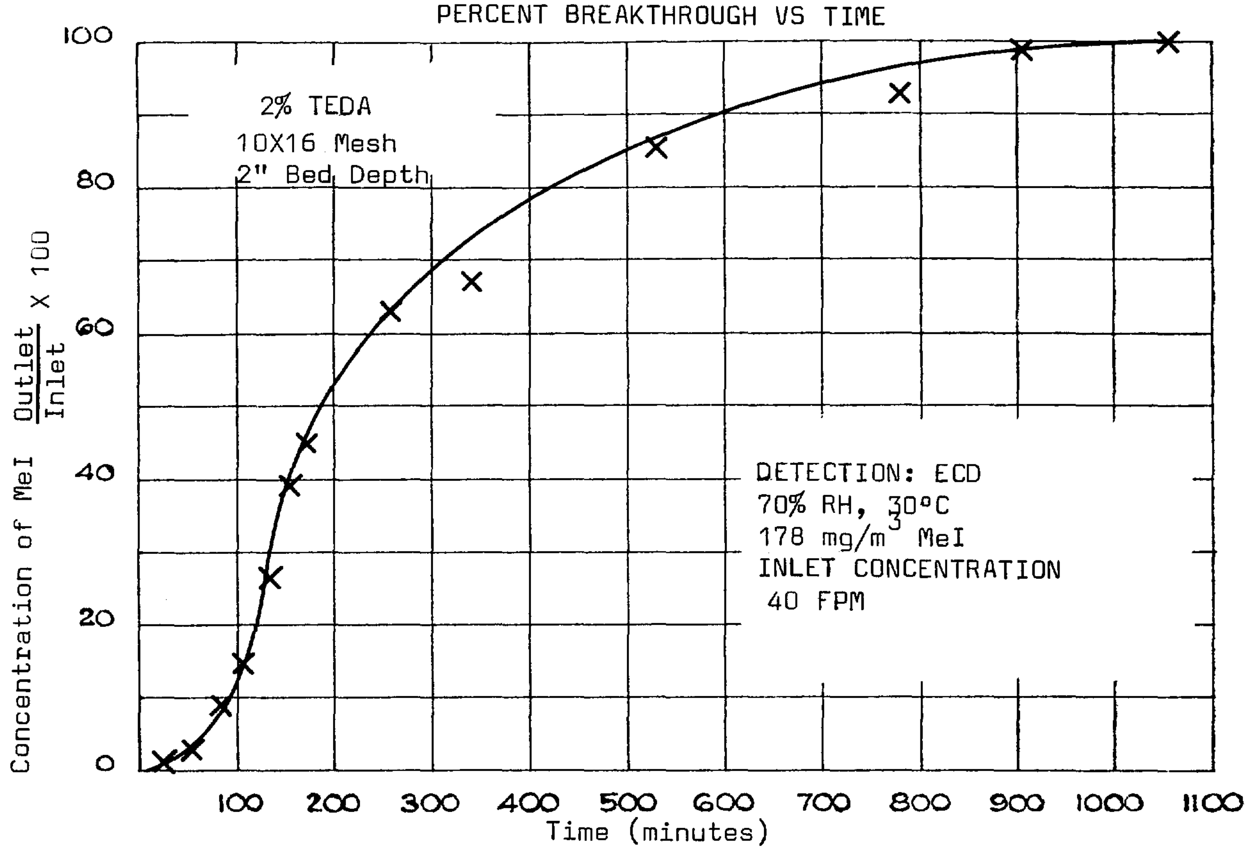


Figure 3
PERCENT BREAKTHROUGH VS TIME

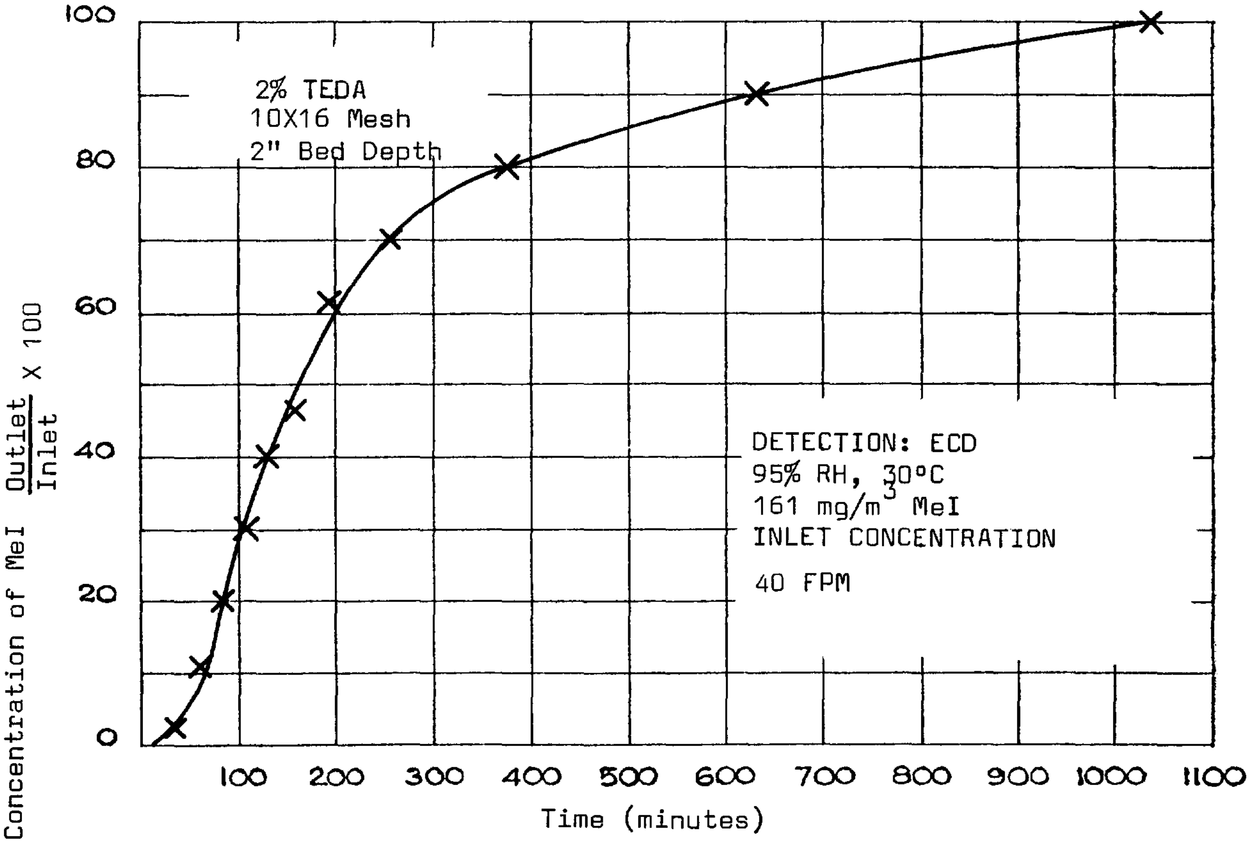


Figure 4
Percent Breakthrough Vs Time

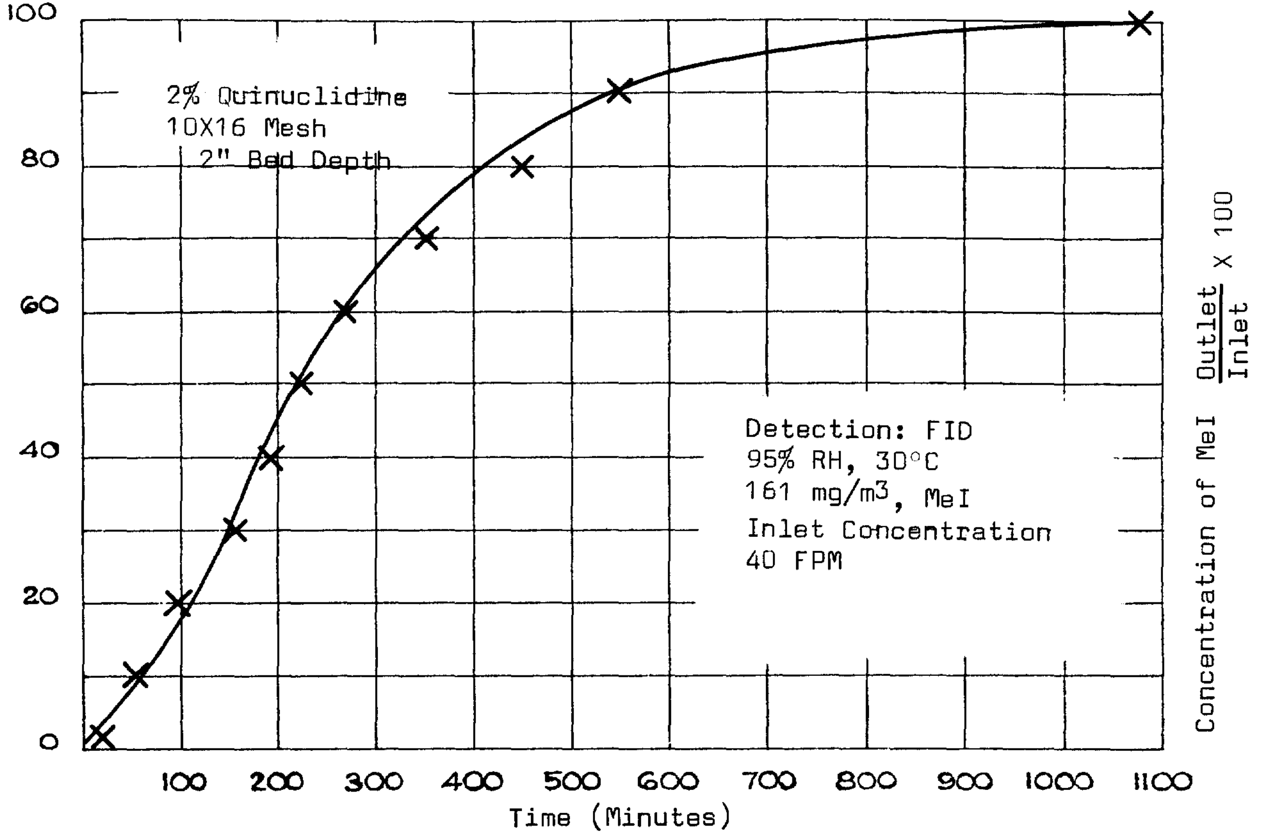
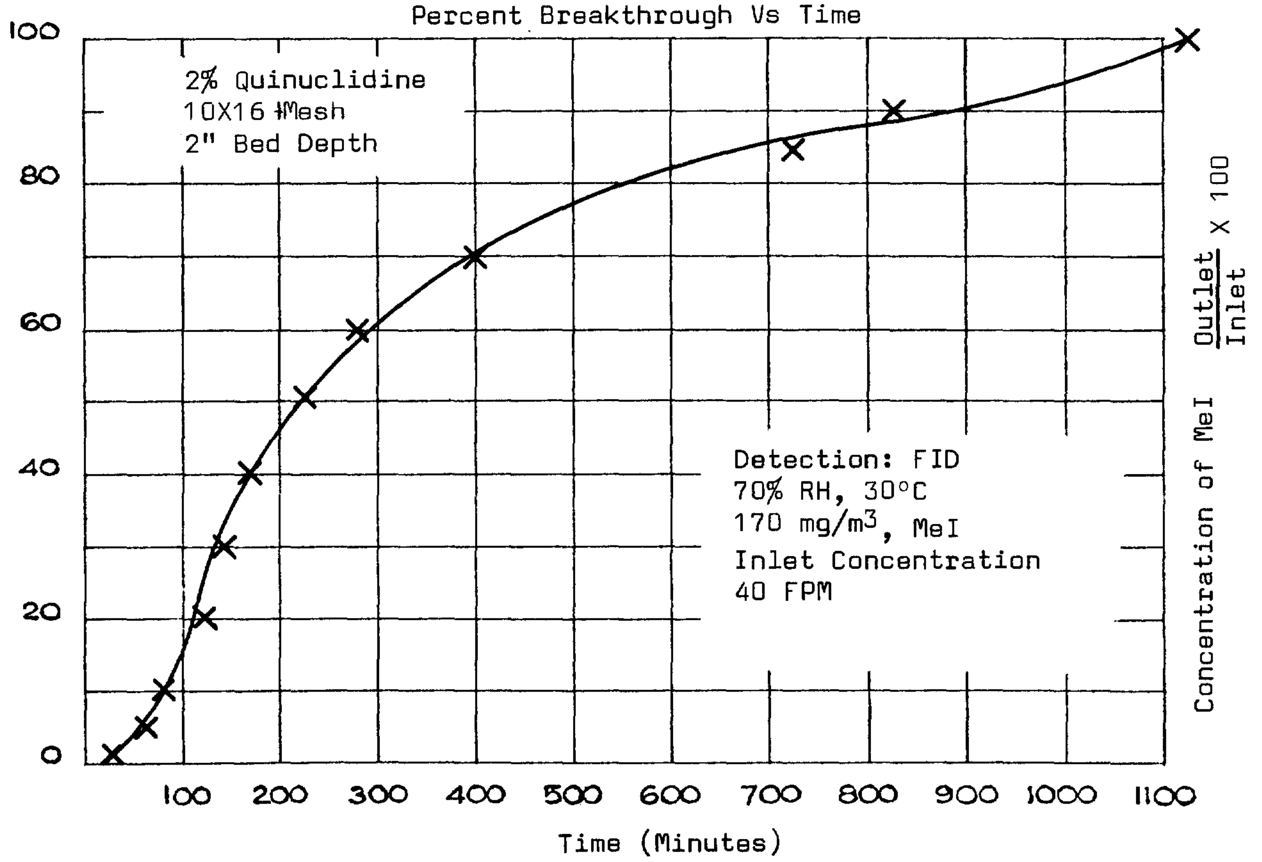


Figure 5
Percent Breakthrough Vs Time



B. Mass Transfer Zone (MTZ) Tests

Breakthrough curves for the adsorption of methyl iodide-127 on the 2% TEDA and 2% Quinuclidine impregnated carbon at 30°C and both at 95% RH and 70% RH are shown on Figures 2 thru 5 for the TEDA and for the Quinuclidine impregnated carbons. On Figures 6 and 7 the breakthrough curves are shown for the unimpregnated substrate carbon under the above conditions.

Table V shows the MTZ length M and rate of travel U calculated from the following equations (10).

$$U = L/t$$
$$M = U\Delta t$$

where:

U = rate of movement (inches per minute)
L = length of carbon bed (inches)
t = time to 50% breakthrough (minutes)
M = MTZ length (inches)
Δt = time to breakthrough-time to saturation (minutes)

TABLE V

SAMPLE	R.H.(%)	M(in.)	U (in./min.)
2% Quin.	95	3.1	3×10^{-3}
2% Quin.	70	3.2	3×10^{-3}
2% TEDA	95	3.2	3×10^{-3}
2% TEDA	70	3.1	3×10^{-3}
Substrate	95	3.5	3×10^{-2}
Substrate	70	2.6	2×10^{-2}

IV. DISCUSSION

All other parameters being equal (i.e., flow, temperature, R.H., etc.) the rate differentiating step for the removal of methyl iodide-131 in case of amine impregnated carbons is the chemical reaction with the CH_3I. Clearly the Quinuclidine performs better than TEDA in case of $CH_3{}^{131}I$ removal, as evidenced by the results in Table I.

However, the $CH_3{}^{127}I$ breakthrough curves for both the 2% TEDA and 2% Quinuclidine carbons at 70 and 95% R.H. (Figures 2 thru 5) while clearly superior to the substrate carbon (Figures 6 and 7) are not sufficiently different from each other to explain the significant difference in $CH_3{}^{131}I$ removal efficiencies. In light of the above results, 2% TEDA and 2% Quinuclidine impregnated carbon were saturated with 160-170 mg/m^3 $CH_3{}^{127}I$ at 95% RH and 30°C. These carbons then were tested for $CH_3{}^{131}I$ removal efficiency to investigate if there were evidence of isotopic exchange with the $CH_3{}^{127}I$-tertiary amine complex. Clearly this is the case as seen in Table II. The 2% Quinuclidine impregnated carbon being significantly more efficient then the 2% TEDA carbon after complexing with $CH_3{}^{127}I$.

Figure 6

PERCENT BREAKTHROUGH VS TIME

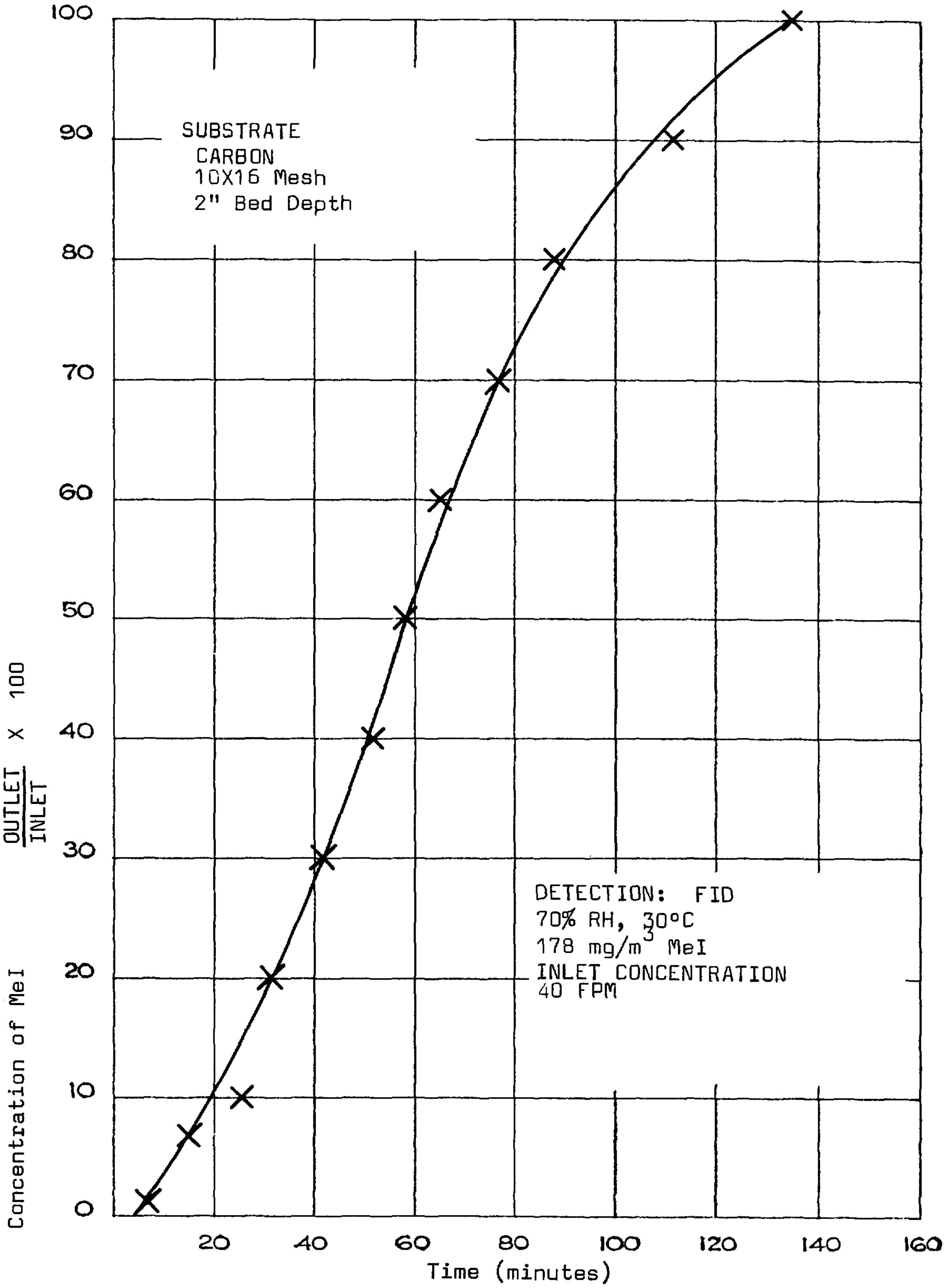
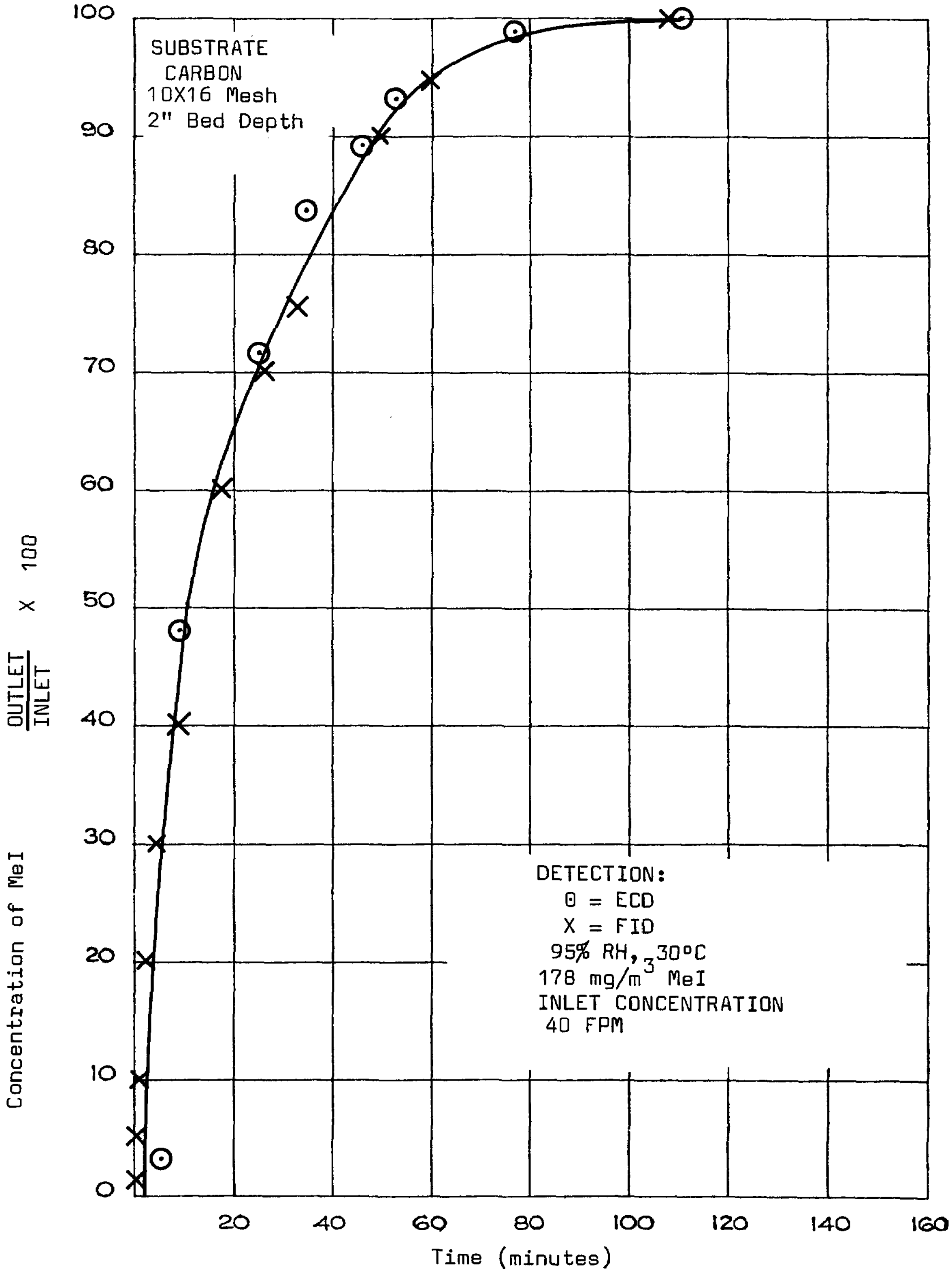


Figure 7
PERCENT BREAKTHROUGH VS TIME



This isotopic exchange with the Quinuclidine $CH_3\,^{127}I$ quaternary complex helps to explain the high efficiencies obtained with this impregnated carbon for removing methyl iodide-131 even though (as seen in Table V and Figures 4 and 5) the $CH_3\,^{127}I$ proceeds through the bed fairly easily. However, in "real life" (i.e., nuclear power plants) the ratio of $CH_3\,^{127}I$ to $CH_3\,^{131}I$ is large and the isotope exchange process has a pronounced if not dominant effect on removal efficiency for ^{131}I containing organic compounds.

Another factor to consider for the type of tertiary amines represented by both TEDA and Quinuclidine are faster reaction rates when compared to straight chain tertiary amines. It has been found (11) that the reaction rate for methyl iodide in nitrobenzene is 60 times faster for Quinuclidine than for triethyl amine at 25°C. This is explained by the sterically unhindered nitrogen atom in Quiniclidine which lowers the activation energy for the resulting quaternary ammonium salt. Much the same would hold true for TEDA.

The stability of the Quinuclidine impregnated carbon has been shown (8) after six months static aging to yield a removal efficiency of 99.89% and in weathering tests at Three Mile Island (12) in which a sample of Quinuclidine impregnated activated carbon was tested after 4 months of dynamic atomospheric weathering with a resultant $CH_3\,^{131}I$ penetration of 0.01% ± .01%. Yet this fact and the above discussion still do not fully explain the high removal efficiency of quinuclidine impregnated carbons when compared with TEDA impregnated carbon (since TEDA has two nitrogen atoms to react). One workable hypothesis might be that since the pores in activated carbon are a non polar environment, the non-polar "end" of the quinuclidine molecule may occupy the active site and leave the "nude" nitrogen atom preferentially oriented to react with methyl iodide or that once one nitrogen in the TEDA forms the quaternary complex it deactivates the other side. Investigation on the impregnant deposition in the activated carbon might help to explain this and other matters more fully (13).

Table III and Figure 1 present removal efficiencies of 2% TEDA impregnated carbon at various humidities. Similar results would be expected for quinuclidine though the data are not complete at the time of this writing. One of the questions in regards to performing test Method A, ASTM D3803 has been the counting error in calculating the efficiency if Xenon-133 is present on the carbon. In Table VI are shown ^{133}Xe dynamic K at various relative humidities and 30°C.

TABLE VI

RH%	WT % H_2O ADSORBED	K cc/g	AVAILABLE PORE VOLUME %
90	21.6	28	1.9
80	20.9	84	5.8
70	19.6	211	14.6
60	19.2	387	26.7
50	10.0	612	42.2
40	4.9	767	52.9
30	3.6	929	64.1
20	2.4	1085	74.8
10	2.0	1340	92.4
5	0.9	1390	95.9

Even though these results were obtained on unimpregnated carbon, the two hours sweep at 95% RH of the test bed (for Method A, ASTM D3803) is more than sufficient to sweep any Xe out of the system.

V. SUMMARY

The mechanism of $CH_3{}^{131}I$ control by tertiary amine impregnated carbons was evaluated. It was found that the primary mechanism of removal is isotope exchange between the $CH_3{}^{131}I$ and the $CH_3{}^{127}I$-amine quaternary salt and the actual complex formation between tertiary amines and CH_3I is of lesser but still a contributing factor.

The data indicates that while the complex forming rates of TEDA and Quinuclidine are nearly identical the isotope exchange rate of the quinuclidine impregnated carbon is significantly superior to TEDA impregnated carbon.

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DISCUSSION

DEITZ: Has the efficiency of the Quinuclidine-impregnated carbons been evaluated after weathering in outdoor air?

FREEMAN, W.P.: Yes, V.R. Deitz reported a penetration of 0.01% ± .01% at the 16th DOE A.C.C. for four months dynamic aging. Our own tests show a Me ^{131}I removal efficiency of 99.89% after a six month static aging.

KOVACH, J.L.: As a coauthor of the paper I would like to express our sincere thanks to Dr. Deitz for reporting the weathered efficiency for the Quinuclidine carbon after four months exposure at an actual reactor site (TMI-II). He reported for the NUCON Q carbon, penetration of 0.01 ± 0.01%, which is one of the lowest penetrations reported for any carbon.

CROSSLIN: Why did you select 2% impregnants over a better carbon with 5% for this test (or report) and what would be the results with the 5% carbon?

FREEMAN: 5% TEDA becomes 2% rapidly! We have used 0.5, 1.0, 1.5 and 2.0% TEDA and Quinuclidine impregnations, not just 2%. We have found that in the plant, the TEDA desorbs from a 5% to a 2% level in a short time. On standard U.S. carbons, 5% TEDA does not meet the ignition temperature requirements of Regulatory Guide 1.52, as it has been reported over the last ten years. For almost all co-impregnated carbons (KI + TEDA), the TEDA content is approximately 2%. We consider these sufficient reasons for evaluating TEDA impregnation up to the 2% level.

BELLAMY: How does the volatility of Quinuclidine compare to that of TEDA?

FREEMAN: The volatility of Quinuclidine is considerable less. It meets the 330°C ignition requirement without the addition of flame retardants.

BELLAMY: In practical terms, I have a concern with TEDA coming off the carbon as I increase the temperature. Should my concern be greater or less with Quinuclidine versus TEDA?

FREEMAN: Less.

DEITZ: You still have to worry. We have shown that TEDA on carbon has some rather interesting properties and no conjecture is needed. Looking at the experimental results, I see that on the carbon there is a reversible reaction between methyl iodide and TEDA. As material ages, you see the disappearance of mass 112 in the mass spectroscope, but you still find good methyl iodide removal. In other words, any tertiary amine remaining is chemically changed on the carbon with time. Yet, it can still trap methyl iodide because the tertiary amine is there. So, even though the TEDA has disappeared, its memory lingers on, in that it has left something on the carbon. We don't know what it is, but it does trap methyl iodide.

EXPERIMENTS ON ADSORPTIVE RETENTION OF NO_x AND KRYPTON FROM DISSOLVER OFF-GAS

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Abstract

A method for separating radioactive krypton from the off-gas of a dissolver in a reprocessing plant based on the principle of adsorption and desorption on adsorbents is described. The laboratory experiments corroborate the feasibility of the individual process steps. The entire process essentially consists of three interconnected stages:

- *Retention of NO_x residues and tritiated water on a molecular sieve and recycling both species with part of the waste gas into the dissolver.*
- *Separation of xenon from the off-gas by activated charcoal with simultaneous concentration of krypton in the off-gas.*
- *Separation of krypton from the residual off-gas by means of preparative gas chromatography and deposition of the pure krypton into storage cylinders containing activated charcoal.*

Based on the experiments a priciple layout for a full scale off-gas cleaning system is described.

I. Introduction

For the separation of the radioactive noble gas krypton from dissolver off-gas at reprocessing plants different physical separation principles can be applied, mainly:

- *rectification at low temperature after liquefaction of the entire off-gas,*
- *adsorption of the krypton in liquids,*
- *adsorption of the krypton on solid adsorption materials,*
- *and possible, permeation of the krypton through semipermeable membranes.*

Based on theses principles a number of process developments have been carried out in different countries (1). Most of the work was done on low-temperature rectification. By this method, a very high decontamination of the off-gas from krypton can be achieved, but the unavoidably high Kr-85 inventory in the complex cryogenic facility is a matter of concern with respect to accidental Kr-85 release and dose rate to plant personnel.

A process for krypton retention by adsorption should significantly reduce these problems. The objective of the experiments on adsorbtive krypton separation from the off-gas is a reliabe prosess with:

- *operation at near ambient pressure and*
- *a low Kr-85 inventory at steady-state operation.*

Both features would reduce the potential for accidental Kr-85 release and high dose rates. Beside this the process should

- *control the residual* NO_x *and tritiated* H_2O *(as well as carbon-14* CO_2*) in the off-gas and*
- *avoid a* O_2 *separation step, like* O_2*-conversion with* H_2 *to* H_2O*, which also eliminates any generation of waste.*

In the case of a low Kr-85 hold-up, it can be expected that there will be no safety risk due to accumulation of ozone and other radiolysis products. An unsafe accumulation of impurities, like methane, in the adsorption columns is not expected either. Any accumulation will leave the facility during regeneration of the columns.

A further principle feature of an adsorption process becomes important when handling radioactive species. This is the implied redundancy of the process because of the different adsorption columns in one line. Under any malfunction of one adsorption step, resulting in desorption of adsorbates, the next down-stream adsorption step will avoid or slow down the release of the adsorbates.(Stand-by units may also serve for this purpose).

A principle disadvantage of an adsorption process is the need for relatively large adsorption columns and their time and energy-consuming regeneration. Therefore - in the application of an adsorption process - it is important to consider the whole dissolver flow sheet for minimizing the off-gas flow.

II. Flow sheet for the proposed adsorption process

Following NO_x*-scrubbing, aerosol and iodine filtration the dissolver off-gas consists of air with the average constituents of 0.5 vol%* NO_x*, 0.5 vol% Xe, 0.05 vol% Kr and is partly saturated with* H_2O*. Takeing these species into account, Fig. 1 showes a principle flow sheet for the adsorptive krypton retention process under consideration.*

In the first process step it is intended that the NO_x*, together with* H_2O *(and HTO), be adsorbed on a molecular sieve. As part of this first step the adsorbed species are to be recycled to the dissolver while the molecular sieve column is regenerated by temperature elevation. The experiments substantiated that it is possible to regenerate the column by increasing the temperature from room temperature to about 200°C under constant flushing of the column with dissolver off-gas; i. e. no additional purge air is necessary.*

As a result, the dissolver off-gas ($\dot{V}_{purge}$*) is partly recycled, which increases the noble gas concentration and decreases the off-gas amount (*$\dot{V}_{off}$*) for the downstream Kr-separation steps.*

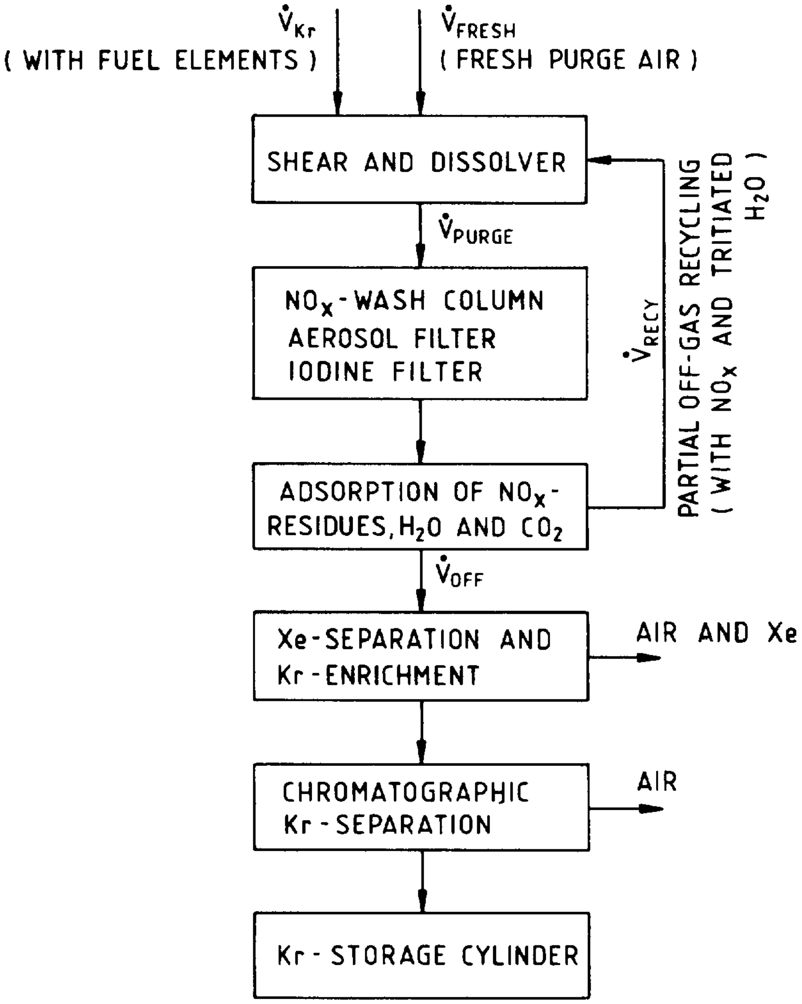

Fig. 1: Principle flow sheet for the integrated krypton separation process by adsorption

The average Kr-concentration (X_{Kr}) in the off-gas is given by $X_{Kr} = \dot{V}_{Kr}/\dot{V}_{off}$ ($\dot{V}_{Kr}$ is the krypton volumn per time, which enters the dissolver with the fuel elements). With $\dot{V}_{off} = \dot{V}_{purge} - \dot{V}_{recy}$ a relation fo the Kr-concentration in the off-gas as function of the recycled off-gas flow ($\dot{V}_{recy}$) can be derived: $X_{Kr} = \dot{V}_{Kr}/(\dot{V}_{purge} - \dot{V}_{recy})$. A graph of this relation (for 30 Nm^3/h off-gas and 0.05 vol% Kr without recycling, assumed dissolver capacity 125 kg/h) is given in Fig. 2.

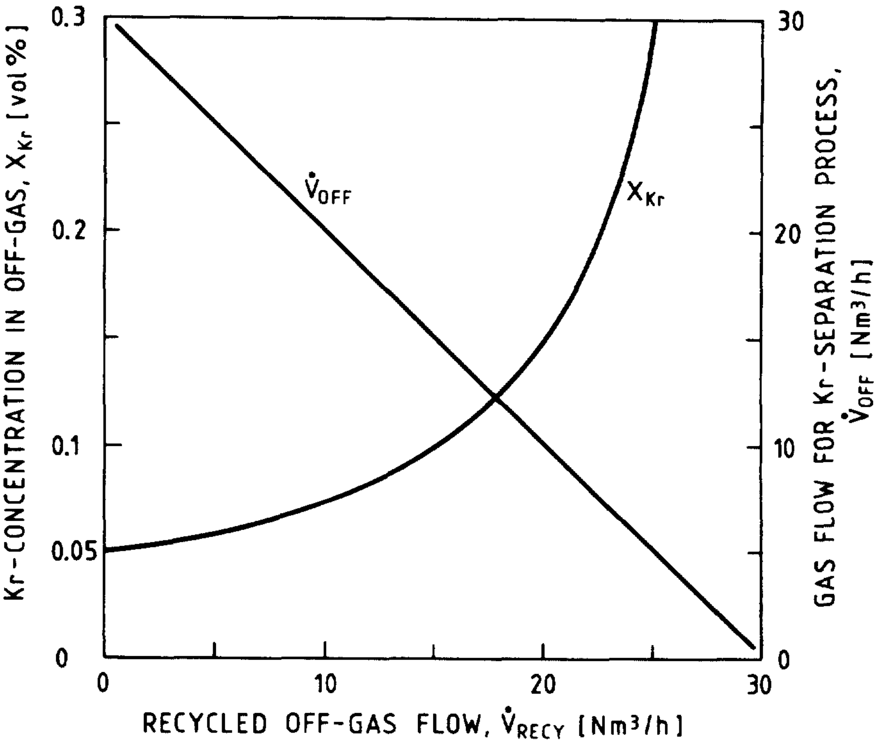

Fig. 2: *Average Kr-concentration in the dissolver off-gas in relation to the recycled off-gas flow for 30 Nm^3/h dissolver purge flow (assumed dissolver capacity: 125kg fuel/h).*

The amount of off-gas which can be recycled, i.e. the minimum of fresh air, depends mainly on the design of the shears as well as on the dissolver operation and has to be determined. A high recycling of off-gas will probably require the addition of O_2 into the dissolver system.

For the control of C-14, the CO_2 has to be retained from the dissolver off-gas. This may be achieved by fixation of the CO_2 on $Ba(OH)_2$ or Ca (OH) as reported (2,3) and could be related to the NO_x-adsorption step.

Following the NO_x-adsorption and -recycling process step a further reduction in the off-gas flow is achieved by a one-step adsorption/desorption process, similar to a process reported by Jüntgen et al. (4). By this process the xenon is completely separated from the off-gas, whereas the krypton is enriched in the off-gas to some degree.

Downstream of this step the off-gas flow will be reduced by a factor of 10 or more; this enables the practical application of a preparative *gas chromatography technique for the final separation of the krypton from the residual off-gas.*

Coupled with this highly efficient separation process, the krypton can be filled - in a final process step - into charcoal containing storage cylinders without handling concentrated krypton in the whole process. The maximum Kr-concentration in any process equipment will be below 1 vol%.

III. Experiments for NO_x and tritium retention on molecular sieve

The dissolver off-gas from the precleaning steps contains about 0.5 vol% NO_2 and NO species as well as water vapour of up to 2 vol%. This water vapour is contaminated by tritium. Recycling of both NO_x and tritiated water into the dissolver is favourable, in accordance with the general rule for waste management: confinement of the individual waste species in one location.

Experiments have been carried out to select a suitable molecular sieve as well as for process control. The flow sheet for the experimental equipment is given in Fig. 3. The molecular sieve in question was filled into glass columns of 200 mm length and 15 to 25 mm I.D. Its dynamic adsorption capacity was determined by passing a mixture of air and NO_x through the column and monitoring the NO_x concentration in the effluent. The air-NO_x gas mixture was prepared by mixing synthetic air and NO from high-pressure gas cylinders and passing this mixture through a 6.2 l hold-up flask for oxidizing the NO to NO_2. At 25°C and a gas flow of 150 l/h (mean residence time 2.4 min) 87 % of the NO reacted with the air-O_2 to NO_2 (for an inlet NO-concentration of 0.63 vol%).

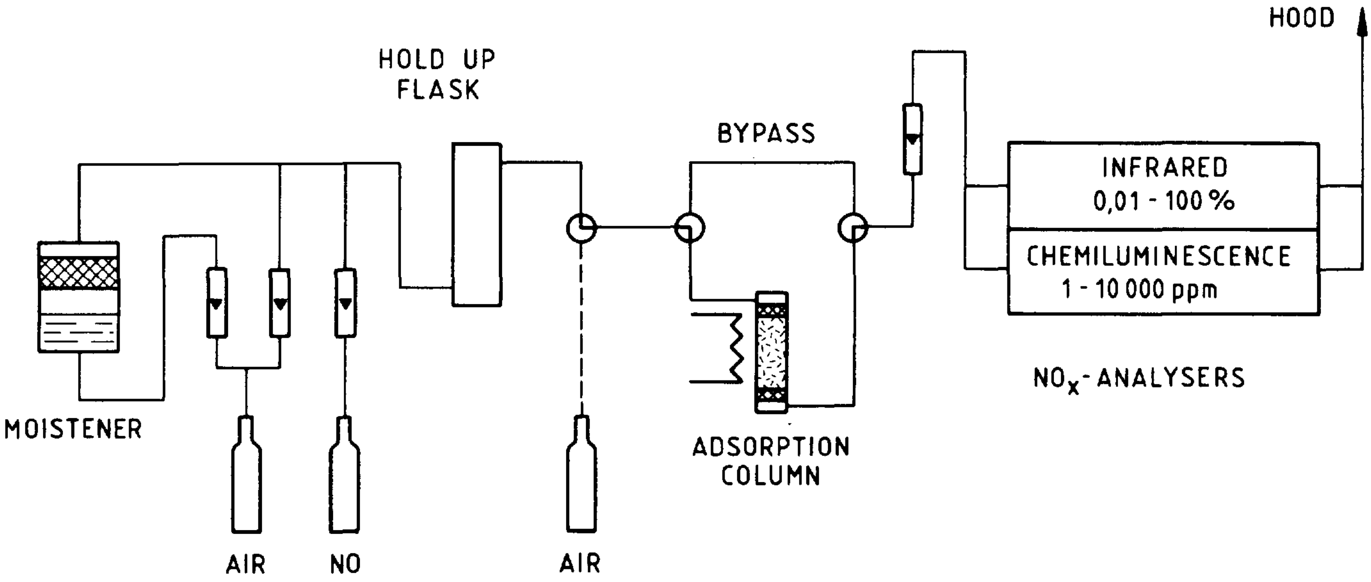

Fig. 3: Flow sheet of equipment for experiments on adsorptive retention of NO_x and H_2O on molecular sieve

Two different inline NO_x analysers were used. For the low NO and NO_x range of 1 ppm up to 0.5 % a chemiluminescence analyser and for higher NO and NO_2 (as well as for CO_2 and H_2O) values of 0.01 % up to 100 % a infrared detector. Measurement by gas chromatography was not feasible.

The parameters for the experiments were chosen so as to be close to the anticipated process parameters. The parameters for the determination of the load capacities (as given in Fig. 4) were:

Column: 15 mm I.D., 200 mm long
Gas flow: 50 Nl/ h (face velocity: 5 m/min)
Gas composition: 79 vol% N_2, 20 vol% O_2, 1 vol% NO_x

The average load capacity (b) of the molecular sieve was defined by:

$$b = \frac{\text{volume of } NO_x \text{ in the column at 0.01 vol\% } NO_x \text{ in the effluent}}{\text{column volume}}$$

Dry Off-Gas

Fig. 4 gives the measured load capacities for different molecular sieves versus the column temperature at loading. The molecular sieve 5 A showed a low, but with the column temperature significantly increasing, load capacity. The maximum capacity is reached at a temperature as high as 135°C. This may be due to chemisorption and/or kinetic effects. Fresh molecular sieves of this type showed about twice the load capacity of used sieves, i.e. during first loading a certain amount of NO_x will be irreversibly captured onto the molecular sieve. For dry gases the sieve showed no degradation during some 50 load/unload cycles; this is not expected for wet gases (5). The molecular sieve "Zeolon 900 Na" from Norton Comp. has much higher load capacities, but showed in principle similar characteristics to the 5 A molecular sieve. The "Zeolon 900 Na" is a synthetic mordenite with a high SiO_2/Al_2O_3 ratio of 10/1 and an effective pore diameter of 7 Å.

The same molecular sieve, but in hydrogen form, "Zeolon 900 H" (8 - 9 Å pore diameter) behaves differently. The load capacity decreases with increasing column temperature as expected, and no irreversible NO_x-fixation was observed during initial loading.

Wet Off-Gas

Only the "Zeolon 900 H" was used in experiments with wet gases. For low H_2O contents in the gas (up to 1 vol%) the load capacity did not decrease under this condition. For about 50 load/unload cycles under wet gas no degradation or decrease of load capacity was observed. This is in accordance with the literature (5,6). The acid resistance of this molecular sieve is due to its high SiO_2 content.

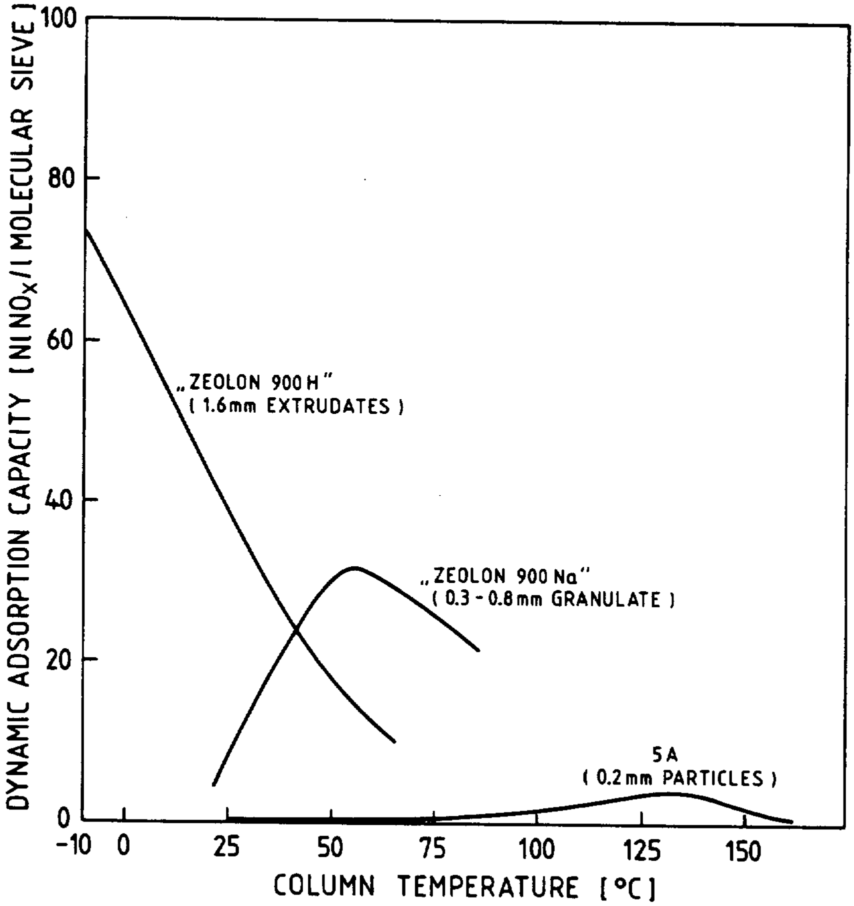

Fig. 4: Dynamic adsorption capacity versus column temperature for some molecular sieves

As NO_2 and H_2O is adsorbed on the molecular sieve HNO_3 is formed and NO liberated ($3\ NO_2 + H_2O \rightarrow NO + 2\ HNO_3$) since NO does not adsorb significantly. The NO again oxidizes to NO_2 with the O_2 from the air. This oxidation is also typically a slow reaction, it seems to be catalysed by the molecular sieve under the condition in question. This can be seen when the whole breakthrough is recorded as wet NO_2 containing air flows through the column. Fig. 5 shows such a breakthrough. The concentration of NO_2 and NO in the wet air at the column inlet was 0.62 vol% and 800 vpm, respectively. When NO_2 starts to breakthrough, no NO is as yet detectable in the effluent. At high NO_2 concentrations of 0.1 vol% and more in the effluent the NO reaches a value of about 100 vpm and stays constant for some time. Finally at full breakthrough of the NO_2, the NO in the effluent reaches a maximum concentration of 300 vpm, which may be compared with the 800 vpm NO at the column inlet.

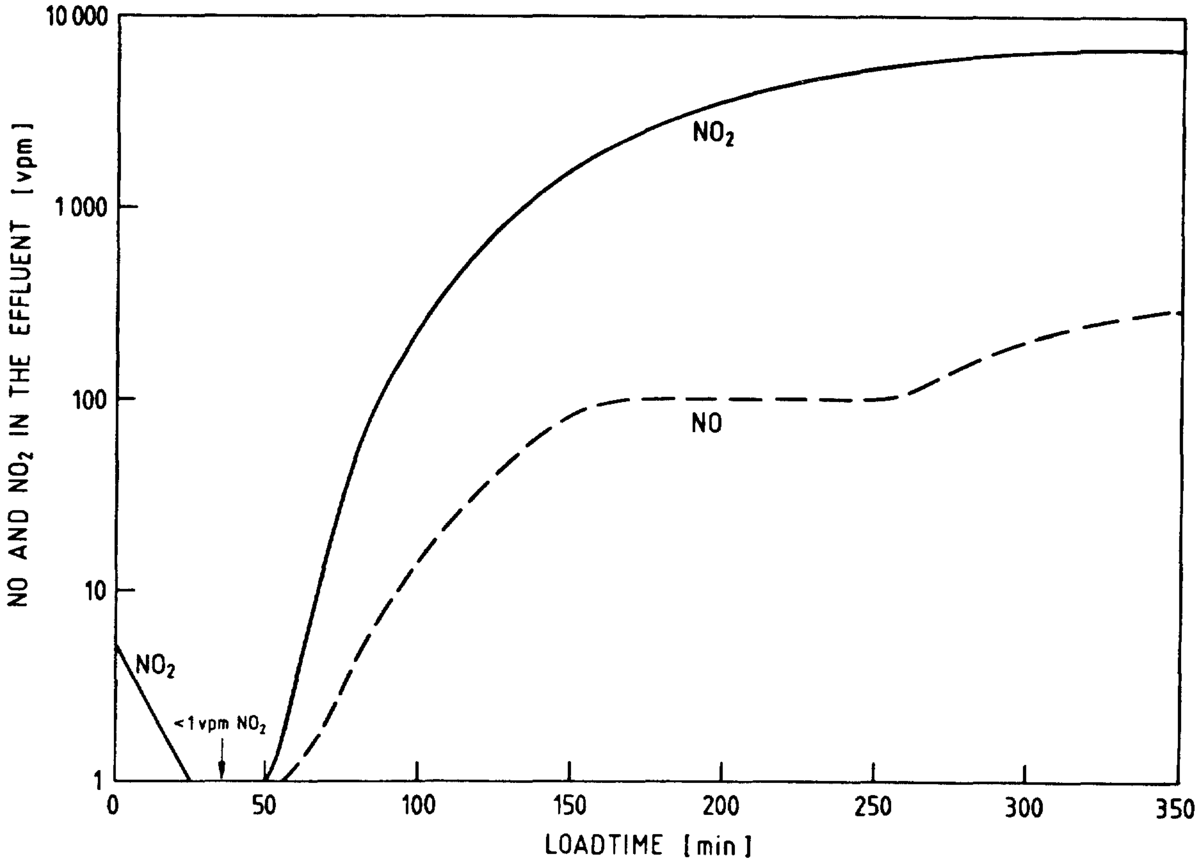

Fig. 5: Full breakthrough of NO and NO_2 through a column filled with "Zeolon 900 H" (column: 24 mm Ø x 200 mm, gas-flow: 150 Nl/h, wet air with 0.63 vol% NO_2 and 800 vpm NO, temperature: 28°C, pressure: 1 bar)

In a glass column the adsorption of NO_2 as well as the formation of HNO_3 on the molecular sieve may also be observed visually. As the brown NO_2-gas adsorbs on the white molecular sieve this also becomes brown. In the case of wet off-gas only a brown adsorption front is established, behind this front the molecular sieve turns white again as colourless HNO_3 is formed.

Process control

The small amount of NO_2 in the effluent during starting of the adsorption -as shown in Fig. 5- is left over from the previous load cycle, since the column was not purged with clean air during previous regeneration at elevated temperature. For unloading, the column was only heated up to 200°C under an unchanged purge flow of wet off-gas containing about 0.5 vol% NO_x.

This method will be used for practical recycling of the NO_x and H_2O together with some off-gas to the dissolver. The diagramm in Fig. 6 gives an impression of this technique. From an ongoing load/unloading of the column two cycles are shown in the diagram. During the process *a flow of 150 l/h of wet air with 0.55 vol% NO_x enters the column continuously. When the NO_x in the effluent reaches a concentration of 100 vpm, the column is placed into an oven at 230°C. During a rise of the column temperature - measured by a thermocouple near the column centre - the NO_x leaves the column rapidly (reaching peak NO_x-concentration of about 5 %) until most of the collected NO_x is desorbed. As the NO_x-effluent concentration tends to reach the inlet concentration, the column is removed from the oven and cooled down to RT, plugging the column for NO_x-passage.*

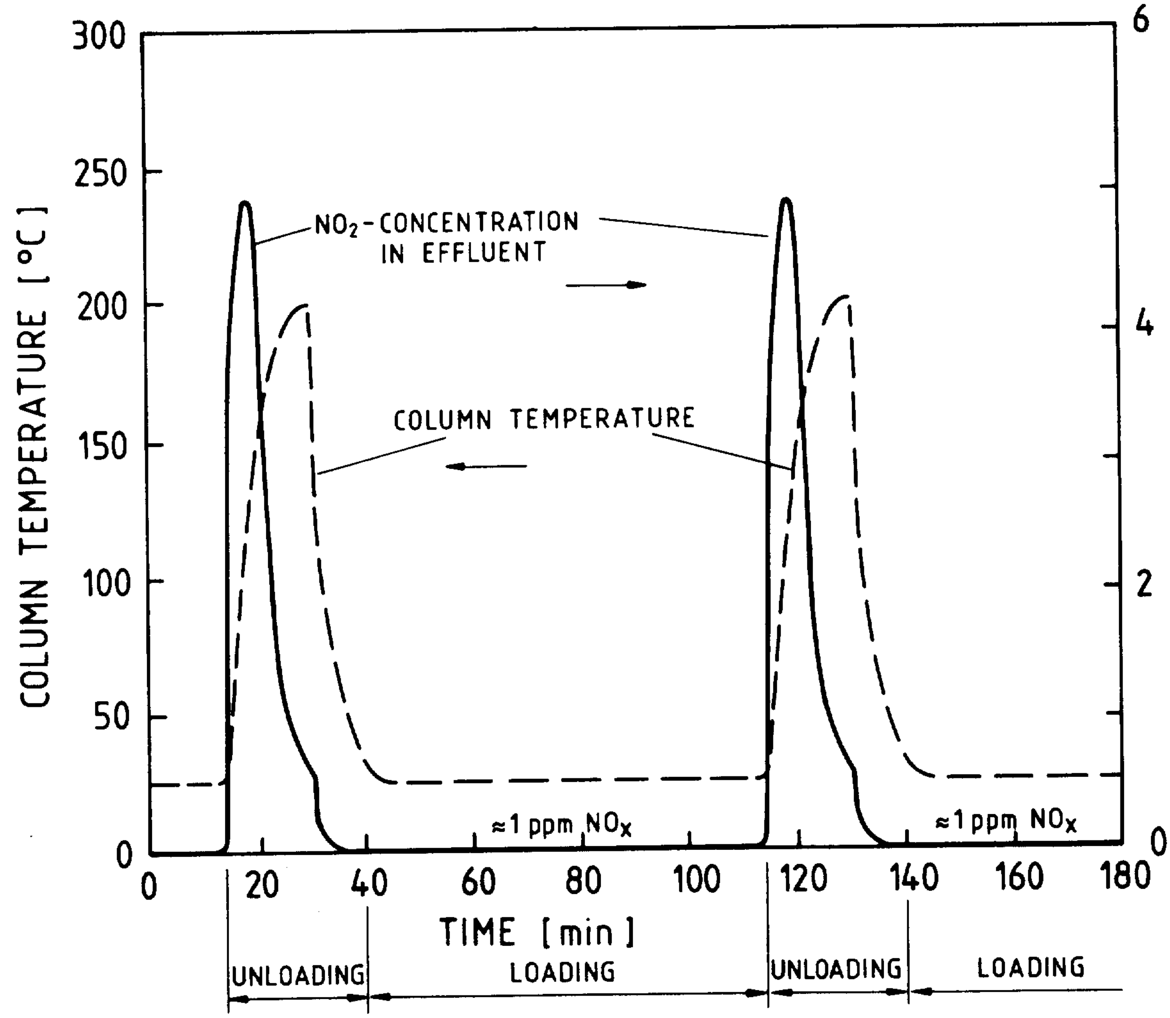

Fig. 6: Periodic adsorption and desorption of NO_2 under continious NO_x-containing air flow at column inlet (column: 24 mm$^{\phi}$ x 200 mm, molecular sieve: "Zeolon 900 H", gas flow: 150 l/h wet air, with 0.5 vol% NO_x, atmospheric pressure)

During column loading the effluent may flow to the down-stream noble gas separation facility, while during column unloading the effluent has to be recycled to the disolver. The minimum gas volume necessary *for column unloading is about 1/3 of the gas volume passing the column during loading.*

IV. Xenon Separation and Krypton Enrichment

After NO_x, H_2O *and* CO_2 *have been separated from the dissolver off-gas, it consists of air with the noble gases Xe and Kr only. In a charcoal column the ratio of the retention time of these gas species (under certain conditions) is e.g.* $(Ar + N_2 + O_2)/Kr/Xe = 3/8/50$. *The difference in adsorption of these gases enables the design of a one-step adsorption process, where Xe is completely separated from the off-gas and the Kr can be, depending on the process parameters, more or less enriched in the off-gas. Experiments for such a process have been reported by Jüntgen et al. (4). Basically, the process is at constant R.T.; the regeneration of the column takes place by evacuation to a low pressure of 30 mbar and under a small purge gas flow; a pumping time of about 15 h is necessary for Xe removal.*

For shorter regeneration time, experiments have been carried out on combined temperature and pressure swing ad/desorption. Fig. 7 gives the flow diagram for the experimental equipment. The adsorption column was placed into an oven and connected with a supply pipe for the gas mixture or pure N_2. *The effluent of the column could be monitored by a thermal conductivity detector. For evacuation of the column a membrane pump was used, venting the effluent into a gasometer.*

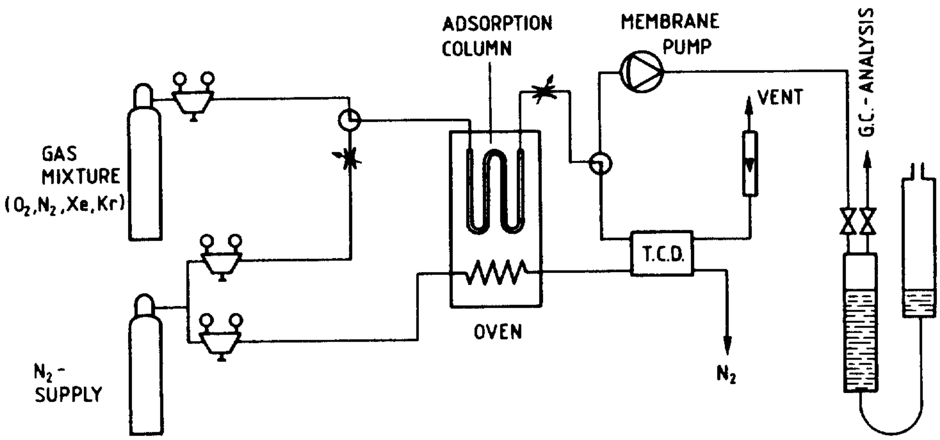

Fig. 7: Flow sheet for the experimental equipment for adsorptive Xe-separation and Kr-enrichment

The column of 4 mm I.D. and 3 m length was filled with charcoal of 0.4 - 0.6 mm grain size. In an initial set of experiments the dynamic adsorption capacity of the charcoal as a function of column temperature and pressure was determined. The diagram in Fig. 8 shows the capacity b (as defined before) versus the column temperature and Fig. 9 the relation of b (of Kr and Xe) to column pressure.

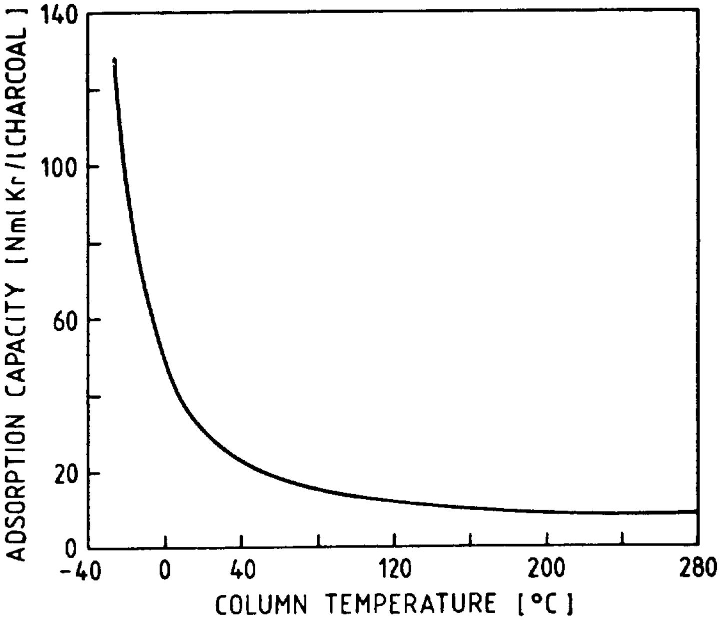

Fig. 8: *Dynamic adsorption capacity of the charcoal for krypton versus the column temperature. (column: 4 mm I. D. x 3 m, gas flow: 22 ml/min, N_2 with 0.2 vol% Kr, face velocity: 1.75 m/min, pressure: 1 bar)*

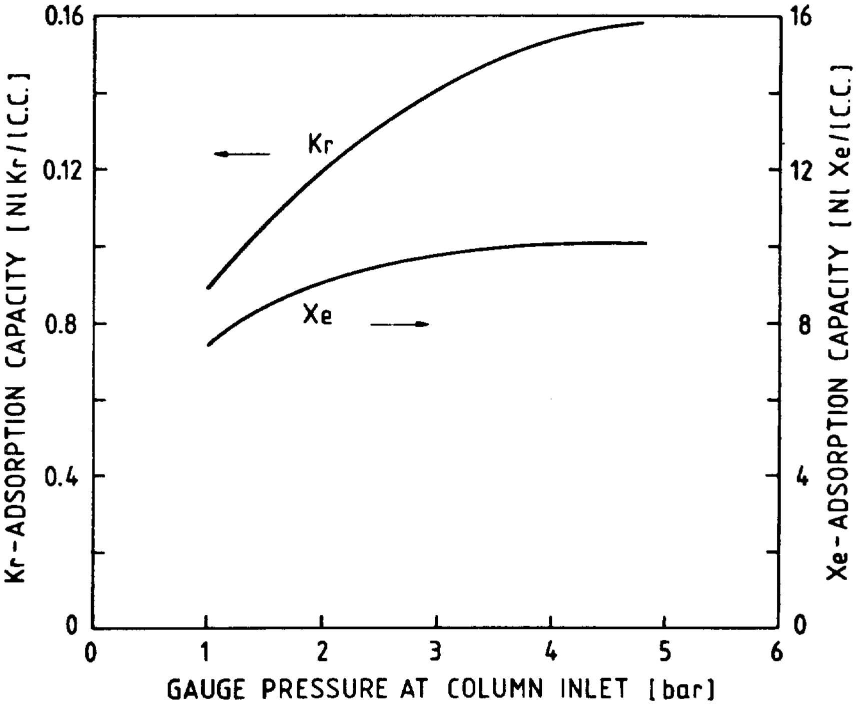

Fig. 9: *Dynamic adsorption capacity of charcoal for krypton and xenon versus column pressure (column: 4 mm I.D. x 3 m, temperature: -10°C, gas-flow: 300 Nml/min of N_2 with 0.2 vol% Kr and 2 vol% Xe)*

The simultanious adsorption of Kr and Xe by charcoal is shown in Fig. 10. It gives the complete breakthrough of both gases through a column of 4 mm I.D. and 6 m length, at e.g. a face velocity of 30 m/min, R.T. and atmospreic pressure. When such a column is only partly loaded with the noble gases, it is possible during unloading of the column to separate both species and to enrich the Kr in the off-gas. E.g. the column may be fully loaded with Kr till the begining of Kr breakthrough, which means a Xe loading of about 1/10 of its full capacity. A possible regeneration of such a column is shown in Fig. 11. The column was heated up from R.T. to 125°C and then evacuated to a minimum pressure of 20 mbar. Within 5 min 500 ml of gas could be pumped from the column having a Kr-concentration of 0.55 vol%, i.e. 2.7 times the inlet Kr-concentration. After additional purging of the column with 100 ml N_2 at about 20 mbar for 10 min, practically all the Kr was removed from the column. Then, during further purging of the column, the Xe was desorbed.

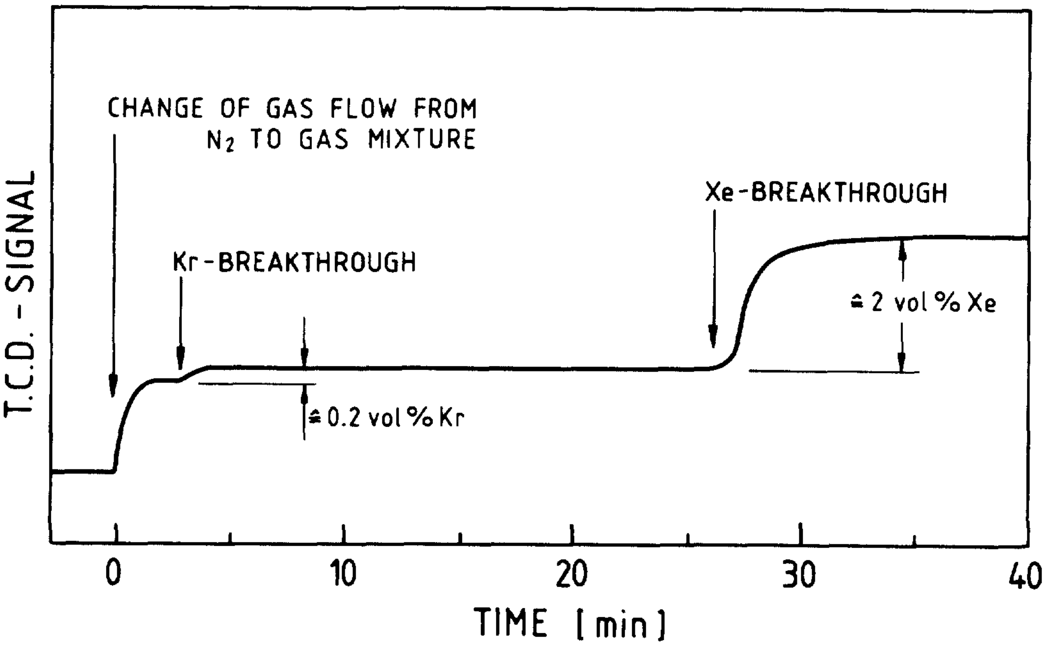

Fig. 10: T.C.D.-signal while passing a N_2-Xe-Kr gas mixture through a charcoal column (column: 4 mm I.D. x 6m, 26°C, gas mixture: 370 ml/min, 2 vol% Xe and 0.2 vol% Kr in N_2)

The average Kr concentration in the whole Kr fraction was 0.46 vol%, i.e. the Kr enrichment factor for this process was only 2.3. This resultcan be improved because the Kr desorbs from the column with a peak-like curve, as can be seen in Fig. 12. In this case, the column was (for higher column utilization loaded at -10°C and 3 bar above atmosperic pressure). During unloading of the column under 100 Nml gas batches the column temperature was raised to +95°C. Under these conditions the Kr-concentration reaches a peak value of 2 vol%, the average Kr-concentration of 0.68 vol% was only

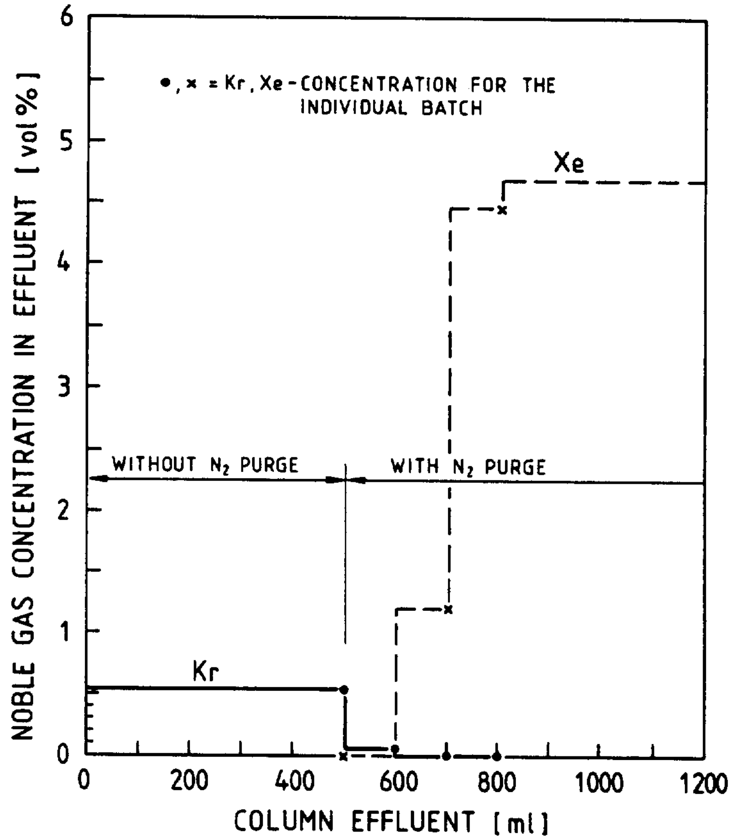

Fig. 11: *Noble gas concentration in the effluent during evacuation at constant temperature*
Column: 4 mm I.D., 6 m length
Loading: till Kr breakthrough for 3.5 min with 365 ml/min (N_2 with 0.2 vol% Kr and 2 vol% Xe) at 26°C and atmosperic pressure
Regeneration: evacuation to 20 mbar at 125°C column temperature

slightly increased. But at the expense of recycling a part of the off-gas the average Kr-enrichment can be considerably increased. When recycling the effluent batches with x_{Kr} outlet $\leq x_{Kr}$ inlet, 300 ml of gas with an average of 0.06 vol% Kr has to be recycled. This would increase the off-gas flow by 10 %. The gas batch of off-gas with $x_{Kr} \geq x_{Kr}$ inlet is then 500 ml with a Kr-concentration of 1.05 vol%, so that the enrichment factor is 5.2.

In the experiments only one kind of charcoal was used. A selection of the most efficient activated charcoal has to be made, as well as the possible application of inorganic adsorbents. Because of the oxygen in the off-gas the use of inorganic adsorbents would be favourable with respect to safety , although their adsorption capacity is typically lower. The application of such adsorbents for processes in question has been reported (7,8).

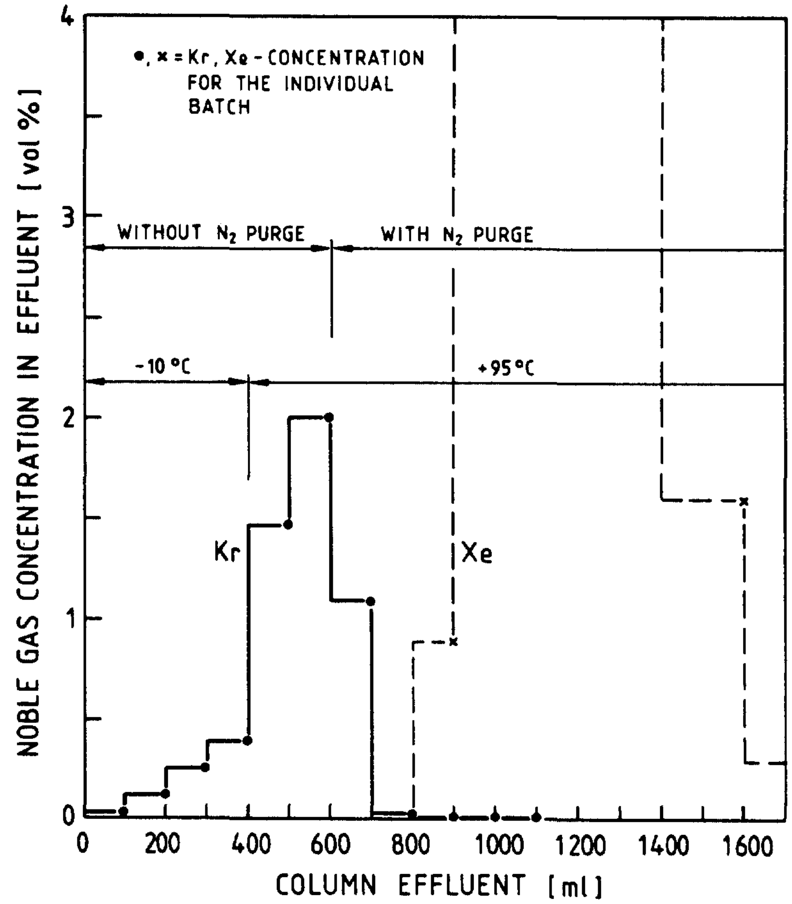

Fig. 12: Noble gas concentration in the effluent during evacuation at elevated temperature
Column: 4 mm I.D., 3 m length
Loading: till Kr breakthrough with a gas flow (0.2 vol% Kr, 2 vol% Xe, balance N_2) of 300 Nml/min for 9 min at -10°C and 3.2 bar above atmospheric pressure
Regeneration: at increasing temperature from -10°C to +95°C and minimum pressure of 20 mbar

V. Krypton-Separation

Since N_2 and Kr have similar adsorption characteristics their separation is laborious. Therefore the potential of preparative gas chromatography was experimentally investigated for this process. In principal, by this process a batch of gas to be separated is flushed by a carrier gas through an adsorption column, in the course of which a multiple-step separation process is achieved. This seems to be necessary for the separation problem in question, but the process requires a high carrier gas flow. Therefore the experiments carried out are mainly directed toward a minimum use of carrier gas. Fig. 13 presents the flow sheet for the experimental equipment. A column filled with charcoal was continuously purged with He and placed into an oven for temperature control. The effluent of the column was monitored by a T.C.D. The most favourable way of loading a batch of off-gas into the column inlet was by means of a load cylinder. During loading, the He-flow was interrupted by a 3-path valve and the intended amount of gas mixture was transferred from the load cylinder into the column within a short period. The batch size of the gas mixture is determined by the pressure in the load cylinder.

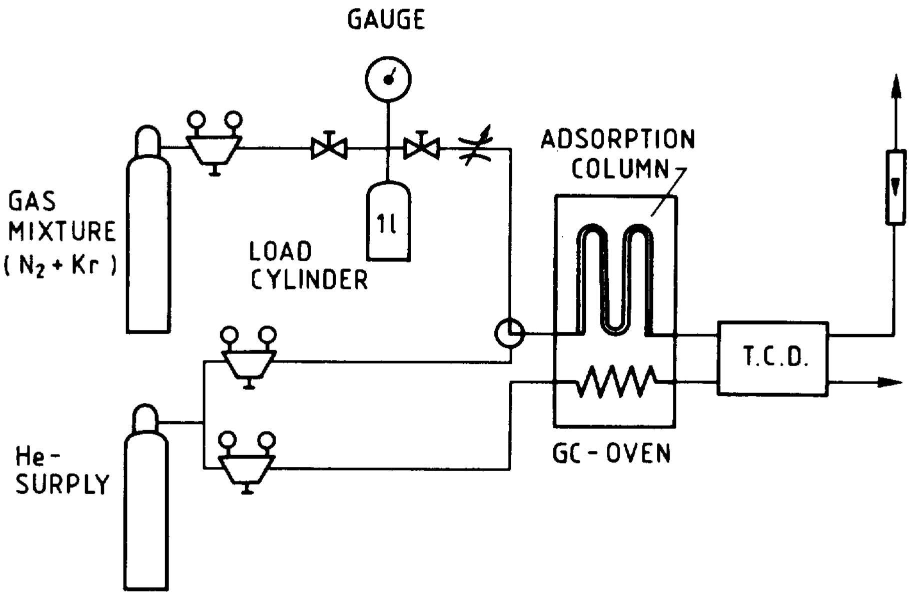

Fig. 13: Equipment for Kr-separation from off-gas by preparative gas chromatography

For the experiments a gas mixture of 80 vol% N_2, 9 vol% O_2, 10 vol% Kr and 1 vol% Xe was used; the column was 4 mm I.D. and 3 m long. At a column temperature of 80°C and a He-flow of 20 ml/min a maximum gas batch of 100 Nml could be completly separated into (N_2 + O_2) and Kr. The chromatogram for this separation is given in Fig. 14. The time for the complete separation cycle (from gas inlet to the end of the Kr-peak) was 18 min, which gives an average gas throughput of 5.5 Nml/min. Under these conditions the minimum ratio of carrier gas to off-gas is $\dot{V}_{He}/\dot{V}_{Gas} = 3.6$. (During the experiments the Xe in the gas mixture was neglected; it will probably smear along the column during column operation but did not influence the operation).

VI. Deposition of the Kr into storage cylinders

The fraction of the effluent containing Kr from the preparative gas chromatography process is a He-flow with about 0.5 vol% Kr. The separation of this Kr from the He can be favourably combined with botteling of the Kr into storage cylinders. A simple experiment has been carried out to demonstrate this. Fig. 15 shows the equipment. In principle a stainless steel cylinder of 4 cm I.D. and 24 length was filled with charcoal and partially submerged into liquid nitrogen. The He, containing Kr was led into the lower part of the cylinder by a small pipe; the outlet from the top of the cylinder was connected to a gas chromatograph.

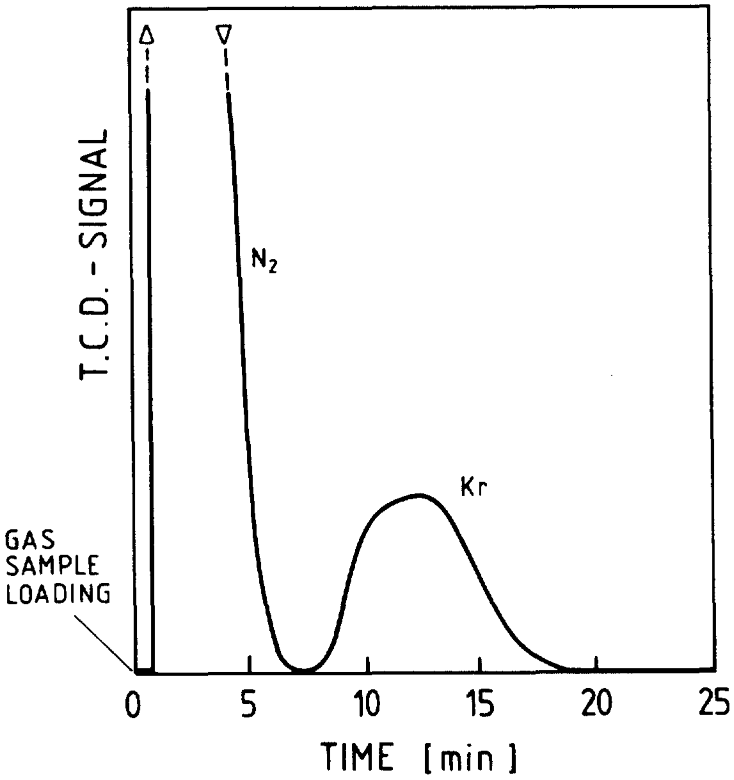

Fig. 14: *T.C.D.-chromatogram for separation of a gas mixture with 10 vol% Kr*
column: 4 mm I.D. x 3m at 80°C
$\dot{V}_{He}$ *= 20 ml/min,* V_{gas} *= 100 ml*

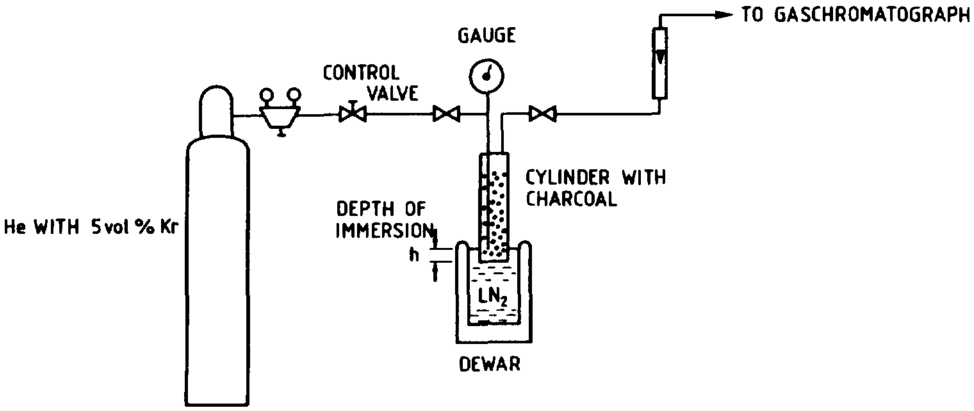

Fig. 15: *Equipment for experiments on the separation of Kr from the He-flow and deposition of the Kr into storage cylinders*

For one specific experiment the parameters were:
charcoal content in the cylinder: 100 g (240 ml) of grain size 0.3 - 0.5 mm,
gas-flow: 80 Nl/h, He with 5 vol% Kr
submerged depth of cylinder into liquid nitrogen: 4 cm.

After a filling time of 100 min under these conditions the pressure difference between cylinder inlet and outlet increased from 0.1 bar to 3 bar, i.e. the inlet pipe plugged. During the whole operation the Kr-concentration at the cylinder outlet was always below the detection limit of 1 vpm.
As the pressure drop increased the inlet and outlet valves of the cylinder were closed and the cylinder warmed up to R.T., the pressure in the cylinder thereby rose to 6.4 bar. With the Kr content in the cylinder of 6.5 Nl, the calculated pressure in the cylinder without charcoal is 28 bar (He content was neglected) i.e. the pressure in the cylinder is reduced by the charcoal by a factor of 4.4.
In this experiment the specific Kr load in the cylinder was 27 Nl Kr/l charcoal. For Kr-85 storage cylinders loadings of 18 to 40 Nl Kr/l charcoal are discussed in the literature (9,10).

VII. Layout of an integrated adsorption process

On the basis of the experimental results a principle layout has been accomplished for Kr-retention from dissolver off-gas by an adsorption process integrated into the general dissolver off-gas cleaning system. This layout is still tentative, since for some process steps further experimental work has to be done for the process scale-up.

For a base, a dissolver of 125 kg/h throughput of fuel is considered. Shears and dissolver are purged with a gas flow of 30 Nm^3/h. Behind the NO_x-wash column, aerosol filter and I-adsorption bed, the off-gas air may contain approximately 0.5 vol% NO_x, 0.5 vol% Xe, 0.05 vol% Kr and 1 vol% H_2O. This gas is forwarded to the adsorptive Kr-retention plant. In Fig. 16 a principle flow sheet is shown for this facility stating the calculated column dimensions.

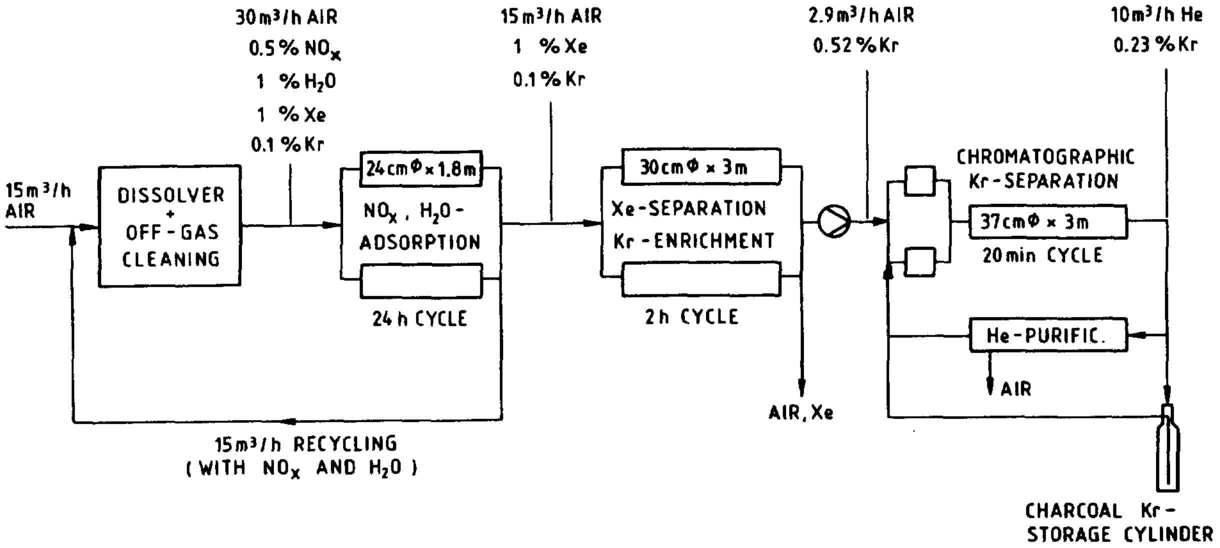

Fig. 16: Schematic flow sheet with estimated column sizes

For the first process step the NO_x and H_2O adsorption column is 24 cm in diameter and 1.8 m long, based on a 12 h loading period. The unloading of the column can be done within 6 h, which gives a standby time of 6 h. For continuous operation 2 columns are necessary. When half the off-gas from the column outlet (together with all the NO_x and H_2O) is recycled to the dissolver, the Kr- and Xe-concentration in the off-gas increases to 0.1 vol% and 1 vol%, respectively, and the remaining off-gas flow for the downstream noble gas separation is reduced to 15 Nm^3/h.

In the second process step the Xe is separated from and the Kr enriched (by a factor of 5.2) in the off-gas by a charcoal-filled column. The dimension of the column is 30 cm Ø and 3 m length, when a cycle time of 2 h is chosen (1 h loading and 1 h unloading). Again, for continuous operation two columns are necessary. The maximum hold-up of Kr in the column is 15 Nl, equivalent to about 1500 Ci Kr-85.

In the third step the krypton is separated from the residual off-gas (an air flow of 2.9 Nm^3/h with 0.52 vol% Kr) by preparative gas chromatography. A single charcoal-filled column of about 37 cm Ø x 3m length is required; the necessary He-flow for its operation will be 10 Nm^3/h. At a cycle time of 18 min, the maximum Kr-hold up in the column is 4.5 Nl (= 450 Ci Kr-85). Since for column loading a load tank is necessary, the whole Kr hold-up in this process step will be about 9 Nl.

Finally, the Kr is separated from the effluent of the chromatography and filled into a storage cylinder which is partially cooled to low temperature. A 50 l cylinder filled with charcoal may collect up to 200,000 Ci Kr-85 (2 Nm^3 Kr). The collection time would be 130 h.

This cylinder has to be handled in a hot cell with e.g. a concrete wall of 1 m thickness. At maximum Kr loading of the cylinder, the radiation dose outside the cell was calculated to 0.01 mrem/h. But besides this the whole adsorptive Kr retention process could be build into a control room with limited access only the adsorption columns would require additional shielding. For the described flow sheet the adsorption columns would contain altogether at maximum 2,500 Ci Kr-85.When placing these columns behind a concrete wall of 45 cm thickness the radiation dose from the whole plant in front of the shielding would amount to 1 mrem/h. With the exception of the adsorption columns, all the equipment such as pumps, valves etc. could be located in front of the shielding giveing free access for control and maintenance.

Acknowledgments

I would like to thank Mr. K. Hein for his experimental assistance and Mr. F. Rohloff for the dose rate calculations.

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DISCUSSION

EVANS: Have you considered the effect of the buildup of ^{85}Rb on the operation of your charcoal beds?

RINGEL: No, so far we have not considered the effect of RbO_2 on the charcoal.

DEITZ: You don't have to worry about that. A little graphite in the charcoal will retain all the ^{85}Rb.

HAAG: For the Zeolon 900H, it appears that H_2O displaces NO_x. Would you comment upon the displacement of CO_2.

RINGEL: NO_2 is not really displaced; rather, HNO_3 is formed. CO_2 is less adsorbed than H_2O and NO_2. That means that CO_2 passes through the column. For 14-C management, CO_2 has to be removed from the off-gas after the "Zeolon H" column.

FORMATION AND BEHAVIOUR OF NITRIC OXIDES IN A CRYOGENIC KRYPTON SEPARATION SYSTEM AND CONSEQUENCES OF USING AIR AS PROCESS GAS

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Abstract

Trace amounts of nitric oxide (NO) would reach the cryogenic columns, for krypton removal, of the off-gas cleanup system of a fuel reprocessing plant because of incomplete removal in the NO_x destruction steps and poor retention on molecular sieve desiccants. A study of the behaviour of NO in the cryogenic test unit KRETA showed an accumulation in the first column which is much less pronounced than predicted by calculations based on published volatility data. This discrepancy was explained by taking into account the dimerization equilibrium of NO in the liquid phase which is concentration dependent.

In the presence of O_2, NO is oxidized rapidly to N_2O_4 at the low temperatures of the column. This oxide is highly insoluble in liquid Kr/Xe mixtures.

If the catalytic O_2-reduction step is omitted and air is used as process gas, appreciable amounts of both O_3 and NO_2 will be formed radiolytically in the cryogenic columns. Calculated concentration levels of O_3 in the first column are between 2 and 3 mole-% in the liquid phase, while NO_2 levels are an order of magnitude lower.

Because CH_4 accumulates to high concentrations in the first cryogenic column, the installation of an oxidation catalyst in the off-gas cleanup system may be necessary.

Test runs with KRETA showed that the column decontamination factor for the rare gases is equally good using air or N_2 as carrier gas.

I. Introduction

Among the impurities which may reach the cryogenic columns of a krypton separation system from the dissolver off-gas of reprocessing plants special attention must be paid to those whose volatility is similar to that of krypton, particulary O_2, CH_4 and NO, because they accumulate in krypton-rich column sections and in the krypton product. These compounds are reactive and may undergo radiolytic and chemical reactions, forming O_3, higher nitrogen oxides, and other, potentially hazardous compounds.

The accumulation behaviour of O_2 and CH_4 in the test unit KRETA (1) had been previously studied (2). It was observed that CH_4 accumulates strongly in the krypton product, and that O_2 leaves the first column via the head.

In order to minimize the concentration of these compounds catalytic reduction of O_2 and residual NO_x with H_2 is included as a precleaning step in our off-gas cleaning scheme (3). Since the handling of large amounts of H_2 may present difficulties in a licensing procedure, a strong incentive exists to omit this step. For that case it is necessary to be aware of the consequences.

In this contribution, we report new experimental results on the behaviour of NO in the first KRETA column, and results of calculations of the radiolytic formation of O_3 and NO_2 in this column if high O_2 concentrations (20%) are present in the feed-gas.

II. Behaviour of NO

1. Accumulation in the first column

The reported boiling point of NO (139 K at 5 bar) is close to that of Kr (144.9 K at 5 bar). So, one could anticipate the accumulation of a high concentration of NO in the krypton product, even stronger than that of CH_4 (2). However, the reported volatility data of NO refer to the liquid, which is highly associated and mainly exists as dimers (4) (equation 1).

$$2\ NO \rightleftharpoons N_2O_2; \qquad \Delta H = -10.5\ kJ/mole \tag{1}$$

In diluted form the vapor pressure of NO is much higher than expected because the fraction of nitric oxide as monomer increases. From the data of Rice (4) the vapor pressure of the hypothetical monomer liquid was estimated. It is given in equation 2.

$$\log p\ (atm) = -\frac{318{\cdot}8}{T} + 3.5596 \tag{2}$$

This vapor pressure is only a little lower than the vapor pressure of O_2 in the temperature range of interest (94 to 180 K).

An expression giving the equilibrium constant for dissociation of the dimer in the liquid phase was derived from the data of Rice (4). The observed gas phase NO concentration profile in the first KRETA column with 2.5 ppm NO in the exit gas was approximately matched with this expression by an iterative technique (equation 3).

$$\log K = \frac{854\ 46}{T} + 6.95 \tag{3}$$

$$\text{where } K = \frac{[NO]^2}{[N_2O_2]} .$$

It was assumed that the heat of dimerization does not vary with the concentration of NO in liquid N_2. The fit of the calculated NO concentrations with the experimental concentration profile in equilibrium with 1 ppm in the feed-gas is shown in fig.1 along with calculated concentration profiles for NO concentrations in the feed gas of 1.3, 1.7, 2.1 and 2.5 ppm.

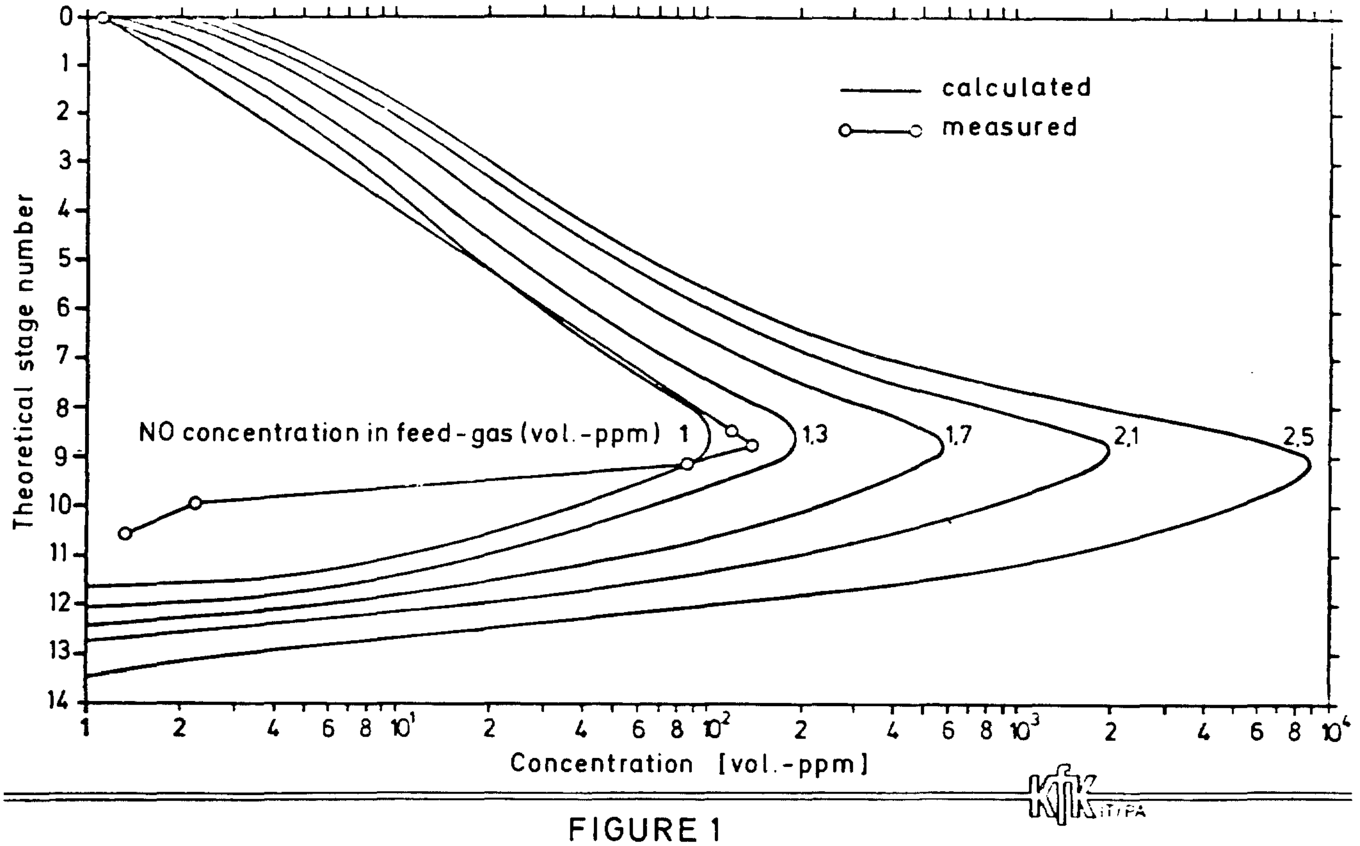

FIGURE 1
Concentration profile of NO in the first KRETA column

In this figure the column length is expressed in terms of theoretical stages. To fit the calculated with the experimental curves it was assumed that one theoretical stage corresponds to two practical stages. Any discrepancies in the fit may be due to incorrect assumptions, e.g. the assignment of the theoretical plate positions, a difference between the actual and calculated temperature profile, of different values of the heat of dimerization and/or the vapor pressure.

When NO is present in concentration of a few ppm or less, it leaves the column via the head and not via the sump as expected previously. If NO is present in larger concentrations the position of the concentration maximum will shift towards the lower column sections.

2. Oxidation of NO

NO can accumulate in the column only in the absence of O_2. In our experiments this condition was fulfilled, since the tank N_2 used as carrier gas contained less than 1 ppm of O_2.

When O_2 was added to the feed-gas, NO was oxidized rapidly according to equation 4:

$$2\ NO + O_2; \longrightarrow 2\ NO_2: \qquad \Delta H = -52.5\ kJ/mole \qquad (4)$$

This is not surprising since the rate constant of this reaction increases by two orders of magnitude when the temperature is lowered from 350 to 90 K (5).

At the low temperatures of the column NO_2 is completely dimerized according to equation 5:

$$2\ NO_2 \rightleftharpoons N_2O_4; \qquad \Delta H = -56.8\ \text{kJ/mole} \qquad (5)$$

In addition, the formation of N_2O_3 is expected (equation 6) since NO and NO_2 are present simultaneously:

$$NO + NO_2 \longrightarrow N_2O_3; \qquad \Delta H = -39.7\ \text{kJ/mole} \qquad (6)$$

The oxidation of NO by O_2 in the first KRETA column was demonstrated by feeding 5 ppm of O_2 to the column which was in equilibrium with 1 ppm of NO in the feed-gas (Fig.2). After one hour

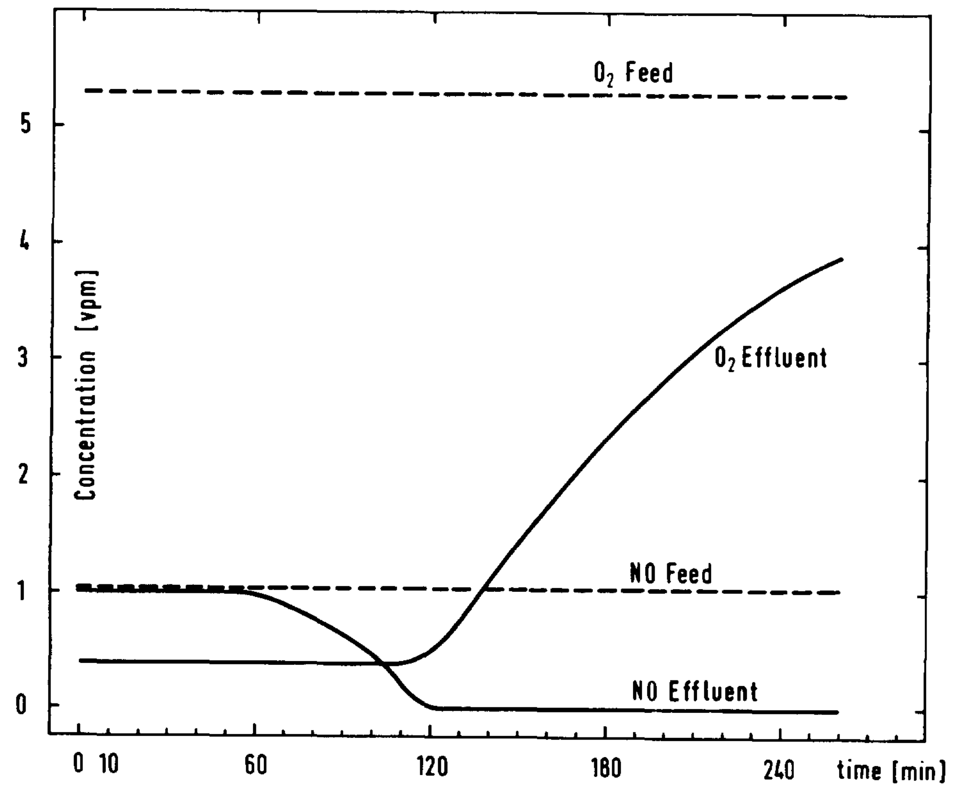

FIGURE 2
Oxidation of NO in the first KRETA Column

the NO concentration at the column head began to decrease indicating that the NO in the column was being oxidized. After two hours this process essentially was completed as indicated by the increasing O_2 concentration at the head. After four hours the column had nearly reached equilibrium with respect to O_2 and no NO could be detected any more.

3. Solubility of N_2O_4

Because of its high boiling point (294 K at 1 bar) NO_2 should accumulate entirely in the reboiler liquid. However, analysis of this liquid showed NO_2 concentrations of only 1-2 ppm throughout the test campaign. This means that the solubility of N_2O_4 in liquid Kr/Xe is extremely low and that most of it must have crystallized (melting point: 262 K). That this indeed had happened was indicated by plugging of a measuring line. However, column operation was not inhibited. At the end of the campaign when all rare gases had been withdrawn from the column the nitric oxides were evaporated and analyzed. A material balance confirmed that during the test campaign practically all of the NO_2 had collected in the column sump.

III. Use of Air as Feed-Gas

1. Column Operation

The cryogenic test unit KRETA was operated continuously for four weeks using air from the environment as carrier gas for the rare gases (typical composition of the feed-gas: 21% O_2, 1% Ar, 400 ppm Kr, 4000 ppm Xe, balance N_2). The steady state concentration profile for O_2 was established in the first column after 12 hours of operation (Fig.3). Maximum O_2 concentrations in the gas phase of the upper column were between 32 and 35%. In the lower column sections O_2 concentrations decreased rapidly to between 10 and 100 ppm. The decontamination factors for Kr and Xe at the column head are determined by the sensitivity of analysis and are 10^3 and 10^4, respectively. These decontamination factors are equal to those determined earlier with N_2 as carrier gas.

The CO_2 in the air (330 ppm) was successfully removed in the adsorber beds preceding the cryogenic unit (test unit ADAMO). During a 24 hour cycle CO_2 broke through the silica gel bed, as expected, but was retained on the following molecular sieve (10 A) bed.

The air at the Karlsruhe site contained 3 ppm of CH_4, which is above the average of 1 ppm. This led to an accumulation in the first column of up to 2200 ppm after three weeks of operation. This amount does not yet correspond to the steady state concentration for 3 ppm in the feed-gas, which is expected to be in the percent range (2).

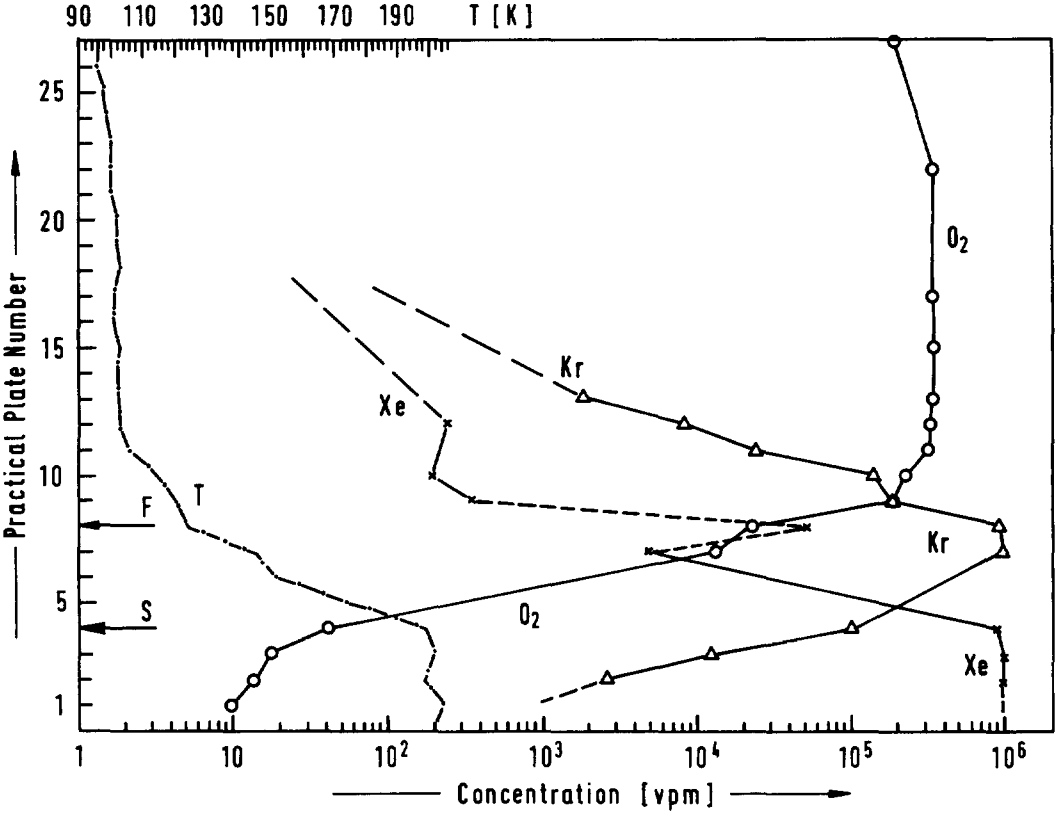

FIGURE 3

Temperature and Concentration Profiles in the first KRETA Column

2. Calculated Formation of O_3 and NO_2

Radiolytic O_3 formation in a cryogenic system containing Kr-85 had been estimated by us previously for three different process versions (2). We repeated this estimate for the process version just described, where very little of the O_2 fed into the first column is carried to the sump product.

The O_3 formation rate F was calculated according to equations 7 and 8:

$$F[\text{mole/h}] = I[\text{eV/h}] \cdot G[\text{n/100eV}] \cdot (6.02\ 10^{23})^{-1}\ [\text{mole/n}] \qquad (7)$$

where I, the radiation dose absorbed is

$$I[\text{eV/h}] = \bar{E}_\beta[\text{eV}] \cdot A[\text{Ci}] \cdot 3.7\ 10^{10}\ [1/\text{s}\cdot\text{Ci}] \cdot 3600\ [\text{s/h}]; \qquad (8)$$

$\bar{E}_\beta$ = 0.225 MeV (average β-energy of Kr-85), n = number of particles and A[Ci] = Kr-85 inventory.

The G-factor for O_3 formation was adapted to the experimental conditions from literature data (6-9) and varied non-linearly depending on O_2 concentration in accordance with literature values (10). The values used are shown in Table I. The G-factors for NO_2 formation were also chosen in accordance with literature values (6) and extrapolated to lower O_2 mole fractions as shown in Table I.

These values are conservative and may be high by a factor of two to three, especially in the case of NO_2.

Table I. G-Factors of O_3 and NO_2 Formation

Mole fraction O_2	G-factor O_3	G-factor NO_2
0.01	3.0	0.1
0.1	5.2	1.0
0.2	7.2	1.7
0.3	-	2.0
0.4	10.2	1.8
0.5	11.0	1.55
0.6	11.6	1.26
0.8	12.2	0.66
0.9	12.3	-
1.0	12.5	0

For the calculation of the O_3 concentration profile the O_3 formed on all 14 theoretical stages of the column was cumulatively added to the feed-gas. Thus O_3 was treated like all other gas components of the rectification mixture. The resulting liquid concentration profile is shown in fig.4.

Because of its low volatility O_3 accumulates in the lower column section just above xenon. Its maximum concentration is 2.3 mole-% in the liquid phase.

The rates of NO_2 formation are given in Table II. Because of its high boiling point and low solubility NO_2 will not build up a concentration profile in the column, but will be collected quantitatively in the reboiler liquid, as pointed out in section II.3. The cumulative formation rate of NO_2 is 85.2 mmole/h or 3.92 g/h.

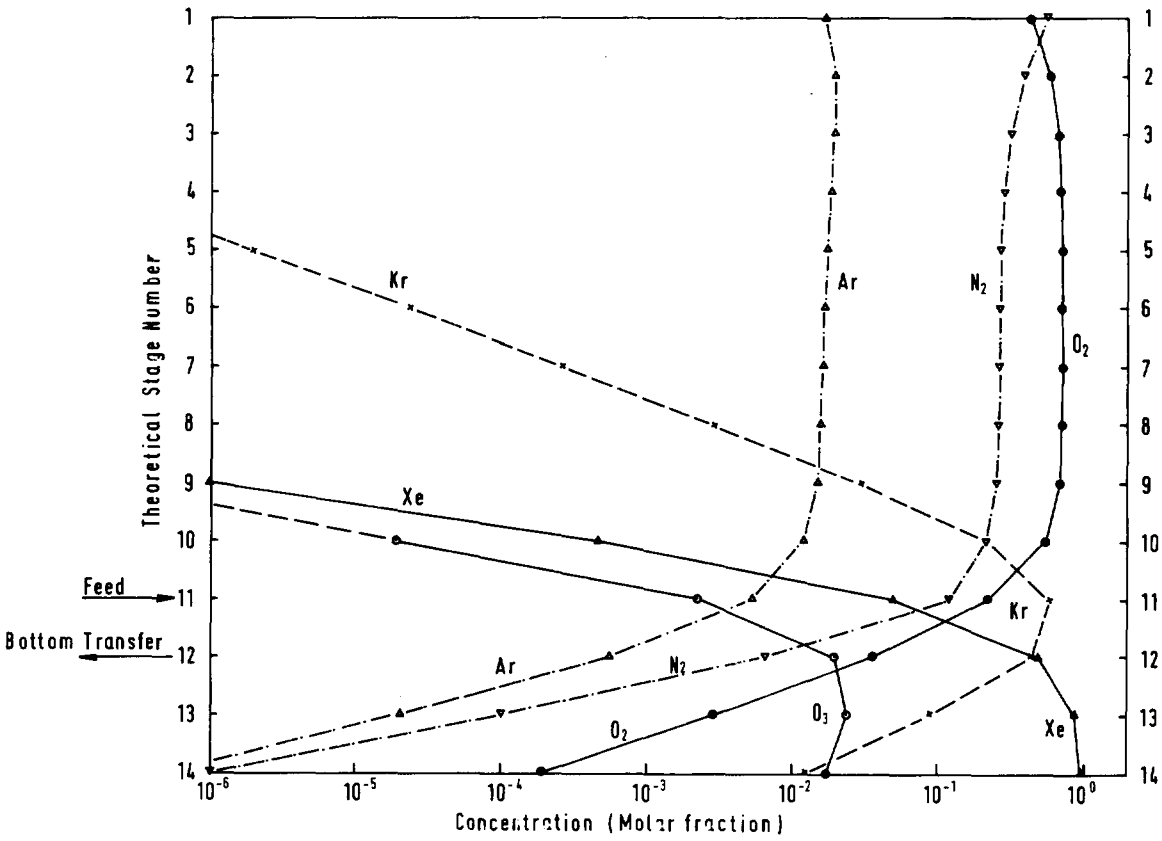

FIGURE 4
Concentration Profiles in the first KRETA Column

Table II. G-factors and Formation Rate of NO_2 in the Liquid Phase of the First Column

Theor. Stage	O_2 conc. vol.-%	G-factor	NO_2 formation mmole/h
1	43.00	1.77	$4.57 \cdot 10^{-9}$
2	58.52	1.35	$1.02 \cdot 10^{-7}$
3	66.35	1.08	$1.01 \cdot 10^{-6}$
4	69.79	0.96	$1.02 \cdot 10^{-5}$
5	71.22	0.91	$1.08 \cdot 10^{-4}$
6	71.82	0.89	$1.16 \cdot 10^{-3}$
7	72.05	0.88	$1.25 \cdot 10^{-2}$
8	71.94	0.88	0.14
9	69.74	0.96	1.55
10	53.92	1.50	18.0
11	21.66	1.71	53.2
12	3.48	0.50	11.4
13	0.28	0.13	0.57
14	0.02	0.09	0.29
			85.2

VI. Conclusions

Concerning the operability of a cryogenic system for the retention of Kr-85 with high O_2 concentrations in the process gas, the following conclusions can be drawn from these experimental results and calculations:

1. O_3 concentrations of 2-3 mole-% seem to be on the limit which can be tolerated. The explosion limit of O_3 in gaseous Kr/Xe mixtures is approximately 7% (11). It must to be kept in mind that in the second column further O_3 enrichment will take place, so that the explosion limit very likely will be exceeded. In any case it is advisable to install a catalyst for O_3 destruction in the transfer line from the first to the second column or within the column itself.

2. NO_2 formation is not a safety hazard but, because of its insolubility may present operational difficulties. Gaseous transfer of the sump product inevitably will lead to serious plugging problems during continuous operation due to excessive accumulation of crystalline nitrogen oxides in the reboiler liquid. A transfer of the reboiler liquid containing solid particles may remedy the problem. If a catalytic reduction step is included in the flow-sheet before the cryogenic section, the problem of NO_2 formation will be greatly reduced but not eliminated. Traces of O_2 passing the reduction unit will still result in the formation of some NO_2.

3. CH_4 is present in air in varying concentrations depending on the location (average content: 1 vol.-ppm). CH_4 reacts at the reduction catalyst with H_2O vapor, which is present if large amounts of O_2 are reduced, to form CO_2 and CO (12). If the catalytic reduction step is omitted and the off-gas contains large amounts of air, significant amounts of CH_4 will accumulate in the cryogenic columns during long term operation. Thus, it may be advisable to install an oxidation catalyst so that CH_4 and other hydrocarbons possibly present in trace amounts are oxidized.

4. Generally, all radiolytic reactions are decreased if the Kr-85 inventory of the columns is reduced. We are installing a new first column in KRETA whose krypton inventory will be a factor of approximately five less than the present column.

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DISCUSSION

BURCHSTED: Do you plan to make experiments relative to the changes you just mentioned?

von AMMON: We will do some experiments with the new column. As to a different flow sheet, there has been no decision made as to how long we will be able to carry on this work.

PENZHORN: I would like to point out that a catalyst is also a good ignitor of an explosive mixture. One must, therefore, be certain that the catalyst is only brought into contact with mixtures having an ozone concentration below the explosive limit.

von AMMON: This is definitely correct; one would have to be very careful in choosing the points where such catalysts are placed. The transfer line between the two columns might be one such ignition point or even the columns themselves, since there are catalysts available which are active even at cryogenic temperatures.

DEITZ: Were organic gases or vapors present in the process gas? These could form explosive compounds, e.g., ozonides, with the ozone present.

von AMMON: I am aware of that problem. When we operated the KRETA unit with ambient air as the carrier gas, we continuously measured a CH_4 content of 3ppm (by vol.) in the feed gas. This is higher than the average methane content of the atmosphere (1 ppm) and dependent on the side. Such a CH_4 content results in a high CH_4 accumulation in the first column during long term operation and would give rise to hazardous reactions in the presence of ozone, nitric oxides, and radiation. So I think it is advisable to install an oxidation catalyst prior to the cryogenic unit to get rid of any organics, including CH_4.

NOBLE GAS REMOVAL AND CONCENTRATION BY COMBINING FLUOROCARBON ABSORPTION AND ADSORPTION TECHNOLOGIES

CONSOLIDATED FUEL REPROCESSING PROGRAM

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Abstract

Since the late 1960s, the Oak Ridge Gaseous Diffusion Plant, in conjunction with the Oak Ridge National Laboratory, has developed a fluorocarbon-based selective absorption system for removal of ^{85}Kr and $^{14}CO_2$ from nuclear fuel reprocessing facilities. Process performance and reliability have been well demonstrated with over 10 years of operation using simulated reactor and reprocessing plant dissolver off-gases and three generations of pilot plant scale equipment. A major development of this work is a combination absorption and stripping column which results in a simplified process with improved reliability and lower cost. The process has shown excellent flexibility in simultaneously removing and concentrating the radioactive gases of interest, i.e., > 99% removal is easily obtainable for Kr, Xe, and CO_2 while concentration factors of three to four orders of magnitude are possible. With the incoming feed gas containing around 10 ppm Kr, the product concentration of Kr from the single column is typically in the 1 to 10% range.

Additional purification of the single-column product allows nearly pure components (> 90% Kr) to be obtained, thereby minimizing final storage or disposal requirements. Several alternatives for product purification have been investigated. In one system, 13X molecular sieve is used to first remove the process solvent vapor. Selective adsorption on 5A molecular sieves and silver mordenite is then used to separately remove the already concentrated CO_2 and Xe, respectively. At this point Kr, which was withdrawn from the column at the percent concentration level, has now been further purified by the removal of the other components and can be collected in a cold trap. This paper summarizes the performance capabilities of the single-column and discusses product purification system options, including selective desublimation, solid sorbent, and cryogenic charcoal adsorption techniques.

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*Research sponsored by the Office of Nuclear Fuel Cycle, U.S. Department of Energy, under contract No. W-7405-eng-26 with Union Carbide Corporation.

Introduction

The fluorocarbon selective absorption process has been developed at the Oak Ridge Gaseous Diffusion Plant (ORGDP) in conjunction with the Oak Ridge National Laboratory (ORNL). Recent development efforts have been predicated on a 1975 Environmental Protection Agency (EPA) ruling that accumulation of ^{85}Kr in the atmosphere from nuclear power operations could not be allowed on a long term basis. Since the necessary control technology was either available or nearly so, the EPA mandated ^{85}Kr removal by 1983. The standard, as finally adopted by the EPA, calls for approximately 87% of fission product Kr to be removed from the LWR uranium fuel cycle.[1] Primarily, this burden falls on the fuel reprocessor since as much as 99% of the Kr would normally be released during the reprocessing step. Similar restric-tions are being considered for ^{14}C.

Since its inception in 1967, the ORGDP fluorocarbon development program has been structured to demonstrate the removal of radioactive noble gases for a number of potential applications. Based initially on reactor safety issues, the fluorocarbon program was verified and proven with three generations of pilot plants. The result of this extended experimental program has been demonstrated pilot plant performance, operability, and tolerance for various feed gas impurities. In recent years, support for the program has been maintained through the Liquid Metal Fast Breeder Reactor (LMFBR) program and currently is continued in conjunction with the Consolidated Fuel Reprocessing Program (CFRP) at ORNL. As currently envisioned, the fluorocarbon process will be employed in an integrated chain of processes designed to collectively decontaminate the off-gas from a reprocessing plant. In this application, the fluorocarbon process will be responsible for the removal of $^{14}CO_2$ in addition to ^{85}Kr.

The main objective of the ORGDP fluorocarbon work is to complete all process development activities necessary to allow the design of a demonstration off-gas decontamination facility. This goal has nearly been realized through the completion of solvent chemistry studies, a reliability analysis, and near completion of the fluorocarbon process and associated peripheral equipment testing.

Much of the current activity has centered on development of the peripheral product purification equipment in order to extend the performance capability of an integrated fluorocarbon system. In the following discussion, performance tests on the fluorocarbon system and verification tests on the product purification sub-system highlight the advantages of combining these two systems to provide simultaneous decontamination and high purity Kr product from dilute radioactive off-gas streams.

Fluorocarbon Process Development

Process Basis

The basis for selective absorption is the solubility differences which exist among the various feed gas components and the particular solvent chosen for the process. The solvent selected for the baseline design is dichlorodifluoromethane, CCl_2F_2, commonly referred to as refrigerant-12 or simply R-12 This particular solvent was first suggested by Steinberg,[2] primarily because of its noble gas capacity, noble gas/bulk gas separation factors, and relatively good thermal and radiation stability, as well as overall process safety and economic considerations. R-12 is one of the major evaporative coolants used in commercial and home refrigeration units, and consequently, a substantial amount of detailed thermodynamic and physical property data are available for the process solvent.

Of course, in the absorption application the most important information needed is the vapor-liquid distribution coefficients of the various feed gas components in the solvent liquid. In conjunction with program goals, a considerable amount of equilibrium vapor-liquid data now exists for solutions of various dissolver off-gases in R-12.[2,3,4,5] A critical review discussing most of the published data has been made by Merriman.[6]

The vapor-liquid equilibrium data for various R-12 binary solutions are summarized in Figure 1.

Process Description

The fluorocarbon process is required to remove volatile radioactive contaminants from nuclear facility off-gas streams and subsequently concentrate the contaminants for long-term radioactive waste storage. Absorption, intermediate stripping, and final stripping operations are required in order to accomplish these two process objectives. A block diagram of one version of the basic process is given in Figure 2. The main separation of radioactive components from the bulk gas is effected in the absorber section. The intermediate or fractional stripper section serves first to remove the coabsorbed carrier gas from the solvent, thereby enriching the remaining dissolved gas in the more soluble components. Secondly, the intermediate stripper collects the product gases prior to removal from the column. The final stripper removes remaining dissolved gases from the process solvent; thus regenerating the solvent for recycle to the absorber. As shown in Figure 3, it is now preferred to perform all process operations in a single combination column. The original process utilized a conventional arrangement of three separate columns.[7] Each column section is filled with a high efficiency wire mesh packing for intimate gas-liquid contacting. Decontaminated off-gas flows from the top of the combination column and regenerated solvent from the bottom, while the fission product gases are collected as a side stream. Support equipment items for the basic process include a reboiler to provide necessary stripping vapor upflow, a solvent condenser, a process gas compressor, a feed gas heat exchanger, a solvent pump, a solvent cooler, storage tanks, and several refrigeration compressors.

The combination column employs an internal condensation zone and soluble gas concentration peak in the intermediate section of the column. The concentration peak is a result of the gross internal condensation of the upflowing stripping vapor from the reboiler

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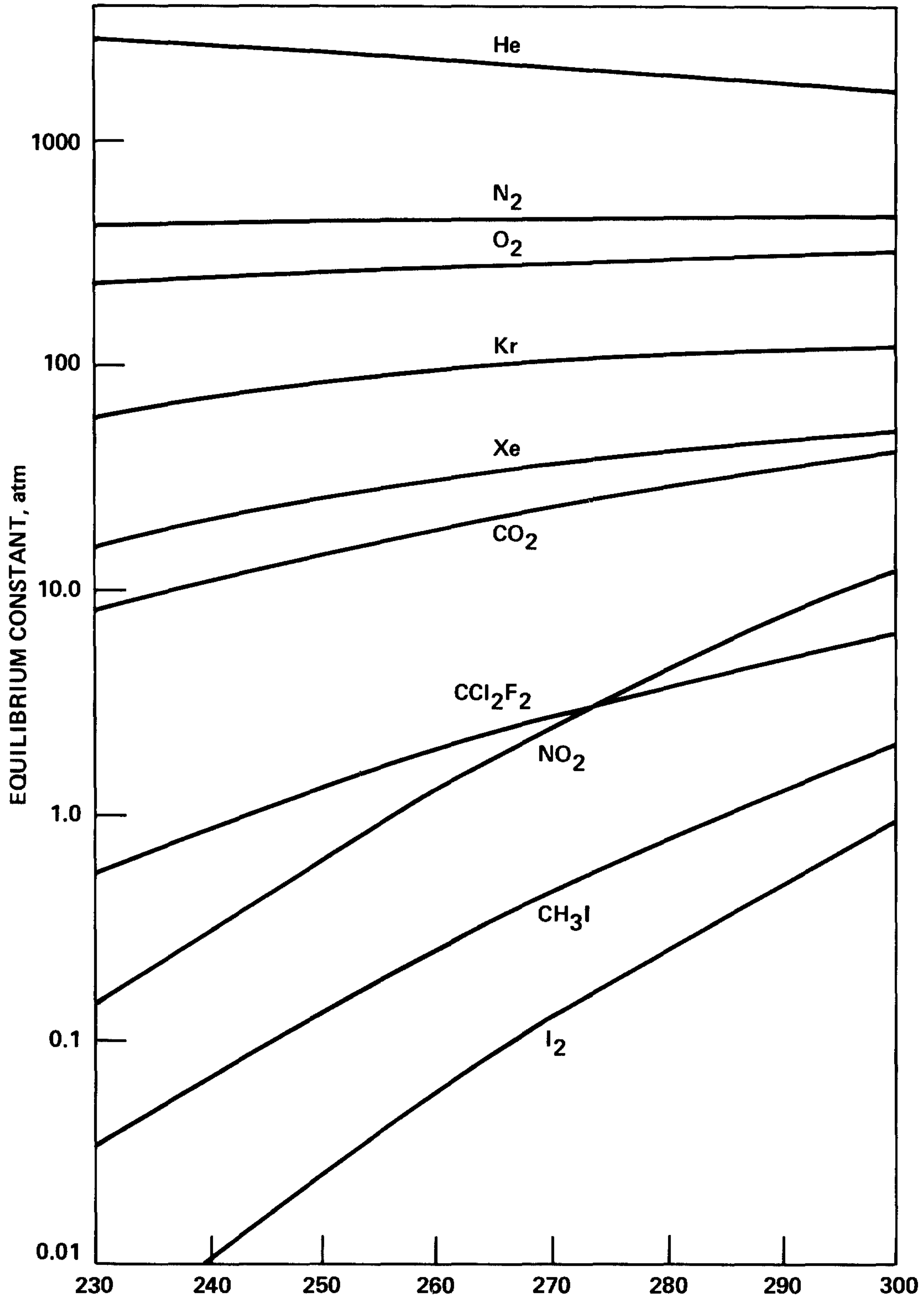

Figure 1
EQUILIBRIUM DISTRIBUTION COEFFICIENTS OF VARIOUS FEED GAS COMPONENTS IN REFRIGERANT-12 (CCl_2F_2)

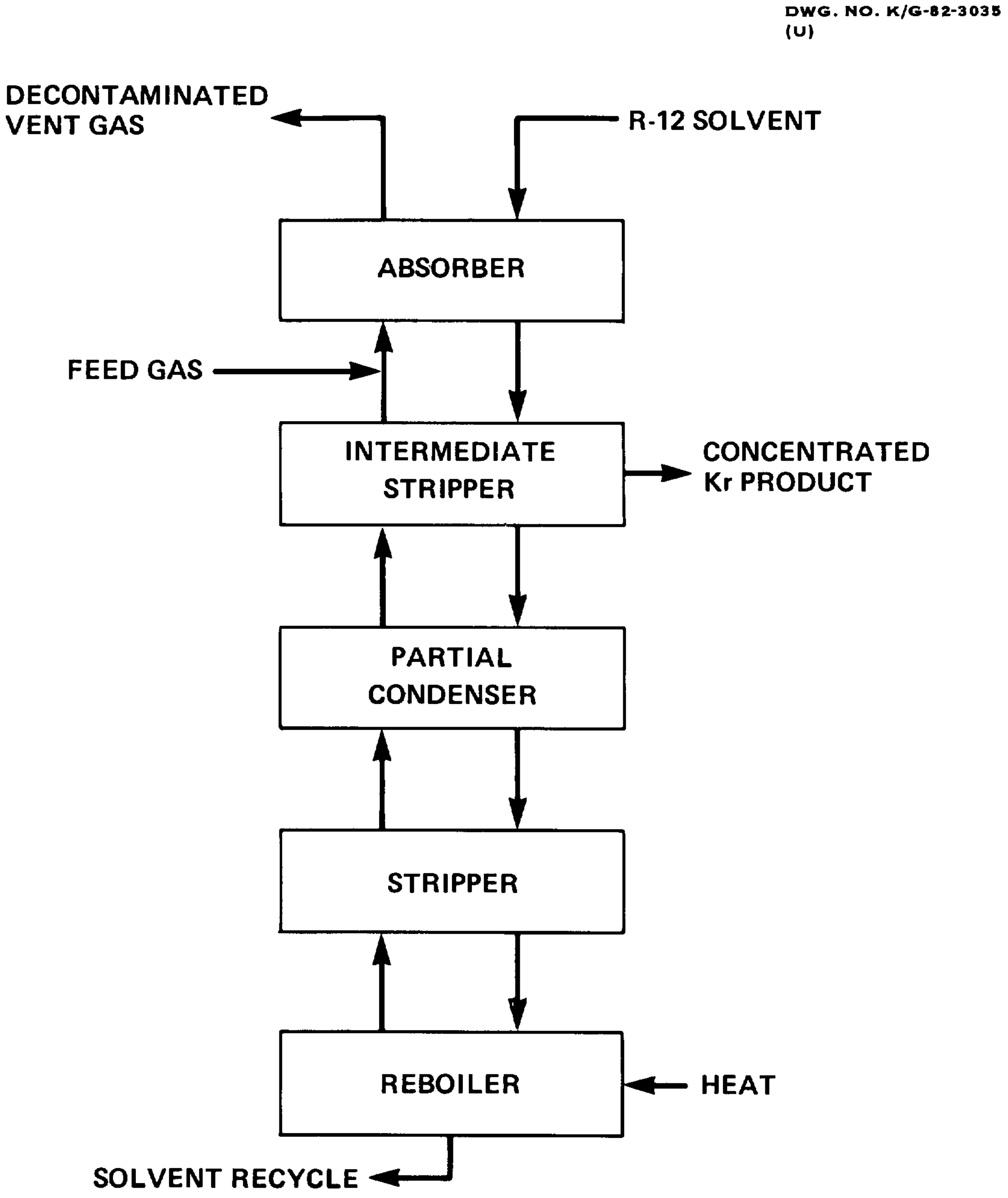

Figure 2
BLOCK DIAGRAM OF BASIC FLUOROCARBON PROCESS

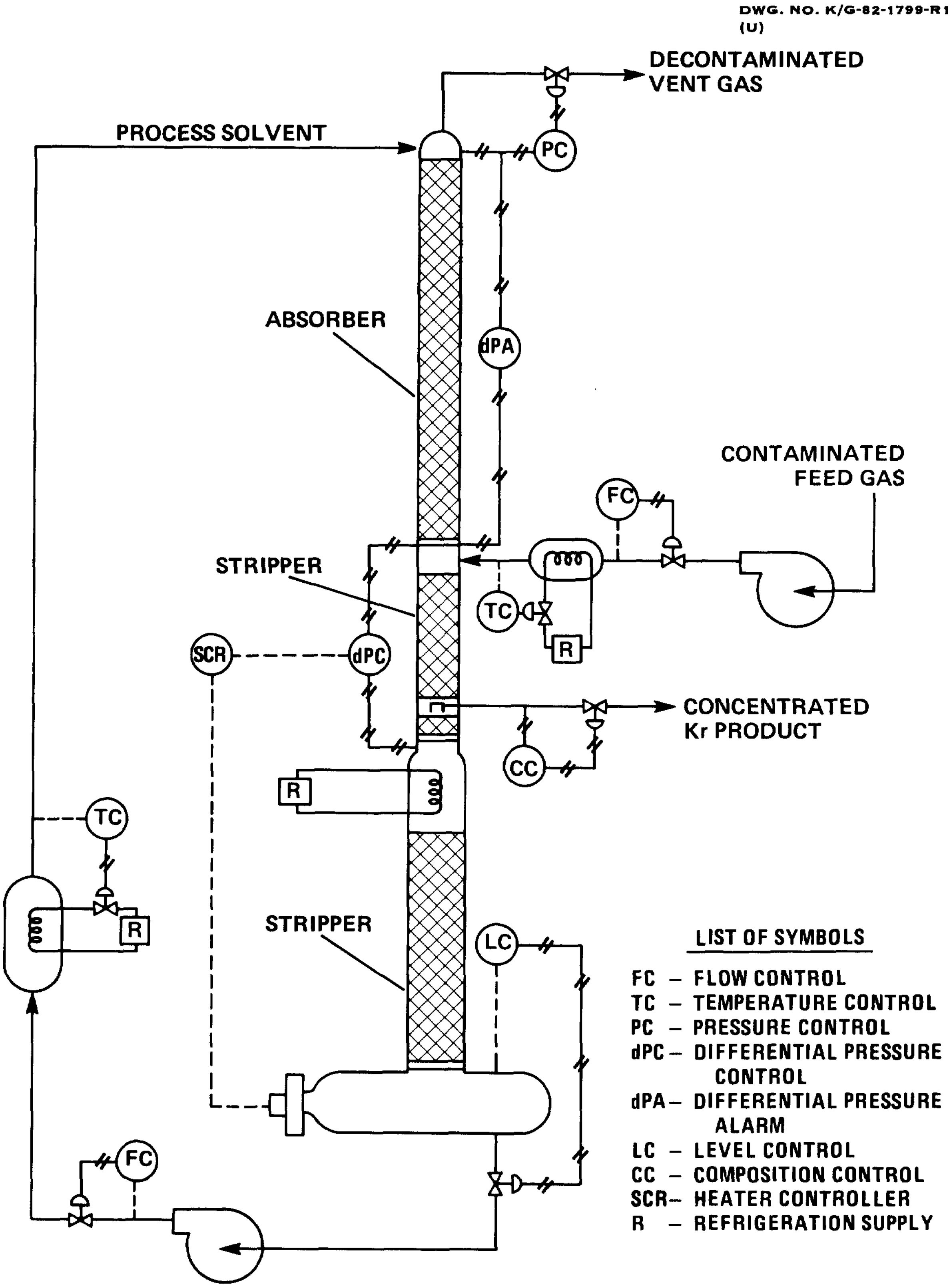

Figure 3
SCHEMATIC OF THE SIMPLIFIED SELECTIVE ABSORPTION PROCESS

as it meets the cold downflowing liquid from the absorbent section. Technical details of the combination column and design models have been described elsewhere.[8,9,10]

The combination column requires substantially less equipment and control instrumentation than the previous more conventional flow sheet utilizing three separate columns. Moreover, because of its greater simplicity, a single column offers numerous operational and economic advantages. The obvious primary advantages include simplified construction, increased reliability, easier operation, lower Kr inventory, lower costs, less hot cell space requirements, and a better demonstrated combined performance of process decontamination factor (DF) and concentration factor (CF). The less significant drawbacks include less freedom in design which requires all column operations to take place at the same pressure; thus, the solvent reboiler temperature is fixed and greater stripper vapor upflow is required. Figure 4 is a photograph of the column. The column is approximately 7.3 m tall and has a nominal flow capacity of 25 m^3/h at STP. The absorber section is 7.6 cm in diameter, while the intermediate stripper is 10.1 cm, and the final stripper is 15.2 cm.

Experimental Testing and Results

Fluorocarbon process performance and general versatility have been well demonstrated on an engineering scale with over 10 years of pilot plant operation using 3 different experimental facilities. Virtually all aspects of the process and many different process options and variations have been examined. Extended pilot plant tests have been conducted with ^{85}Kr, ^{133}Xe, and ^{131}I, with and without various feed gas impurities such as CO_2, NO_2, N_2O, NO, and H_2O. These tests show that better than 99% of the feed gas Kr can be efficiently removed from such carrier gases as air, N_2, Ar, He, and H_2.[10] Feed gas impurities have little discernible effect on either the short-term process operability or noble gas removal performance.

It is important to note that the combination column design must accommodate a high Kr DF as well as a high CF within a single column. In this regard, a great deal of experimental data has been taken with the combination column to verify control and performance. These data have confirmed much of the previous 3-column work and more importantly provide the designer with a roadmap of suitable operating conditions that will allow high DFs and CFs simultaneously with the control philosophy to maintain them.

Figure 5 depicts Kr concentration and temperature profiles in the combination column for a typical test run demonstrating high DFs and CFs simultaneously. A Kr process decontamination factor of 500 and concentration factor of nearly 10,000 were achieved with a feed gas containing 11 ppm Kr, in this case. The plot shows all concentrations normalized to the feed position which was assigned an arbitrary value of 1. Note the direct correlation of the internal condensation zone (as indicated by the temperature profile) with the krypton concentration peak location. Repeated tests have consistently shown that during normal steady-state operation this

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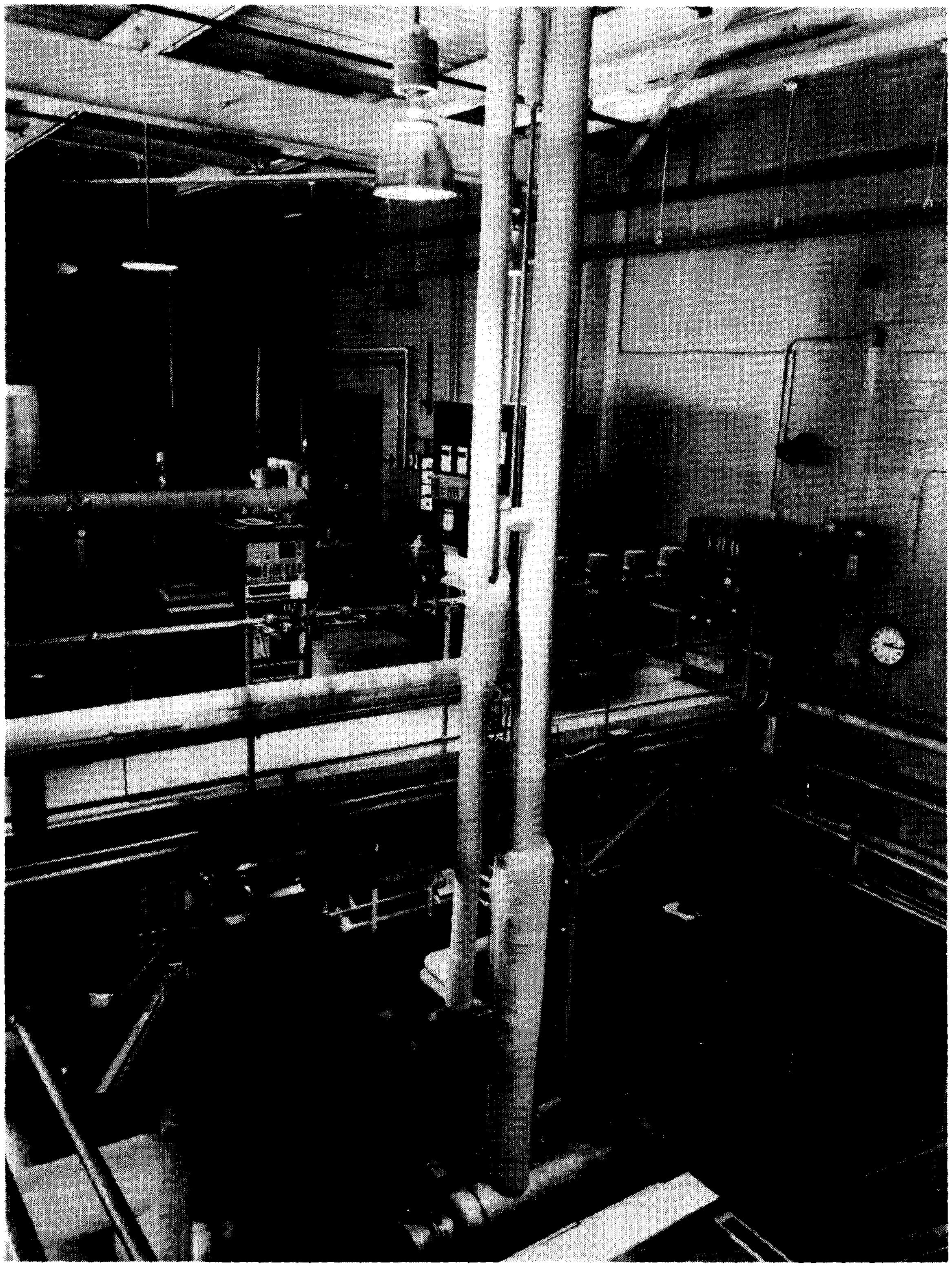

Figure 4
VIEW OF THE COMPACT COMBINATION COLUMN

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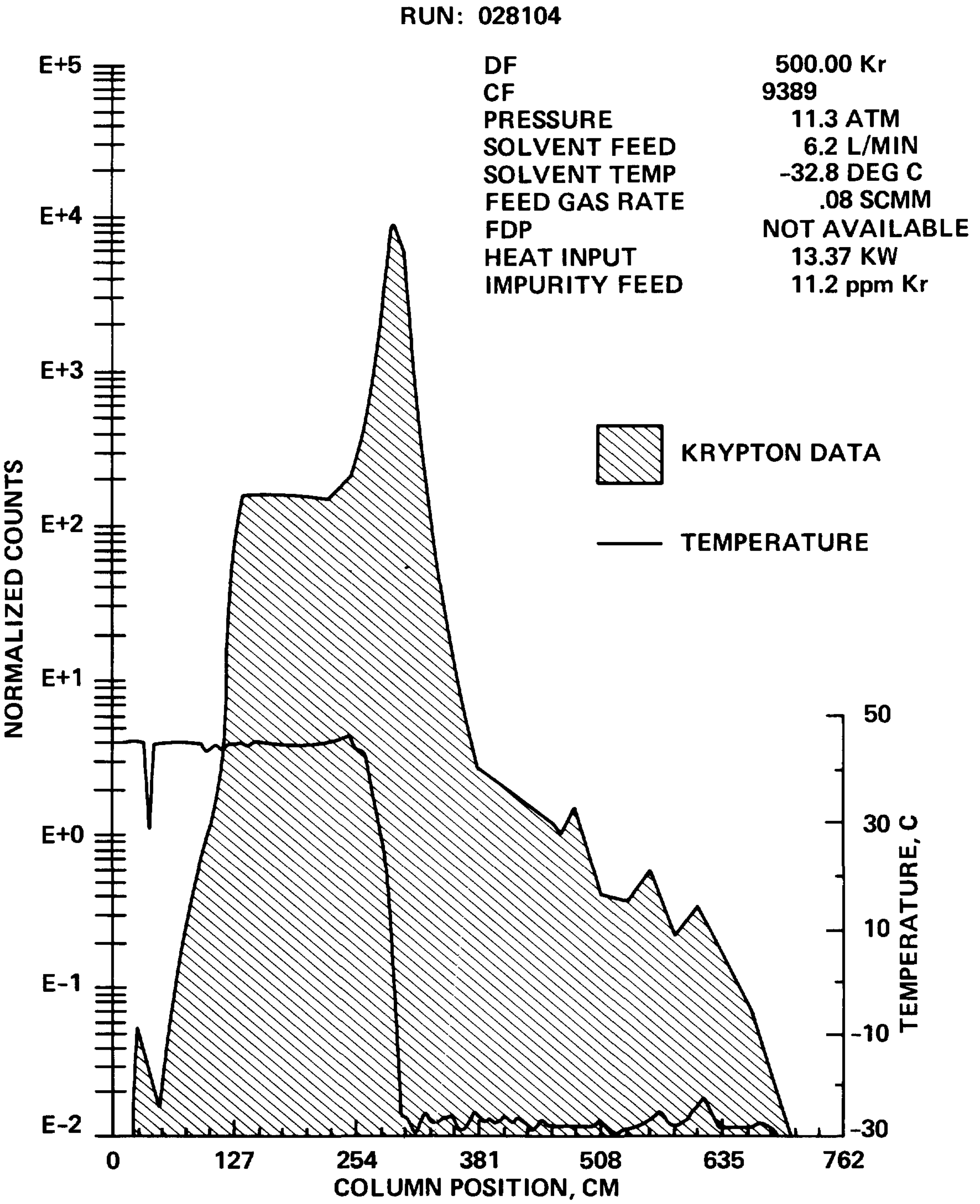

Figure 5
TYPICAL Kr CONCENTRATION PROFILE AT A LOW GAS FLOW RATE

correlation holds. External temperature monitoring can be used to locate the concentration peak. The stability of the condensation zone, and hence the krypton product withdrawal point, depends upon good column pressure and reboiler controls. Excellent column control was accomplished through the use of conventional control devices as indicated in Figure 3. Several performance related characteristics (DF versus absorption factor (kg/l), DF versus feed gas flow rate, etc.) of the combination column have been published by Eby, et al., in a recent paper presented at the Workshop on Dissolver Off-Gas in Karlsruhe, Germany, and will not be repeated here.[11] In summary, that work verified the excellent performance capability, stability, and controllability of the combination column.

Product Purification System

Basis

The capability to provide a high purity Kr product via fluorocarbon absorption alone does exist. German researchers, using fluorocarbon absorption at low temperatures (-145°C) and low pressures (1 atmosphere), have demonstrated 98.9 to 99.9% Kr purity.[12] The Xe and Kr separation, in this method, is attained with two separate columns to individually absorb, concentrate and strip the Xe and Kr, respectively. The removal of Xe and CO_2 in the first column greatly reduces the impurities present in the Kr product. Additionally, over 99.99% of the Kr was separated from the process Xe. In this particular case, one of the main intents was to produce a high purity Xe product for resale. In contrast, the approach of the Oak Ridge fluorocarbon process has primarily been to accomplish the separation of the noble gases from the bulk gas. The subsequent separation of Xe from Kr for high product purity, if desired, can then be effected externally from the fluorocarbon process.

While processing a feed gas containing 10 ppm Kr, relatively high concentrations (> 10%) of Kr have been obtained from the combination column product stream directly. However, final Kr disposal requirements may dictate further purification. Additional purification is preferred, for example, where ultimate disposal methods are expensive or would require prohibitively large storage areas. It is not clear at this point what final product purity will be required, however, because the method and form for final disposition has not yet been determined. The goal of the product purification system in the interim is to further concentrate the Kr product taken from the fluorocarbon absorption process to a level near 90%. This concentration level will satisfy any of the disposal processes currently being considered; i.e., ion implantation, zeolite encapsulation, or high pressure bottling. Once the decision is made, the product purification train will be tailored to meet the needs of the specified process. If high pressure cylinders are to be used, it might be best from a licensing aspect to keep the product Kr purity in the level of 1 to 10% to effectively limit the curies and associated heat generation per cylinder. Ion implantation methods, on the other hand, would favor the highly concentrated Kr product.

Depending on the actual operating conditions and feed gas concentrations, the product from the fluorocarbon process will typically contain 1 to 10% Kr with a balance of R-12 vapor, CO_2, Xe, N_2, O_2, and Ar (in relative order of abundance). Once the R-12 is removed, Xe and CO_2 will be the main constituents in the combination column product. Generally, the concentration ratio of Xe and CO_2 to Kr in the feed gas is maintained in the product, thus limiting the purity of the Kr obtainable from a single column fluorocarbon system alone. Xenon, if not removed from the product, increases storage volume requirements by more than a factor of 5.[13]

With these considerations in mind, considerable effort has been directed towards improving and revising the product purification system. Through the years, many different methods for separating and concentrating the fluorocarbon process product have been considered. These have included a second combination column which would fractionate the product stream, similar to the function of the second column of the Idaho cryogenic process, releasing Kr gas as an off-gas product with the more soluble components, i.e., Xe and CO_2, concentrated in a side stream product. Other options considered have included low temperature separation techniques such as cryogenic charcoal adsorption and selective desublimation (cold trapping), as well as the application of various solid sorbents for specific removal of individual components. While there is not room in this paper for a thorough review of these various techniques, a summary of their applicability to the fluorocarbon purification train is appropriate. Since the bulk of the gas separation takes place via noble gas absorption, the product from the primary separation column is reduced to less than 1% of the total feed gas flow. Studies and experience have shown that at these low flow rates, solid sorbent methods combined with simple cold trapping have a particular advantage where simplicity and cost become important and the main purpose is to prepare the Kr for storage. Subsequent sections discuss three attractive methods for additional product concentration, selective desublimation, solid sorbents, and cryogenic charcoal. Experimental results with proposed flow sheets are included.

Selective Desublimation

In the mid 1970's, studies were first initiated at Oak Ridge to evaluate methods for removing impurities from the product of the fluorocarbon process. A cold trapping scheme was investigated which subsequently identified selective desublimation (cold trapping) as a technique for purification of the fluorocarbon product.[11] This approach capitalizes on a natural phenomena considered to be one of the major problems associated with the cryogenic scrubbing process for Kr removal; namely, Xe freezeout. Desublimation utilizes the difference in the vapor pressures of the various product gases as shown in Figure 6. It should be recognized that the wider the difference in vapor pressures, the greater the potential for separation by fractional desublimation. Thus, by controlling the operating temperature, cold traps were operated to allow selective separation of the product gases.

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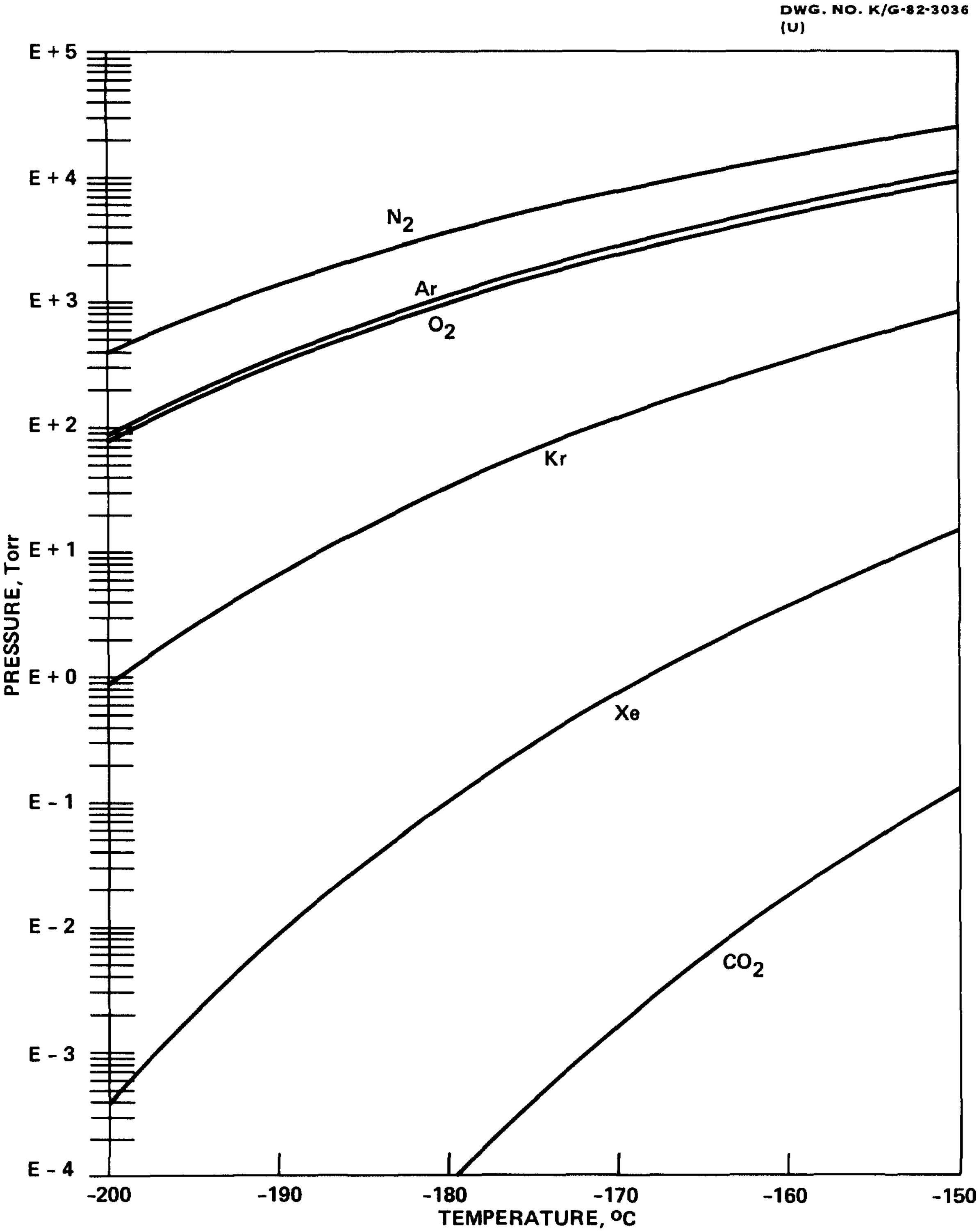

Figure 6

VAPOR PRESSURE VS. TEMPERATURE
FOR VARIOUS FLUOROCARBON PRODUCT COMPONENTS

Figure 7 is a schematic of this system. Following a 13X molecular sieve to first remove R-12 vapor, two batch operated cold traps are used to concentrate the Kr product to high purity. The first trap removes the Xe and CO_2 allowing the Kr and remaining noncondensible gases such as N_2, O_2, and Ar to pass through to a colder, second trap where the Kr is collected. Table I summarizes the theoretical removal capabilities of this system as applied to a typical product from the fluorocarbon process.

Experimental testing has verified much of this theoretical capability with tests conducted over a wide range of temperatures, pressures and several gas compositions. A complete discussion of this work will be published at a later date. For the purposes of this paper only a brief summary will be given. First, operating the cold trap at -165°C for CO_2 removal did show excellent removal and concentration of the CO_2 from the Kr stream. Similarly, other tests at colder Kr trapping temperatures allowed Kr removal with concentrations >88% Kr. In addition, one important capability of this system is the fact that no mechanical pumping is used or needed. The combination column operating pressure is easily sufficient to promote flow throughout the product purification system. Also, in the product cold traps, sublimation of the collected product provides sufficient pressure for cryogenic pumping to storage cylinders without mechanical compression. Pressures consistently > 200 psig have been obtained after warmup of collected product. In addition to providing pumping pressure, the warmup procedure can be used to further separate desublimed product gases. Kr contamination in the Xe and CO_2 solid due to entrainment can be minimized by this procedure. Figure 8 shows a controlled sublimation from a trap containing N_2, Xe, Kr, and O_2. In this case, bulk Kr and Xe separation was achieved in a single cold trap. As the trap was allowed to warm up the bulk of the more volatile Kr was selectively sublimed prior to sublimation of Xe. Thus, if Kr contamination should occur in the Xe and CO_2 trap, this method could be used to keep the less volatile product at a higher purity.

When the Kr inlet concentration is high (> 15%), a problem with this system might be encountered as some Kr may desublime along with the CO_2 and Xe. Cryogenic temperatures with either frequent cycling or a relatively large trap volumes are necessary for CO_2 and Xe removal since they constitute the bulk of the product gases from the fluorocarbon product. For these reasons, solid sorbents were considered as an alternate product purification route to allow simplification of the control concerns and possibly lower operating costs. In this case, a Kr cold trap is still preferred for final Kr-N_2 separation.

Solid Sorbent Studies

In 1976, trapping studies were initiated to evaluate solid adsorbents for removing R-12 vapor from the Kr product. Experiments proved the 13X molecular sieves to be an excellent trapping material for the process solvent. Summarizing this work, the trap effluent from the 13X bed typically contained less than 1 ppm R-12 with bed loadings as high as 30 weight percent R-12 over a wide range of R-12 feed compositions and flow rates.10

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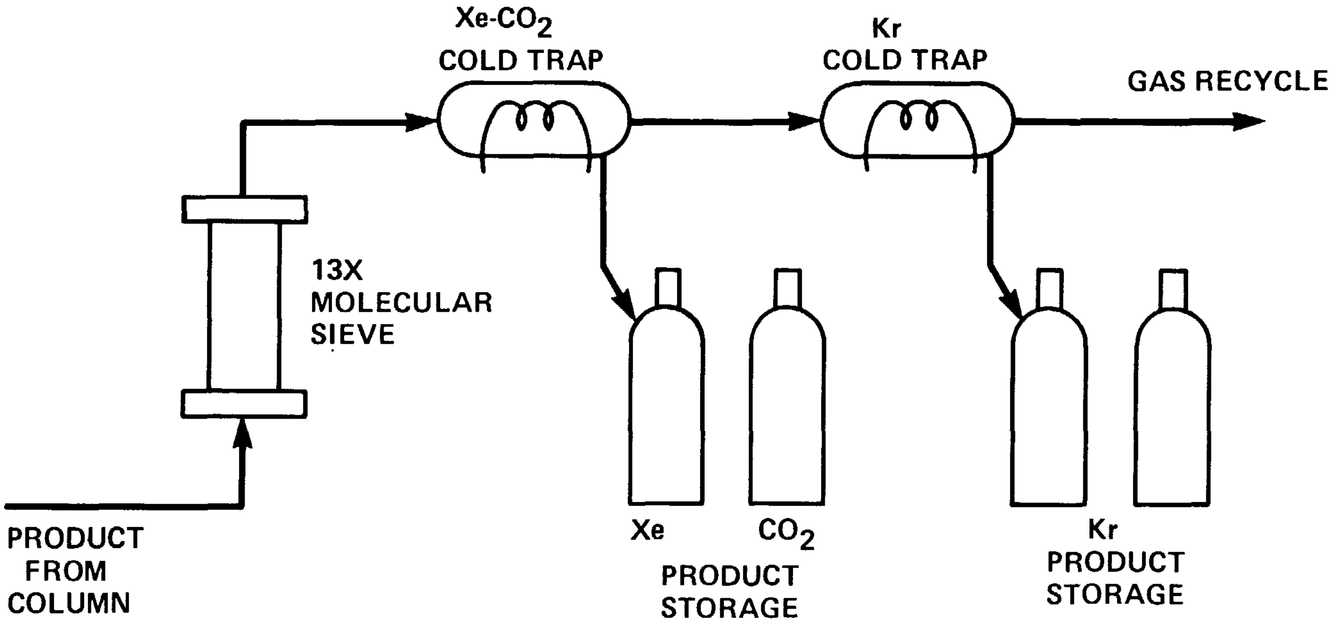

Figure 7

PRODUCT PURIFICATION SCHEMATIC UTILIZING TWO COLD TRAPS

Table I

THEORETICAL REMOVAL CAPABILITIES FOR THE SELECTIVE SUBLIMATION SYSTEM*

	Trap I			Trap II		
Temperature	117K			80 K		
Pressure	1280 Torr			860 Torr		
Component	Effluent Concentration %	% Removal	Product Concentration %	Effluent Concentration %	% Removal	Product Concentration %
CO_2	28 ppm	~ 10	85.75%	0.88 ppb	~ 100	.015
Xe	0.48	99.7	14.25%	4.5 ppm	99.93	2.14
Kr	22.1	0	0	.4601	98.38	97.84
O_2	15.5	0	0	19.9	0	0
Ar	1.1	0	0	1.4	0	0
N_2	60.8	0	0	78.2	0	0

*Based on a typical product from the fluorocarbon system of 78% CO_2, 13% Xe, 2% Kr, 5.5% N_2, 1.4% O_2 and 0.1% Ar.

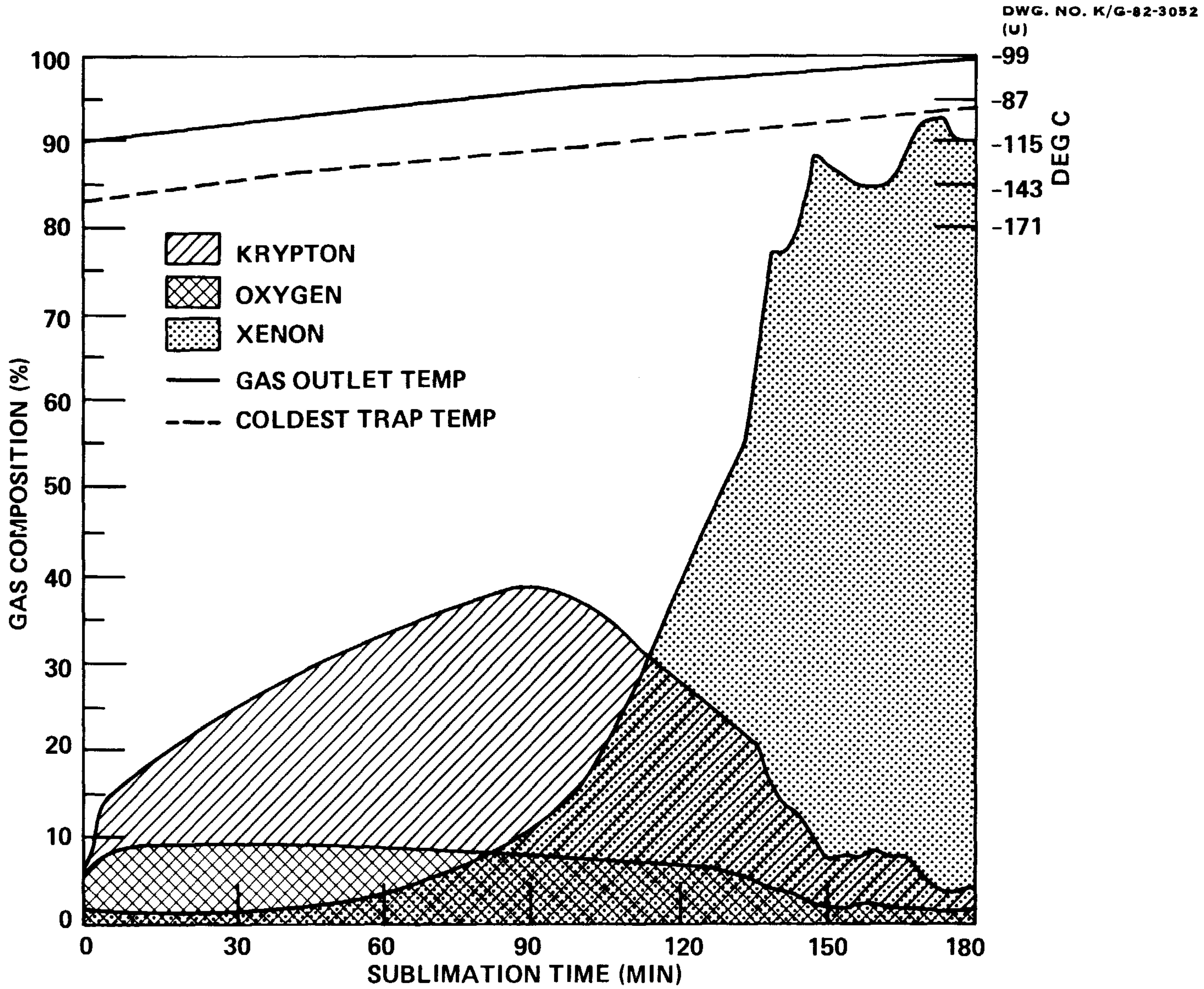

Figure 8

CONTROLLED SUBLIMATION OF Kr and Xe

In the same time frame, Forsberg was studying separation of Kr from CO_2 and O_2 using a 5A molecular sieve.[15] His tests were conducted with 1% mixtures of Kr in gas streams containing 90+ % CO_2 and a few percent O_2 with the sieve bed temperature maintained at 0°C. He found the 5Å molecular sieve to be quite capable of selectively removing CO_2 from Kr while partially separating the O_2 from Kr. The maximum concentration of Kr obtained in these tests was in the range of 50 to 60% with CO_2 loadings averaging 95 standard cm^3/(gram of sieve). The CO_2 loading corresponds to 18.7% of the bed weight. Since the typical product from the fluorocarbon system contains CO_2 as a bulk gas with a few percent Kr, one would anticipate, based on the Forsberg data, that separation of Kr from CO_2 could be similarly accomplished in the fluorocarbon product purification environment. Certainly the potential of this method applied to the product purification system is high. Since the sieve trap operates at temperatures around 0°C, the big problem and cost of thermal cycling cryogenic cold traps for CO_2 removal is replaced by a much less energy intensive regeneration cycle. Furthermore, ORGDP tests have indicated that the effluent from 5A molecular sieve traps prior to breakthrough will contain only a few ppm CO_2. This is approximately an order of magnitude better than the capability of the CO_2 cold trapping method.

Recently, the ORGDP experimental program was expanded to include testing of silver zeolite for Xe removal as well as 13X and 5A molecular sieves for R-12 and CO_2, respectively. The use of a silver-exchanged synthetic mordenite zeolite (AgZ) is recommended by Pence and Kirstein for removal of Xe from streams containing Kr.[16] They estimate that separation of Kr from the Xe should provide a DF on the order of 10^2 to 10^3 in an AgZ bed operated at 15°C.

A schematic of the proposed product purification system based on molecular sieve technology is shown in Figure 9. In verification tests of this system, analyses showed R-12, CO_2, and Xe removals from the product were greater than 90% when their respective sorbents of 13X, 5A, and silver zeolite were used. Furthermore, loadings on the beds averaged 13.7% for R-12 on 13X, 17% for CO_2 on 5A, and 8.8% for Xe on silver zeolite. While certainly not conducted under optimum conditions, these tests did verify previous work which identified separational capabilities of the various adsorbents and provided the feasibility for Kr purification to any level desirable for the fluorocarbon process. Studies are being performed to optimize on the basis of performance, cost, and required control standards.

Cryogenic Charcoal

Certainly the most proven of all Kr purification methods is cryogenic charcoal adsorption which is capable of providing research grade purity Kr. This method has been used in the Isotope Sales Department at ORNL for more than 20 years to purify Kr. A flow sheet of this system is shown in Figure 10.

In the ORNL cyrogenic charcoal system, a carbon reactor operating at 800°C is used to decompose nitrogen oxides, but only if the concentration in the feed is greater than 5%. The feed is then

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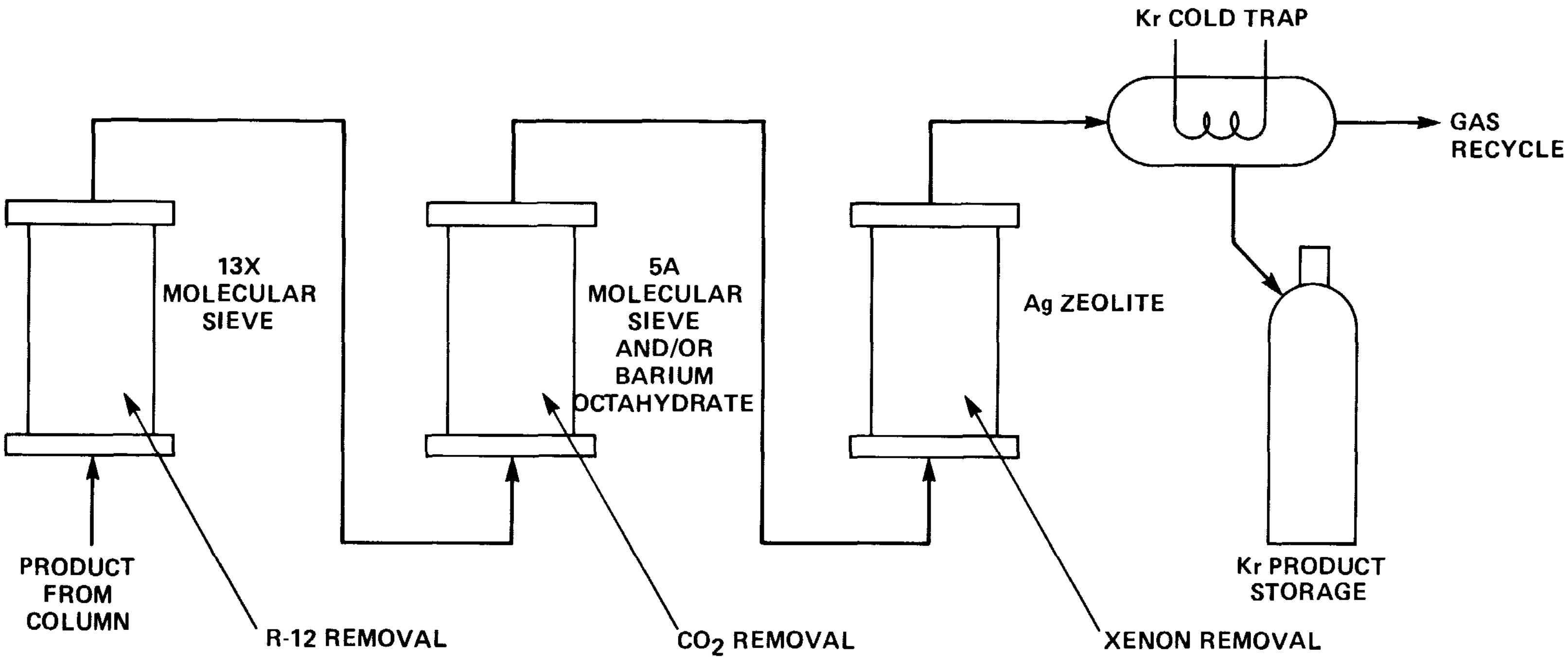

Figure 9
SCHEMATIC OF PRODUCT PURIFICATION SYSTEM

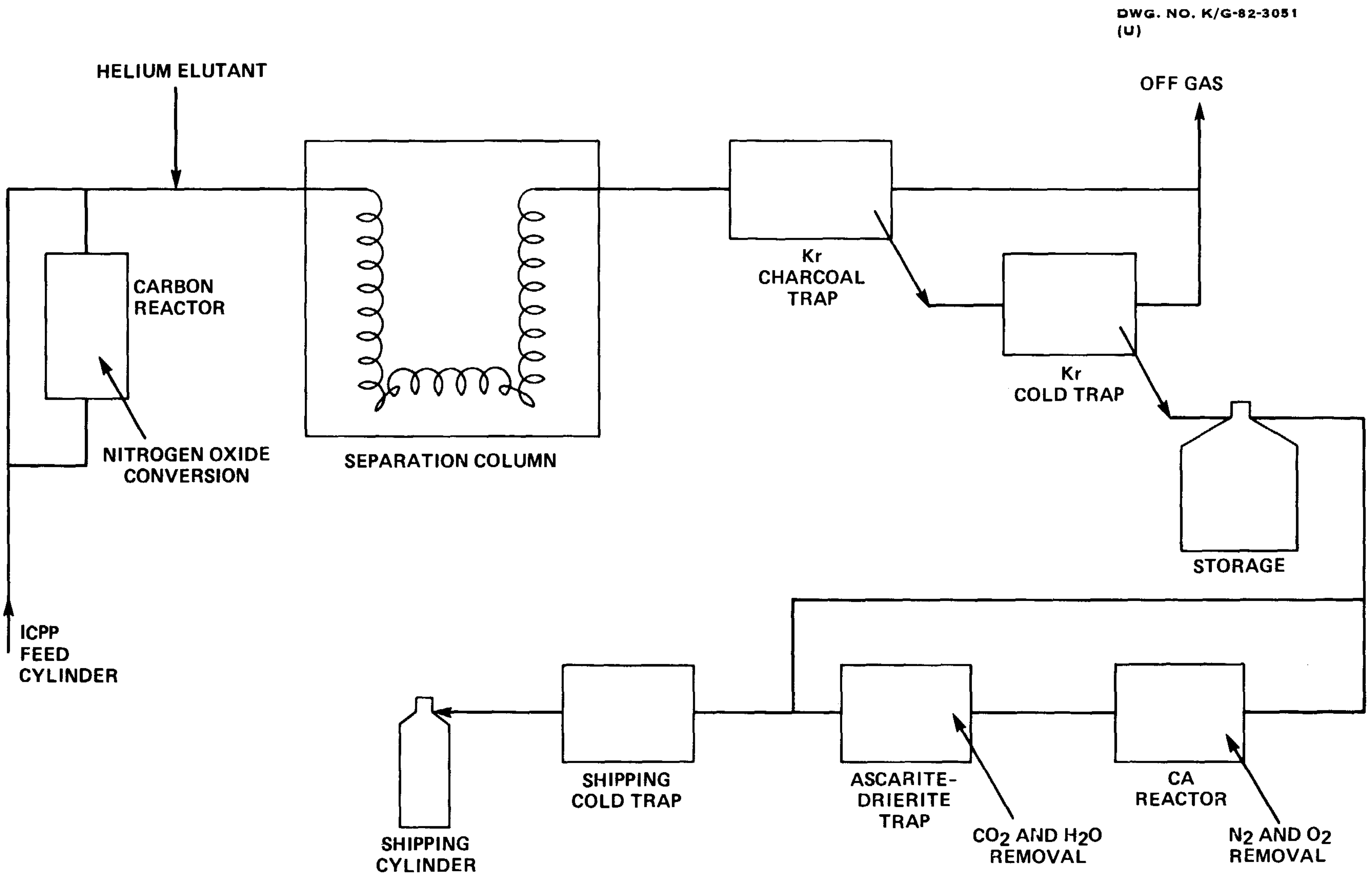

Figure 10

SCHEMATIC OF CRYOGENIC CHARCOAL KRYPTON PURIFICATION SYSTEM passed to the separation column which consists of a helically wound tube filled with activated charcoal and cooled by liquid N_2 to -80°C. The feed gas adsorbs on the charcoal and distributes the various components along the column according to the molecular weight. The lighter components (N_2, O_2) penetrate to the end of column with Kr being adsorbed in the center and Xe at the beginning. Adsorption on the column is continued until a predetermined concentration of Kr has been loaded. Once the feed flow is shut off, a helium purge is started and the column is allowed to warm up. The helium removes the various components as they desorb. When Kr breakthrough is detected, the off-gas flow is diverted to a carbon trap which is cooled to -195°C. This trap separates the krypton from the helium elutant. A transfer by heating and freeze-out in a cold trap allows further purification of the Kr. After noncondensibles have been pumped from the trap, the Kr is evaporated into a storage tank. At this point, if analysis shows less than 98% Kr, further purification can be made if desired. A hot calcium reactor operating at 750°C can be used to remove O_2 and N_2. Similarly, an unheated ascarite-drierite trap is used to remove any residual CO_2 and H_2O.

In reviewing the cryogenic charcoal system, several important characteristics become evident. First, while a batch system, the capacity of cryogenic charcoal adsorption is quite high. In addition, the existence of approved handling, transport, and operational procedures at the ORNL facility, considering the base of experience, provides great incentive towards further application of this system. Moreover, successful operation has fully demonstrated and proven the technique; including, the use of cryogenic pumping for the safe transfer and pressurization of the radioactive product. Cryogenic pumping applies the vapor pressure of cold trapped materials which, when warmed, vaporize to provide sufficient pressure for transfer and storage.

It should not be forgotten that the main purpose of the ORNL facility has been to sell ^{85}Kr. Indeed, the marketing of ^{85}Kr may very well provide an economically sound alternative to permanent storage and is discussed here since it may impact ^{85}Kr recovery methods. Currently, ^{85}Kr is used in many applications from leak testing in the semiconductor industry to its use in thickness gauges for manufacturing operations. Industrial use of ^{85}Kr continues to increase but is restricted due to the very low current supply and resulting high price. In a scenario with large scale reprocessing facilities and subsequent recovery operations, ^{85}Kr could potentially become very plentiful resulting in a seemingly inexhaustible supply. Marketing of ^{85}Kr could become very competitive since the saved cost of permanent disposal methods would be added to the revenues from Kr sales. Furthermore, the low price could attract many new users. Several of these, i.e., light sources and heat source applications, require large amounts of ^{85}Kr. Some applications may also require enrichment of the ^{85}Kr isotope; thereby acquiring the ultimate in low pressure concentration. ORNL has also provided enrichment services for many years using the thermal diffusion separation method. Krypton mixtures containing 5% ^{85}Kr can be enriched to 40% ^{85}Kr in the Oak Ridge equipment. This further volume reduction might be beneficial.

Conclusions

In general, the performance data of the combination column, in conjunction with previous 3-column testing, provides more than sufficient information to design an effective, efficient, safe, and reliable Kr removal system. No further process development work needs to be done.

With regard to the product purification studies, the feasibility of several methods to separate major components from the fluorocarbon product stream has been demonstrated. Verification tests at ORGDP and preliminary work done by others have shown that 13X and 5A sieves can be used effectively to separate R-12 and CO_2, respectively. In addition, should Xe removal be required for Kr product concentration, several methods have been tested and have demonstrated operational feasibility. Tests are currently being conducted to optimize the final purification steps.

In summary, by combining fluorocarbon absorption with selective desublimation and solid adsorption, the technology exists to provide efficient removal and concentration of Kr, Xe, and CO_2 from radioactive off-gas streams which will meet and/or exceed current proposed standards and requirements. It should be noted, however, that most of the development work has been performed without the benefit of a "real" reprocessing plant feed. Legitimate concerns have been expressed about the process effects of plant levels of radioactivity, process behavior of minor chemical plant impurities, and their various pertinent interactions, and overall reliability and controllability of an integrated off-gas system. Our current efforts are being directed toward the conceptual planning of an integrated hot off-gas facility which would offer a timely opportunity for overall process demonstration.

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DISCUSSION

MONSON: How guickly can you start up the system and what is its application to reactor emergency confinement?

LITTLE: Start up of the single column fluorocarbon system is very rapid, typically less than two hours from dead start to near equilibrium of all systems (including refrigeration systems). Feed gas decontamination can begin after approximately 30 min. with improving performance as equilibrium is reached. Fluorocarbon absorption is, indeed, ideally suited to emergency reactor situations since impurity tolerance and removal capabilities for iodine, NO_x, and Xenon, as well as Kr, make the system extremely versatile in the sort term. Shortly after the incident at TMI, a proposal was submitted to DOE for this specific application.

HUTTER: If higher Kr concentrations than 90% are required, what are the additional cleaning steps, and what Kr concentration do you expect will be necessary for commercial use?

LITTLE: It is our belief that Kr purity in the 90 to 95% range would be acceptable to commercial users, and that with optimization, this could easily be obtained with solid sorbent purification equipment. As has been demonstrated at ORNL, cryogenic charcoal is used to produce greater than 98% Kr product and if this level is required, this system might be considered for final purification.

PENZHORN: I understand that some ozone can build up during fluorocarbon absorption. We looked into the explosion limit of ozone in R-12 and found it to be approximately 20 mol % O_3 in CCl_2F_2. It is, therefore, much higher than that in oxygen (about 11 mol %) and in noble gases (about 7-8 mol %). Furthermore, the pressure ratio (maximum pressure over initial O_3 pressure) is much lower than that when O_2 or Kr are used as diluents. We, therefore, feel that the O_3 1R-12 system is comparatively safe.

LITTLE: Your comment underlines the inherent safety of the fluorocarbon system as it concerns the ozone hazard. Thank you.

BURCHSTED: It is worth noting that we have a fluorocarbon that is used as a fire protection agent which is snubbing explosions in the 20% range.

RINGEL: Could you give a number for the typical krypton hold-up in the whole process at steady state conditions? When Xe and CO_2 are frozen out, what is the Kr contamination in the Xe and CO_2 ice?

LITTLE: The typical holdup, or inventory, of Kr in the fluorocarbon system is approximately equivalent to the amount of Kr contained in four hours of feed gas. Although not measured in our system, some small amount of Kr is definitely adsorbed in the Xe-CO_2 solids. This is one of the reasons we began investigating solid sorbents for final product purification. It illustrates one of the advantages of solid sorbents over cold trapping methods for separation.

BURCHSTED: Do you propose to store the xenon in krypton as gases in gas bottles?

LITTLE: The small effort that we have been working on in Oak Ridge really does not address the disposal mechanism. At this time, gas bottling is used just because it is the simplest. That does not solve the big problem.

HAAG: Would you give us an idea of the size of a combination column for the treatment of 500 ft^3/min of off-gas?

LITTLE: Scaleup studies of the fluorocarbon system have been experimentally investigated. Direct scaleup of the system requires only an increase in the column cross sectional area proportional to the square root of the flow rate increase. The diameter of the column absorption section corresponding to 500 CFM would be about 17 in. (44cm.)

FAILURES IN AIR-CLEANING, AIR-MONITORING, AND VENTILATION SYSTEMS IN COMMERCIAL NUCLEAR POWER PLANTS (JANUARY 1, 1978 THROUGH DECEMBER 31, 1981)

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Abstract

An analysis of Licensee Event Reports submitted by commercial nuclear power plant operators during the four year period, 1978 through 1981, showed that from 11% to 17% of those reported by PWR installations and from 20% to 29% of those reported by BWR installations, pertained to air treatment systems. The majority of these pertained to problems in air monitors. Problems with gaseous and particulate radiation monitors accounted for 68% of the air monitoring events in PWR installations and for 41% of those in BWR installations. Failures in the sampling portion of the air monitors accounted for 31% of the LERs in this category for PWR installations and 29% for BWR installations. Thirty four percent of the air monitoring failures in BWR installations were in hydrogen and oxygen monitors. Although information needed to prevent and/or correct these problems is available, it is not being effectively utilized. This is well illustrated by the major role that human errors continued to play in these failures. Although this is due to a number of factors, a primary reason is a shortage of personnel who are knowledgeable about HVAC systems, in general, and about nuclear air cleaning technology, in particular. To correct this situation, the authors recommend an increase in the training of both nuclear power plant personnel and members of the NRC staff in these subject areas.

I. Introduction

In a nuclear power plant, there is a variety of systems that provide a safe environment to personnel and equipment during normal operations. These include heating, ventilating, and air conditioning systems that service the control room, the spent fuel pool area, the auxiliary and radwaste area, and the turbine area. There are also specially engineered air-cleaning, air-monitoring and ventilation systems that are needed to assure safe shutdown of a plant, or that service equipment required following an accident. Finally, there are related systems that monitor the temperature, pressure, and concentrations of particulates and gases (both stable and radioactive) in air handling systems and the spaces they serve. In addition, there are systems that provide protection against fires within various plant spaces. There are also monitoring devices that assure the proper operation of important post-accident air cleaning and pressure reduction systems, such as the suppression pool space in a BWR installation. The purposes of this study were to review Licensee Event Reports (LERs) pertaining to failures in these types of systems over the four year period from January 1, 1978, through

December 31, 1981, to interpret these data in terms of the lessons to be learned, and to recommend steps for minimizing the occurrence of similar events in the future. This report extends and updates a previous study(1) covering the period from January 1, 1975, through June 30, 1978.

Serving as sources of information for this study were the individual LERs as issued by utility plant operators, the monthly summaries of such data prepared by the Nuclear Regulatory Commission (NRC)(2) and the annual summaries published by the Nuclear Safety Information Center at the Oak Ridge National Laboratory.(3-8) Also serving as valuable data sources were the "Information Notices" of the Office of Inspection and Enforcement, the bimonthly "Power Reactor Events"(9) and the quarterly "Reports to Congress on Abnormal Occurrences,"(10) issued by the NRC. During the time period covered, approximately 14,100 LERs were submitted, of which over 2400 (17%) pertained to failures in air-cleaning, air-monitoring and ventilation systems.

The average annual number of LERs from all causes reported for each nuclear power plant during the 4 year period covered ranged from 47 to 57 for boiling-water reactor (BWR) installations and from 47 to 52 for pressurized-water reactor (PWR) installations (Table 1). This closely parallels data reported in our earlier study.(1) In terms of the percentage of the events that pertained to failures in air treatment systems, however, the number have shown a definite increase in recent years. For example, 20% of the LERs reported for BWR installations in 1978 pertained to failures in air treatment systems; by 1981 this had increased to 33%. Similarly, the percentage of LERs pertaining to air treatment systems for PWR installations was 11% for 1978; by 1981 this had increased to 17%.

As an approach to the analysis and interpretation of these data, discussion is first presented on failures that are specific to BWR installations. This is followed by a similar discussion of events specific to PWR installations. Finally, items common to both types of plants are reviewed.

II. Specific Failures in BWR Installations

Details of LERs pertaining to air-monitoring, air-cleaning and ventilation units within specific systems for BWR nuclear power plants are summarized in Table 2. As reported in our previous paper,(1) a large percentage of these events continue to be associated with the equipment designed to sample and monitor the performance of ventilating and air-cleaning systems, rather than in the systems themselves. In fact, an analysis of the data shows that, for BWRs, this percentage has increased from an average of about 48% for the previously reported 3-1/2 year period to almost 61% for the 4 year period covered here. Further analyses of these data (Table 3) show that about 29% of the failures in the monitoring equipment occurred as a result of deficiencies in the air-sampling portion of the system. This represents a reduction from the value

(41%) reported in the previous study.(1) Although this decrease may be indicative of corrective actions that have been taken relative to this aspect of the problem, it could also be due, in some degree, to changes in the manner in which the data are reported and tabulated. The basic reason or reasons for the change are not known.

Other changes noted in the data in Table 2, as contrasted to observations during the previous study, include the marked increase in airborne releases from Coolant Purification Systems, and in failures of blowers, isolation valves and dampers in s econdary containment and in atmospheric monitoring systems in the turbine building. Continuing at a high rate were failures in atmospheric sampling and monitoring systems in secondary containment and in off-gas systems.

Failures Associated With Primary Containment

For BWR installations, there was a relatively large number of failures related to diluting, inerting and ventilation systems associated with primary containment, as well as in jet systems important to proper operation of the torus. Data show that, for the four year period covered by the study, there were 101 LERs related to deficiencies in the nitrogen purge or ventilating system (Table 2). Primary among the events in this category were problems with the containment atmospheric dilution (CAD) tank, leakage in the purge inlet valves and torus purge outlet valves, and problems with containment ventilation supply isolation valves. The most frequent problem with the CAD tank was insufficient nitrogen in storage due to evaporation and/or leaks, failures in the pressure control valve, faulty level monitors, or personnel errors in failing to replace nitrogen that had been used. The more common sources of problems with the purge valves were deformed or improperly adjusted stem seals, depressurization of inflatable disc seals, deterioration of the disc to seat mating surfaces, and dirt on the limit switch. Failures in the containment supply isolation valves included inoperability of a transistor in the power supply to the containment vacuum relief control system which would have prevented closure of the isolation valves, closure times that were in excess of the allowable limits due, for example, to excessive wear in the valve's air operating piston, instances in which supporting brackets for the valve operator were found not to meet seismic requirements, and personnel errors in which valves were left more fully open than allowable during power operations.

Data also show that there was a total of 72 failures of vacuum breakers between the torus and drywell and between the suppression chamber and the reactor building. There was also a total of 41 malfunctions of the water level indicators within the torus (Table 2). Because of the anticipated air cleaning contributions of the torus or suppression chamber following a loss of coolant accident, these events were considered to be important in terms of the study being reported here.

Causes of the failures of vacuum breakers included inoperability of the valve due to the pneumatic cylinder piston sticking in misposition, failure of the solenoid valve that controls the air supply to the vacuum breaker, defects in the differential pressure reset switch, and improper calibration of the differential pressure switch. One event was due to plant personnel covering the suppression chamber vacuum breaker inlet pipe with a plastic bag, during a leakage test, and neglecting to remove it after the test was completed.

A review of reports on torus water level indicator malfunctions revealed a range of causes. Several involved changes in the differential pressure between the torus and the drywell, including malfunctions of the vacuum breakers. In one case, the process of inerting the containment led to a positive differential pressure which caused a reduction in the water level indication. In another case, plant personnel opened the vacuum breakers during an operations surveillance test. This reduced the dry well to torus differential pressure and allowed the vent pipe downcomers to fill with water. This, in turn, resulted in an indicated lowering of the torus water level beyond the limits allowed on the Technical Specifications.

Other failures of torus water level indicators were due to stuck float chambers, dirty electrical connections, and draining of the reference leg of the transmitter. One event was reported in which poor ventilation in the recorder cabinet resulted in excessive temperatures which, in turn, caused the power supply output to fluctuate. Personnel errors also contributed to water level indicator malfunctions. These included an event in which personnel failed to properly backfill the torus water level instrument sensing lines after outage modifications; a second event involved the inadvertent disconnecting of the input signal cale to the recorder terminal.

Failures in Containment Spray Systems

Records for the four years covered by this study showed a total of 36 events involving failures of Containment Spray Systems (CSS) in BWR installations (Table 2). In several instances, the CSS drywell pressure switches were found to trip at values greater than those specified. This was attributed to instrument set point drift. In a related event, it was found that eight drywell pressure switches were inadvertently isolated due to closure of the instrument panel valves. Such closure isolated the safety-related instruments that were designed to automatically actuate reactor protection, the main control room environmental control system, emergency core cooling, and primary and secondary containment isolation systems if a Loss-Of-Coolant Accident (LOCA) had occurred. With the loss of high drywell pressure instrumentation, automatic initiation of the depressurization system, which functions during a small break LOCA, would not have occurred and a scram signal would not have been actuated by high drywell pressure.

Subsequent investigation showed that a technician closed the isolation valves on the instrument panel, believing they were drain valves. To prevent a similar occurrence in the future, the licensee plans to revise instrument valve lineup procedures for safety-related systems to include valve identification numbers and independent verification, and to color code valves to safety-related instruments with green signifying normally closed valves and red signifying normally open valves.

In another instance, the water level in the intake structure to one of the emergency water service loops dropped below the pump suction lines. This resulted in the loss of one of the CSS loops. The cause was the collection of excessive debris on the intake structure screens which restricted the amount of water available.

Another problem in Containment Spray Systems involved leaks in a heat exchanger nipple between a water box and a relief valve on the service water side. This was attributed to corrosion that was accelerate by galvanic action.

Failures in Hydrogen Monitoring and Control

The data also indicate that there has been a significant increase in recent years in the number of failures in systems for monitoring hydrogen and oxygen within primary containment and other air spaces within BWR nuclear power plants (Table 3). Whereas for calendar years 1975 through 1977, the number of such events ranged from only 7 to 11 per year, during 1978 there were 34 such failures, during 1979 there were 55, during 1980 there were 78 and during 1981 there were 95 (Table 4). Some of these failures were due to high ambient temperatures within analyzer cabinets. Many of these situations were directly attributed to inadequate ventilation. Similar increases have been noted in the number of failures of iodine and particulate monitors and temperature monitors. The reasons for these increases are not known.

As would be expected, the inoperability of such equipment can seriously hamper the effectiveness of hydrogen control systems. This may well be a matter that needs attention. Failures in hydrogen monitors can also lead to other types of problems as was exemplified by an event at a BWR installation in 1979. This event resulted in the release of airborne radioactive materials to the environment and occurred while plant personnel were returning a hydrogen analyzer in the off-gas recombiner system to service. Because the analyzer was leaking, noble gases were permitted to flow to the off-gas recombiner room, through the reactor building ventilation system, and out the plant's main stack. The total release, however, which occurred over a period of about 20 minutes, was limited.

In 1980, an equipment manufacturer discovered a design defect in the discharge valve of a sample pump on his hydrogen analyzer. The problem was that when the valve was isolated, it deadheaded the pump and could have led to rupture of the diaphragm. Two modes of failure were identified: (a) release of containment gas; and (b) system inoperability. Corrective action for analyzers already installed included installation of a bypass line around the pump and installation of an interlock to trip the pump upon isolation of the discharge valve.

The use of hydrogen recombiners themselves can lead to still other types of problems. In one reported instance, leakage of the mechanical compressor within such a recombiner, and the accompanying increase in pressure within the system, resulted in the release of airborne radioative material through the reactor building vent. During the preheating of the off-gas lines during startup operations at another BWR installation, moisture entered a recombiner and reduced its capacity. The reason for this occurrence was that the preheater temperature was too low. This event, which was repetitive, led to excessive hydrogen concentrations in the off-gas lines.

Failures in Standby Gas Treatment Systems

A variety of failures have been reported relative to the performance of Standby Gas Treatment (SBGT) systems. These include hydrogen explosions, inadvertent water deluging of the charcoal adsorbers, and failure in the functioning of the valves that must open to place such systems into operation.

At a BWR installation in 1979, a station operator noticed water leaking from the carbon adsorber housing for the SBGT system. Investigation showed that the fire protection deluge system had actuated. The cause was found to be inadequate latching surface area between the deluge valve clapper and latch. This permitted the clapper to open and spray the charcoal. Corrective action consisted of replacing the clapper and latch assembly and adjusting them to ensure that adequate seating area was established between the latching surfaces. The carbon adsorber was dried out and placed back in service.

At another BWR installation in 1979, monthly surveillance showed that the plant service water supply isolation valves for the SBGT charcoal filter protection deluge valves were in the closed position. Investigation revealed that the valves had been closed to prevent spurious trips of the systems caused by low plant service water pressure, and deluge valves that were over-sensitive to pressure. The interim corrective action was to maintain the valves in the manual model with break-away locks, and to switch the water supply from the plant service water to fire protection water. It was thought that this would provide reliable deluge valve operation with the higher pressure in the fire protection water system. However, subsequent checking showed that the fire protection deluge system would not meet seismic and redundancy requirements. A design study was initiated to determine an appropriate solution to the problem. One possibility was to install deluge valves that were less sensitive to low water supply pressures.

At another BWR installation in 1979, while decreasing the reactor water level preparatory to maintenance of the reactor cleanup system, a reactor low water level signal was actuated. This, in turn, should have initiated the start of both the SBGT trains. Although the "B" train did start, the "A" train did not. Investigation showed that a movable contact cover on the relay that starts the "A" train was misaligned. The cover was adjusted and all similar relays were checked.

In preparing for repairs on the SBGT System at another BWR installation, operations personnel closed the normally open isolation valve in the suction line for train "B". Train "A" was operable at the time. Later, after concluding the repairs on the "B" train, a repairman misinterpreted the SBGT system configuration and proceeded to work on the "A" train. This error was due, in part, to the failures of operations personnel to tag "closed" the manual valve in the cross time line in train "B". As a result, train "B" was unavailable for use but was thought to be inoperable by control room personnel; train "A", which was thought by control room personnel to be available for service, was actually out of commission. Because of the mixup, the total system was unavailable for a period of approximately eight hours. Records indicate, however, that the repairman was in the fan room approximately half of the time and would have noted and corrected the condition if the fan had started.

III. Specific Failures in PWR Installations

Details of LERs pertaining to air-monitoring, air-cleaning, and ventilation units within specific nuclear power plant systems for PWR installations are summarized in Table 5. Again, it may be noted that a large number of the reported events related to the equipment designed to sample and monitor the performance of ventilating and air-cleaning systems. An interesting aspect of the newer data is the significant change since the previous study. For calendar years 1975 through 1978, the percentage of the total air system failures that involved air monitoring units was about 32%; for calendar years 1979 through 1981, this had increased to 54%, making it comparable to the situation for BWR installations (Table 3). With the increasing use of air-cleaning, air-monitoring, and ventilation systems in PWR installations, it may well be that both types of installations share common problems and that the newer data simply reflect this.

Further analyses of the newer data (Table 5) show that for PWR installations the percentage of the total air monitoring events that involved failures in the air sampling portion of the systems was about 31%. Although this is comparable to the newer data for BWR installations (about 29%), it again represents a reduction from the value of 38% calculated on the basis of the data for the years 1975 through mid-1978. As stated earlier, whether this represents an improvement in the performance of sampling systems, or simply reflects a change in the reporting of the data, is not known at this time.

As may also be noted from the data in Tables 5 and 7 (as contrasted to the data reported in the earlier study), there appears to be a marked increase in the number of failures of recombiners in primary containment, in dampers or fans in the emergency ventilating systems and in emergency air sampling and monitoring systems for control rooms, and in atmospheric sampling and monitoring systems for the turbine building and the main stack discharge. Also of interest is the relatively large number of failures of radiation monitors attributable to the deterioration of mechanical components. New requirements relative to upgrading of equipment and to increasing the frequency of inspections and reporting, imposed following the accident at Three Mile Island, Unit 2, may account for some of these increases.

Failures Resulting in Major Degradation of Primary Containmennt

Two events occurred during 1978 at PWR installations that resulted in loss of automatic closure capability for certain large sized isolation valves in the containment ventilation systems while the valve were open for containment purging operations. The automatic closure feature was lost because the signals that are intended to initiate automatic closure under certain accident conditions were either bypassed or over-ridden and therefore ineffective. Normal purging activities do not require the negating of any automatic closure signals. If a design basis accident had occurred under these conditions, the offsite consequences would have been exacerbated. In addition, the performance of the Emergency Core Cooling System (ECCS) may also have been degraded due to a decrease in the pressure buildup inside containment during the accident. The only means the operator would have had to identify the valve status would have been the valve position indication.

The basic causes of these events were procedural inadequacies and design deficiencies. The NRC subsequently required licenses to commit to stop purging during operation or to provide a basis why purging during operation should be permitted. The basis for allowing limited purging included demonstration of the capability of the valves to close under postulated accident conditions, demonstration that ECCS performance would be acceptable under purging conditions, confirmation of conformance purge and isolation instrumentation and control circuit design with IEEE standards, and demonstration of the acceptability of the radiological consequences of the design basis LOCA initated during purge operations. In addition, the NRC advised licensees of the necessity for proper management controls for the use of manual over-ride of safety signals during non-emergency conditions.

In another instance, a containment purge damper was repositioned during welding operations to avoid damage to the charcoal filters in the purging line. Without the filters in the system, any release of airborne radioactive materials within containment would have had direct access to the ambient environment. Purging was subsequently re-established after the damper was set back in the proper position.

In somewhat similar event, it was discovered in 1979 that, during leak tests, two manual valves in a 4-inch bypass line around the main containment purge valve were locked in the open position. Had an accident occurred while these valves were locked open, a significant release of radioactive material could have occurred. Had such a release occurred, the investigation showed that there was no instrumentation to identify the open valves as the cause.

The initial design purpose for the bypass system was to provide a long term hydrogen control capability for the containment atmosphere following a design basis accident. It was intended that after about 30 days following an accident, when conditions permitted, the system could be manually valved to vent the containment atmosphere through high efficiency and charcoal filters. Since the components in the bypaass line beyond the two manual isolation valves were not designed for the severe service they would be exposed to with the valves open during the initial pressure surge of an accident, significant uncontrolled release could have occurred. High radiation in the vicinity of the bypass line would make immediate closing of the valves, even if identified as the source of leakage, an extremely hazardous operation.

The basic cause of this event was human error in the make-up of the master containment integrity valve line-up checklist and in the filter efficiency test procedure for the bypass line. The NRC subseuently issued an order requiring that an appropriate review of checklist and procedures be performed to avoid repetition of such events.

Failures Resulting in Minor Degradation of Primary Containment

Inspection during normal operations at a PWR installation in 1978 revealed that the containment air sampling inlet isolation valve was closed. This caused two containment radiation monitors to be out of service. Further investigation revealed that the valve had failed shut when a transformer crew was routinely changing gas bottles. A sudden pressure lockout of the tertiary auxiliary transformer occurred, causing a loss of power to the valve which was designed to fail shut under these conditions. At the time of the loss of power, the operator observed from the radiation monitor panel that all indications were normal. He failed to check the valve position indication, however, to verify that a sample path existed and the valve remained shut for approximately 39 hours. Additional study identified a leakage path through the cover gasket on the particulate monitor cabinet permitting flow through the sample lines even with the valve closed. This prevention actuation of the low flow alarm when the valve was shut. The length of time the gasket had been leaking could not be determined.

Corrective action consisted of replacing the gasket and reminding operations personnel of the need to utilize other status indications (valve positions as well as flow, pressure, temperature, etc.) to verify proper system alignment.

At another PWR installation in 1980, it was found that three limit switches, that were not sealed, could become submerged following a LOCA. In a submerged condition, these switches would be susceptible to failure and could lead to inadvertent opening of the letdown isolation. Corrective action included immediate placement of the switches in the closed position prior to resetting containment isolation. Longer range corrective action consisted of properly sealing the switches.

In 1981, the containment air particulate detector sample valve was discovered open in a PWR installation. Investigation revealed that the one-inch valve had been open for several days, and that a small release of radioactive material had occurred during this period. The release path was from the containment through the sample line to the auxiliary feed pump area to the atmosphere. Although the loss of mass from the containment had been observed, it was not brought to the attention of plant management.

Failure in Containment Fan Cooling Unit

At a PWR installation in 1980, there were significant multiple service water leaks in the containment fan cooling units, which permitted water to discharge directly onto the containment floor. Approximately 100,000 gallons of water spilled onto the containment floor before the incident was discovered. Because the water level rose sufficiently high to wet several feet of the reactor pressure vessel lower head, there resulted an unanalyzed thermal stress condition of potential safety significance. Although there were several avenues through which the plant operators should have been alerted to the leakage, the moisture level indicators within containment did not indicate unusual conditions since they were designed to detect pressurized hot water or steam leaks and were not sensitive to the lower airborne moisture levels resulting from relatively small cold water leaks. The two containment sump pumps, which should have cut on to remove the water as it accumulated, were inoperable, one due to blown fuses and the other due to binding of its controlling float. The two containment sump water level indicating lights were stuck on, leaving the operator with no operable instrumentation to measure containment water level. The two submersible pumps in the cavity under the Reactor Pressure Vessel were ineffective since they pump onto the containment floor. Thus, an event originating in leakage from the containment fan cooling units was compounded into a major problem due to a combination of circumstances.

Failure in Containment Spray Systems

Inadvertent actuation of Containment Spray Systems (CSS) has occurred at several PWR installations in recent years. In addition, there have been other types of failures in these systems.

While the reactor was in a cold shutdown condition, an auxiliary unit operator erroneously opened a containment spray valve. This valve, which is located in the auxiliary building, isolates the Residual Heat Removal (RHR) system from the containment spray heater. Approximately 40,000 gallons of primary water and 65,000 gallons of refueling water storage tank water were sprayed into the containment building.

The auxiliary unit operator had been asked to verify that the containment spray valve from the RHR system was physically closed and sealed. Due apparently to miscommunications, he opened the spray valve and the valve remained in this position for 35 minutes. Evacuation of workers, who were inside containment at the time, was hampered by darkness, since most of the light bulbs burst when sprayed with the water. Containment purge, which was in progress at the beginning of the event, was discontinued and was not resumed until later in the cleanup phase, after licensee engineering assured that the moisture within containment would not damage the shield building ventilation exhaust filters.

The primary cause of the event was determined to be lack of adequate oral communication between the unit opeerator and the assistant unit operator. It should also be noted that the event occurred during a transition period between a preoperational plant and an operating plant mode. The operating staff was supplemented for the preoperational phase, and communication channels were not clearly understood.

During operation of the RHR System at another installation, leakage was observed from the upper containment spray nozzles. Investigation revealed that the check valves in the lower containment spray header were installed in the reverse direction. Subsequent review of the records indicated that this situation resulted from improper reinstallation of the check valves, following preoperational testing of the CSS a year earlier. The valves had been removed for the installation of temporary piping associated with the testing procedure. When the temporary piping was removed, the check valves were reinstalled backwards. These check valves are located in the lower CSS header and, as designed, cannot be flow tested.

A design change to eliminate the necessity for removing the valves for testing purposes is under consideration. In addition, procedural changes were made requiring verification of proper flow through all of the final containment spray check valves.

In another event, it was discovered that a spray additive isolation valve was locked shut. This occurred during a periodic check of the spray system during normal power operations. This condition would have prevented automatic sodium hydroxide injection into the CSS in the event that operation of the system had been needed. Because the lack of spray additive injection would have been indicated on the control board, the situation would probably have been quickly noted in an accident and corrected.

Investigations revealed that during earlier surveillance testing of the sodium hydroxide addition valves, the operator had inadvertently locked the valve shut. Corrective measures included reinstruction of all operators on the importance of maintaining proper valve lineups, with special emphasis on safety-related systems and those circumstances where valve position indication is not available to control room personnel.

At another installation in 1981, an inadvertent spray down of containment occurred while personnel were conducting an operability test of the refueling water/containment spray pump. The failure occurred due to leaking butterfly valves in the discharge of the pumps. Approximately 1500 gallons of water were discharged into containment.

Another example of human error contributing to deficiencies in the CSS occurred at a PWR installation in 1980 when maintenance personnel were told to repair a low pressure safety injection pump. Due to a verbal communication error, the personnel began to disassemble one of the containment spray pumps, thus rendering this train of the CSS inoperable. The plant was at 100% power at the time.

In another event, there was a failure to return three recirculation valves in the CSS to their normally locked-shut position, following routine testing of the system. This resulted in a condition in which this safety system could not have performed its intended function had an accident resulted in the release of radioactive materials into containment. This situation was also directly attributable to human error.

Failures Resulting in Airborne Releases to Auxiliary Building

There have been several reported events that resulted in releases of radioactive noble gases to the auxiliary building. One event followed a turbine-reactor trip sequence, with subsequent opening of the main steam dump valves. When the Reactor Coolant System (RCS) temperature decreased below the steam dump setpoint, however, one steam dump valve failed to close. This resulted in RCS depressurization and a low pressurizer pressure signal, which initiated the safety injection. Although the transition from injection mode to the normal charging mode of operation was made in a slow and cautious manner (so as not to overpressurize the RCS), this evolution resulted in overfilling the Volume Control Tank (VCT). When the pressure in the VCT exceeded the relief valve setpoint, the letdown water and gasses were discharged directly to the high level liquid waste tank. Normal action at this point could have been the release of noble gases from the waste tank through the vent line and through the plant process vent. At one point in the vent line, however, a flange had been disconnected. This permitted the release of noble gases into the auxiliary building. The gases were then vented through the plant charcoal and high efficiency particulate air filters and then out the plant ventilation vents.

At another PWR installation, a release of radioactive noble gases to the auxiliary building occurred as a result of the deborating ion exchanger having been left open to the plant venting system in preparation for transferring resin. Since the outlet valve to the VCT had not been fully shut due to wire wrapped around the valve stem, this pressurized the ion exchanger and backed up radioactive water into the vent piping. The vents were closed within five minutes and leakage was confined to the event system piping. Corrective action in both cases was primarily procedural in nature.

In 1979, a tube rupture in a drain cooler for the low pressure feedwater heater led to extraction steam backing up in the feedwater heater. This, in turn, led to a turbine and reactor trip with subsequent opening of the main steam dump valves. Because one valve stayed open, safety injection was initiated leading to high pressure in the reactor coolant system. The relief valve on the VCT lifted, transferring coolant to the high level waste drain tank which, in turn, released dissolved noble gases to the auxiliary building via the waste system vent. Because of design and construction errors, the vent line from the high level waste drain tank was not connected to the auxiliary building stack which had a radiation monitor and block valve. As a result, about 7.5 curies of noble gases were released into the auxiliary building, which had to be evacuated. Compounding the problem was the fact that control room personnel has used a pencil and paper clip to defeat a spring operated switch on the VCT automatic level control. This led to the overfilling of the VCT and resultant lifting of the relief valve.

Failures Resulting in Airborne Releases from Boron Recovery Systems

Two events occurred at a single PWR installation in 1981 which involved the boron recovery system and led to inadvertent airborne releases. The first event occurred when a manual valve was left partially open, allowing gases generated during boron recovery to be vented directly to the plant stack. The second release occurred about a week later when an operator, as part of normal procedure, switched from the start-up gas vent to the running-gas vent as the system reached normal temperature and pressure. Although the running gas vent ties into the waste gas processing system, there is an additional connection to the plant stack through two valves in series that are normally closed. These valves had been inadvertently left open. The release was detected and terminated when the stack monitor alarmed.

Failures Resulting in Airborne Releases to the Environment

Several events have been reported that resulted in releases of airborne radioactive materials to the environment. One of these involved the failure of a rupture diaphragm in a degasifier. Gases in the degasifier were then released to the stack, along with about 800 gallons of radioactive water which were also carried over into the stack and then settled at the base. In the main, it was concluded that this release involved design errors. These included the use of a rupture diaphragm for overpressure protection in a system containing potentially radioactive gases and liquids, and use of a single control relay which, upon failure, may cause pressurization of the degasifier system up to the rupture diaphragm actuation pressure.

As a result of this event, re-evaluation is being given to the use of rupture diaphragms where relief valves, or relief valve/rupture disc combinations, may greatly reduce releases. In addition, it may be that overpressure protection discharges should be diverted to other tanks to prevent release to the environment.

In another instance, radioactive material contamination of the soil near a nuclear power plant was observed. Investigation revealed that this was probably due to atmospheric fallout of particulate material which had been exhausted from the plant stack during containment purge following explosive plugging of steam generator tubes. Subsequent review revealed that the steam generator manways were not covered, and that the purge system was not equipped with HEPA filters.

Failures Involving Ion Exchange Resins

While transferring resin and dewatering the Spent Resin Dewatering Tank at a PWR installation in 1979, a slug of water entered the process vent blower and filter via the tank vent. This caused the vent to cease, the blower to stop, and resulted in wetting of the waste gas charcoal filter system. After the water was drained from the system, the HEPA filters were replaced and the charcoal filters were repacked and re-installed.

During preparations for backflushing the cation demineralizer in the Chemical and Volume Control at a PWR installation in 1981, resin material entered the reactor coolant letdown line through a partially open demineralizer inlet isolation valve. The resin then plugged the reactor coolant filter and subsequently entered the Volume Control Tank, where about one pound was charged into the reactor primary cooling system and partiaally plugged the reactor coolant pump seal injection filters. During the subsequent replacement of the plugged filters, a 3/4 inch drain valve was inadvertently left open and this allowed letdown water to drain continuously to the auxiliary building drain tank, which subsequently overflowed into the building sump. Out-gassing from the water resulted in a release of noble gases into the auxiliary building and then offsite through the exhaust ventilation system.

Failures in Hydrogen Monitors

As mentioned previously, there has been an increasing number of failures reported in the performance of hydrogen analyzers in BWR installations. Similar problems exist at PWR installations (Table 4). These types of analyzers appear to be particularly susceptible to moisture. In one PWR installation in 1981, failure of a hydrogen analyzer was determined to be due to the analyzer temperature switch being exposed to ambient air due to lack of insulation. At another PWR installation during the same year, a relief valve on the Waste Evaporator Condensate Recovery Tank lifted. The steam release resulted in excessive moisture buildup on components in a hydrogen analyzer making it inoperable. In this case, consideration is being given to rerouting the relief valve steam release to another area.

During construction at another PWR installation, it was found that the hydrogen analyzers could not be continuously calibrated, as required. For proper calibration, such analyzers require a constant amount of reagent gas (air) flow. In the system described, this gas was supplied by the control air system. Due to the variable demand on this system by other sources, and since there were no provisions for a reagent gas supply pressure regulator, the control air pressure varied, resulting in variations in the reagent gas flow to the analyzer and inaccuracies in its calibration. Corrective action was to install a pressure regulator in the reagent supply line.

Failure Resulting in Explosion in Waste Gas Tank

A number of situations have occurred in which there have been explosions in BWR offgas systems. In fact, since 1970 about 50 explosions related to the processing of hydrogen-bearing waste gases from such installations have been reported.[11] In 1981, a similar problem occurred at a PWR installation during the venting of radioactive gases to the waste gas decay tank through the cryogenic waste gas treatment system. As processing began, difficulty was experienced in adjusting the flow rate through the system. Investigation determined that a reducing valve which controls downstream gas pressure into the gas treatment system was cycling. While attempting to alleviate this problem, an operator noted "popping" noises, apparently originating in the piping downstream of a reducing valve. Sometime thereafter, an explosion of the mixture occurred. Fire alarms were observed in the control room and personnel operating the gas treatment system were notified. These personnel reported a loud noise, apparently from the gas decay tank area.

Subsequent investigation showed that the damage to the waste gas decay tank was apparently limited to the manway area and the manway bolting. The source of the ignition was apparently the oxygen recombiner located in the cryogenic waste gas treatment system. At oxygen concentrations greater than 3%, the chemical reaction of the recombiner can generate temperatures above the ignition temperature for an oxygen-hydrogen combination. Although the manufacturer of the unit provides an oxygen analyzer with this system, it was inoperable at the time of the event. Local ignition of the hydrogen-oxygen atmosphere evidently created pressure spikes that caused the control valve to cycle, resulting in the "popping" noise, previously mentioned. During one of the local ignitions, the flame front propogated upstream of the control valve and ignited the gas mixture in the tank.

Subsequent investigation into the cause of the high oxygen concentrations in the waste gas system revealed high oxygen concentrations in the station's nitrogen system. The source of the oxygen was identified as instrument air leaking through check valves at the cross connections between instrument air and nitrogen lines. Corrective measures included physical separation of the instrument air system and the station's nitrogen supply, and the use of bottle gas instead of the nitrogen system. In addition, procedures were revised to prohibit operation of the waste gas treatment system when oxygen concentrations are above 3%.

IV. Problems Common To BWR And PWR Installations

As containment designs, safety systems, and normal and accident monitors in BWR and PWR installations share an increasing number of common characteristics, many of the problems in the operation of the air cleaning systems in the two types of installations tent to overlap. Discussed below are problem areas noted in this study which tended to be common to both types of power plants.

Potential Failures in Containment Purge and Isolation Systems

During 1979 and 1980, a range of problems were discovered in the design of the containment purge and venting systems of several BWR installations. One indication was that there would be a potential loss of secondary containment if primary containment purging were underway during hot standby or power operation concurrent with a Loss of Coolant Accident (LOCA). Calculations showed that the pressure surge in the ductwork associated with the purging system could cause failure of the dampers and/or ductwork. Similar analyses for other BWR installations showed that the pressure transients associated with an accident could damage the air operator mechanism and cause failure of the ventilation isolation valves for the reactor containment. The cause of these problems was attributed to inadequate specifications in the original designs.

Similar analyses, for both BWR and PWR installations, showed that the containment isolation valves as well as the containment purge valves were not designed to close against the differential pressures that might accompany a design basis LOCA unless the valves were operated partially closed. This proved to be a generic problem common to a number of installations.

Related potential defects in Heating, Ventilating, and Air Conditioning (HVAC) and containment purging systems were also discovered in the review of the designs of BWR and PWR installations during this same period. In one instance, it was found that the containment purge system ductwork did not comply with the thickness criteria. Because the metal used was thinner than prescribed, the possibility arose that damage to the ductwork during a LOCA might interfere with the ability of the containment isolation valves to close. In a second instance, this time at a BWR installation, it was discovered that the HVAC ductwork on the emergency diesel generator bay could collapse as a result of negative pressures induced by a tornado. Since a tornado could result in a loss of off-site power, the diesel generators would be required to bring the plant to a safe shutdown. Corrective action was to reinforce the ductwork and to consider the possible addition of pressure relief dampers.

In a related event, it was found at an operating PWR installation that the safeguards area exhaust system, which would provide post-LOCA ambient cooling for the recirculation spray and low head safety injection pumps, was not entirely seismically designed. The specific defect was that the fan discharge ductwork, up to and including the ventilation stack, was not designed to Seismic Category I requirements. Corrective action consisted of modifying the auxiliary building central area ventilation exhaust system to ensure operability following a seismic event.

Other Failures in Valves and Dampers

As may be noted from the previous discussion, the discovery of potential failures in valves associated with air ventilation and isolation systems is common. Failures of dampers is also common. Dampers fail to open, fail to close, or leak after closure. The principal causes are improper installation, nonfunctioning sensors and controllers, incorrectly positioned damper actuators and linkages relative to control motors, and degradation of sealing surfaces by dirt and mechanical damage.

During construction of a BWR installation in 1981, it was found that the tack welds that connect the shaft to the damper blades on two safety related automatic dampers failed during an attempt to open the blade. These dampers were in the HVAC system for the emergency diesel generators. The defect resulted from the inadequacy of the materials used in the damper shafts and/or the use of inappropriate welding procedures.

Other areas within this same plant that were potentially affected by this same problem included the SBGT System and the HVAC systems in the control room, the switchgear and battery room, and the standby service water building. Inadequate environmental control in the control room could result from the loss of function of the standby fresh air system, and the secondary containment integrity could be jeopardized by inadequate performance of the SBGT system.

In another event at a PWR installation in 1980, the control room operator observed that the position indication for the ECCS room ventilation exhaust damper had been lost. Attempts to move the damper were unsuccessful, and it was declared inoperable. Attempts to determine the cause of this malfunction were unsuccessful. The damper was manually closed.

Deficiencies in Fans

Problems with fans have been reported both in operating plants and in those under construction. At one PWR installation under construction, onsite inspection of the fan motors showed that the grease originally placed in the bearings had hardened and, when new grease was added, the old grease was forced into the motor windings. Investigation showed that the grease relief tubing in the fan motor was undersized.

In another PWR installation, initial startup testing showed that all eight fans in the diesel generator room exhaust system exhibited excessive vibration. Investigation showed that all the fans lacked structural rigidity.

At still another PWR installation, it was found that data supplied for the containment fan coolers and used in the LOCA-ECCS analysis represented the capacity of a single fan rather than the combined capacity of the four coolers. Provision of cooling, in excess of that assumed, would reduce containment pressure following a LOCA below that anticipated. This, in turn, could result in peak fuel cladding temperatures being in excess of the predictions.

During construction and testing of a BWR installation in 1981, it was found that flow rates were low. This condition was true for the HVAC systems supplying the control room, fuel handling area, drywell, and radwaste and turbine buildings, and could have prevented equipment in these areas from performing their intended safety functions. The cause of this situation was not immediately revealed.

Contamination of Air Systems

In late 1981, the NRC reviewed a number of problems relating to contamination of air systems in operating nuclear power plants. The review indicated that air-operated components and systems will occasionally become inoperable due to contamination with oil, water, dessicant, and rust or other corrosion products. Examples of such problems were reported in at least four different PWR installations during 1980 and 1981. In one case, an air-operated control valve failed to stay open, resulting in both residual heat removal trains becoming inoperable. This failure was attributed to the accumulation of water at the lowest point in the air system lines which coincided with the valve location. At another PWR, a pneumatically operated globe valve failed to close within the time required by the Technical Specification. Investigation revealed the presence of dessicant at the air discharge port. In a third event, the containment air sample valve failed to close during the monthly containment isolation operability test. Failure was found to be due to oil contamination in the instrument lines. In a fourth case, the isolation valve for service water to containment failed to close while a containment isolation valve test was being performed. Failure of the instrument air filters allowed small particles of dessicant to enter the air lines, preventing the solenoid air control valve from operating.

In another event at a PWR installation, failure on a non-filtered vent heater isolation valve to close was traced to its actuating piston becoming stuck due to dirt in the air supply. The source of the problem was a physical interconnection of the instrument and service air systems.

A related situation, which occurred twice at a BWR installation, involved the leakage of contamination from the radwaste system into the service air system, which serves as a source of breathing air for personnel using supplied air respiratory protective equipment. By means of an interconnection to the radwaste system, the facility also used the service air system to provide a source of compressed air during the backwash cycle of the demineralizer filter element. The compressed air provided the motive force for reverse water flow through the filter element and was being used to perform this function when the two incidents occurred. Liquid from the radwaste system leaked past a check valve and a process valve. Examination revealed the presence of dirt deposits in the check valve and the air operated ball valve.

During construction of a BWR installation in 1978, it was found that the air handling unit blower, as originally designed, discharged directly from the air handling unit into the control room air supply ducting. This arrangement could have resulted in pressures inside the air handling unit case that would be lower than the pressure in the surrounding HVAC equipment rooms and this, in turn, could have led to in-leakage of unfiltered air into air handling units. The possibility for airborne radioactive contaminants existing within the HVAC equipment rooms resulted from the fact that HVAC equipment room heating, ventilating and air conditioning was provided by critical switch gear room HVAC equipment. The air supply for the critical switch gear room HVAC equipment was from the inle plenum area which also served the control room HVAC systems during normal operation. This plenum inlet may be exposed to radioactive material releases following accident conditions.

Unless this deficiency were corrected, it was estimated that the infiltration of airborne radioactive contaminants into the control room following a LOCA could have resulted in a 30-day integrated dose to the control room operators in excess of specified limits. Corrective action included (a) isolating the control room HVAC equipment in separate leak tight rooms, (b) enclosing the air handling unit in an additional pressurized case, and (c) replacing the existing air handling unit blower with a separate blower at the air handling unit inlet.

Since other nuclear power plants use service air as a source for breathing, it is important that precautions be taken to prevent contamination of the breathing air source. The plant supply of compressed air should not be used for breathing purposes unless it has been specifically modified and properly adapted for such use.

Effects of Extreme Temperatures

During the period covered by this study, a variety of failures were reported due to high temperatures which were, in turn, most commonly caused by inadequate ventilation. In one BWR installation, the High Pressure Coolant Injection (HPCI) system did not manually inject due to the pump discharge valve failing to open. The source of the problem was failure of the windings on the motor to the valve due to its limited duty cycle and the high temperature and humidity in the HPCI room. This was a repetitive occurrence.

In a PWR installation, analyses showed that the fan cooling system was inadequate to maintain the design capability of the emergency diesel generators during periods of hot weather. The cause of this problem was believed to be due to an improper pitch setting on the cooling fan blades.

High ambient temperatures were also found to be the cause of a number of failures in air sampling and monitoring equipment in PWR installations. This included failurs of post-accident radiation monitors within containment. An interesting case was that in which access barriers to several service water pump motors were removed to provide better ventilation. Later it was realized that the access barriers also served as missile shields for the pumps.

It is important to note also that high ambient temperatures can lead both to failures in monitors as well as to the output of erroneous data. An example was the case of high drywell temperature in a BWR installation (due to ineffective ventilation) which caused the water level indicators to oscillate. The high temperature caused the reference legs to flash, inducing the oscillations.

Low temperatures can also cause problems. One such event involved failure of the air conditioning compressor in the control room at a PWR installation. The increase in the viscosity of the oil at the low temperature caused it to be displaced from the compressor crankcase to the evaporator coil.

Over the past few years, there have been a dozen or more events reported that have involve instrument or sampling lines that have become inoperative due to cold weather. Some of the commonly reported causes of line freeze-up was the absence of heat tracing or adequate insulation, de-energized heat trace circuits, space heater failures, and improper thermostat settings or sensor location for the heat tracing. Since a number of these failures have involved radiological effluent sampling lines, including those which provide data on the operation of air cleaning systems, the NRC staff issued a report[12] urging that proper attention be given to this subject. This report pointed out that there may be a need to develop better design requirements, acceptance criteria and review procedures for heat tracing.

V. Commentary

Although this study covered a wide range of events, several aspects appear to deserve special comment.

Failures in Air Monitoring

The data summarized here reveal a continuation of the failures in the equipment that monitors the performance of air cleaning and ventilation systems. This is particularly true with respect to radiation monitors and hydrogen and oxygen monitors. An average of over 23% of all the LERs reported by the operators of BWR installations during the four years covered by this study were in air cleaning, air monitoring and ventilation system. Of these, almost 61% involved failures in air monitors, and, of this number 41% were in radiation monitors (gaseous and particulate) and 34% were in hydrogen and oxygen monitors (Table 6). Thus *of all the LERs* that were reported by BWR installations from 1978 *through 1981*, 11% involved either radiation monitors or hydrogen and oxygen monitors (Table 6 and 8).

The percent of all LERs that involved failures in air-cleaning, air-monitoring and ventilation systems in PWR installations was much less than in the case of BWR installations, averaging about 14% for the four years covered by this study. However, the data show that over half (54%) of all the reported failures in such systems were in air monitors (Table 6). Although the number of failures in hydrogen and oxygen monitor was low, the number of failures in radiation monitors (gaseous and particulate) was again relatively high (Table 8). For example, of all the failures in air monitors reported for PWR installations, over 68% involved radiation monitors. Thus, *of all the LERs* that were reported for PWR installations from 1978 *through 1981*, almost 5% involved radiation monitors.

Of the failures in air monitors, data for BWR and PWR installations combined show that about 30% were in the sampling portions of the systems. Of these failures, moisture and dust appear to be major contributing factors. From the standpoint of sampling pumps, moisture in sampling lines causes carbon vanes to swell and seize. In addition, corrosion of the carbon vanes can cause abnormal wear, resulting in loss of adequate sample flow or deposition or carbon particles in the pump bearing.

On several occasions, both high and low ambient air temperatures contributed to failures of sampling lines and sample pumps. High temperatures, for example, can lead to the loss of lubrication and subsequent bearing seizure, unless lubricants and bearings are designed specifically for high temperature service.[12]

Of the increasing number of events involving failures of hydrogen and oxygen monitoring systems, of note were the incidents in which a leaking hydrogen analyzer permitted noble gases to escape to the environment from a BWR off-gas system and in which an exposion occurred in a PWR waste gas decay tank. The latter event might have been averted if an oxygen analyzer had been operable.

In terms of averting hydrogen buildup problems, the importance of the proper performance of ventilation and air circulation systems should not be overlooked. For example, the operation of fans within containment after an accident is important to assure proper mixing and burning of hyrdogen gas in ice condenser containments equipped with igniters. Without such mixing, it is postulated that hydrogen might accumulate and burn in the lower compartment and this, in turn, could lead to overpressurization of the upper compartment.

Failures Associated with Surveillance Testing

Another observation was the large number of problems that occurred as a result of mistakes made during surveillance testing. For example, performance of a radiation monitor surveillance test at PWR installation in 1981 resulted in a loss of supply power to the containment atmospheric particulate and gaseous radioactive material monitors. This resulted from uninsulated portions of the power cable to one monitor coming into contact with the proper supply fuse to another monitor on the rack.

At another PWR installation in 1980, there was an inadvertent release of radioactive gas to the atmosphere due to failure of the rupture disc installed to protect the reactor containment from overpressurization. The rupture of the disc occurred during the containment integrated leak rate test. Failure occurred at a pressure below that for which the disc was designed.

One of the most common air cleaning systems whose testing leads to problems in the containment spray system. There have been a number of occasions in which the valve alignment, following tests of the spray pumps, has not been repositioned for proper response in an emergency. In addition, there have been instances (for example, at one PWR installation in 1981) in which the NaOH spray additive tank isolation valve had been found locked in the closed position, making the spray additive system inoperable. Locking out of such valves is a part of the routine surveillance tests. It would appear that positive design changes should be sought in order to permit testing of such systems in the operating mode anticipated under accident conditions, or to institute some other means for assuring in a positive manner that the systems will be returned to the proper operating configuration following surveillance testing.

Systems Interactions

Many cases were noted in which equipment provided to assure the proper operation of one system led to the failure of another. A typical example was the inadvertent opening of sampling lines to air monitors which led, in turn, to excessive containment leakage. There were other examples in which the proximity of radiation monitors to other components within PWR installations resulted in false alarms. One case involved a relatively high short-term release of noble gases through a plant's stack. Due to the proximity of the sampling lines for the stack monitor to the radiation detector in the steam generator monitoring system, the latter monitoring system was actuated. As a result, selection of proper locations for sampling lines for stack radiation monitoring systems was re-evaluated.

In another instance, a stack monitor gave an indication of a high rate of release of particulate radioactive material. Subsequent investigation, however, showed that the alarm resulted from a relatively high concentration of krypton-85 being detected erroneously in the particulate radiation channel of the detector. Since the particulate channel in this type of detector is specifically designed to detect beta radiation emanating from particulates trapped on the filter surface, beta radiation from high concentrations of krypton-85 gas in the sampling flow path will trigger a significant response from the detector. This type of false indication can be eliminated by calibrating the particulate channel to subtract out or ignore beta radiation associated with the noble gas.

VI. Conclusions And Recommendations

If maximum benefit is to be gained from the analyses of the data presented in this report, several questions must be addressed. The first concerns the relative significance of the various findings and observations cited, the second concerns the basic causes of the events (especially the role of human errors), and the third concerns the delineation of specific recommendations to avoid repetition of similar events in the future.

Relative Significance of the Events

Most people would agree that failures that involve systems important to safety are significant since such events represent a breakdown in the barriers provided for protecting the health and safety of the public and plant workers. Most people would also agree that failures that do not involve systems important to safety are probably not significant. At the same time, however, determination of the importance of failures in systems, such as those designed to monitor the quantities of radioactive materials being released to the environment, becomes more difficult. If nuclear power plant operating personnel have no data, or are being provided inaccurate data, on environmental radionuclide releases, they will not be able to know whether their plant is being operated safely. Falling into a similar category are failures that reduce the confidence of nuclear power plant personnel in the protection that should be provided to them by various engineered safety features. Although such failures would be difficult to designate, it has been reported, for example, that control room operators lack confidence in the HVAC and air cleaning systems provided for their protection in case of an accident. This situation could lead to impairments in their performance in case of an accident and this, in turn, could lead to decreased safety in terms of their capabilities to protect the health and safety of the public. Another troublesome group of failures are those that occur repetitively. Whether they involve a system important to safety or not, repetitive failures are indicative of inadequacies in overall plant operation. On this basis, such failures should be carefully reviewed and evaluated.

Since, for purposes of this review, the LERs were separated into those involving BWR installations, those involving PWR installations, and those common to both, the significance of the events will be addressed in this same manner.

(1) BWR Installations

In terms of BWR installations, the failures that were considered significant were as follows:

(a) Failure in vacuum breakers between the torus and drywell and between the suppression chamber and reactor building

These failures, coupled with those involving water level indicators in the torus are indicative of a degradation in the anticipated heat suppression and air cleaning functions of the torus or suppression chamber in case of a loss of coolant accident.

(b) Failures of containment spray systems

Although many of these failures were due to set point drift in the drywell pressure switches, loss of such instrumentation would have negated automatic initiation of the depressurization system and the accompanying scram, both of which are supposed to function in case of a small break LOCA.

(c) Failures in hydrogen and oxygen monitors

These failures represented almost 5% of all LERs reported for BWR installations for the four year period covered by this study. Since many of these were repetitive and since the inoperability of such monitors can seriously hamper the effectiveness of hydrogen control systems (and thus increase the potentiality for hydrogen explosions), this is considered to be a matter that needs attention. Although not regarded as serious from the standpoint of the general public, hydrogen explosion can be very serious in terms of power plant workers. To the extent that they impair the performance of the workers, they may also have implications relative to the health and safety of the public.

(2) PWR Installations

In terms of PWR installations, the failures that were considered significant were as follows:

(a) Degradation of primary containment

These failures were caused primarily by loss of automatic closure capability for certain large sized isolation valves while they were open for containment purging operations. Because these situations could have resulted in large environmental airborne releases following failure of the reactor cooling system, the NRC Staff had previously cited these as Abnormal Occurrences and had taken steps to correct them.

(b) Fan cooling unit leak

Although an isolated event, this failure was an excellent example of the potential detrimental effects of systems interactions. The event resulted in flooding of the containment floor. This, in turn, led to wetting of the reactor pressure vessel lower head, and resulted in an unanalyzed thermal stress condition of potential safety significance. Again, the event was cited by the NRC Staff as an Abnormal Occurrence and measures have been taken to prevent its recurrence.

(c) Failures in containment spray systems

The more significant failures in this group were those that resulted in the non-availability of the containment spray system. This system is an important engineered safety feature both for assuring pressure reduction and containment integrity as well as for assuring the removal of airborne radionuclides following an accident. Of interest here is the fact that essentially all of the failures cited occurred as a result of direct human error.

(3) Problems Common to BWR and PWR Installations

Of the failures cited as being common to both BWR and PWR installations, the following were considered significant:

(a) Potential failures in containment purge and isolation systems.

Although no such failures have occurred, analyses of the designs of containment purge and venting systems in both BWR and PWR installations showed that the pressure surge in the purging system ductwork could cause failures in the dampers and/or the ductwork, and that the containment purge valves were not designed to close against the differential pressures that might accompany a design basis LOCA. Because of the importance of such systems in containing potential airborne releases accompanying an accident, these findings were considered significant.

(b) Other failures in valves, dampers and fans

This review showed that failures in valves, dampers and fans associated with air ventilation and isolation systems are common. Since the satisfactory performance of certain air systems, such as those that assure the habitability of control rooms, is essential under accident conditions, many of these failures are significant.

(c) Hydrogen explosions

As noted in the text, about 50 explosions related to the processing of hydrogen-bearing waste gases have occurred at BWR installations since 1970. In 1981, a similar problem occurred at a PWR installation during the venting of radioactive gases to the waste gas decay tank. As previously mentioned, such events can be very serious in terms of potential injuries to power plant workers.

(d) Contamination of air systems

Several of these failures involved leakage of radioactively contaminated air into the service air system, which serves as a source of breathing air for personnel using respiratory protective equipment. Although not of significance from the standpoint of the safety of the public, this could result in unnecessary exposures of plant personnel and is therefore significant. In plants designed for the chemical processing of spent fuels, service air systems and air breathing systems are carefully separated. A similar requirement might be appropriate for nuclear power plants.

Basic Causes of the Failures

As noted in the discussion of specific events, human errors continued to play a major role as a causative factor in Licensee Event Reports for both BWR and PWR installations. This is exemplified by the large number of failures that occurred as a result of surveillance testing. In an earlier study(1) covering the time period from 1975 through 1977, we reported that from 46% to 69% of the LERs occurred as a result of human error. Data tabulated for the study reported here indicate that human error played a role in only 16% to 27% of the events in BWR installations, and only 17% to 28% of the events in PWR installations (Table 9). In reporting these contrasts, however, it is important to note that the data for this newer study were based on the contributions of human errors as reported by the Licensees. In the previous study, the values were estimated on the basis of an examination of the events themselves.

For several reasons, we believe that the data reported by Licensees on the contribution of human error to the LERs analyzed in the current study are too low. For example, each of the percentages would have been increased by about 5% if the LERs attributed to improper calibration of air monitoring instruments had been classified as being due to human error. Related studies conducted by the NRC staff relative to human errors underlying pump and valve related events showed that, when LERs were reviewed and analyzed without regard to the cause assigned by the Licensees, the contributions from human errors were significantly higher than reported.(13) This is a segment of the LER reporting system that needs additional review and evaluation.

Further analyses of the reported data on human errors show that, for 1978 through 1981, 16% were attributable to inadequacies in administrative procedures, 33% were attributable to inadequacies in engineering design and installation, and 51% were directly attributable to operating and personnel errors.

Recommendations for Action

Discussion with experts in the field of air-cleaning, air-monitoring and ventilation show that the information needed for preventing most of the failures cited in this report is available. The major problem is that this information is not being effectively utilized. Although this situation can be attributed to a number of factors, several stand out.

One is the diversity of groups within the NRC that have responsibilities in this field. An example is the review of control room ventilation systems. Review of the design of these systems in terms of safety significance, such as the single failure criterion, is the responsibility of the Auxiliary Systems Branch; consideration of the design in terms of control room habitability is the responsibility of the Accident Evaluation Branch; consideration of the design in terms of fire protection is the responsibility of the Chemical Engineering Branch; consideration of the adequacy of the design in terms of air filtration is the responsibility of the Effluent Treatment Systems Branch. What appears to be lacking is a group that looks at the total system with respect to its air treatment functions and assures that the design is satisfactory. Similar problems may exist with respect to evaluations of the construction, maintenance and operation of such systems. We recommend that consideration be given to developing better coordination among the various NRC groups responsible for these activities.

A second factor that may contribute to the problem is a shortage, on the part of both Licensees and the NRC staff, of personnel who are knowledgeable about HVAC systems, in general, about nuclear air cleaning technology, in particular. To correct this situation, we recommend that the NRC take steps to increase the training provided to nuclear power plant personnel in these subject areas. Similar training should be provided to members of the NRC staff.

Another factor is the failure on the part of Licensees to apply corrective measures that address the basic causes of the events. All too frequently, the corrective measures applied address the symptoms of the problems without addressing their underlying cause.(14) This is a chronic problem that needs to be given more attention both by Licensees and the NRC staff. Perhaps the recommended increased training for people responsible for HVAC and air cleaning systems will help in this regard.

In addition to these considerations, it is important that the air-cleaning, air-monitoring and ventilating equipment and components installed in nuclear power plants meet minimum standards. That this is not the case has been reported in another paper presented at this Conference.(15) Tests of HEPA filters, purchased from seven selected U.S. manufacturers, showed that not one was in compliance with current standards. With some 17 U.S. companies now manufacturing and selling such filters, we recommend that the NRC reconsider its policy not to have the certification of such filters confirmed by one of the test stations of the U.S. Department of Energy.

Lastly is the matter of making sure that the NRC Staff has all the available data for assessing problems associated with air cleaning systems. Through inspections of such systems conducted by private contractors and consulting organizations, a wealth of supplementary information on deficiencies in such systems has been developed. Because many of the problems uncovered do not involve violations of Technical Specifications, and therefore do not result in the issuance of an LER, they are not made known to the NRC. Since these data would be useful and valuable in improving procedures for eliminating failures in air-treatment systems, we recommend that arrangements be explored to have such data made available to the NRC Staff. Perhaps the Institute of Nuclear Power Operations could be of assistance in this regard.

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Table 1: Overall Tabulation of Licensee Event Reports

	Power reactors		All events		Air-cleaning events**		
Year	Reactor type	Number operating*	Total number	Number per reactor	Total number	Number per reactor	Percent of total
1978	BWR	24	1193	50	239	10.0	20%
	PWR	41	2036	50	232	5.7	11%
1979	BWR	26	1324	51	278	10.7	21%
	PWR	42	1959	47	225	5.4	11%
1980	BWR	26	1560	60	335	12.9	21%
	PWR	42	2191	52	316	7.5	14%
1981	BWR	26	1461	56	417	16.0	29%
	PWR	42	2403	57	400	9.5	17%

* As of July 1 of the given year. For calendar years 1979 through 1981, TMI-1 and TMI-2 were considered to be operating reactors.

** Includes events pertaining to failures in Air-Cleaning, Air-Monitoring and Ventilation systems.

Table 2: Summary of Licensee Event Reports Relating to Air-Monitoring, Air-Cleaning and Ventilation Systems (Boiling-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

System	Component	Nature of problem	Number of events			
			1978	1979	1980	1981
Primary Containment	Atmospheric monitoring system	Failure in sampling or monitoring system	91	73	98	114
	Diluting, inerting, or ventilating system	Deficiencies in nitrogen purge or ventilating system	30	22	20	29
		Deficiencies in filter system	2	1	3	2
	Torus	Failure of vacuum breakers	21	17	16	18
		Improper water level or indicator malfunction	10	7	9	15
	Containment spray system	Deficiencies in operation of valves	2	1	4	7
		Failure of supporting equipment	5	4	3	10

Table 2: Summary of Licensee Event Reports Relating to Air-Monitoring, Air-Cleaning and Ventilation Systems (Boiling-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

System	Component	Nature of problem	Number of events 1978	 1979	 1980	 1981
Reactor cooling system	Coolant purification system	Airborne Release	0	10	14	12
		Failure in Control Instrumentation	0	5	6	7
	Leak detection system	Failure of particulate sampler	0	2	4	2
	Injection and isolation system	Isolation of high-pressure coolant injection system	2	7	7	4
		Isolation of reactor core isolation cooling system	2	5	2	3
Secondary containment (reactor building)	Atmospheric monitoring system	Failure in sampling or monitoring system	18	11	20	27
	Diluting and ventilating system	Failure of blowers, isolation valves, or dampers, or cooling water flow	1	10	12	21

Table 2: Summary of Licensee Event Reports Relating to Air-Monitoring, Air-Cleaning and Ventilation Systems (Boiling-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

System	Component	Nature of problem	Number of events 1978	1979	1980	1981
Standby gas-treatment system	Air-flow system	Failure of blowers, low flow, train overheated excessive moisture	11	7	12	12
	Filter system	Failure of control unit	0	6	7	6
		Adsorbers depleted or absent, filter plugged	2	5	7	11
	Fire-protection system	Flooding of charcoal filters	2	2	2	1
Off-gas system	Gaseous and particulate monitoring system	Failure in sampling or monitoring system	13	15	21	45
	Air-flow system	Failure of drain line, leaks in line	4	5	3	6
	Filter system	Excessive pressure drop (plugged filter)	0	1	6	1

Table 2: Summary of Licensee Event Reports Relating to Air-Monitoring, Air-Cleaning and Ventilation Systems (Boiling-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

System	Component	Nature of problem	Number of events			
			1978	1979	1980	1981
Control room or building		Fires or explosions	1	0	0	0
	Combustible gas control	Excessive hydrogen concentration	0	10	5	5
	Sampling and monitoring system	Failure in sampling system	0	16	9	6
	HVAC and Ventilating system	Failure of monitor	2	2	3	3
		Failure in emergency ventilation system	6	4	12	7
Turbine room	Atmospheric monitoring system	Failure of radiation monitor	1	3	11	13
	Airborne radioactive release control	Excessive airborne release	0	0	0	1

Table 2: Summary of Licensee Event Reports Relating to Air-Monitoring, Air-Cleaning and Ventilation Systems (Boiling-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

System	Component	Nature of problem	Number of events 1978	 1979	 1980	 1981
	Ventilating system	Lack of interlocks on supply and exhaust fans	1	4	4	4
Main stack discharge system	Gaseous and particulate monitoring system	Failure in sampling or monitoring system	8	8	10	14
	Air-flow system	Inadequate flow	4	3	1	3
Waste Processing Building	Atmospheric monitoring system	Failure of radiation monitor	0	2	1	4
	Ventilating system	Airborne release	0	5	1	1
	Waste-gas tank	Failure of isolation system	0	4	2	3
	Fire protection system	Failure of monitor	0	1	0	0
		Total	239	278	335	417

Table 3: Summary of Licensee Event Reports Relating to Air-Monitoring Systems (Boiling-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

Nature of problems		Number of events			
General	Specific	1978	1979	1980	1981
Failure of sampling system	Leaking or plugged sampling line	8	2	3	7
	Moisture in sampling line	11	2	5	4
	Failure of sampling pump or motor	10	19	21	42
	Failure of valves	9	13	17	24
	Design, maintenance, or operator error	6	4	6	13
Failures of radiation monitor (gaseous)	Improper calibration or instrument drift	8	9	4	13
	Failure of detector or electronics	16	7	10	6
	Condensation in detector well	4	4	4	1
	Failure of electrical system	5	9	2	12
	Failure of chart recorder	1	4	0	2
	Design, maintenance, or operator error	2	5	8	13
	Indeterminant malfunction	2	0	1	2

Table 3: Summary of Licensee Event Reports Relating to Air-Monitoring Systems (Boiling-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

Nature of problems		Number of events			
General	Specific	1978	1979	1980	1981
Failure of iodine and particulate monitors	Failure of detector or electronics	0	2	8	3
	Failure of electrical system	1	0	1	1
	Human and design errors	0	1	0	3
Failure of hydrogen or oxygen monitor	Improper calibration or instrument drift	3	10	12	22
	Failure of sensor or electronics	8	10	16	12
	Failure of electrical system	1	9	8	12
	Failure of chart recorder	0	1	4	3
	Design, maintenance, or operator error	2	10	17	8
	Indeterminant malfunction	2	2	3	0
Failure of pressure monitor	Improper calibration or instrument drift	20	8	8	9
	Failure of electrical system	1	8	10	9

Table 3: Summary of Licensee Event Reports Relating to Air-Monitoring, Systems (Boiling-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

Nature of problems		Number of events			
General	Specific	1978	1979	1980	1981
	Failure of chart recorder	1	1	4	2
	Design, maintenance or operator error	5	2	4	5
Failure of temperature monitor	Failure of detector or electronics	0	5	4	4
	Failure of electrical system	1	13	6	16
	Failure of chart recorder	3	1	10	5
Failure of chlorine monitor	Failure of detector unit	0	5	2	1
Failure of fire and smoke protecting system	Failure of detector	3	3	0	7
	Inadvertent actuation of spray system	4	2	1	2
	TOTALS	137	171	199	263

Table 4 -- Summary of Licensee Event Reports Involving Failures in Hydrogen and Oxygen Monitors (Jan. 1, 1978, through Dec. 31, 1981).

	Number of Reported Events*	
Year	BWR Installations	PWR Installations
1978	34	10
1979	55	9
1980	78	11
1981	95	22

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* These numbers include failures in the sampling systems for these monitors. Therefore, the numbers shown here are not the same as those in Tables 3 and 6.

Table 5: Summary of Licensee Event Reports Relating to Air-Monitoring, Air-Cleaning and Ventilation Systems (Pressurized-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

System	Component	Nature of problem	Number of events			
			1978	1979	1980	1981
Primary containment	Atmospheric monitoring system	Failure of sampling or monitoring system	89	88	96	141
	Diluting or ventilating system	Deficiencies in purge (ventilation) system	24	20	37	20
		Deficiencies in filter system	8	11	13	10
		Deficiencies in air-cooling system	29	9	15	17
	Emergency combustible gas control	Failure of recombiners	0	13	16	12
	Containment spray system	Spray system not available	17	8	10	9
		Performance degraded	8	4	6	7
	Containment isolation system	Failure of vacuum breaker or isolation valve	2	2	3	3

Table 5: Summary of Licensee Event Reports Relating to Air-Monitoring, Air-Cleaning and Ventilation Systems (Pressurized-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

System	Component	Nature of problem	Number of events			
			1978	1979	1980	1981
Reactor cooling system (primary)	Pumps, valves, pressurizer, sensing lines, etc.	Excessive airborne release	11	6	4	7
Control room	Normal ventilating system	Failure of dampers or fans, or design error	2	3	9	12
		Failure of heaters, cooler, or compressors	3	2	11	4
	Emergency ventilating system	Failure of dampers or fans, or design error	5	10	15	21
		Leak in header	2	3	3	1
	Emergency sampling and monitoring system	Failure of chlorine or radiation detector	2	10	12	27
Enclosure building	Ventilating system	Water in off-gas pipe	0	0	0	2

Table 5: Summary of Licensee Event Reports Relating to Air-Monitoring, Air-Cleaning and Ventilation Systems (Pressurized-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

System	Component	Nature of problem	Number of events 1978	 1979	 1980	 1981
Fuel storage building	Ventilating system	Degraded charcoal filter or fan	1	3	5	6
	Atmospheric monitoring system	Failure of radiation monitor	1	3	3	5
Auxiliary building	Atmospheric monitoring system	Failure of radiation monitor	3	1	7	7
	Ventilation system	Failure of dampers or fans, or loss of power	3	3	7	11
		Filter plugging or heater failure	1	1	2	2
Diesel generator room	Ventilating system	Failure of dampers or fans, or design error	1	2	1	2
	Atmospheric monitoring system	Failure of radiation monitor	0	0	2	1
		Failure of temperature sensor	1	0	0	0

Table 5: Summary of Licensee Event Reports Relating to Air-Monitoring, Air-Cleaning and Ventilation Systems (Pressurized-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

System	Component	Nature of problem	Number of events 1978	1979	1980	1981
Turbine building	Atmospheric monitoring system	Failure of radiation monitor	3	5	8	14
	Ventilating, and HVAC system	Failure of air cooler	1	3	3	5
Waste-processing system	Waste gas decay tank	Excessive airborne release	2	1	7	6
	Waste gas surge tank	Excessive airborne release	1	1	3	1
	Waste gas vent header	Failure of radiation monitor on loop seal	0	2	1	2
		Excessive airborne release	4	0	0	3
		Deficiency in charcoal bed	0	0	1	0
		Isolation valves fail to close	2	1	2	3

Table 5: Summary of Licensee Event Reports Relating to Air-Monitoring, Air-Cleaning and Ventilation Systems (Pressurized-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

System	Component	Nature of problem	Number of events			
			1978	1979	1980	1981
	Liquid waste system	Excessive airborne release	0	0	0	0
	Sampling and monitoring system	Failure of sampling system	0	1	5	6
	Iodine removal tank	Hydrazine level low	1	0	0	0
Main stack discharge system	Gaseous and particulate monitoring system	Failure of sampling or monitoring system	4	9	10	24
	Air-flow system	Failure of exhaust fan	0	1	3	3
		TOTALS	232	225	316	400

Table 6: Overall Summary of Total Licensee Event Reports and Those Pertaining to Air-Cleaning, Air-Monitoring and Ventilation Systems in BWR and PWR Installations (Jan. 1, 1978 through Dec. 31, 1981)

Type of Installation	Total Number of LERs	Number & Percent of LERs Pertaining to Air Related Systems*		Number & Percent of LERs Pertaining to Air Monitors		
		Number	Percent	Number	Percent of Total	Percent of Those Pertaining to Air Related Systems*
BWR	5538	1261	(23%)	770	(14%)	(61%)
PWR	8589	1171	(14%)	629	(7%)	(54%)
TOTALS	14127	2432	(17%)	1399	(10%)	(57%)

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* Includes all LERs pertaining to failures in Air-Cleaning, Air-Monitoring and Ventilation systems.

Table 7: Summary of Licensee Event Reports Relating to Air-Monitoring Systems (Pressurized-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

Nature of problems		Number of events			
General	Specific	1978	1979	1980	1981
Failure of sampling system	Leaking or plugged sampling line	0	1	1	3
	Moisture in sampling line	1	1	1	3
	Failure of sampling pump or motor				
	Electrical	0	4	2	3
	Mechanical	20	25	30	38
	Failure of valves	5	14	11	14
	Design, maintenance or operator error	8	0	3	8
Failure of radiation monitor (gaseous)	Improper calibration or instrument drift	5	2	9	7
	Failure of detector or electronics	14	7	8	16
	Condensation in detector	0	1	3	5
	Failure of electrical system	10	5	12	20
	Failure of chart recorder	1	4	1	2
	Design, maintenance, or operator error	7	4	11	20
	Indeterminant malfunction	2	2	1	3

Table 7: Summary of Licensee Event Reports Relating to Air-Monitoring Systems (Pressurized-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

Nature of problems		Number of events			
General	Specific	1978	1979	1980	1981
Failure of iodine and particulate monitors	Failure of detector or electronics	3	8	4	6
	Failure of electrical system	5	6	5	5
	Failure of chart recorder				
	Design, maintenance, or operator error	5	6	7	9
Failure of hydrogen or oxygen monitor	Improper calibration or instrument drift	0	1	1	5
	Failure of sensor or electronics	1	1	3	2
	Condensation in sensor	0	3	1	3
	Design, maintenance, or operator error	2	1	4	5
	Indeterminant malfunction	0	0	0	2
Failure of pressure monitor	Improper calibration or instrument drift	3	9	3	4
	Failure of detector or electronics	3	7	12	4

Table 7: Summary of Licensee Event Reports Relating to Air-Monitoring Systems (Pressurized-Water Reactors, Jan. 1, 1978 - Dec. 31, 1981)

Nature of problems		Number of events			
General	Specific	1978	1979	1980	1981
	Design, maintenance, or personnel error	4	7	1	4
	Indeterminant malfunction	0	0	4	1
Failure of temperature monitor	Failure of detector or electronics		3	1	4
	Failure of electrical system		2	2	9
	Failure of chart recorder		1	2	3
	Indeterminant malfunction	1	0	0	0
Failure of chlorine monitor	Failure of detector unit	1	2	10	20
Failure of fire and smoke protection system	Failure of detector	1	2	2	4
	Inadvertent actuation of spray	0	3	2	2
	TOTALS	102	132	157	237

Table 8: Relative Distribution of Failures in Air-Monitoring Equipment (Jan. 1, 1978 - Dec. 31, 1981)

	BWR installations				PWR installations			
	Within primary containment		Within all systems		Within primary containment		Within all systems	
Type of monitor	Number	Percent	Number	Percent	Number	Percent	Number	Percent
Radiation monitors (gaseous)	59	15%	275	36%	181	45%	304	48%
Radiation monitors (particulate)	22	6%	39	5%	101	25%	128	20%
Pressure monitors	75	19%	100	13%	59	15%	68	11%
Hydrogen and oxygen monitors	207	52%	262	34%	35	9%	52	8%
Temperature monitors	30	8%	68	9%	24	6%	28	4%
Chlorine monitors	0	0%	8	1%	0	0%	33	5%
Fire and Smoke detector	3	1%	18	2%	6	1%	16	3%
TOTALS	396	101%	770	100%	406	101%	629	99%

Table 9: Contributions of Human Errors to Failures in Air-Cleaning Air-Monitoring, and Ventilation Systems in BWR and PWR Installations (Jan. 1, 1978, through Dec. 31, 1981)

	Air-cleaning events (BWR installations)			Air-cleaning events (PWR installations)		
Year	Total Number	Number attributed to human error	Percent attributed to human error	Total Number	Number attributed to human error	Percent attributed to human error
1978	239	65	(27%)	232	37	(25%)
1979	278	44	(16%)	225	38	(17%)
1980	335	53	(16%)	316	88	(28%)
1981	417	79	(19%)	400	104	(26%)

DISCUSSION

FISH: Is the noted increase in LERs a result of an increase in events or a better reporting system?

MOELLER: The increase is undoubtedly due in a major way to the increase in recent years in the number of commercial nuclear power plants in operation, as well as backfitting requirements developed as a result of the Three Mile Island accident. Unfortunately, the LER system does not provide data on failure rates; therefore, we do not know if the newer data reflect an increase in the rates of failures in air cleaning systems.

SCUDDER: In response to your challenge to utilities to become a part of this conference: can you suggest data compilation methods, format, sampling, etc. so that the utilities can become a useful filter/adsorber part of the data base?

MOELLER: In response to your inquiry, I want to offer the following comments relative to ways in which utility personnel might become more active in matters pertaining to air cleaning. Although there are several approaches you might take, let me offer the following suggestions. 1) Could you present a paper at the next Conference in which you share with other participants a listing of your major air cleaning problems and needs? If you covered subjects not covered by the LER system, this would be especially helpful. 2) What specific follow-up do you do on air cleaning LERs that are issued by your staff? Are you satisfied with the corrective actions taken? Which specific failures have you found most difficult to correct? 3) What has been your primary source of information on their subject? How adequate is the guidance provided by NRC Regulatory Guide (1.52) and professional society standards (ANSI/ASME N509 and N510)? 4) Have you developed inhouse competence in air cleaning or do you depend primarily on outside consultants and industrial organizations? How do you check designs provided to you to be sure they are adequate? 5) From the standpoint of inhouse competence, how have you trained your people? Which specific courses have you found helpful and where? To what extend have you incorporated air cleaning technology into the training programs for your plant staff? 6) There is a possibility that air cleaning failures may not be included in future NRC reporting requirements. To what extend do you believe INPO might be helpful in compiling such data and sharing it among the utilities? Would you be willing to assist in such an effort?

Undoubtedly there are additional areas that you might suggest. Basically, my thought would be to encourage you to write up your thoughts, experience, criticisms and suggestions, and to share them with other participants at the Conference. Such an exchange should be mutually beneficial.

CLOSING REMARKS OF SESSION CHAIRMAN:

Dr. Yusa discussed the use of silver-exchange alumina for iodine adsorption. His work has shown that depletion of the silver ion on alumina is substantially less than that in silver zeolite, and, therefore, produces higher removal efficiency than the zeolites. The specification of the porosity of the alumina is a novel advance.

Dr. Deitz described environmental tests at the Naval Research Laboratory to examine the performance of weathered charcoals under simulated accident conditions. One encouraging result he reported is a significant recovery of efficiency for trapping organic iodine compounds after irradiation. Requirements of the Regulatory Guide appear to be quite reasonable.

Dr. Freeman provided a comparison of two tertiary amine impregnants, TEDA and quinuclidine, for trapping methyl iodide by activated carbon. He found that the primary mechanism involved in trapping radioiodine is isotopic exhange between the radioactive iodine in the air stream with the normal iodine of the impregnant. He also found that the quinuclidine impregnant shows better effectiveness that TEDA.

Dr. Ringel discussed first, the removal of NO_2 using molecular sieves (the removal of ^{85}Kr for dissolver off-gas by sequential adsorption and desorption using molecular sieves.) On the basis of the experimental work, KFA has developed a tentative design process layout which utilizes the molecular sieve approach. Although the influence of the rubidium was not explored, the discussion at the end of the paper indicated that this should be no problem.

Dr. von Ammon described the behavior of nitric oxides in cryogenic separation systems and the effect of high oxygen concentrations in the carrier air. The work shows that the solubility of N_2O_4 in liquid krypton/xenon is extremely low, and that practically all of the NO_2 is collected in the column sump after the noble gases have been extracted. He also discussed the radiolytic generation of ozone and the possbility of ozone explosions in operating systems. He pointed out that a catalytic converter in systems of this type is essential.

Mr. Little stated that 86-90% of Kr must be removed under upcoming EPA regulations. He reported on the performance of a system based on a combined absorption and adsorption process for meeting this requirement. He concluded that the technology to meet the coming EPA regulation in fuel processing operations does exist today.

Dr. Moeller continued the analysis of LERs started at the 15th Air Cleaning Conference. The analysis shows air cleaning system events have increased from 11% in the 15th to 17% at this time for PWR's, and from 20% at the 15th to 29% at this Conference.