SESSION XI

REMOVAL OF NOBLE GASES, TRITIUM, AND ^{14} CARBON

Wednesday, August 4, 1976
CHAIRMAN: J. A. Buckham

OPENING REMARKS OF SESSION CHAIRMAN:

This session deals with the removal of gaseous isotopes which could be responsible for relatively low radiation exposures to the public. Because of the low resulting radiation exposures from release, no consensus has yet been reached on whether to remove these isotopes and, if so, when to start and to what degree to do it. It is fitting that there is such an international representation at this conference and, notably, in this session, because this really is an international problem. The low-level doses caused by these effluents would, in large measure, be coming from a uniform distribution of the isotopes in the world's atmosphere. Thus, the consensus I referred to should almost surely be an international consensus. It is significant that eight of the nine papers in this session deal with noble gas removal, which is a direct indication of the state of technological development in this general area. It is also significant that the papers deal largely with removal and cover lightly, if at all, what to do with the removed isotopes. I believe this fact brings up another significant general point in this whole area that cannot be overemphasized: that is, to assure that we have an adequate storage or disposal method before undertaking isotope removal. We must keep in mind that in removing these isotopes, we are converting a low-dose, high-probability risk to a high-dose, low probability risk--we hope. Since this conference is being held in Idaho, it is fitting to draw an analogy with a hydroelectric system where this conversion was improperly made, namely, the recent failure of the Teton Dam. One of the major justifications for construction of the Teton Dam was flood control--namely, the prevention of periodic, relatively small spring floods. This low-exposure problem was prevented this May, but in June, when the defective dam broke, the result, as you know, was a devastating loss of hundreds of millions of dollars and, miraculously, only eleven lives. Therefore, as we listen to these papers on removal, we should also keep in mind the necessity of developing disposal and containment methods for the removed isotopes so that the net result of our efforts is not another Teton Dam disaster.

THE DELAY OF XENON ON CHARCOAL BEDS

G. Collard, M. Put, J. Broothaerts, W.R.A. Goossens

S.C.K./C.E.N.
Mol (Belgium)

Abstract

The dynamical adsorption of Xenon on a fixed bed of charcoal type RBL-3 has been investigated in a 15 cm diameter column applying a ^{133}Xe pulse. The experimental break-through curves were fitted by the Gaussian relationships proposed by Underhill. All data are summarized by a Van Deemter's equation the parameter values of which have determined by non-linear regression analysis of the results.

I. Introduction

The radioactive level of the gaseous effluents from a nuclear power station depends on the performance of the gas cleaning techniques in use. Up to now, it is common practice to use buffer tanks - called delay tanks - as a mean to reduce the radioactive content of the gaseous effluents of a nuclear reactor. This technique relies on the knowledge that roughly 98 % of the instant radioactivity of the noble off-gases is caused by short-lived Xenon and Krypton isotopes.

The delay of a few weeks, generally obtained now in buffer tanks, does however not satisfy anymore the "as low as practicable" principle that has to be fulfilled in the future. Therefore, fixed beds of charcoal have been proposed. A Xenon delay time of about fifty days with a corresponding noble gas de-activation factor of about 700 is now accepted for design purposes (1).

In this context SCK/CEN at Mol has performed the following three studies :

- comparison of the Xenon adsorption capacity of European charcoals;
- study of the dynamical adsorption on a selected charcoal ;
- study of the behaviour of this latter in a pilot reactor.

This paper treats the dynamical adsorption of Xenon on a fixed bed of charcoal in order to obtain the necessary design equations. A European charcoal type RBL-3 has been chosen since this material showed a high adsorption capacity in the preliminary comparative study (2).

II. Experimental procedure

The experimental apparatus consists of three parts :

- the gas inlet where mainly stable Xe is traced with ^{133}Xe ;
- the proper adsorption column ;
- the outlet characterization section to measure the tracer concentration at any moment.

Figure 1 shows the different parts of the experimental apparatus, a view of which is given on figure 2.

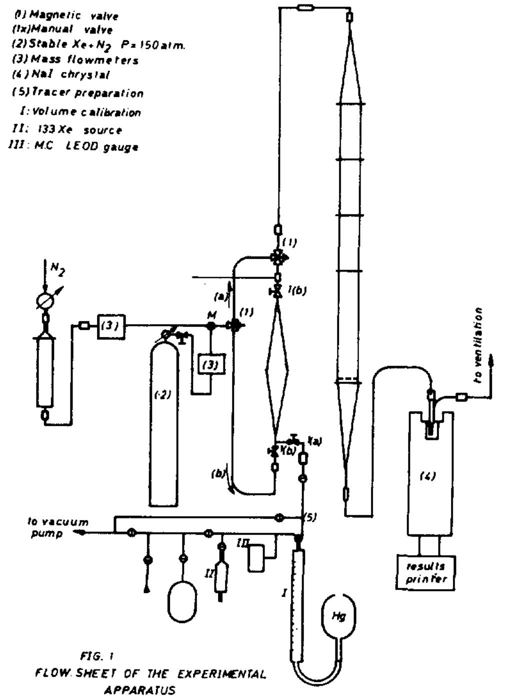

FIG. 1
FLOW SHEET OF THE EXPERIMENTAL APPARATUS

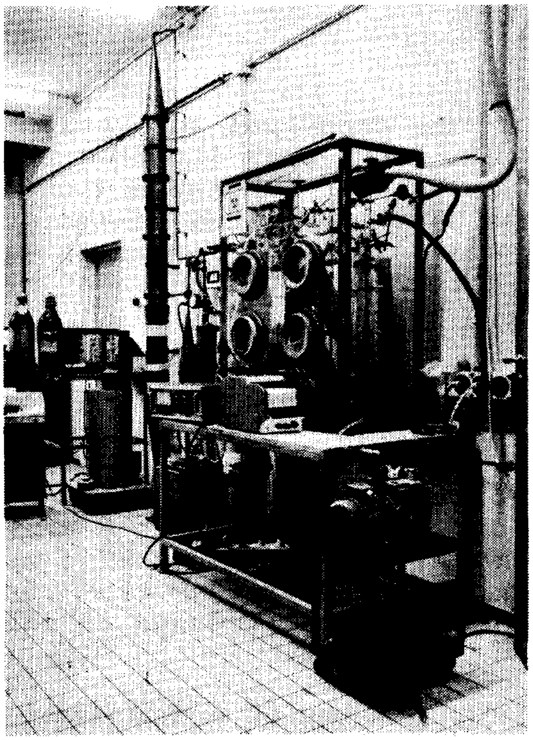

Fig. 2 Vew of the plant

In the gas inlet system a main feed stream, generally dry nitrogen, has been mixed with a side stream containing 8,000 ppm by volume of ^{131}Xe in order to obtain a Xenon inlet concentration between 50 and 600 ppm by volume. In a few runs, humid air at a relative humidity between 50 and 65 % was used as carrier gas.

The adsorption column consisted of 15 cm diameter tube, 2 m long mounted in a vertical position. This column was loaded with activated charcoal cylinders 3 by 3 mm to a height of 0.8 m. The total gas flow rate varied between 14 and 84 $10^{-6}m^3s^{-1}$. In some final runs with dry air, the charcoal height was increased to 2 m and the gas flow rate was varied between 4.4 and 695 $10^{-6}m^3s^{-1}$.

The gas mixture passed the column until saturation. At that moment, a pulse of radioactive ^{133}Xe was introduced by directing the main streaum for a while along a chamber previously filled with a mixture of nitrogen and ^{133}Xe at the initial Xenon inlet concentration. In this way, the radioactive pulse did neither change the over-all Xenon inlet concentration nor the steady state of the column. Moreover, entrance effects were minimized by using inlet and outlet cones with an angle of 10°C.

The break-through of the radioactive pulse was measured on line by gamma counting during 100 s with the help of a sensitive well-type NaI crystal. The dead time between consecutive countings varied from 260 to 1700 s depending on the gas flow rate used. The counting apparatus was connected to a teletype for printing and for punching on a tape which could be analysed straigth on a digital computer.

III. Mathematical analysis of the experimental data

In the computer analysis, the mean and the variance of each experimental curve were calculated. Further, each set of data points was fitted by a Gaussian function (3) and also by the Thomas's function (4). In both cases, the parameter values of these functions were calculated by minimizing the sum of the squares of the vertical distance between each experimental point and the corresponding function value. Both fittings showed no distinguishable difference, their resulting variances always differing less than 1 % from the variance of the experimental data. Therefore the Gaussian approximation was retained and Underhill's model (3) was applied.

Finally the linearity of the adsorption isotherm was verified and the dependence of the Gaussian parameters on the gas flow rate was determined.

IV. Results

The experimental conditions and data obtained are summarized in table 1.

IV.1. Capacity of the coal (fig. 3)

The capacity of the coal under these dynamical working conditions was derived by applying

$$q = \frac{G.C.t_{o.5}}{M} \qquad (1)$$

where :

q = adsorption capacity of the charcoal : $Nm^3Xe.kg^{-1}coal$

G = carrior gas flow-rate : Nm^3s^{-1}

C = Xenon concentration : $Nm^3Xe.NM^{-3}$ carrier-gas

$t_{o.5}$ = mean stay time of Xe in the bed : s

M = mass of the bed : kg

Table I.; Experimental results : Carrior gas - dry nitrogen

	I	II	III	IV	V	VI	VII	VIII	IX	X
Run	Column height (m)	Gas flow-rate m^3s^{-1}	Xe concentration ppm volume	Mean stay time of Xenon (t.o.s) 10^3s	Mean stay time of carrior gas of empty column s	Delay Factor $\frac{IV}{V}$	Variance of Gaussian approxim. 10^3s	Number theoretical plates	Height of a theoretical plate $10^{-2}m$	Coal capacity $10^{-3}\ Nm^3kg^{-1}$
1	0.8	2.1 10^{-5}	200	202	673	300	22.7	79.2	1.01	0.14
2		1.4 10^{-5}	200	307	1009	304	37.6	66.8	1.20	0.14
3		8.3 10^{-5}	200	49	170	291	5.5	79.6	1.01	0.13
4		8.3 10^{-5}	200	48	170	282	5.5	75.3	1.06	0.13
5		8.3 10^{-5}	150	48	170	282	5.6	75.6	1.06	0.10
6		8.3 10^{-5}	100	47	170	276	5.3	82.6	0.97	0.07
7		8.3 10^{-5}	50	50	170	294	5.6	79.8	1.00	0.03
8		2.1 10^{-5}	200	187	673	278	20.9	80.1	1.00	0.13
9		2.1 10^{-5}	150	209	673	310	23.8	78.4	1.02	0.11
10	2.0	1.4 10^{-5}	300	695	2523	275	51.4	182.9	1.09	0.19
11		20.8 10^{-5}	300	51	170	300	4.0	164.9	1.21	0.20
12		8.3 10^{-5}	300	126	495	296	8.3	231.5	0.87	0.20
13		11.1 10^{-5}	300	98	318	308	6.1	254.5	0.79	0.21
14		5.5 10^{-5}	75	220	638	346	13.1	284.0	0.70	0.06
15		30.5 10^{-5}	75	37	115	322	3.2	131.6	1.52	0.05
16		25.0 10^{-5}	75	42	140	300	3.7	129.7	1.54	0.05
17		0.4 10^{-5}	600	2377	8835	270	255.9	86.3	2.32	0.41
18		55.5 10^{-5}	75	21.2	64	331	2.2	89.4	2.28	0.06
19		69.4 10^{-5}	75	16.8	51	330	2.0	72.2	2.77	0.06

This adsorption capacity depends on the partial of Xenon. Expressed in usual units, the following dependence was found :

$$q = 0.91 \quad 10^{-3} \; p \qquad (2)$$

where the partial pressure of Xenon p, is expressed in mm Hg

$$1 \text{ mm Hg} = \frac{1}{133} \text{ Pa}$$

This expression differs slightly from the equation

$$q = 1.13 \; 10^{-3} p^{1.07} \qquad (3)$$

obtained under conditions in the preliminary comparative study (2) by regression analysis of the experimental results.

Both expressions (2) and (3) indicate that the partial pressure of Xenon is the only important parameter influencing the adsorption isotherm ; the composition of the carrier gas being either dry air or nitrogen showed no effect at room temperature.

The linearity of the adsorption isotherm makes the delay factor of the charcoal bed independent as well of the Xenon concentration as of the gas flow rate. This delay factor generally is put equal to the ratio of Xenon mean residence time to the mean residence time of the carrier gas in the empty column. It depends on the characteristics of the coal used and on the main gas component absorbed while other gaseous compounds (for example, humidity) might disturb the phenomena. The delay factor of Xenon has a value of the order of 300 for the coal studied.

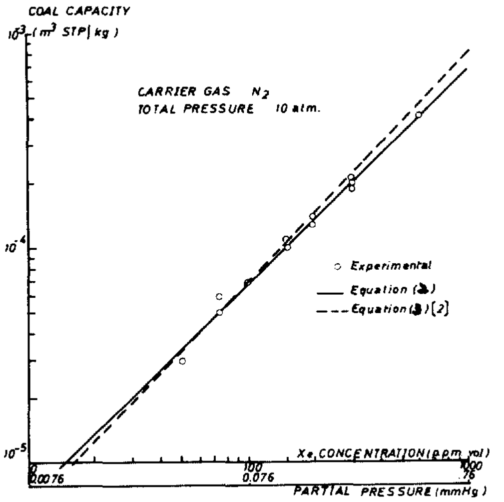

FIG. 3 ISOTHERM OF XENON ADSORPTION AT 25° C

2. Effect of gas flow rate on the variance of the break-through curve (3)

In Underhill's model, the number of theoretical plates, N, is expressed by

$$N = \frac{t_{0.5}^{2}}{\sigma 2} \qquad (4)$$

with σ = variance of the break-through curve (s)

Moreover, the length of a theoretical plate H is given by

$$H = \frac{L}{N} \tag{5}$$

with : L = bed length (m)

According to Van Deemter the length of a theoretical plate for a given process is the result of three phenomena so that the following relationship exists :

$$H = \frac{A}{Vi} + B + C\ Vi \tag{6}$$

where V_i is the superficial velocity.

Equation (6) can be generalized and written in non-dimensional nummbers (3)

$$h = \frac{a}{v_i} + b + c\ v_i \tag{7}$$

where h = reduced height of a theoretical plate

v_i = reduced interparticle velocity.

The values of the coefficients in the latter two equations were determined for the conditions of this study by non-linear regression analysis between the experimental N value and the operating value of the superficial velocity.

This analysis gives the following expression

$$H = \frac{4.62\ 10^{-6}}{V_i} + 5.1\ 10^{-3} + 0.45\ V_i \tag{8}$$

or

$$h = \frac{0.82}{v_i} + 1.7 + 0.35\ v_i \tag{9}$$

Figure 4 shows that the curve related to equation (8) fits quite well the experimental values of the height of a theoretical plate.

Figure 5 illustrates for typical working conditions how good the experimental points are fitted by the Gaussian function the parameters values of which were calculated by applying equations (1), (2) and (8).

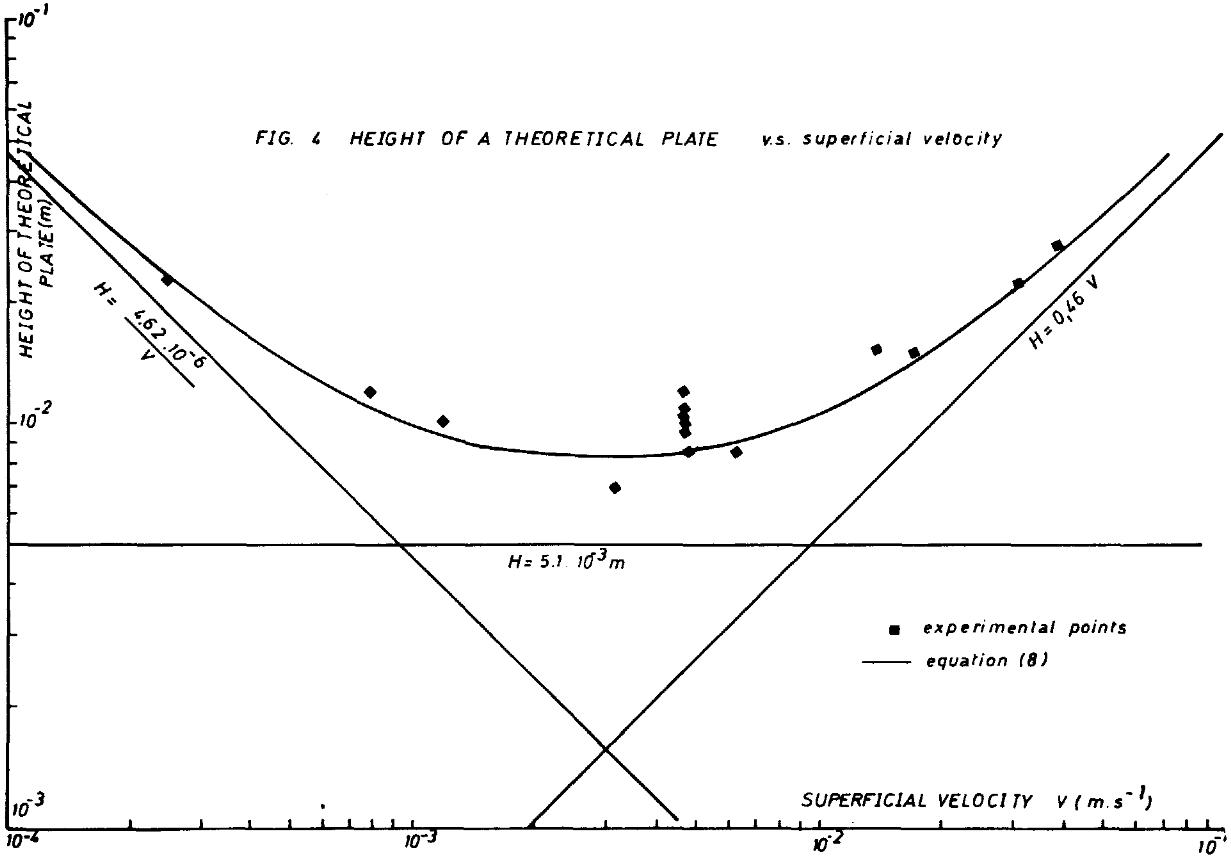

FIG. 4 HEIGHT OF A THEORETICAL PLATE v.s. superficial velocity

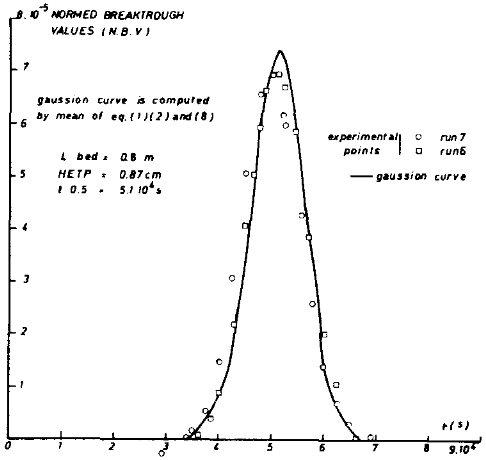

FIG. 5 ILLUSTRATION OF THE UNDERHILL'S MODEL

V. Additional experimental results

In order to evaluate the influence of humidity on the performance of the charcoal, five additional runs were done on the 0.80 m long bed. The conditions and results of these tests are summarized in table 2.

Table 2 : Experimental results; carrier gas : humid air

Run	Gas flow rate $m^3\ s^{-1}$	Xe conc. ppm	Relative humidity at 25°C %	Mean stay time of the 10^3 s	Delay factor	Variance σ 10^3 s	Number of theoretical plates	Height of a theoretical plate 10^{-2}m
20	5.5 10^{-5}	600	60	33	96	3.6	87.1	0.92
21	5.5 10^{-5}	600	53	43	125	4.5	94.0	0.85
22	8.3 10^{-5}	200	64	20	118	2.3	73.1	1.09
23	8.3 10^{-5}	600	64	18	106	2.1	69.3	1.15
24	8.3 10^{-5}	50	66	18	106	2.2	70.0	1.14

By comparing the values of tables 1 and 2, it can be seen that the delay factor is reduced by a factor 3 at 60-65 % relative humidity. Nevertheless, the height of a theoretical plate is only slightly influenced.

VI. Further work

Based on the results obtained so far((2) and present work) a pilot delay bed has been constructed on the off-gas systems of the pilot nuclear power station BR3 (10 MWe). This delay system consists of two columns 0.5 m in diameter and 5 m in height connectable in parallel or in serie. The reception runs will start as soon as BR3 will be put on power.

VII. Conclusion

In order to reduce radwaste of L.W.R. gaseous effluents, a complete study has been undertaken at SCK/CEN. The first two parts of this study have been completed, the results of which can be used to compare different European coals and to design delay beds for Xenon in dry or humid air or nitrogen. The effect of coal ageing, radioactivity and other reactor parameters will be studied in the near future and will allow to design delay beds for the retention of Xenon from reactor effluents on mathematical bases.

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DISCUSSION

UNDERHILL: Your equation nine has coefficients which are very similar to those found in experiments which I carried out earlier using krypton at the temperature of dry ice. I believe that the values of the first two coefficients in this equation are not strongly dependent upon the temperature of fission gas that is used in the adsorbent experiments. I think the closeness of agreement between your results and the ones I have under quite different conditions may indicate that these values can be used as general values for experiments of this type. The first two coefficients should be determined by the packing of the bed and the third should be dtermined by diffusion of the fission gas in the adsorbent particles.

COLLARD: I agree completely with you and I think most people acknowledge it. Moreover, the exchange zone is so small that it will never influence very much the performance of the column. Therefore, these studies must be performed to know the range of usable gas velocities, but not to fix them in a narrow range.

UNDERHILL: One final point. I took the data that I had in these earlier experiments and examined them by using moment analysis. It did not make much difference in the values of the coefficients, but the moment analysis technique is mathematically exact. It's an exact solution to the mathematical equations for the transfer through adsorption beds. Having a mathematically exact solution allows you to take data from columns of all sizes and compare them without having to use full scale data. You do not merely rely on the Gaussian approximations.

The point is that it includes all kinds of factors and is far more general than, say, using something of the Thomas equation and, yet, is quite a simple technique.

COLLARD: Yes, I think most people acknowledge it, but there are a number of complex factors such as the exchange zone being so small that it will never influence turbulence.

RIVERS: As you stated in your presentation, the correlations on page 6 do not provide reasonable descriptions of the device. Without going deeply into filtration theory, more reasonable correlation forms might be:

For downstream concentration,

$$C_0 = C_i \, e^{-K \, L^m \, D_p{}^n} \qquad (1)$$

where C_i is inlet concentration. Taking logs,

$$\ln(C_0/C_i) = -K \, L^m \, D_p{}^n$$

$$\text{and } \ln(C_i/C_0) = \ln K + m \ln L + n \ln D_p \qquad (2)$$

The values of K, m and n are easily evaluated. Could you provide your data for such an evaluation? For pressure drop, we could use:

$$\Delta P = K \, G^p \, D_p{}^q$$

and proceed as before.

GOSSENS: We can not agree with your first sentence as you stated it. The correlations on page 6 are regression equations for the data obtained using the technique of parameter planning. These equations reflect an exact description of the data points but do not describe the performance of the device, as such, so that interpolations and extrapolations give only reasonable estimates. If correlation (1) of your question is applied on our factorial design data [this implies two "ln" in the left side of equation (2) and not one "ln" as indicated in your letter], the following constant values are obtained:

$K = 3.11$
$m = 0.31$
$n = -0.33$

The following table indicates that, in this way, a description of the data points can be obtained with the same degree of accuracy as that given by the first regression equation on page 6 of our paper.

values for ln $\frac{C_i}{C_o}$	
data point values	calculated values
4.868	4.908
4.193	4.146
6.376	6.320
5.277	5.345

We did not measure the pressure drop, but rather, the pressure increase per hour.

THE RELEASE OF ADSORBED KRYPTON AND XENON FROM SPILLED CHARCOAL

D. W. Underhill
Harvard Air Cleaning Laboratory
Boston, Massachusetts

Abstract

The rate of release of the fission gases, krypton, and xenon, depends on the depth of the spilled charcoal, the decay constant of the fission gas, and the initial distribution of fission gas within the spilled charcoal. A mathematical analysis of the rate of release is presented here which takes into account the initial distributions which may be encountered in practice. It is found that: (1) fission gases more than 15 cm from the surface generally decay within the charcoal before diffusing to the surface; (2) xenon isotopes diffuse relatively slowly and that the release of xenon can be protracted over several days and (3) the initial distribution has a strong effect on both the rate of release and the fraction of fission gas released. These equations can be applied to the release of fission gases from a charcoal adsorption bed following rupture (as for example by an earthquake). It is suggested that in order to minimize the possible release of fission gases during such an incident that during normal operation a charcoal adsorption bed be operated at a flow rate above a certain minimum for this would prevent the adsorbed fission gases from being contained within a shallow area from which their release could be relatively rapid.

I. Introduction

The use of charcoal in fission gas holdup systems has several advantages. The first and most important is that the use of a charcoal adsorbent considerably reduces the volume of the holdup system. Another advantage is that if there were a rupture in a holdup tank, the fission gases would be retained in the charcoal far longer than they would be in the ruptured tank. This paper addresses the problem of calculating the retention of krypton and xenon in charcoal spilled from a holdup bed. If these calculations prove useful in the design of nuclear containment systems, particularly if they are helpful in reducing redundant conservatism, they will have served their purpose.

II. Diffusion of Krypton and Xenon in Bulk Charcoal

The first step in calculating the loss of fission gases from spilled charcoal is to determine the diffusion coefficient for the fission gases within the bulk charcoal. The formula used for this purpose is:

$$D = \gamma_g f_g D_g + \gamma_c f_c D_c \tag{1}$$

where D = diffusion coefficient for fission gas in bulk charcoal, cm^2/sec

γ_g = tortuosity factor for diffusion in the interparticle void volume, dimensionless

f_g = fraction of the fission gas, at equilibrium, in the interparticle void volume, dimensionless

D_g = diffusion coefficient for fission gas in the carrier gas at ambient temperature and pressure, cm^2/sec

γ_c = tortuosity factor for diffusion through the matrix of the charcoal, dimensionless

f_c = fraction of the fission gas, at equilibrium, within the adsorbent particles, dimensionless

D_c = diffusion coefficient for fission gas within an adsorbent particle, cm^2/sec

The above equation can be criticized for neglecting the coupling of diffusion between the inter- and intraparticle volumes. This simplification is valid because D_c is generally very small. In practice the term D_c can usually be neglected and D calculated as:

$$D = \gamma_g f_g D_g \tag{2}$$

The next step is to determine reasonable values for γ_g, f_g, and D_g. The value for γ_g, as determined from many experiments in gas chromatography and chemical engineering, has a range of 0.5 to 0.9. In the results given in Table 1 a value of 0.6 was assigned to γ_g. The factor f_g can be determined from:

$$f_g = \frac{\varepsilon}{\rho K} \tag{3}$$

where ε = fractional interparticle void volume, dimensionless

ρ = bulk density of the charcoal, gm/cm^3

K = bulk adsorption coefficient for the fission gas, cm^3/gm.

The diffusion coefficient, D_g, may be estimated using the equation of Kirschfelder, Bird, and Spotz(1).

By means of the above formulas, estimates were made of the bulk diffusion coefficients for krypton and xenon in a commercial charcoal (Barneby Cheney type 483/AK). Experimental measurements are also available giving the measured coefficients for bulk diffusion(2). The results are shown in Table 1. As the predicted diffusion coefficients relied on estimated values for K, ε, and γ_g, the agreement between theory and experiment is as good as could be expected.

III. Integration of the Basic Differential Equation

The next step is to calculate the change in concentration across a large mass of spilled charcoal. If diffusion and radiodecay are the controlling factors, mass transfer is described by the following partial differential equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \lambda C \qquad (4)$$

where D = diffusion coefficient for fission gas within bulk charcoal, cm^2/sec

C = concentration of fission gas within the bulk charcoal curies/cm^3

λ = decay constant for fission gas, sec^{-1}

t = time, seconds

x = vertical distance, cm

Three boundary conditions are required for the solution of the above equation. The first comes from the assumption that fission gas at the bottom of the spill is not expected to diffuse appreciably into the floor. Then:

$$\frac{\partial}{\partial x}(C\ (x=0,\ t>0)) = 0 \qquad (5)$$

The second assumption, that the charcoal is spilt to a height, L, and that at the surface of the charcoal, equilibrium exists between the charcoal and a large volume of fresh air, leads to the equation:

$$C(x=L,\ t>0) = 0 \qquad (6)$$

The most difficult boundary condition to establish is the initial distribution of fission gas within the spilt charcoal. It is known that in the intact holdup beds before spillage occurred, the concentration of each isotope will be an exponential function of distance. We should consider the most dangerous type of spill to be one in which the most contaminated charcoal is nearest the surface of the spill. This is an extremely conservative assumption - perhaps to the point of being unrealistic - for it is far more likely that a spill would lead to mixing of the charcoal and that as a result there would be no significant concentration gradient in the charcoal. Nevertheless both cases can be examined if the concentration of fission gas is assumed to have the following initial distribution with respect to the height above the floor.

$$C(t=0) = C_o e^{-\alpha(L-x)} \qquad (7)$$

where C_o = the concentration of fission gas initially at the surface of the spill, curies/cm^3

α = exponential coefficient describing the initial distribution of fission gas within the charcoal, cm^{-1}. The factor, α, will equal zero is the charcoal is thoroughly mixed in spilling.

The integration of Equation 4 by means of a Fourier series leads to the following equation for the total fraction of the curies originally contained within the charcoal that would be released by time t.

$$f = \sum_{N=1}^{\infty} \left(\left(\frac{8 + \dfrac{(-1)^N\, 16\, \alpha\, L\, e^{-\alpha L}}{(2N-1)\pi}}{(2\alpha L)^2 + (2N-1)^2\, \pi^2} \right) \Bigg/ \left(\frac{\alpha L \left(1 - e^{-\left(\frac{D\pi^2 (2N-1)^2}{4L^2} + \lambda\right)t}\right)}{\left(1 + \dfrac{4\lambda L^2}{D\pi^2 N}\right)(1 - e^{-\alpha L})} \right) \right) \tag{8}$$

As t→∞ the above equation converges to:

$$f = \frac{D\alpha^2 \left(\operatorname{sech}\left(\sqrt{\frac{\lambda}{D}}\, L\right) e^{-\alpha L} - 1\right) + \alpha \sqrt{\lambda D}\, \tanh \sqrt{\frac{\lambda}{D}}\, L}{(\lambda - D\alpha^2)\,(1 - e^{-\alpha L})} \tag{9}$$

If it is assumed that good mixing of the fission gases has taken place within the charcoal at the time of the spill, then $\alpha=0$ and:

$$f = \sum_{N=1}^{\infty} \left(\frac{8}{(2N-1)^2\, \pi^2} \right) \left(\frac{1 - e^{-(D\pi^2\, (2N-1)^2 + \lambda)t/L^2}}{1 + \dfrac{\lambda L^2}{D\pi^2 N}} \right) \tag{10}$$

And under these conditions as t→∞:

$$f = \frac{\tanh \left(\sqrt{\frac{\lambda}{D}}\, L\right)}{\sqrt{\frac{\lambda}{D}}\, L} \tag{11}$$

Only one factor remains unresolved before calculations can be made, and that is the maximum value for α. But this factor can be determined from the fact that the concentration difference across the spilt charcoal should be no greater than that existed in the charcoal in the intact holding bed. The difference in concentration, or more precisely the ratio between the highest concentration and the lowest concentration in the intact bed should be given by:

$$\frac{C}{C_o} = e^{-\frac{km\lambda}{v}} \tag{12}$$

where k = adsorption coefficient for fission gas, cm^3/gm

m = grams of adsorbent

λ = decay coefficient for fission gas, sec^{-1}

v = flow of air through bed during normal operation, $cm/^3sec$

The ratio of the highest to lowest concentration in the spilled charcoal is given by:

$$\frac{C}{C_o} = e^{-\alpha L}, \tag{13}$$

therefore, the maximum value for α is:

$$\alpha = \frac{km\lambda}{vL}. \tag{14}$$

IV. Estimated Releases from Spilled Charcoal

The results obtained using the equations developed in the previous section are shown here in a series of graphs. Figures 1-4 illustrate the loss of krypton and xenon from charcoal spills in which there was an initially homogeneous distribution of krypton and xenon in the spilled charcoal. By comparison of the results shown in these figures it is immediately apparent that (1) the release of krypton is more rapid than for xenon, (2) that the fraction that is released from a spill increases with increasing half life, and (3) that the deeper the spill the smaller the fraction of the fission gas that is released.

The effect of spill depth is clearly shown in Figures 5 and 6, which give the total fraction that can be released as a function of the depth of the spilled charcoal. Note that for beds several times deeper than $\sqrt{D/\lambda}$, the fractional release is equal to $\sqrt{D/\lambda}$ /L.

The final two graphs show the effect of both bed depth and the initial distribution of fission gas on the total fraction of fission gas that will be released. For values of $\alpha L >> 1$, the fractional release can be appreciable. The real danger brought to light by this analysis is that if the fission gases are concentrated into a small volume of charcoal, then spillage of this highly active charcoal could result in a significant release of fission gas. It is suggested that in order to minimize the possible release of fission gases during such an incident that during normal operation a charcoal adsorption bed be operated at a flow rate above a certain minimum for this would prevent the adsorbed fission gases from being contained within a shallow area from which their release could be relatively rapid.

V. Summary

The results presented here give estimates of the loss of krypton and xenon by diffusion from spilled charcoal. In making these estimates the following steps were taken.

1. A theory developed for diffusion in bulk charcoal.
2. Measurement of diffusion rates and finding results which agreed with theoretical analysis.

3. Development of a theory to predict the loss of radioactive fission gases from spilled charcoal.

It has been the purpose of this paper to show what degree of the activity contained within a spill can be expected to be released and thereby give design engineers the ability to make reasonable estimates of accident conditions.

Table I Predicted and measured bulk diffusion coefficients.

		Bulk Diffusion Coefficient, cm^2/sec	
		Predicted	Measured
Fission Gas	Krypton	2.1×10^{-3}	1.6×10^{-3}
	Xenon	9×10^{-5}	7×10^{-5}

References

1. R.H. Perry, ed., Chemical Engineers' Handbook, 4th edition, McGraw Hill, New York, 1963 (Equations 14-57).

2. D.W. Underhill, "Release of Krypton and Xenon from Spilled Charcoal." Accepted for publication in Nuclear Science and Engineering.

DISCUSSION

PALMER: It would seem to me that these calculations are of academic interest only. In other words, if an accident occurred of such magnitude to spill the charcoal, there would be enough other serious hazards that the release of the adsorbed krypton and xenon would be a minor concern.

UNDERHILL: That is not always true. This analysis was developed to learn what would happen if there were a severe earthquake in a nuclear reactor complex. The working assumption in the analysis is that the reactor itself would be designed to withstand an earthquake of any magnitude considered possible, but that the fission gas holdup beds were not so designed.

WATT: At the loading that you suggested, I am wondering whether decay heat would not produce sufficient temperature differences in various portions of the beds to produce convective flow rather than pure diffusion.

UNDERHILL: That is a good question. There is a minimum loading of fission gas required for heating effects to become important. I calculate that, at a loading of 100 Ci of Xe-133/kg of charcoal that the initial temperature rise would be 0.1°C/day, and in the absence of connection and thermal diffusion, the charcoal would reach a maximum of 0.7°C above its surroundings. At this loading, thermal effects are not important.

Krypton isotopes at the same initial loading would give a similar initial temperature increase, but as a result of the shorter half life of the krypton isotopes, the final temperature rise would be considerably less.

Finally, it would appear that even if the interior of a mass of spilled charcoal were to heat up, cooling of the surface areas of the charcoal by thermal diffusion would create a retentive layer which would effectively adsorb the fission gases released from the interior. This phenomenon deserves further study.

MEARDON: Has there been or is there to be consideration given to an accident condition involving the combustion of the charcoal bed? This would seem to be a maximum credible accident for this type system.

UNDERHILL: That is not always true - this analysis was developed to learn what would happen if there were a severe earthquake in a nuclear reactor complex. The working assumption in this analysis is that the reactor itself would be designed to withstand an earthquake of any magnitude considered possible, but that the fission gas holding beds were not so designed.

DEVELOPMENT OF THE CRYOGENIC SELECTIVE ADSORPTION-DESORPTION PROCESS ON REMOVAL OF RADIOACTIVE NOBLE GASES

T. Kanazawa, M. Soya, H. Tanabe, B. An
Kobe Steel, Ltd., Kobe, Japan.

Y. Yuasa, M. Ohta, A. Watanabe, H. Nagao, A. Tani,
Nippon Atomic Industry Group Co., Ltd., Kawasaki, Japan.

H. Miharada,
Tokyo Shibaura Electric Co., Ltd., Tokyo, Japan.

Abstract

Cryogenic selective adsorption-desorption process was developed as an effective means of removing the radioactive noble gases. A series of experiments and evaluation studies have been performed to develop a new type off gas clean up system which adopted the above process to remove the noble gases from the off gas streams of nuclear facilities.

The fundamental processes of our proposed clean up system are as follows; 1) Noble gas enrichment process to remove and enrich the radioactive noble gases from off gas, 2) Oxygen removal process to remove oxygen and oxide impurities from enriched gas and 3) Storage process to store enriched gas into cylinder. For the first process, the "selective adsorption-desorption" method was adopted. The laboratory scale experiments were performed to investigate the breakthrough and enrichment. And the engineering scale experiments are being carried out to confirm them. For the second process, "metal getter absorption" method has been developed. The static experiments were performed with heated zirconium metal getter. And the dynamic experimental apparatus is constructed and will be operated. For the third process, "adsorbent packed cylinder" method has been developed. From the laboratory experiment, it has been proved to have several advantages.

This investigation showed that the proposed methods could be applied to the off gas clean up system of the nuclear facilities.

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   - 3.1 General Description and Definition
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     - 3.3.1 Test Plant
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4. Oxygen Removal Process
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   - 4.2 Study of Dynamic Experimental Apparatus

5. Storage Process
   - 5.1 Experimental
   - 5.2 Results and Discussion

6. Conclusion

1. Introduction

A majority of the present BWR power plants equip with charcoal delay beds operated at ambient or reduced temperature for their off gas clean up systems. These charcoal beds will delay noble fission gases long enough to allow the shorter lived nuclides to decay to a small fraction of their original activity, and total activity release to the environment is controlled enough below 'as low as reasonably achievable' criteria. However, as they have no decay effect to the longer lived nuclides such as Kr-85, the obtainable decontamination factor (DF) of this delay bed type system will not be able to exceed about 10^4. The DF of some conventional delay bed systems with several ten tons of charcoal is estimated as about 10^2, and almost two hundred tons of charcoal will be required for the DF of 10^4.

Consequently, for the future power plants near populous area or to build several of them in one site, it will be significant to develop a new type of off gas clean up system which should be constructed at reasonable cost compared with the delay bed type system and is able to remove even long life noble gas nuclides such as Kr-85.

From this point of view, we have started to study a total system which could effectively remove radioactive noble gas nuclides from off gas streams of nuclear facilities and store them safely for a long time period. For the noble gas enrichment process, the most important process of the total off gas clean up system, the "selective adsorption-desorption" method[1)] has been developed and been proved to be promising for our purpose by the laboratory scale experiments. For the storage process, "adsorbent-packed cylinder" method has been developed. From the laboratory scale test, this storage method has been proved to have several advantageous points compared with conventional cylinder method. In case the oxygen gas in off gas stream is not removed prior to the enrichment process, oxygen and some gaseous oxide impurities in enriched gas should be removed prior to its long term storage. For this oxygen removal process, "metal getter absorption" method has been developed. Based on the experimental results of these methods, a feasibility study for the applicability of these methods to BWR off gas clean up system has been performed. Also, engineering test plant scale test facility for the enrichment process has been constructed, and its performance are now being studied.

In this article, the details of our new off gas clean up system will be shown. Also, the results of the laboratory experiments for individual processes in the total off gas clean up system and some of the results from performance test of the engineering test plant for the noble gas enrichment process will be discussed.

2. Proposed Off Gas Clean Up System

A total off gas clean up system could consist of several subsystems. Prior to determining the construction of these subsystems or their individual processes for our total system, evaluation studies concerning safety, economy, performance and others of the many existing processes have been performed. As a result, several criteria to develop our off gas clean up system have been settled. Although the details of the discussions for this studies will not be shown here, some of the representative criteria are as follows ;

1. apply the "selective adsorption-desorption" method to the noble gas enrichment process,
2. operate as many subsystems under subatmospheric pressure as possible,
3. remove oxygen and gaseous oxide impurities after noble gas enrichment process,
4. adopt synthetic zeolite beds rather than reversing heat exchanger to remove moisture and carbon dioxide before cooling the off gas flow,
5. circulate the enriched gas on the adsorption bed batchwise between the bed and off gas inlet flow until the required enrichment are obtained,
6. adopt two adsorption beds system rather than three beds system for the noble gas enrichment, and
7. adopt cryogenic "adsorbent-packed cylinder" method to eliminate any compressors for the transportation of the enriched gas to a storage container.

Based on these considerations, a total process as shown in Fig. 1 has been proposed for our off gas clean up system.

Description of the Proposed Total Process

BWR off gas is extracted from the main condenser via the steam jet air ejector (SJAE) and transferred to the plant off gas system. Its constituents are air introduced into the condenser by leakage, hydrogen and oxygen produced by radiolytic decomposition of the coolant water, small amounts of short-lived gaseous activation products, fission gases and a large volume of steam. As shown in Fig. 1, most of steam, hydrogen, oxygen and activation products are removed at an off gas pre-treatment section, recombiner and cooler, which is the same section as in conventional off gas line, resulting the principal off gas constituents are air containing moisture, carbon dioxide and noble gases.

The effluent stream of the pre-treatment section enters the moisture/ carbon dioxide remover, the main portion of which consists of two adsorption beds filled with synthetic zeolite, where moisture and carbon dioxide are removed and their effluent concentration are made of the order of ppm. Since synthetic zeolite can adsorb more or less noble gases, it should be noticed that radioactivity could come out at regenerating step of the bed. At the regenerating step of the moisture/carbon dioxide remover bed, noble gas, CO_2 and moisture are desorbed in this order with increasing temperature. In our process utilizing this desorption characteristic, decrease of overall decontamination factor of the system which possibly arises from this step is eliminated by returning the initially desorbed gas, which contains most of all noble gases having been adsorbed on the bed, to the SJAE.

The effluent of the moisture/carbon dioxide remover then flows through the heat exchanger, where it is cooled to -170°C. Most of cooling source is provided with effluent stream from cryogenic adsorption bed and shortage of the cooling is supplemented with liquid nitrogen.

Subsequently, cooled off gas enters the cryogenic adsorption bed, where noble gases are removed from off gas stream, returns to the heat exchanger and is utilized as cooling source as mentioned above, and finally is released from the plant stack to the atmosphere.

Noble gas concentrator consists of two adsorption beds. Off gas or effluent of the heat exchanger, first enters one of these beds. At the time when the exit krypton concentration reaches a certain level, the flow pass is changed to the second bed (adsorption step). Then the first bed is regenerated and recooled. The present method has the special characteristics in this regeneration step. That is, the desorbed gas is recycled to SJAE (recycle step) for a certain times after a conventional regeneration step, and then the bed undergoes the following two different types of succeeding processes, regeneration at low temperature and pressure (selective desorption step) and regeneration step with increasing temperature. The selective desorption process is also conducted with increasing bed temperature but still at relatively low temperature, for instance from -170°C to -100°C. At this range of temperature increase, most of all nitrogen and oxygen adsorbed on the bed are desorbed, but yet noble gases are almost completely kept adsorbed on the bed. The desorbed gases at this step are returned to the inlet of SJAE. Thus the noble gases are doubly concentrated at the adsorption step first and then at this selective desorption step. So, the authors have named this concentration process as selective adsorption-desorption method. Concentrated noble gases are finally desorbed from the bed by raising the bed temperature up to 50°C ~ 100°C, and are sent to the noble gas storage system.

In regard to conventional noble gas enrichment methods, both thermal swing and pressure swing methods can get relatively low enrichment factor

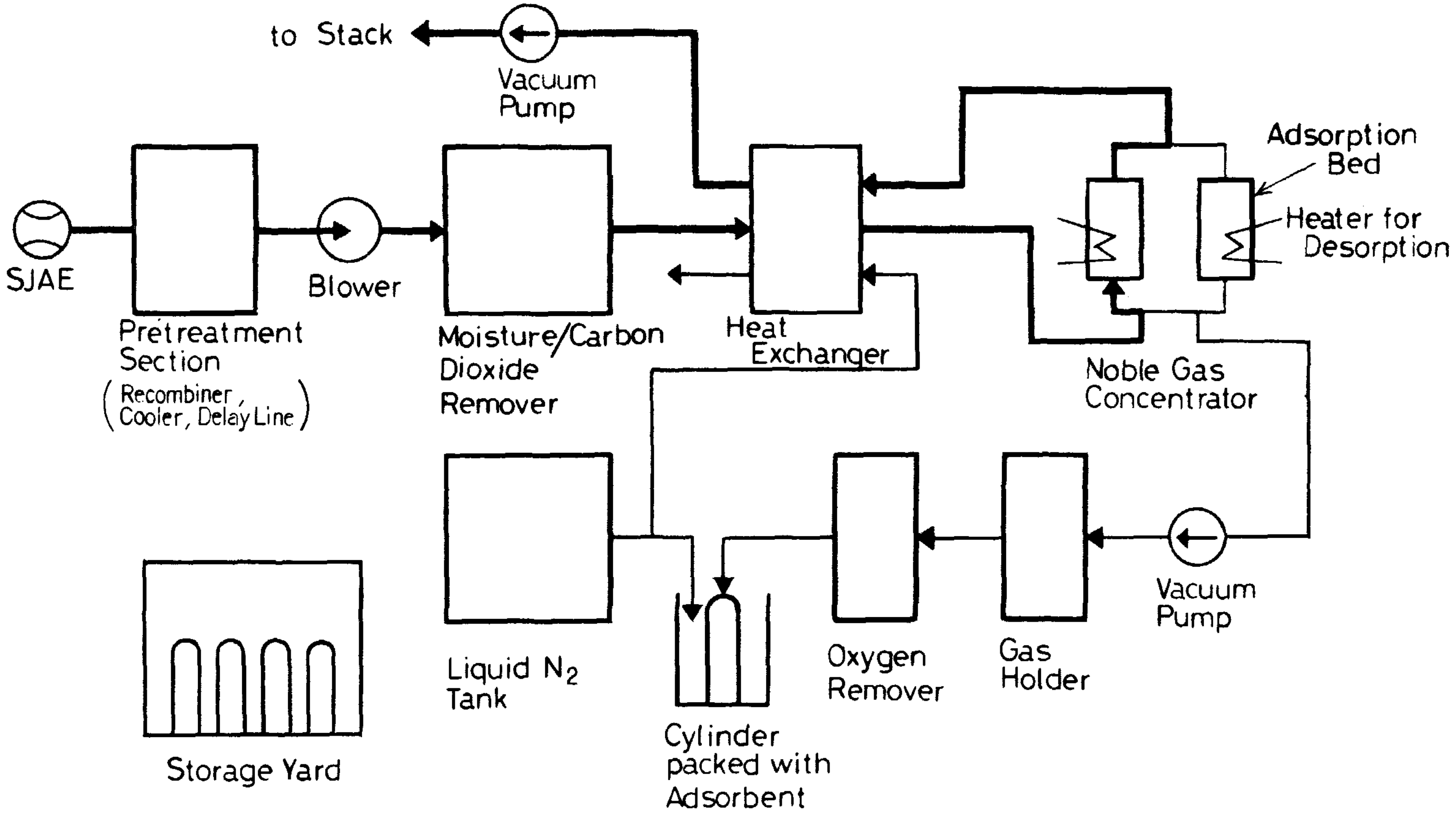


FIG. 1 THE SCHEMATIC FLOW DIAGRAM OF THE PROPOSED OFF GAS CLEAN UP SYSTEM FOR BWR PLANT

with a single stage enrichment system such as described above, and may require double or more stages to get the sufficient noble gas concentration for the purpose of the permanent storage. This was a significant disadvantageous point of the noble gas enrichment system using the adsorption method. The authors believe this problem has been resolved by combining recycle technique with present selective adsorption-desorption method as mentioned above. Besides, the present noble gas concentrator is operated at subatmospheric pressure through all the processes, and this is another advantageous point of the present method.

Inlet flow to the storage system contains not only concentrated noble gases but also nitrogen, oxygen, ozone and other gaseous impurities. In order to store these concentrated gases safely for an extended period, it is required to remove not only ozone and other impurities but also oxygen which might have possibility to change to ozone during storage. So, the proposed system equips with oxygen (and other gaseous oxide impurities) remover. "Metal getter absorption method" is to remove oxygen and to decompose ozone and nitrogen oxide by letting them contact with some kinds of metals. For instance, zirconium metal does not absorb noble gases at all while it absorbs a large amount of oxygen at elevated temperature. It also absorbs nitrogen, but the absorption rate of nitrogen is so far less than that of oxygen that it can be regarded as a selective absorbent of oxygen. Inlet flow to the storage system first passes through the oxygen remover utilizing this Zr getter absorption method, and then enters the storage section.

The main part of the storage section consists of metallic cylinder in which a certain type of adsorbent is packed. The cylinder is cooled with liquid nitrogen when the gas from the noble gas concentrator is required to deliver for storage. With this cooling of the cylinder, the system requires no pumps or compressors for the transportation of the concentrated gas between the gas holder and the storage cylinder by the adsorption power of cooled adsorbent in the cylinder, and furthermore the system can be operated at subatmospheric pressure. At the completion of the storage period, the cylinder is sealed, left to room temperature and transported to the storage yard. Internal pressure of the cylinder at room temperature is kept lower by the action of adsorbent packed in the cylinder than the case the cylinder contains no adsorbent.

3. Cryogenic Adsorption-Desorption Process

3.1 General Description and Definition

The noble gas concentrator can be divided into two charcoal beds (A, B), valves and piping. A typical cycle of operation of the two charcoal beds, based on one day switching interval, is shown schematically in Fig. 2. The cyclic process, as shown in the figure, is fundamentally composed of four steps.

1) Selective Adsorption Step

The feed is passed through a cooled bed until the breakthrough of krypton is detected. Radioactive noble gases are removed from the feed by being adsorbed on adsorbents. Noble gases enriched on adsorbents are desorbed at regeneration step.

2) Regeneration Step (- recycle step or storage step)

The bed is evacuated with raising temperature to 50°C - 100°C following the selective adsorption step or selective desorption step. Desorbed gases are recycled to the feed at recycle step, and are transferred to the next oxygen removal process at storage step. In order to achieve greater DF by the cryogenic adsorption process, it would be necessary to purge the bed with clean gas at this step.

3) Selective Desorption Step

After selective adsorption step, the bed as being kept at low temperature is evacuated to a desired pressure with a vacuum pump. Since noble gases are not desorbed so easily as carrier gas, because of the difference of physical properties such as mass transfer resistance and adsorption potential between them, the ratio of noble gases content to the carrier gas becomes greater in the bed.

4) Cooling Step

After the regeneration step, the bed is cooled to a desired temperature and kept waiting for the next cycle.

The cryogenic adsorption-desorption process, as previously mentioned, plays the roles of both removing radioactive noble gases from off gas streams and enriching noble gases. The efficiency of the former or its DF could be estimated by using the breakthrough curve of noble gases, and the characteristics of the latter could be described with enrichment factors at the selective adsorption step, the recycle step or the selective desorption step. These outlines are described below.

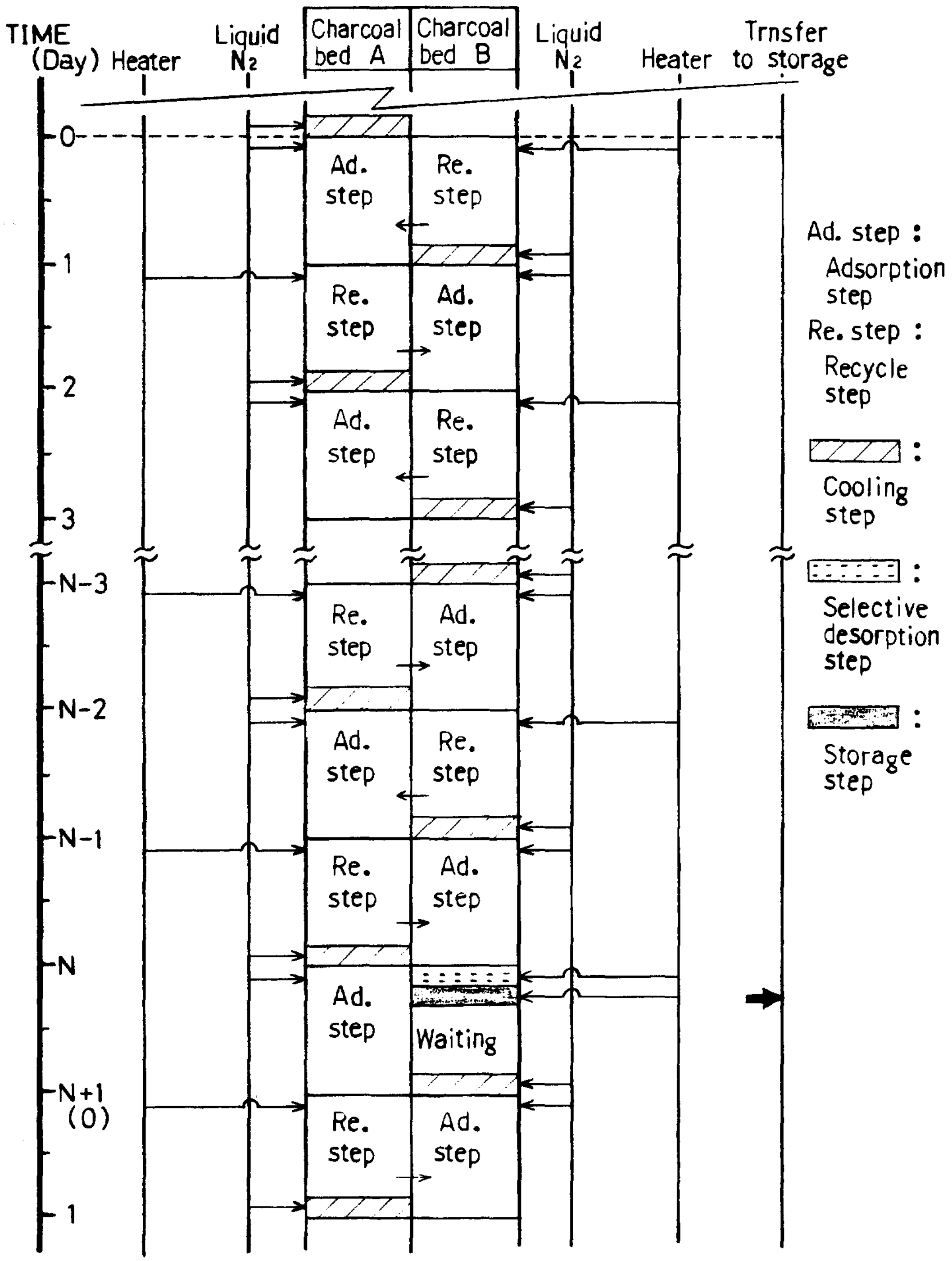


FIG. 2 THE TYPICAL CYCLE OF TWO CHARCOAL BEDS OPERATION

Definition of DF and Analytical Method of Breakthrough Curve

DF could be expressed by a breakthrough curve of non-active krypton and decay effect of radioactivity in the bed as follows,

$$DF \cong \frac{\sum_i A_i(Kr) + \sum_j A_j(Xe)}{t_B^{-1}\int_0^{t_B} \frac{C}{Co} \sum_i A_i(Kr) e^{-\lambda_i \cdot t} dt} \quad \text{-----} \quad (1)$$

where,

$A_i(Kr)$: release rate of radioactive krypton at an entrance of the bed (μCi/sec)

$A_j(Xe)$: release rate of radioactive xenon at an entrace of the bed (μCi/sec)

C/Co : breakthrough curve of non-active krypton ($-$)

t_B : breakthrough time (sec)

i, j : nuclide

λ_i, λ_j : decay constant (1/sec)

Since the adsorption coefficient of xenon is greater than that of krypton, it has been postulated that xenon does not appear in the effluent at the breakthrough of krypton ($\leq 10^{-2}$). In order to evaluate DF by the equation (1), it is necessary to establish an analytical method of the measured breakthrough curve and a method to calculate the breakthrough curve under given conditions. Although the various methods to analyze, and calculate the breakthrough curve had been proposed, the method proposed by Rosen[2)] was adopted in this article. A material balance and linear-equilibrium relationship give

$$\left.\begin{aligned} \varepsilon D\frac{\partial^2 c}{\partial x^2} &= \gamma\frac{\partial q}{\partial t} + \varepsilon\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x}\ , \\ \gamma\frac{\partial q}{\partial t} &= K_F a_v\ (C - q/K) \end{aligned}\right\} \quad \text{-----} \quad (2)$$

using the boundary conditions q=0 for t=0, $x \geqq 0$ and C=Co for $t \geqq 0$, x=0, and neglecting the diffusion term, $\varepsilon D\frac{\partial^2 c}{\partial x^2}$, the approximate solution to the equations (2) is

$$C/Co = e^{-(\zeta+\theta)} Jo\,(Z_i\sqrt{\zeta+\theta})$$
$$+ \int_0^{\zeta} e^{-(\mu+\theta)}\, Jo\,(Z_i\sqrt{\mu\cdot\theta})\, d\mu \qquad \text{-----} \quad (3)$$

$$\zeta = \frac{K_F a_V}{\gamma K}\left(t - \frac{x}{u/\varepsilon}\right), \quad \theta = \frac{K_F a_V}{u}\cdot x$$

Under the condition $\theta \gg 1$, the equation (3) is able to be approximated with equations,

$$C/Co = \frac{1}{2}\,(1 + \mathrm{erf}\ E) \qquad \text{---------} \quad (4)$$

$$E = \frac{\zeta-\theta}{2\sqrt{\theta}} = \frac{1}{2\gamma}\sqrt{\frac{u\cdot K_F a_V}{xK^2}}\,t - \frac{1}{2}\sqrt{\frac{x\cdot K_F a_V}{u}} \qquad \text{-----} \quad (5)$$

where,

Co : concentration of krypton in the feed (mol/cc)

C : concentration of krypton in gas phase at distance along charcoal bed, x and time of adsorption process, t (mol/cc)

D : diffusion coefficient of krypton in air (cm^2/sec)

Jo : Bessel function of zero order

K : adsorption coefficient $(\frac{mol}{g} / \frac{mol}{cc})$

$K_F a_V$: total mass transfer coefficient (1/sec)

q : amount of krypton adsorbed per unit mass of adsorbent (mol/g)

t : time of adsorption process (sec)

u : superficial velocity (cm/sec)

x : distance along charcoal bed (cm)

ε : void fraction of charcoal bed (–)

γ : bulk density of charcoal (g/cm^3)

Adsorption coefficient K and total mass transfer coefficient $K_F a_v$ are calculated by applying the equations (4) and (5) to a measured breakthrough curve. Breakthrough curve under any conditions can be counter-calculated from the equations (4) and (5) for given values of K and $K_F a_v$.

Definition of Enrichment Factor

We have defined the enrichment factor of noble gases as the ratio of noble gases content in the bed to that in the feed. From the definition, total enrichment factor, Ψ , is described as follows,

$$\Psi \simeq \frac{[\text{noble gases/carrier gas (in the bed)}]_a}{[\text{noble gases/carrier gas (in the feed)}]} \tag{6}$$

where, the suffix, a , shows that selective desorption step has been conducted.

The equation (6) can be described as follows.

$$\Psi = \Psi_1 \times \Psi_2 \tag{7}$$

where,

$$\Psi_1 = \frac{[\text{noble gases/carrier gas (in the bed)}]_b}{[\text{noble gases/carrier gas (in the feed)}]} \tag{8}$$

$$\Psi_2 = \frac{[\text{noble gases/carrier gas (in the bed)}]_a}{[\text{noble gases/carrier gas (in the bed)}]^b} \tag{9}$$

and the suffix, b, shows that selective adsorption step has been conducted.

The equation (9) can be transformed into the next equation.

$$\Psi_2 = \Psi_8 \times \eta \tag{10}$$

where,

$$\Psi_8 = \frac{[\text{carrier gas (in the bed)}]_b}{[\text{carrier gas (in the bed)}]^a} \tag{11}$$

$$\eta = \frac{[\text{noble gases (in the bed)}]_a}{[\text{noble gases (in the bed)}]^b} \tag{12}$$

From the equations (7) and (10), total enrichment factor is presented as follows,

$$\Psi = \Psi_1 \times \Psi_3 \times \eta \qquad \text{--------} \quad (13)$$

The enrichment factor at selective adsorption step, Ψ_1 , is transformed by taking account of recycle step as follows,

$$\Psi_1 = \Psi_O \cdot (N + 1) \qquad \text{--------} \quad (14)$$

where,

Ψ_O : enrichment factor at selective adsorption step without recycle step

N : number of recycle

After all, total enrichment factor can be described as follows.

$$\Psi = \Psi_O \cdot (N+1) \times \Psi_3 \times \eta \qquad \text{--------} \quad (15)$$

In case breakthrough point is 10^{-2} for krypton, the enrichment factor, Ψ_O , of krypton can be approximately described from the equations (4) and (5) as follows.

$$\Psi_O \cong \frac{u \cdot \frac{273}{T} \cdot P}{q_{carrier} \cdot \gamma \cdot L} \times t_B \cong \frac{273 \cdot P}{q_{carrier} \cdot T} \left[1 - 3.3 \sqrt{\frac{u}{L \cdot K_F a_V}} \right] \cdot K \qquad \text{----} \quad (16)$$

where,

L : bed length (cm)

P : pressure in bed (atm)

$q_{carrier}$: amount of carrier gas adsorbed per unit mass of adsorbent (STP-cc/g)

T : bed temperature (K)

3.2 Laboratory Scale Experiment

Some breakthrough curves were measured with a laboratory scale apparatus to obtain adsorption coefficients and mass transfer coefficients, and to compare the measured breakthrough curves with the calculated breakthrough curves from the equations (4) and (5). Some basic data for enrichment factors shown in this paper were selected from the data which we had reported at 13th AEC Air Cleaning Conference[1).

Besides, based on these results, an engineering test plant has been constructed and experiments are being performed with the plant. Such engineering scale experimental results will be shown in the next chapter "Engineering Scale Experiment".

3.2.1 Experimental

Apparatus and Method

Although components of noble gases in the off gas stream were krypton and xenon, krypton was used as adsorbate in this work, because xenon was adsorbed easily and not desorbed easily in comparison with krypton.

The apparatus used in this work, shown schematically in Fig. 3, was designed to be able to perform adsorption experiment and desorption experiment, using krypton tagged with Kr-85 as adsorbate.

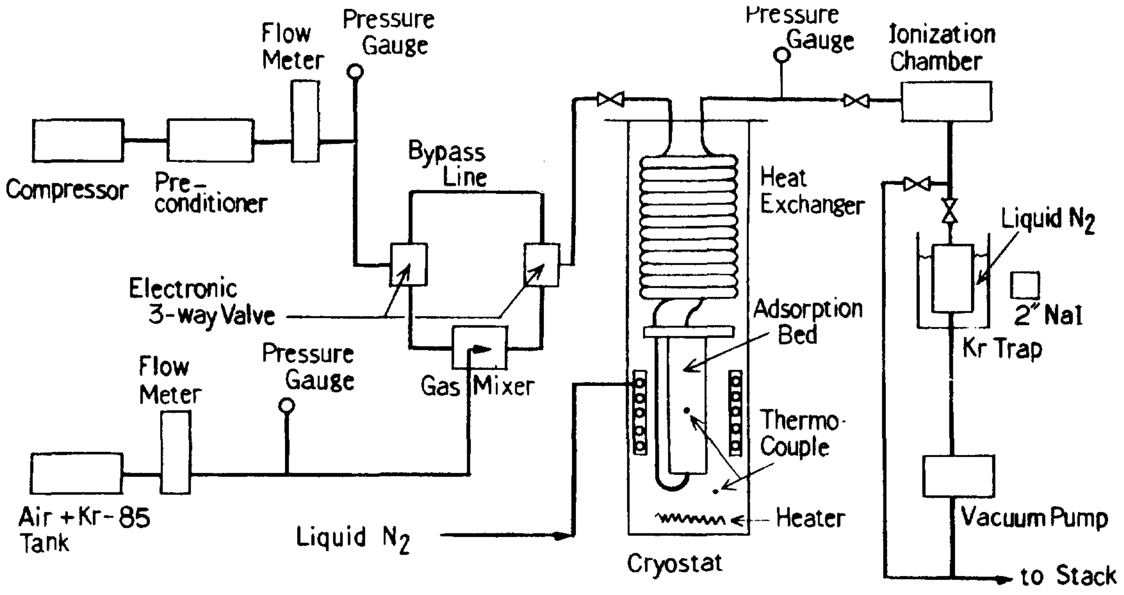


FIG. 3 SCHEMATIC DIAGRAM OF LAB-SCALE EXPERIMENTAL APPARATUS

The adsorption experiments were carried out by passing the feed through the adsorption bed cooled to a desired temperature. While the effluent was monitored with an ionization chamber to measure the breakthrough curve of krypton tagged with Kr-85. After adsorption experiments had been performed, the desorption experiments were conducted by evacuating the bed under low temperature through a Kr trap which was located in exhaust line, where Kr-85 was monitored with a NaI (Tl) scintillation detector to measure the amount of desorbed krypton.

An adsorption column which held the bed was placed in a cryostat, which was controlled over a range of temperature from -50°C to -150°C by using a heater and liquid nitrogen. The temperature of the cryostat was maintained within ± 1°C of the set point for the adsorption experiment and within ± 5°C of the set point for the desorption experiment. The adsorption column was a cylinder with a diameter of 2 inches filled with adsorbents.

Inlet and outlet lines from the column were of 1/2 in. outer dia. copper tubing, and were silver-soldered together in parallel for a length of 3.2 m to effect heat transfer from the incoming to the outgoing gas.

The Kr trap was a glass cylinder which was about 3 cm in diameter and 15 cm in effective length, filled with activated charcoal and immersed in liquid nitrogen. It was confirmed that the Kr trap was able to collect more than 90% of desorbed krypton.

The feed was made up by mixing air supplied by a compressor and krypton - dry air gas mixture tagged with Kr-85 which was stored at high pressure in an air - Kr-85 tank. Moisture and carbon dioxide in the air supplied by the compressor were removed with the preconditioner, which was composed of molecular sieves beds and cooler.

Breakthrough Curve, Adsorption Coefficient and Total Mass Transfer Coefficient

The adsorption coefficients and the total mass transfer coefficients were calculated by applying the equations (4) and (5) to the measured breakthrough curves. The theoretical breakthrough curves obtained by adopting these calculated coefficients are compared with the measured breakthrough curves.

Enrichment Factors

The enrichment factor, Ψ_0 , at the selective adsorption step was calculated by the equation (16) using the coefficients K and $K_F a_v$ obtained in this work and the amount of carrier gas adsorbed per unit mass of adsorbent, $q_{carrier}$, which was measured with a B. E. T. apparatus.

In order to determine the enrichment factor, ψ_2 , at the selective desorption step, the factors ψ_3 and η defined in the equations (11) and (12) were estimated by the methods shown below.

The counting rate of Kr-85 collected in the Kr trap was measured during the selective desorption experiment. After the selective desorption experiment, the bed was heated to 50°C and the amount of remained air in the bed was determined from the pressure and the volume of the column with the correction of the air amount adsorbed on adsorbents at the temperature of 50°C. Then, the column was evacuated to 10^{-2} Torr through the Kr trap and the counting rate of the Kr trap was measured at the Kr trap. ψ_3 and η were estimated from these data by using the equations shown below.

$$\psi_3 = q_{\text{carrier}} / q'_{\text{carrier}}$$

$$q'_{\text{carrier}} = 0.845\, V_d P + q''_{\text{carrier}}$$

$$\eta = 1 - A/B$$

where,

A : counting rate at the Kr trap after the selective desorption experiment, but before the bed heating to 50°C

B : counting rate at the Kr trap after the bed was heated to 50°C and evacuated to 10^{-2} Torr

P : pressure in the column when the column was heated to 50°C (atm)

q'_{carrier} : amount of remained carrier gas in the bed after the selective desorption process (STP-cc/g)

q''_{carrier} : amount of carrier gas adsorbed at the temperature of 50°C and the pressure of P, measured with the B. E. T. apparatus (STP-cc/g)

V_d : dead volume of the column (cm^3)

Experimental Condition

Some of the experimental conditions are summarized as follows,

Adsorbents : activated charcoal "Shirasagi G-A" (see Table 1)

Bed size : 2 inches diameter and 11.7 to 19.4 cm in length

Carrier gas : air

Feed concentration
: 1 ppm Kr. by volume, tagged with Kr-85

Temperature at the adsorption experiments
: -50°C to -150C

Pressure at the adsorption experiments
: 1 atm

Air flow rate at the adsorption experiments
: 1 cm/sec in superficial velocity

Pumping speed at the desorption experiments
: 11 ℓ /min to 14 ℓ /min at the standard temperature of 30°C

Temperature at the desorption experiments
: fixed temperature at the adsorption experiments and raising temperature from -150°C to -100°C

Ultimate pressure at the desorption experiments
: 10 Torr

Table 1 Properties of Adsorbents

		Charcoal			Molecular Sieves
		Kurale 4GA	Shirasagi G-A	VRG	MS 5A
Base		Coconut	Coconut	Coal	Zeolite
Shape		Cylindrical pellet	Cylindrical pellet	Granular	Granular
Size (Ave.)	Dia.	3.8 mm	4.0 mm	1.0 mm	
	Leng.	7.7 mm	4.1 mm	(14 mesh)	(60-80 mesh)
Apparent Density		0.78 g/cm^3	0.68 g/cm^3	0.82 g/cm^3	0.9 - 1.3 g/cm^3
Bulk Density		551 g/ℓ	459 g/ℓ	529 g/ℓ	639 g/ℓ

3.2.2 Results and Discussion

Breakthrough Curve, Adsorption Coefficient and Total Mass Transfer Coefficient

The measured breakthrough curve, taken from a typical run , is shown in Fig. 4 together with representative experimental conditions. The solid lines in the figure are the breakthrough curves calculated by the equations (4) and (5). The experimental data are fitted quite well by the theoretical curves.

In Fig. 5, the obtained adsorption coefficients are plotted against inverse temperature. The data for the temperature -15°C to 40°C in the figure are the experimental values that we measured previously for the same adsorbent. The data could be fitted by a straight line on a semilog paper at a temperature above -100°C, and the fitting line becomes gradually curved at the lower temperature by the reason of the interference effect which may be due to the increase in the amount of adsorbed carrier gas on adsorbents.

The total mass transfer coefficient calculated from the measured breakthrough curves was 2.1 ± 0.4 sec^{-1} at the temperature -150°C to -50°C. According to our experiments performed previously for the same adsorbent, values of the coefficient were 12 sec^{-1} at 40°C and 5 sec^{-1} at 0°C. Based on these results, it is clear that the total mass transfer coefficient becomes smaller at the lower temperature and the dependency of the coefficient on the temperature is relatively small at the lower temperature. The coefficient might be affected considerably by the gas pressure in the bed and the superficial velocity; the effect of these parameters was not investigated in this work, however. The conditions in this work were as follows.

Pressure : 1 atm
Superficial velocity : about 1 cm/sec

Enrichment Factor

The enrichment factor, ψ_0 , shown in Fig. 6 was calculated by the equation (16) using the experimental data which were obtained under the conditions as follows.

Bed size : 2 inches in diameter and 19.4 cm in length (same as the bed size at the selective desorption experiments)
Breakthrough point : 10^{-2}
Pressure : 1 atm
Superficial velocity : 1 cm/sec

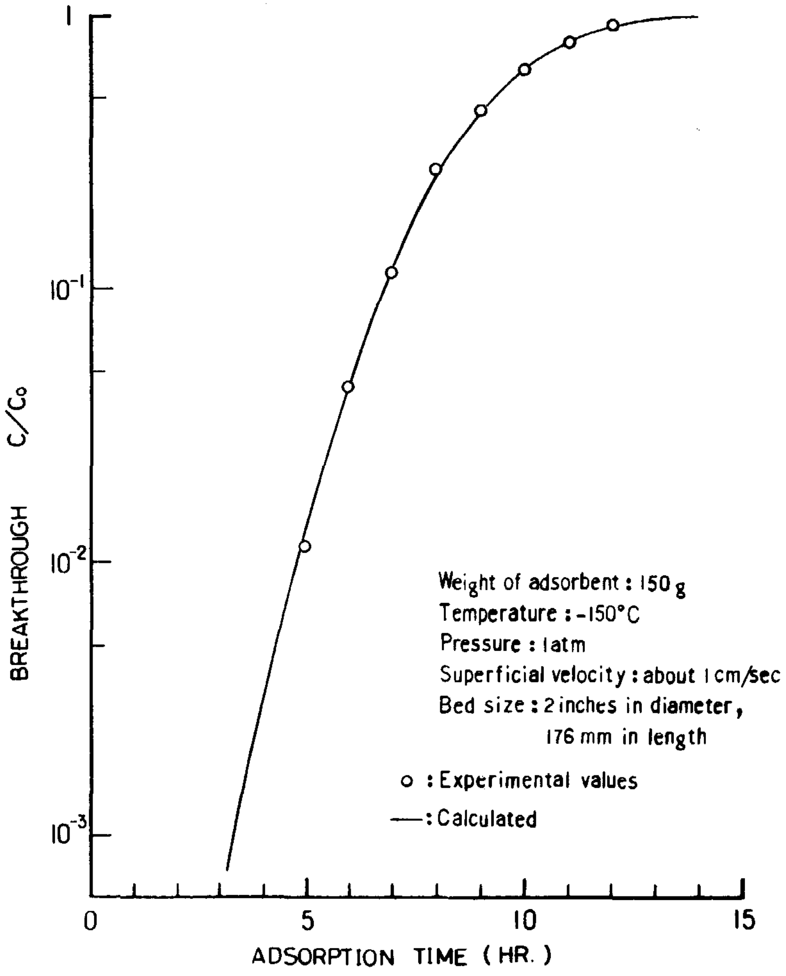


FIG. 4 BREAKTHROUGH CURVE BY LAB-SCALE EXPERIMENT

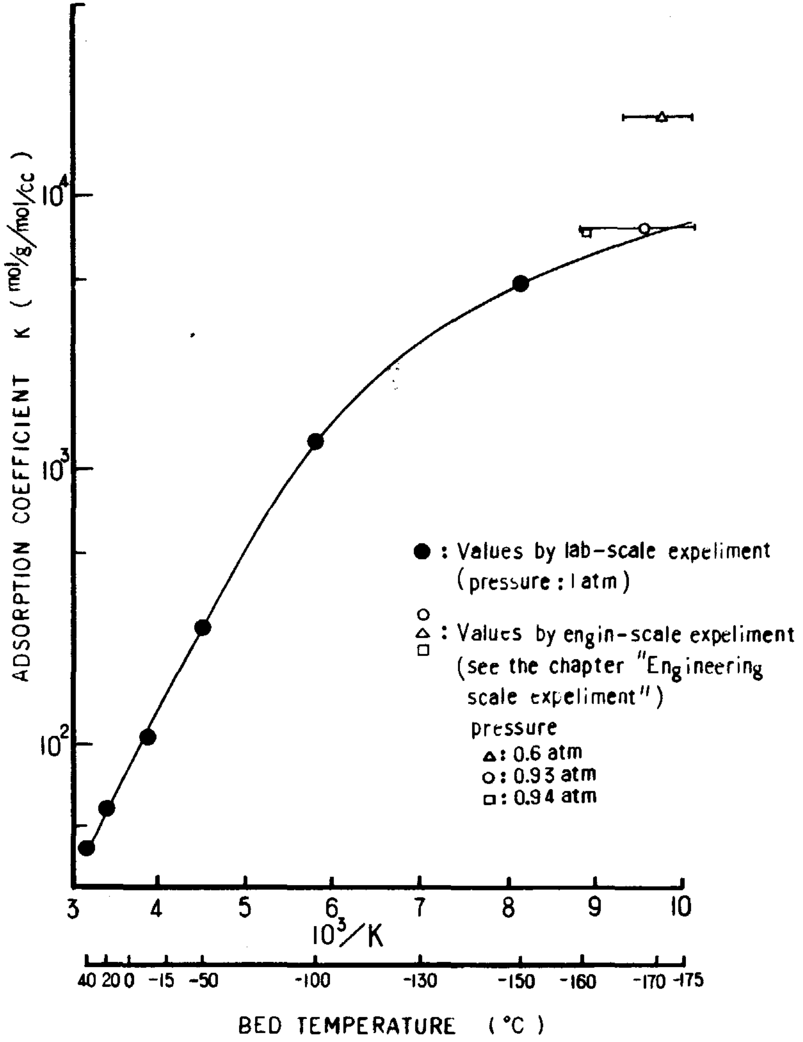


FIG. 5 ADSORPTION COEFFICIENT

Since properties of the factors, Ψ_2, Ψ_8 and η at the selective desorption, defined in the equations (9), (11) and (12) were discussed previously in the 13th AEC Air Cleaning Conference, only the experimental values of the factors will be shown here. In Fig. 6, the factors Ψ_8 and Ψ_2 are shown with the factor Ψ_O and the total enrichment factor, Ψ, calculated by the equation (7). The desorption rate of krypton at the selective desorption, $1-\eta$, are shown in Fig. 7. The data labelled with a mark * in Fig. 6 and 7 are the experimental values which were obtained by evacuating the bed with increasing the temperature -150°C to -100°C. The other data in the figures are the experimental values obtained by evacuating the bed at the fix temperature.

It could be concluded from these results that the equations (4) and (5) proposed by Rosen were suitable to the breakthrough curve analysis and the enrichment factor was increased without noticeable increase of krypton desorption rate by evacuating the bed with increasing temperature. In order to confirm whether the above conclusions are applicable to an actual scale facility or not, an engineering test plant has been constructed and the experiments are being performed, which will be presented in the next chapter "Engineering Scale Experiment .

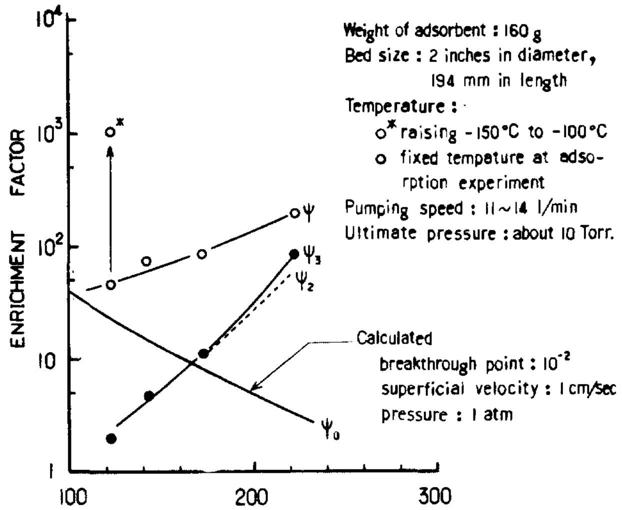


FIG.6 ENRICHMENT FACTORS AT LAB - SCALE EXPERIMENT

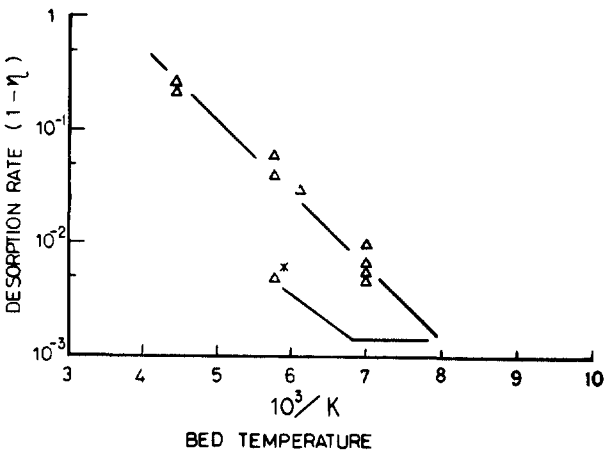


FIG.7 DESORPTION RATE OF ADSORBED Kr AT SELECTIVE DESORPTION LAB - SCALE EXPERIMENT

3.3 Engineering Scale Experiment

An engineering test plant for adsorption-desorption experiments has been designed and constructed utilizing the data of adsorption-desorption in laboratory scale experiment, and performance is now examined. This report shows the interim results.

3.3.1 Test Plant

A process flow diagram of the test plant is shown in Fig. 8 and the photographs are shown in Fig. 9.
Experiments are performed by passing the air with about 1 ppm Kr tagged with Kr-85 in down flow through the adsorption bed of charcoal. The air of 50 Nm^3/hr is intaked and pressurized to 1.2 kg/cm^2 Abs. by main blower and fed to one of the moisture/carbon dioxide remover towers after pre-cooled to 10°C. Moisture and carbon dioxide are removed to the levels of less than 1 ppm and 2 ppm respectively in towers packed with adsorbent, "Zeorum F-9".

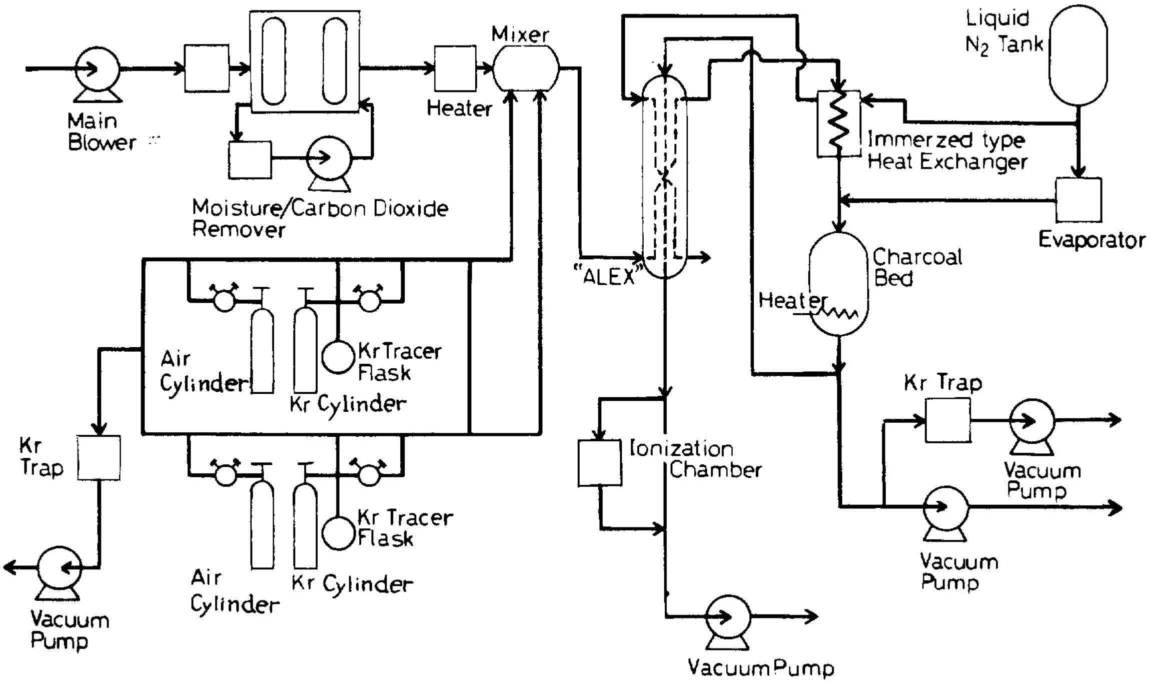
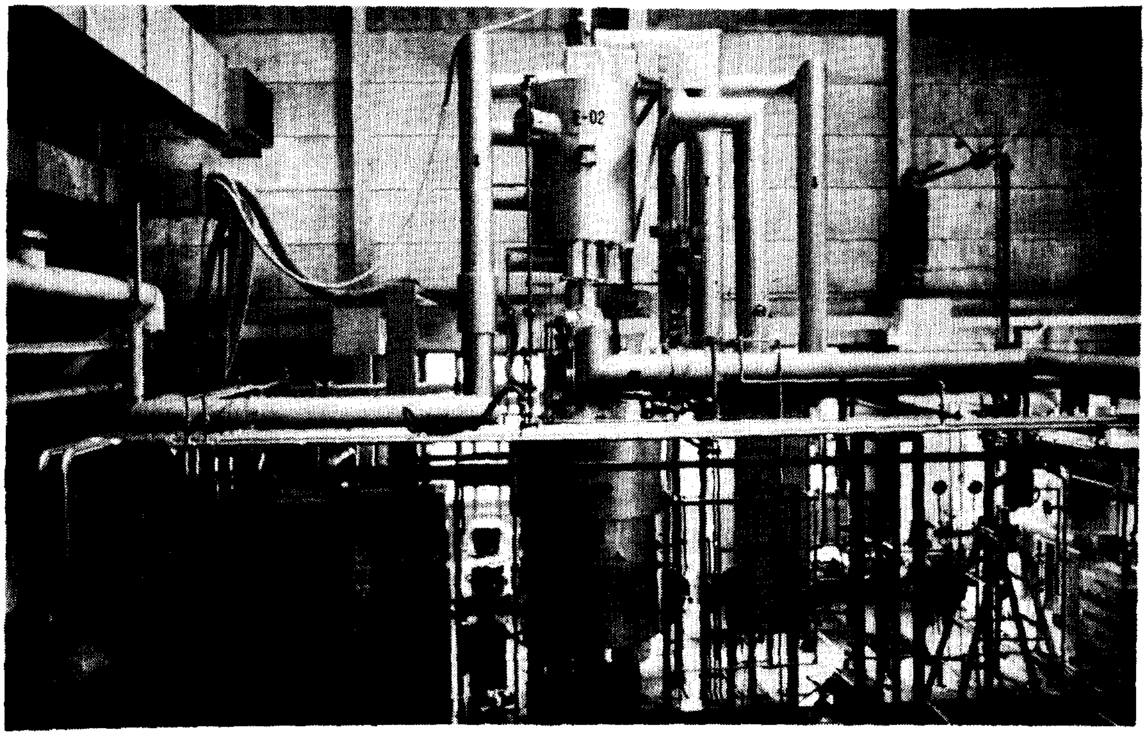
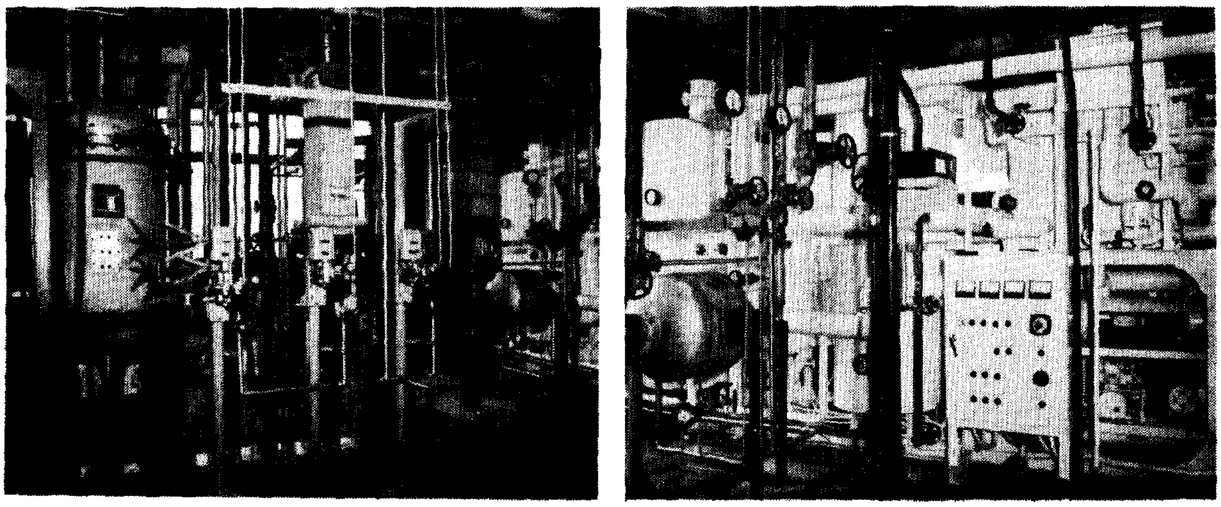


FIG. 8 PROCESS FLOW DIAGRAM OF ENGINEERING SCALE TEST PLANT



TOTAL VIEW OF TEST PLANT



CONCENTRATOR AND
HEAT EXCHANGER

MOISTURE/CARBON DIOXIDE
REMOVER

FIG. 9 PHOTOGRAPHS OF ENGINEERING SCALE TEST PLANT

When one of towers is in adsorption step, the other is in regeneration step or in cooling step, and the path of feed gas is automatically changed every 8 hours. After the tower in adsorption step is saturated with moisture and carbon dioxide, the adsorbents are heated up to about 300°C for regeneration, and are purged with purified gas of 10 Nm^3/hr from the other tower.

In this remover, both internal and external heatings are adopted to get the high removal efficiency of moisture and carbon dioxide for the prevention of blockage in small piping lines at the low temperature section.

Dried feed gas of 40 Nm^3/hr tagged with Kr-85 at the gas mixer goes into the "ALEX" heat exchanger. The feed gas is cooled down in this heat exchanger and is further cooled down in the next immersed type heat exchanger. The temperature of the effluent gas from the immersed type heat exchanger is controlled from about -185°C to -190°C by means of controlling the level and the pressure of liquid nitrogen in the heat exchanger.

Then the effluent gas is fed into the charcoal bed which has been sufficiently cooled down prior to the adsorption experiment by cold nitrogen gas, and the temperature of the charcoal bed is kept at -160°C to -170°C by the cold of the feed gas itself during the adsorption experiment. Krypton tagged with Kr-85 in the feed gas is adsorbed in the charcoal bed and the effluent gas from the bed is exhausted by a vacuum pump. A part of the effluent gas is passed through an ionization chamber which measures the breakthrough curve of krypton. The pressure in the charcoal bed is controlled at the range of 0.6 ata to 1.0 ata by regulating the valves at the suction of the vacuum pump and the outlet of the moisture and carbon dioxide remover. The charcoal bed is 750 mm in diameter and 300 mm in depth.

Raschig rings are packed at the upper and down sides of the bed and six semicircle heaters of total capacity of 30 kW are buried in the charcoal bed. In this experiment 46 kg of "Shirasagi G-A" charcoal was packed. The bed temperature is measured with the C-C thermocouples at nine locations. Cold nitrogen for the low temperature section is supplied from the liquid nitrogen tank, using a liquid nitrogen line for the immersed type heat exchanger and a cold nitrogen gas line for pre-cooling of the charcoal tower. Urethane foam is used to insulate the low temperature section for the convenience of various works such as changing of adsorbents.

For the selective desorption experiment, two vacuum pumps and a Kr trap are installed. One of the pumps of a pumping speed of 3 m^3/min is used for the evacuation of the bed. The other pump of a smaller pumping speed is used for sampling a portion of desorbed gas. The sampled gas is collected in the Kr trap and monitored by NaI (Tl) scintillation detector. The Kr trap is packed with charcoal and immersed in liquid nitrogen.

3.3.2 Experimental

Cooling

It is needed to pre-cool the charcoal bed prior to the adsorption experiment. In this plant, the bed is pre-cooled by feeding cold nitrogen gas directly to the bed to shorten cooling time and to reduce a consumption of liquid nitrogen. After passed through the bed, nitrogen gas is fed into the "ALEX"heat exchanger, cools the low temperature section and is exhausted. While this pre-cooling operation, liquid nitrogen is supplied to the immersed type heat exchanger. When the temperature of the charcoal bed reached to about -170°C, the supply of cold nitrogen gas was stopped, and a stabilizing operation was started. When the temperature was balanced in the "ALEX" heat exchanger a vacuum pump was started for the normal operation.

Adsorption Experiment

When the normal operating conditions were obtained, the adsorption experiment was started by injecting Kr-85 tracer into the feed gas. Kr-85 in the effluent gas from the charcoal bed was measured by the ionization chamber.

a) Preparation of Kr-85 Tracer

The Kr-85 tracer supplying section was composed of two series of a Kr tracer flask, an air bombe, a Kr bombe, one charcoal trap and one vacuum pump. About 100 mCi of Kr-85 in a Kr tracer flask was sucked into a Kr bombe, well evacuated beforehand and was diluted with air to a certain concentration.

b) Measurement of Breakthrough

The concentration of Kr-85 in the effluent gas from the charcoal bed, C, was measured by the ionization chamber. On the other hand, the concentration Kr-85 in the feed gas, Co, was measured by passing the feed gas directly in the ionization chamber.

The breakthrough ratio (C/Co) was calculated from C and Co. The adsorption coefficient, K, and the total mass transfer coefficient, $K_F a_v$, were calculated from the breakthrough curve with Rosen's equations (4) and (5).

Desorption Experiment

When the adsorption experiment was finished, the charcoal bed was isolated from the feed gas line. The selective desorption was performed by heating and evacuating the bed. A portion of krypton desorbed from the bed during the selective desorption experiment was trapped in the Kr trap and was measured by the NaI (Tl) scintillation detector. When the selective desorption was finished, the bed was heated to about 100°C. From the temperature and the pressure of the bed, the enrichment factor at the selective desorption step was calculated in the same way as the laboratory scale experiment.

After that, the bed was evacuated and the desorption rate of krypton in the effluent gas was measured by the NaI (Tl) scintillation detector in the same way as the selective desorption step. The experimental conditions were shown in Table 2.

Table 2 Experimental Condition

Charcoal Bed Size : 750 mm in diameter and 300 mm in length
Adsorbent : Shirasagi G-A pelletized coconut base charcoal, 46.3 kg

At the Adsorption Step

Pressure : 0.6 atm and 0.94 atm
Temperature : -160°C to -170°C
Feed Gas Flow Rate : 40 Nm^3/hr.
Conc. of Kr in the Feed Gas : 1 ppm
Superficial Velocity : 1.6 cm/sec (at 0.6 atm) and 1.0 cm/sec (at 0.94 atm)

At the Selective Desorption Step

Increasing Rate of Bed Temperature : ≃25°C/hr
Pumping Speed : ≃80 m^3/hr
Temperature of Bed : -100°C
Pressure in Bed : 20 to 25 mmHg

3.3.3 Results and Discussion

Cooling

The charcoal bed and the "ALEX" heat exchanger were cooled down by cold nitrogen in a relatively short time of about 2 hours and 0.5 hour respectively. However, it took much more time to stabilize the bed temperature after setting the pressure and flow rate under the experimental conditions succeeding to the pre-cooling. The amount of liquid nitrogen consumed in pre-cooling was 700 Nm^3, for the fill-up of the immersed type heat exchanger and 100 Nm^3 for cooling down of the charcoal bed by cold nitrogen gas. Consumption of liquid nitrogen during the adsorption experiments was about 40 $\mathrm{Nm}^3/\mathrm{hr}$.

Breakthrough Curve

Breakthrough curve for the run No. 3 is shown in Fig. 10 with experimental conditions. And E-t curves for the run No. 1, No. 2 and No. 3 are shown in Fig. 11, 12 and 13 with the change of the bed temperature during the adsorption, where E was derived from the breakthrough ratio (C/Co) using the equation (4). In the run No. 1 and No. 2, a small change of the bed temperature was observed.

Presumably owing to this fractuation of the temperature, E-t curves were not linear and the gradients of the curves were in correspondence with the change of the bed temperature. In the run No. 3, ten more hours than run No. 1 and No. 2 was devoted to the temperature stabilization for the confirmation of above mentioned problem. Even in this run, the change of the temperature could not be avoided. However, the influence on the curve was smaller and the curve became linear except the initial part. Calculating the adsorption coefficient, K, and the total mass transfer coefficient, $K_F a_v$, from the breakthrough curve of this run,

$$K = 7,300 \ \frac{\mathrm{mol}}{\mathrm{g}} \Big/ \frac{\mathrm{mol}}{\mathrm{cc}}$$

and,

$$K_F a_v = 1.0 \qquad 1/\mathrm{sec}$$

for the adsorption pressure of 0.94 atm and temperature of -160°C. This value of 1.0 1/sec for $K_F a_v$ seems too small for this experimental conditions. This might be attributed to the slight high temperature at the beginning of the adsorption. In the run No. 1 and No. 2, the method by Rosen is not effective for the calculation of K owing to the non-linearity of the E-t curves. So, the K values are derived approximately from the equation shown below using the time $t_{0.5}$ which gives the C/Co ratio of 0.5.

$$K = \frac{u \cdot t_{0.5}}{\gamma \cdot L}$$

This K value will be larger for the initial high temperature and smaller for the lower temperature in one test run and was shown in Table 3 and Fig. 5.

Fig. 5 shows the K value depends on the gas pressure and gets larger with the decrease of the gas pressure. This will be explained by the idea that the decrease of co-adsorbed carrier gas amount in low gas pressure raises the adsorption capacity of Kr, because the co-adsorbed carrier gas hinder the adsorption of Kr. We could not quantitatively evaluate the effect of the gas pressure on Kr adsorption owing to the scarcity of data and the change of temperature, however it will be said that the effect of gas pressure is greater at low temperature than at the ambient temperature.

At the ambient temperature, the decrease of pressure leads to the shortening of the hold up time of Kr because of the larger effects of gas velocity than the co-adsorption. On the contrary, pressure decrease raise the hold up time at the low temperature as in this experiment. In the following experiment, we exclude the temperature fractuation and make much more data to obtain the accurate K and $K_F a_v$ and the pressure dependence.

Enrichment Factor by Desorption

Enrichment factors by the selective desorption and the desorption ratio of Kr from the bed are shown in Table 3.

Table 3 Enrichment Factor

Run	K	Enrichment factor	Kr desorption ratio
No. 1*	20,000	~ 25	0.5 %
No. 2*	7,600	25 ~ 30	0.7 %
No. 3	7,300	25 ~ 30	2.3 %

* K values were derived from the above equation.
These runs were stopped before 100% breakthrough.

Enrichment factors obtained in this engineering scale experiments are in conformity with the value of 40 in the laboratory scale experiments.

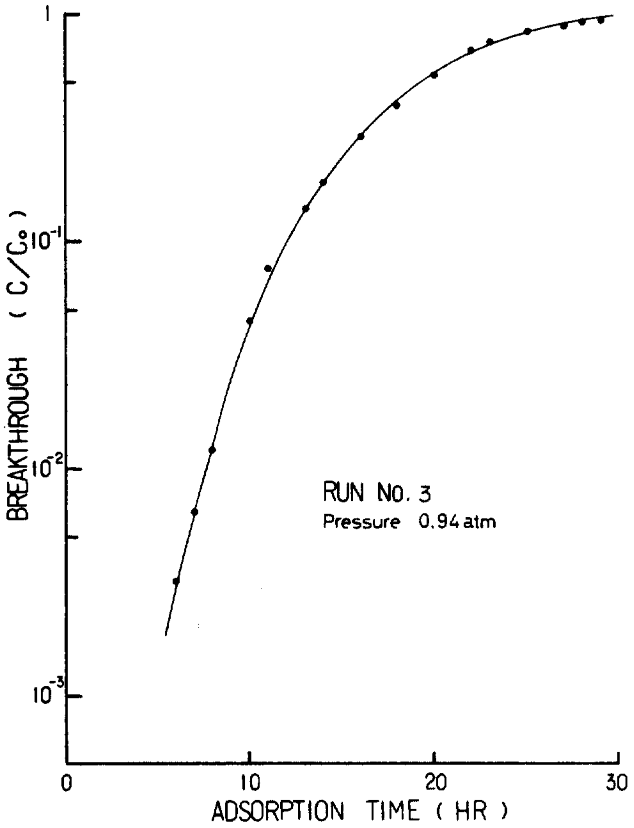


FIG. 10 BREAKTHROUGH CURVE

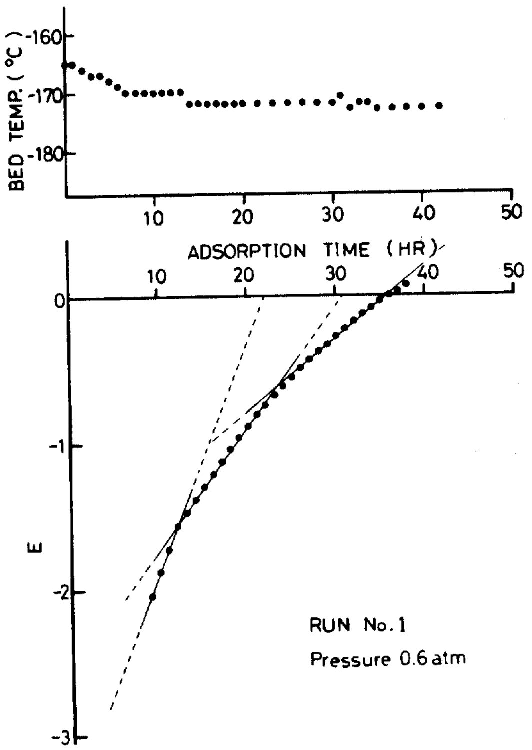


FIG. 11 E-T CURVE & BED TEMP.

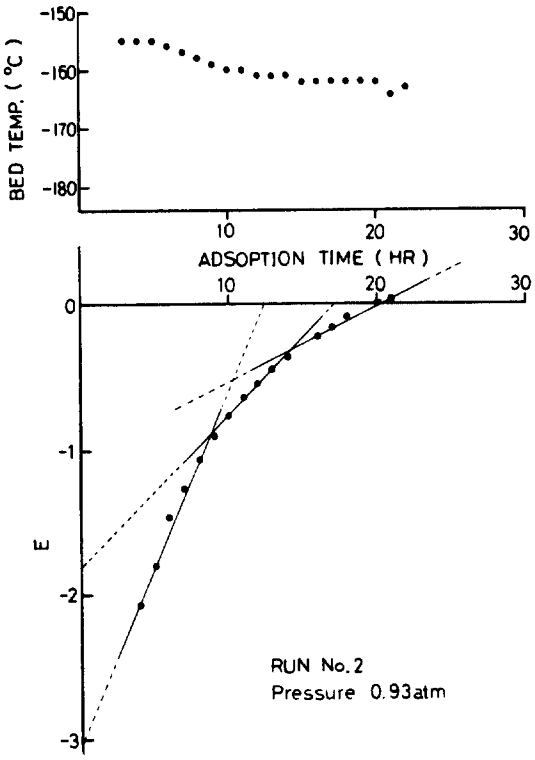


FIG. 12 E-T CURVE & BED TEMP.

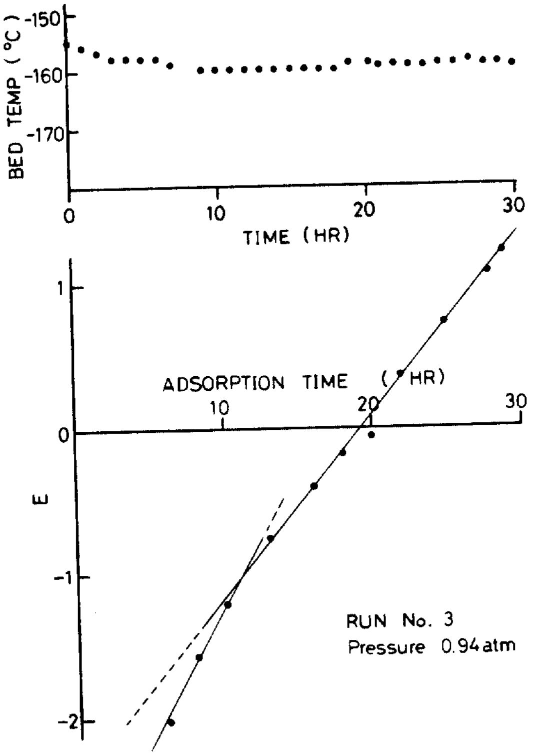


FIG. 13 E-T CURVE & BED TEMP.

4. Oxygen Removal Process

As described in Chapter 2, "metal getter absorption" method has been studied for the oxygen removal process, and the applicability of the method to the actual plant is experimentally being investigated. Two kinds of experiments were conducted. One was that sample gas was reacted with metal getter in a closed vessel during a constant time (static experiment), and the other was that sample gas was reacted with metal getter under a constant flow rate of the same magnitude as expected in the actual plant (dynamic experiment). In this report, results from the static experiments and the description of the dynamic experimental apparatus are presented.

Transition metals of the fourth group such as Zr, Ti and Hf and of the fifth group such as V, Nb and Ta are well known to have the characteristics to absorb nitrogen and oxygen and not to absorb noble gases in the field of vacuum technology.[3) However most of the studies in this field have focused their concern on the studies of fundamental metal-gas reaction and reported data are limited to those obtained under high vacuum conditions and/or single component gas reaction. The data required for the discussion in the present study are those for the metal to multi-component gas reaction under atmospheric pressure.

Authors chose Zr metal as most promising gas absorbent or getter, and first have carried out the laboratory scale experiment to know its absorption capacity and absorption rate of concerned gases in air under atmospheric pressure. Air was chosen because its component is similar to that of enriched gases. Also, data for some pure gases were obtained.

4.1 Static Experiment

Apparatus and Method

The static experimental apparatus is shown in Fig. 14. Reaction tube made of quartz (80 cc) can be heated over a range of temperature from 100°C to 900°C by an electric furnace and controlled at a constant temperature within ± 5°C. Before the absorption experiments, a Zr sample washed in acetone and dried was put into the reaction tube and it was evacuated to a vacuum of 10^{-2} mmHg. Then, the specimen was heated to a predetermined temperature and the reaction tube was evacuated continuously for about two hours.

After that, sample gas was introduced into the reaction tube to a certain pressure from a gas cylinder. When the sample gas was a single component, reacting amount of sample gas was determined from the pressure change. And when the sample gas was a multi-component, reacting amount was determined by the volumetric method with mass spectrometry. The weight gain of the Zr sample was determined from these results.

Experimental Condition

The experimental conditions are summarized as follows.

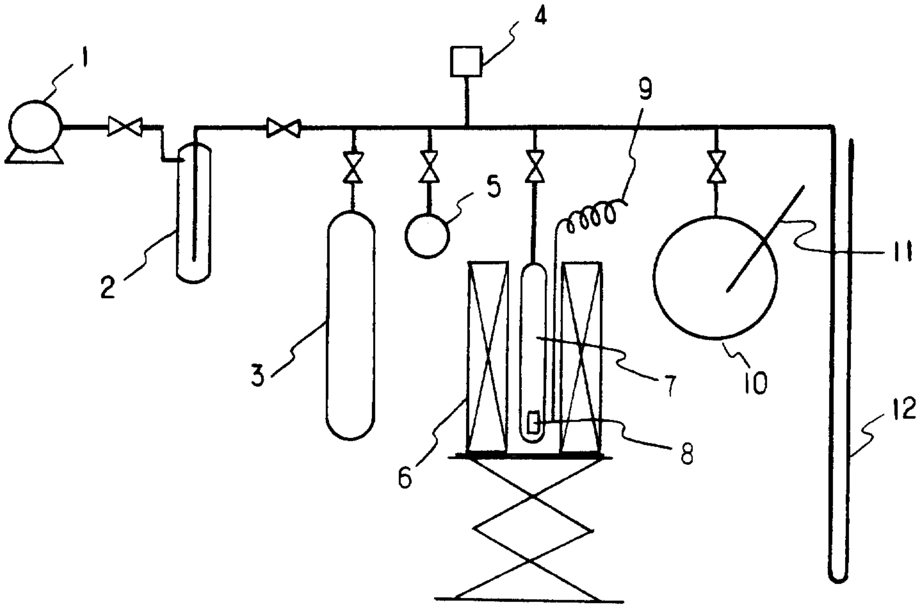
Specimen : Zr foil (20μ m thick), weight 10 - 100 mg
Zr sponge (5 - 8 mm$^{\phi}$ beads),
weight 100 - 500 mg

Sample gas : N_2, O_2, Kr, Xe, NO_2
(each purity $\geqq$ 99.5 vol.%)
Air

Loading pressure : 20 - 700 mmHg

Reaction temperature : 400 - 800°C

Reaction time : 5 - 300 min



1. Vacuum Pump 2. LN_2 Trap 3. Gas Cylinder 4. Diaphragm Vacuum Gauge
5. Gas Sampler 6. Electric Furnace 7. Reaction Tube 8. Specimen
9. Thermocouple 10. Gas Holder 11. Thermometer 12. Manometer

FIG. 14 STATIC EXPERIMENTAL APPARATUS

Results and Discussion

Changes of the weight gain of Zr foil are plotted against time in Fig. 15 and 16 with temperature and loading pressure. From Fig. 15, it is realized that both Zr-O_2 and Zr-N_2 reactions follow the so-called parabolic law expressed by the following equation :

$$W^2 = kt \quad \text{-------} \quad (17)$$

where,
w : weight gain (g/cm^2)
k : parabolic rate constant (g^2/cm^4·min)
t : reaction time (min)

Fig. 16 shows the weight gain for oxygen (or nitrogen) in air is not different from that for pure oxygen (or nitrogen). From this fact, it would be said that the absorption rate for oxygen was not affected by the existence of nitrogen. The same experiments were performed for Zr sponge and it was clarified that the parabolic law was also effective and absorption rate for oxygen was independent of the existence of nitrogen. From the experimental results, its reactive surface for oxygen was determined as about 50 cm^2/g. It was also found that the reaction rate constant or weight gain between Zr and oxygen (or nitrogen) were independent of the loading pressure and dependent on the temperature. These results well agree with several previous reports.

The temperature dependence on oxygen and nitrogen for the temperature range from 600°C to 800°C is described in the following equations (18) and (19) respectively.

$$k = 0.11 \exp\left(-\frac{32000}{RT}\right), \text{ for oxygen} \quad \text{-----} \quad (18)$$

$$k = 0.20 \exp\left(-\frac{48000}{RT}\right), \text{ for nitrogen} \quad \text{-----} \quad (19)$$

From Fig. 15 and 16, the weight gain of oxygen is found to be greater in one or two order than that of nitrogen. In experiments with pure krypton or pure xenon at 700°C, these gases were not absorbed in Zr at all as expected.

The consumption of metal getter should be taken into account from the economical point of view, and would be strongly dependent on the absorption capacity of Zr for oxygen. Oxygen was absorbed by Zr to 45 at.% in the experiments and so it may be thought its absorption capacity is at least 45 at.%.

As described before, enriched gas contains small amount of ozone and nitrogen dioxide besides oxygen, and these must also be removed before storage. Ozone can be expected to decompose thermally at high temperature.

Nitrogen dioxide also seemed to decompose, although no data were reported about it. In order to confirm this expectation, nitrogen dioxide was examined in the same manner as pure oxygen at 700°C and 100 Torr. As the result, nitrogen dioxide was found to decompose into oxygen and nitrogen as expected, and they were absorbed in the zirconium with each absorption rate.

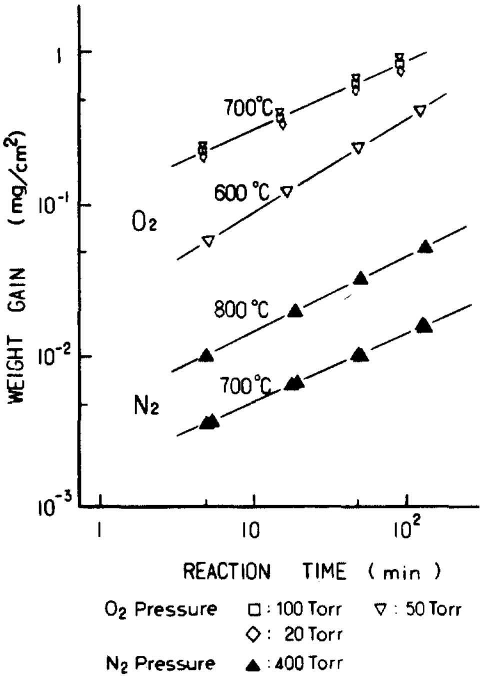


FIG. 15 REACTION OF Zr FOIL WITH O_2 AND N_2

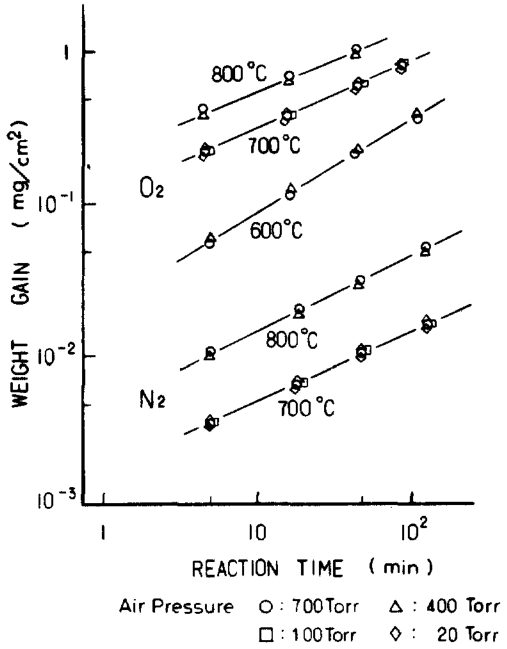


FIG. 16 REACTION OF Zr FOIL WITH AIR

4.2 Study of Dynamic Experimental Apparatus

Based on the static experimental results, the dynamic experimental apparatus was designed as follows. In order that the oxygen concentration in the effluent gas from Zr bed is almost equal to zero, the following equation should be established.

$$t \geq \tau \qquad \text{-----} \quad (20)$$

where, t : contact time (min)
τ : time required for oxygen removal (min)

and,

$$t = \frac{W/\rho}{F} \times \left(\frac{273}{T}\right) \qquad \text{-----} \quad (21)$$

From the static experimental results,

$$\tau = \frac{(Wo/A)^2}{k} \qquad \text{-----} \quad (22)$$

$$A = W \times 50 \times 10^3 \qquad \text{-----} \quad (23)$$

$$Wo \cong Ft \times \frac{1}{5} \times \frac{32}{22.4} \qquad \text{-----} \quad (24)$$

where,

W	:	weight of Zr sponge (kg)	
ρ	:	packed density of Zr sponge (=2.2)	(kg/ℓ)
F	:	air flow rate	(Nl/min)
T	:	reaction temperature	(K)
k	:	Zr-O_2 reaction rate constant	($g^2/cm^4 \cdot min$)
A	:	surface area of Zr sponge	(cm^2)
Wo	:	weight of oxygen	(g)
R	:	gas constant	(cal/mole·k)

Therefore,

$$k \geq 1.6 \times 10^{-11} \frac{F}{W} \times \left(\frac{273}{T}\right) \qquad \text{-----} \quad (25)$$

or

$$\frac{F}{W} \leq 6.5 \times 10^{10} k \times \left(\frac{T}{273}\right) \qquad \text{-----} \quad (26)$$

The equations (26) shown in Fig. 17 indicates that, if dynamic experiment is performed at reaction temperature of 500°C with 1 kg of Zr sponge, air flow rate should be less than 20 Nl/min. In order to confirm the expectation, a dynamic experimental apparatus has been constructed and dynamic experiment is being performed.

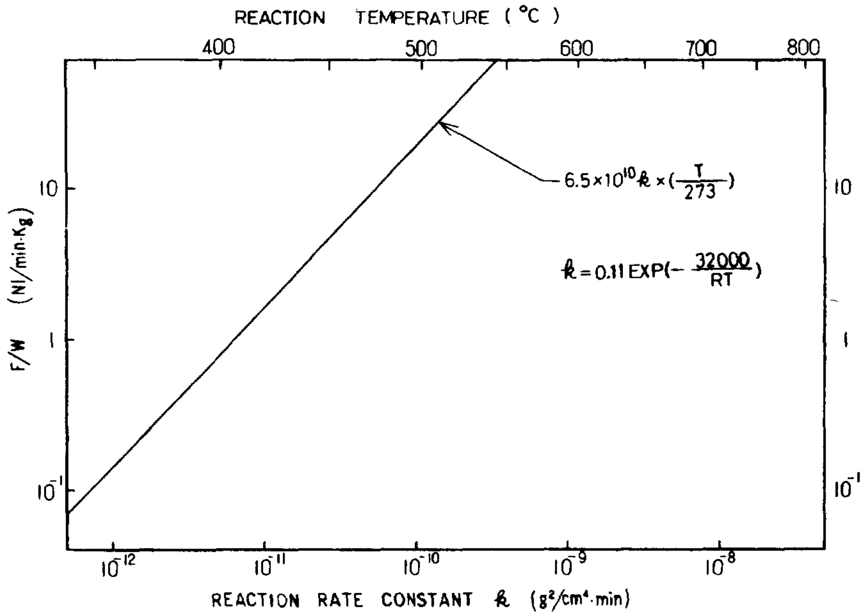


FIG. 17 ESTIMATION OF DINAMIC EXPERIMENT

5. Storage Process

As to the storage of the radioactive noble gases, various methods[4] are proposed and investigated. Among them, the method to compress the gas into a cylinder will be most promising at the present stage, thinking of the practicability, economy and safety. However, this method necessitates the use of compressors in the high radioactive lines and the operation at high pressure, and these demands cause the problems of the leakage of the compressed radioactive gas, the recovery of the residual gas in the connecting lines and overpressurization of a cylinder. As the storage process handles the most high radioactive gas in the total system, even a small leakage cannot be permitted, otherwise DF of the total system will be spoiled to a great extent. To eliminate these problems, a new storage process has been developed and examined. This process consists of a gas holder always operated at subatmospheric pressure, a cylinder packed with adsorbent and a cold bath.

The radioactive gas from the cryogenic adsorption process is once stored in the gas holder and then sucked into the cylinder by adsorption pump mechanism with cooling down the adsorbent in the cylinder. At this time, the cylinder is isolated, taken out of the cold bath and transferred to the pertinent storage yard. Pressure in the cylinder gradually becomes higher with the rise up of the adsorbent temperature. However, the equilibrium pressure at the ambient temperature is about one third of that of the conventional cylinder method. In our method, compressors and pumps are eliminated from the process and the gas is always handled at the pressure below one atmospheric. So, the above mentioned problems can not be expected.

5.1 Experimental

Apparatus and Method

A flow sheet of the experimental apparatus and equipment's sizes are shown in Fig. 18. Equipments are in about one hundredth scale of the assumed actual plant system. Before the experiments, adsorbent was heated to 85°C and evacuated to 0.1 mmHg to remove the adsorbed moisture and impurities. Pure nitrogen gas was used as the process gas, because the majority of the assumed radioactive gas is nitrogen (about 90%). The volume of the gas sucked into the cylinder was calculated using the volume and pressure of the gas holder. Adsorption was started simultaneously with cooling down by liquid nitrogen, and the pressure and adsorbent temperature were measured. After the completion of adsorption, the cylinder was isolated and warmed up to the ambient temperature from 25°C to 40°C. Adsorbents used are 3 charcoals, "Kurale 4GA", "Shirasagi G-A" and "VRG" and molecular sieves 5A. Their properties are shown in Table 1.

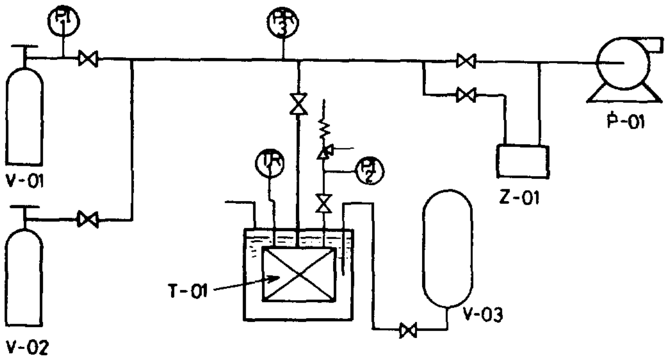


FIG. 18 FLOW SHEET OF EXPERIMENTAL APPARATUS

EQUIPMENTS

No.			
V-01	N_2 Cylinder	Volume	50 l
V-02	Gas Holder	〃	10 l
V-03	Liq. N_2 Tank	〃	20 l
T-01	Cylinder	〃	0.3 l
Z-01	Cold Trap		
P-01	Oil Rotary Vacuum Pump		

INSTRUMENT

No.	
PI-1	Bourdon's Tube, Range 0 ~ 800 mmHg
PI-2	〃 , 〃 0 ~ 25 kg/cm^2
PR-3	Pirani Gauge, Range 200 ~ 1×10^{-3} mmHg
TR-1	C-A Thermocouple

5.2 Results and Discussion

Pressure obtained by Adsorption

The pressure and temperature of adsorbent were plotted against the adsorption time in Fig. 19. Pressure in the cylinder reached to 1×10^{-3} mmHg by every adsorbents as shown in the figure. Both cooling down and adsorption should be started up simultaneously to reduce the necessary time for the operation using the thermal conductivity of the process gas.

Cylinder Pressure during Storage

Results are shown in Fig. 20 and 21. Cylinder pressure was about one third of that of the conventional cylinder method as shown in Fig. 20, and was in the following order. "Kurale" < "Shirasagi" < "VRG" < MS 5A
As Fig. 21 shows, there is no remarkable increase of the cylinder pressure at the temperature from 25°C to 40°C. Although the temperature rise due to decay heat is anticipated in the actual plant, the large part of radioactivity of the off gas from the nuclear power plant is attributed to short lived nuclides and so the decay heat shortly becomes negligible after the storage. By our calculations, the temperature rise at the center of a cylinder with charcoal is about 20°C just after the storage and becomes nearly zero in a week.
Next items will be the future subjects to be examined.

1) Stability of adsorbent properties, especially adsorption capacity in long term storage.

2) Investigation as a whole system including handling, radiation shielding and remote control.

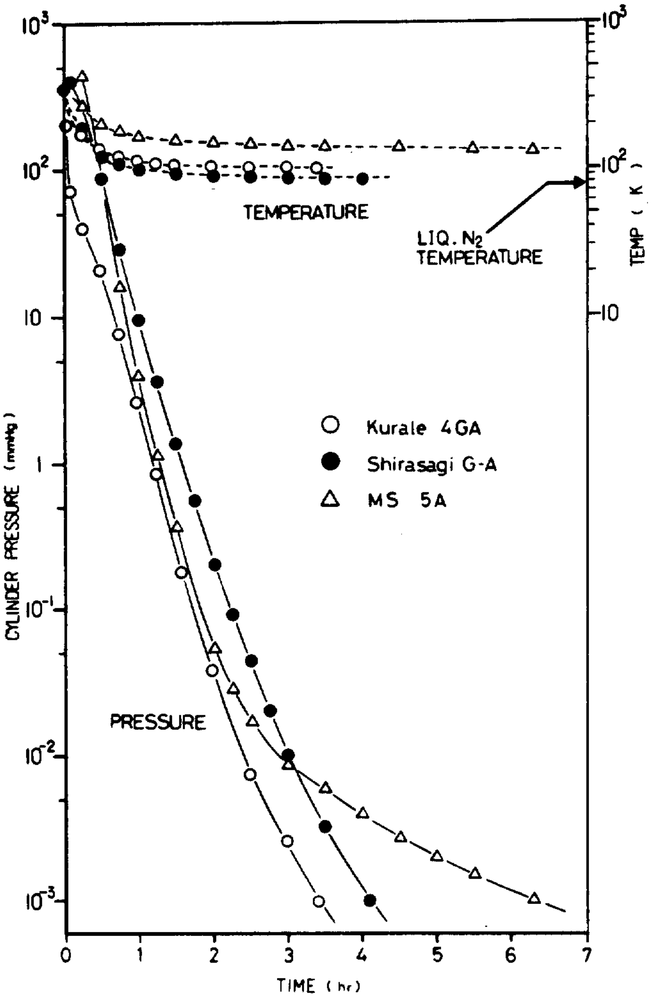


FIG. 19 PRESSURE AND TEMPERATURE AFTER START UP OF COOLING DOWN AND ADSORPTION

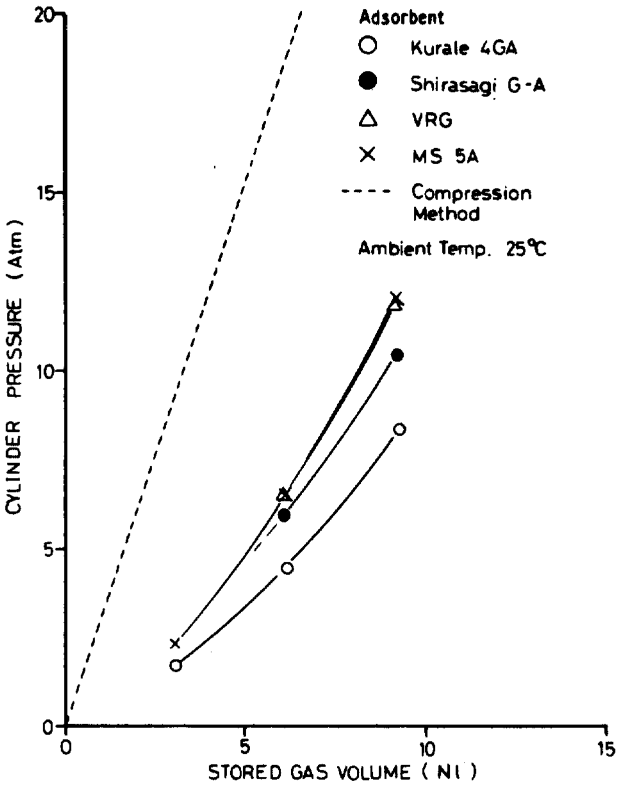


FIG. 20 CYLINDER PRESSURE VS. STORED GAS VOLUME

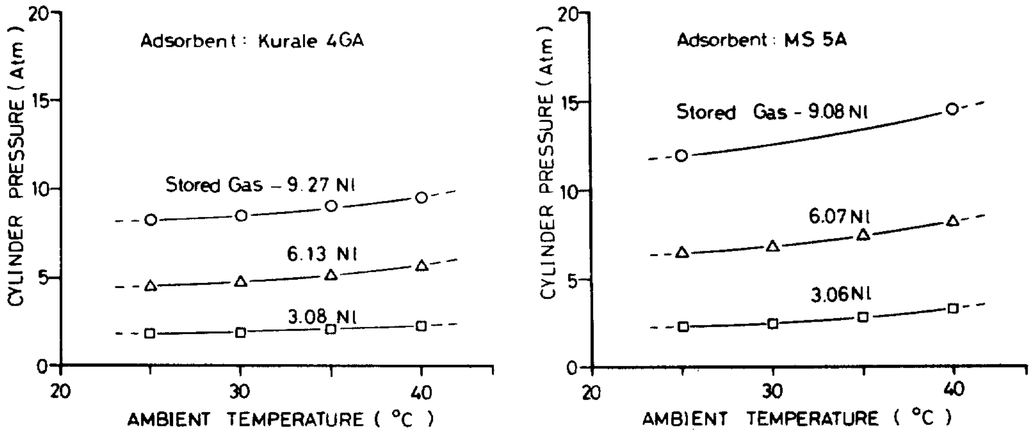


FIG. 21 EFFECT OF TEMPERATURE ON CYLINDER PRESSURE

6. Conclusion

It was proved that our proposed methods would be effective to recover radioactive noble gases from off gas streams of nuclear facilities. However, further investigation is necessary to settle some interesting problems obtained from a series of experiments.

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DISCUSSION

STUART: We have built a similar system installed at Point Beach, a PWR with low oxygen content. For BWR's with high oxygen we recommend use of an inorganic adsorbent to avoid the potential problem of interaction of charcoal saturated with oxygen enriched air. Have you considered this safety issue?

TANABE: We have done a safety analysis involving ozone and oxygen. By the current analysis, we don't expect much difficulty with handling ozone in the charcoal bed. However, the actual behavior of ozone and oxygen has to be found out by future experimental work.

STUART: I think you may be right on ozone. We have a limited amount of data which indicates that it is formed. It may be simultaneously destroyed within the adsorbent bed. I think that additional data must be obtained.

KNECHT: Can this process be scaled up for 85 Kr removal from a commercial scale fuel reprocessing plant (1,400 ton per year scale)? If so, I would be interested in a comparison with other processes currently being considered such as cryogenic distillation and liquid fluorocarbon absorption.

TANABE: Engineering scale data will be obtained by future experiments.

14th ERDA AIR CLEANING CONFERENCE

SEPARATION OF THE FISSION PRODUCT NOBLE GASES KRYPTON AND XENON FROM DISSOLVER OFF-GAS IN REPROCESSING HTGR-FUEL

J.Bohnenstingl, S.H. Djoa+), M.Laser, St.Mastera, E.Merz, P.Morschl

Kernforschungsanlage Jülich GmbH
Institute for Chemical Technology

5170 Jülich / Germany

Abstract

This paper describes a process developed for the retainment and separation of volatile (^{3}H, $^{129+131}$J) and gaseous (^{85}Kr, Xe) fission products from the off-gas produced during dissolution of HTGR-fuel. To prevent unnecessary dilution of liberated noble gases by surrounding atmosphere, a helium purge-gas cycle is applied to enable a coarse fractionating of krypton and xenon by cold-trapping at about 80 K after precleaning the gas stream. The process consists of the following steps:

- deposition of droplets and solid aerosols
- chemisorption of iodine on silver impregnated silica gel
- catalytic removal of nitrogen oxides and oxygen
- drying of the process gas stream
- final filtering of abraded solids
- deposition of xenon in solid form at 80 K and low subpressure
- deposition of krypton in solid form at 80 K after compression to about 6 bar
- decontamination of ^{85}krypton-containing xenon by batch distillation for eventual industrial utilization
- removal of nitrogen and argon enrichment during continuous operation in the purge-gas stream by inleaking air with charcoal.

A continuously operating dissolver vessel, closed to the surrounding atmosphere, yields a very high content of noble gases, f.e. 0.35 vol % krypton and 2.0 vol % xenon. The presented off-gas treatment unit is operated in cold runs with 1/3 of the full capacity and can treat about 1 m^3 STP/h helium, corresponding to a quantity of about 10,000 MW$_e$ HTGR-fuel reprocessing plant.

1. Introduction

The principle waste products from the nuclear power program resulting from the fission process are radioactive fission products. Whereas high-level radioactive wastes have been carefully stored under surveillance, it has been customary up to now either to discharge low-level streams directly to the environment or to give them the minimum treatment necessary to decrease the activity below specific levels.

Several gaseous (^{85}Kr, Xe) and volatile (^{3}H, $^{129+131}$J) radionuclides pose problems which are not already solved by the present state-of-the-art technology with the existing commercial reprocessing plants. Since the delaytime between fuel discharge from the nuclear power reactor and fuel reprocessing is usually more than 150 days,

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+) Kernforschungsanlage Jülich GmbH
Central Division for Advanced Technology

the short-lived products decay to insignificant low-levels during this cooling period. However, ^{85}Kr with a half-life of 10,76 years remains a potential hazard for many years. To avoid local release problems and long-term build-up in the atmosphere, ^{85}Kr must be separated at suitable points at a reprocessing plant and stored for a long period of about 100 years to allow a substantial decay. To keep the radiation dose to the population as low as possible the Commission for Radiation Protection of the Federal Republic of Germany recommends a limitation of the ^{85}Kr release for a reprocessing plant to a value of 10^6 Ci/year. This limitation requires a decontamination factor of $\geq$ 100 for any ^{85}Kr separation process being applied [1].

Although, at present, several cryogenic separation techniques for ^{85}Kr based upon the principle of liquefaction of air are under advanced development [2, 3, 4, 5, 6, 7] careful considerations of the costs and the risk analysis during hot operation as well as positive consequences of the dissolver vessel development encouraged us to initiate the development of a somewhat simpler but very effective equipment. The costs of the above mentioned techniques are very sensitive to the off-gas volume which have to be treated. Therefore, special precautions should be taken to prevent disadvantageous dilution of the liberated fission product noble gases by inleaking air or instrument air.

The main objective of the R&D program of the Kernforschungsanlage Jülich GmbH is the development of the HTGR and the closing of the thorium fuel cycle. Therefore, also the noble gase separation techniques are specially designed for HTGR-fuel reprocessing.

2. HTGR-fuel reprocessing off-gas treatment

In the course of reprocessing spent HTGR-fuel elements, essentially all of the gaseous and volatile radioactive nuclides are released during the head-end treatment, which includes

- crushing and burning the graphite matrix of the fuel element with oxygen, air or oxygen enriched air and
- dissolution of the remaining oxide ash or particles, respectively, in Thorex-reagent.

For both head-end steps specific off-gas treatment units are under development in the KFA: The AKUT-process [8] for the burner off-gas and a helium purge-gas cycle for the dissolver off-gas resulting from an advanced type of continuously operating closed dissolver unit [9]. This type of dissolver has been developed in our institute [10] to simplify the arising off-gas problems. Its main component is a dissolver vessel closed to the surrounding atmosphere suited for the application of a helium purge-gas cycle. Therefore, the resulting off-gas is relatively rich in fission product noble gases.

In a reprocessing plant, serving for about 10,000 MW_e, approximately 240 kg/day heavy metal are dissolved yielding about 3.6 l STP/h krypton and 19.9 l STP/h xenon. The ^{85}Kr release will amount to about 350 Ci/h.

The other components of the helium-stream are nitrogen oxides, iodine, water vapor, droplets and solid aerosols as well as traces of inleaking air. No major alterations in the off-gas composition are expected during continuous operation of the dissolver. The equipment has been designed for the treatment of the mentioned fission product noble gas rich helium carrier gas stream with a through-put of 3 m^3 STP/h helium. Flow-rate and composition of the gas stream leaving the dissolver unit are listed in table 1.

3. Process description

Utilizing a carrier gas two advantages may be obtained: Firstly, an influx of relatively large quantities of air is prevented by taking constructive measures. Secondly, owing to the quantity of carrier gas supplied, the total partial pressure of krypton and xenon in the gas stream can be adjusted to such an extent that in the first succeeding cooling of the gas mixture by means of liquid nitrogen, xenon is deposited in solid form. In order to minimize the quantity of additionally frozen krypton as well as krypton dissolved in solid xenon, it is desirable to keep the partial pressure of krypton and xenon in the gas mixture as low as possible. It has been found advantageous to add to the liberated noble gases such a quantity of helium that the total partial pressure of krypton plus xenon is lowered to about 16 mbar or below. At such a partial pressure the precipitated solid xenon is contaminated with only about 0.1 vol % krypton.

3.1 Separation of contaminants from the helium-stream

In addition to helium and the fission product noble gases the gas mixture contains carbon dioxide, nitrogen oxides, iodine, water vapor, droplets and solid aerosols as well as small traces of air components (O_2, N_2, Ar).

To prevent freezing out and eventual plugging of piping and valves in the cryogenic part of the unit these contaminants must be removed by a gas clean-up system. To achieve this removal the following subsystems are applied:

- filtering of droplets aerosols
- filtering of solid aerosols
- chemisorption of iodine on silver impregnated silica gel (AC-6120)
- catalytic decomposition of the nitrogen oxides and simultaneous deposition of oxygen
- deposition of carbon dioxide and water vapor by adsorption on molecular sieve
- final filtering of abraded solids.

In order to obtain a higher deposition efficiency of iodine on the sorption material AC-6120 [11] the accompanying nitrogen oxides are advantageously removed after iodine filtering. At present the main experimental work is done on cryogenic separation of the noble gases. Therefore the preclean-up system provided for hot operation is only discussed concisely. A schematic block-diagram reviews the necessary processing steps (Figure 1).

a. Filtering of droplet aerosols

Before entering a droplet aerosol filter the temperature of the off-gas stream is lowered by a water-cooled radiator to about 20 °C. Consequently, condensating water is deposited together with droplet aerosols in a suitable filter. A spraying system consisting of a spray pot and a spraying pump is additionally installed to improve the self-purification of the filter from simultaneously deposited solid aerosols. By this equipment the off-gas stream is fogged. For this type of filter, f.e. in the case of a fibrous ring-layer filter, a deposition efficiency of 99.997 % for particles < 3 μ is guaranteed by the manufacturer. But up till now no utilization in nuclear technology has taken place.

b. Filtering of solid aerosols

For the removal of eventually present solid aerosols, a commercially available solid aerosol filter is put in line. Usual high-efficiency aerosol filters of the special class S result a deposition efficiency for solid aerosols of < 0.3 μ particle size to equal or better than 99.96 %. To avoid a watering of this filter the gas stream is heated to about 80 °C.

c. Chemisorption of iodine

Subsequently, the temperature of the gas stream is raised to about 150 °C to favour an optimal iodine sorption. This is achieved by fixation in two alternately operated filter cartridges, filled with the sorption material AC-6120 [11], a silver impregnated product on the basis of amorphous silicic acid. To measure and to check the efficiency of the iodine filtering device, a test filtering cartridge has been installed in the hot cells to be operated in connection with the continuous dissolver under hot conditions.

d. Catalytic separation of nitrogen oxides and inleaking oxygen

The catalytic reduction of the nitrogen oxides takes place by reaction with added hydrogen. The required temperature of about 600 °C is obtained applying an electric heater in connection with a temperature controller. The catalyst is used as bulk material laying on a conic sieve plate to enable a withdrawal to a material handling system by means of a vibrator after being spent. The function of the catalyst is controlled by measuring the oxygen and nitrogen oxide concentration before and after the catalyst bed. The outcoming hot gas mixture is than cooled down from about 700 °C to 20 °C and again condensed water is removed. Any condensed water resulting in the course of this treatment is withdrawn applying a special retainment device.

e. Process gas drying

The helium-stream will contain water vapor, corresponding to a dew-point of about 20 °C, the cooling water temperature, traces of carbon dioxide and ammonia. Prior of the low temperature separation, they will be removed by adsorption in a gas dryer filled with molecular sieve material. After a break-through of the humidity, adjusted to a limiting value of the dew-point of - 80 °C is reached, an automatical change-over to a stand-by dryer is initiated by a hygrometer, installed behind the dryer. Simultaneously, the water is withdrawn from the loaded dryer by means of a closed recovery cycle at a temperature of about 250 °C. Soon after the regeneration is finished the dryer is cooled down automatically to operating temperature.

f. Absolute filters

Before entering the cryogenic unit, the precleaned off-gas stream must pass alternately operated absolute filters of the HEPA type to guarantee complete removal of any abraded solid particles still present in the gas stream.

3.2 Cryogenic separation and concentration of the fission product noble gases and final purification of nonradioactive xenon

Separation of the crude krypton and xenon product obtained and further purification of the xenon fraction achieved by a cryogenic system including

- two precoolers
- two pairs of alternately operated cold-traps for deposition of solid xenon and solid krypton at 80 K
- two high-pressure tanks for intermediate storage of liquid or gaseous noble gas fractions
- a low temperature distillation column for decontaminating ^{85}Kr containing xenon batches
- a charcoal adsorber bed
- a cooling tank for liquid nitrogen.

The components of the separation system are filled into a vacuum container (height: 3.6 m; diameter: 1 m) evacuated by a high-vacuum pumping station to 10^{-5} Torr. Figure 2 gives a full-view illustration of the complete plant. A schematic flow-sheet of the process is shown in figure 3.

The gas mixture arising from the preclean-up system consists mainly of helium, krypton and xenon. After entering the cryogenic part, the preconditioned gas passes a cold-trap for depositing xenon in solid form at the boiling temperature of liquid nitrogen ($\sim$ 80 K). In order to minimize thermal losses, a heat-exchanger is interconnected before the traps to precool the gas stream. The heat-exchanger is designed for lowering the temperature of the gas mixture to about 20 $^{\circ}$ above the temperature at which freezing of xenon in the cold-trap starts so that a freezing out and eventual plugging of piping and valves is avoided with certainty. Then the deposition of xenon is carried out at a low subpressure of 0.7 bar to lower the krypton-content in solid xenon to about 0.1 vol %. Deposition efficiences of $> 3 \cdot 10^3$ were achieved for xenon. In cold runs the capacity of the separators was determined to be 0.48 kg, corresponding to a loading period of 4 hours.

Then the xenon-free gas mixture is sucked from the Xe-separator by a pump (Figure 4) to be compressed by a compressor (Figure 5) to at least 6 bar. To regulate the through-put the high-pressure and low-pressure sides of the compressor are connected with a regulator valve. The compressed mixture flows to the second cold-trap to deposit krypton in the same way. At operation pressure the deposition efficiency is only about 80 %. After expansion to operation pressure of the dissolver vessel by a pressure reducing valve, remaining rest-krypton containing helium is recycled to the dissolver equipment to enable further loading with liberated fission product noble gases.

The separators are subdivided into individual chambers by radially extending thermal conducting copper sheets. Through those the waste gas flows in axial direction, entering in the upper part of the container, called the precooling zone. It is precooled by residual gas mixture which leaves the cold-traps counter-currently. In order to provide optimal deposition areas of maximum size in the freezing zone, the number of copper sheets in the lower part is doubled in relation to the number in the precooling zone. The cooling of the deposition surfaces is effected by a tubular jacket filled with liquid nitrogen. During the regenerating period the liquid nitrogen for cooling the freezing zone is discharged to a collecting vessel. The deposited solids are rapidly thawed by a heating coil extending around the jacket.

When a sufficient quantity of xenon and krypton, respectively has been deposited, the pressure drop in the separator increases to a limiting value, so that the gas feeding is routed automatically to the second separator, while the loaded one is regenerated. To guarantee a continuous operation of the process in connection with the fuel dissolver the separating units are installed in parallel connection.

To recover deposited xenon from one of the cold-traps the container is heated to about 160-165 K to melt xenon, which is contaminated with small amounts of krypton, and to feed it through a flow metering device to a high-pressure bomb for intermediate collection or to introduce it directly to the still of the rectifying column.

The krypton deposited in the second separator in high-purity form is recovered by heating to about 120 K to enable the liquid flow to an intermediate collection tank from which it might be filled directly into steel cylinders for final storage. To remove ^{85}Kr to a content of 3 µCi ^{85}Kr/m^3 STP xenon and to get an extremely pure xenon for eventual industrial application, the previously deposited xenon-fraction must be refined. This is achieved by rectification. Therefore about 4.5 kg xenon-charges are transferred periodically to the still to be boiled under nearly total reflux. This takes place at a pressure of 2-3 bar and a temperature of about 162 K at the condenser of the rectifying unit. The cooling energy required is generated by a refrigerant which is circulated through four pipes between the condensator and the refrigerator. While ^{85}Kr-free, high-purified xenon is withdrawn from the bottom of the still to a high-pressure intermediate collection bomb by gravity feed and then to steel cylinders for further use, the Kr-fraction with some impurities of xenon is recycled from the top of the column to the helium purge-gas cycle.

In first runs unsatisfactory decontamination factors of $\sim 10^6$ were obtained. To obtain a decontamination factor of $> 10^9$, about 1 l STP of inactive krypton is added to the Xe-batch ($\sim$ 800 l STP xenon) to repeat rectification. Applying this technique, a ^{85}Kr-content of < 3 µCi ^{85}Kr/m^3 STP xenon is achievable.

To avoid an enrichment of inleaking air components (N_2, Ar) in the carrier gas stream, this must be purified from time to time by passing over a charcoal adsorber bed.

Cooling of the different components of the recovery system is achieved in all cases by liquid nitrogen from a 100 l storage tank located inside the vacuum container. The charging preferably takes place in accordance with the principle of communicating tubes.

The complete cryogenic system is controlled automatically by a computer program.

Because the possibility of malfunction never can be excluded the cryogenic unit is connected with an additionally installed safety system including collection tanks for a total gas volume of 3 m^3 to take up the whole radioactive gas inventory of the several plant components. The connecting tubes are encapsulated by a second containment.

3.3 Bottling of the noble gas products

Pure fission product krypton and inactive xenon from the separators, respectively from the bottom of the rectifying column are transferred to the bottling system to be filled into steel cylinders and to be weighed. The piping and valves are inside of a second gas-proof containment to prevent outleaking of radioactivity. The bottling is operated automatically. Standard 50 l steel cylinders can be filled up to a pressure of 100 bar in the case of krypton and 200 bar in the case of xenon. A 50,000 MW_e HTGR-reprocessing plant for example will produce approximately 30 cylinders/yr for krypton and 90 cylinders/yr for xenon. The radioactivity of ^{85}Kr per 50 l steel cylinder amounts up to about $5 \cdot 10^5$ Ci.

4. Conclusion and outlook

In summary the developed process is suitable to enable an economical separation of fission product krypton from the off-gas liberated during continuous dissolution of spent HTGR-fuel. The krypton-content of the deposited fraction in the Kr-separator is always 100 %. Furthermore, the process provides an economical method to produce high-purity and inactive xenon from nuclear fuel reprocessing for sale or further industrial application. However the most important incentive to initiate the development of this process is the small ^{85}Kr inventory arising during hot operation. In comparison to the principles of conventional air liquefaction processing, the ^{85}Kr inventory in the plant is lower by a factor of about 10^4.

The unit presented is operated with nonradioactive noble gas mixtures. At present and for the very next future experiments with nonradioactive noble gases will be continued to obtain optimal operation parameters. Then the behaviour of the unit will be tested with traces of ^{85}Kr. The result obtained from cold and tracer runs will give valuable information for the design of a dissolver off-gas clean-up system in a HTGR-fuel reprocessing prototype plant.

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	l STP/h	Ci/h	g/h	vol %
helium	~ 1000	-	-	97.14
xenon (stable)	19.9	-	-	2.0
krypton (stable)	3.36	-	-	0.34
krypton-85	0.24	~ 350	-	0.024
iodine-129	-	$3.5\cdot10^{-5}$	0.22	-
tritium	-	$7.5\cdot10^{-2}$	-	-
water vapor	-	-	22.55	-
nitrogen oxides	~ 5.0	-	-	~ 0.5

Table 1: Flow-rate and composition of the off-gas stream leaving the dissolver equipment

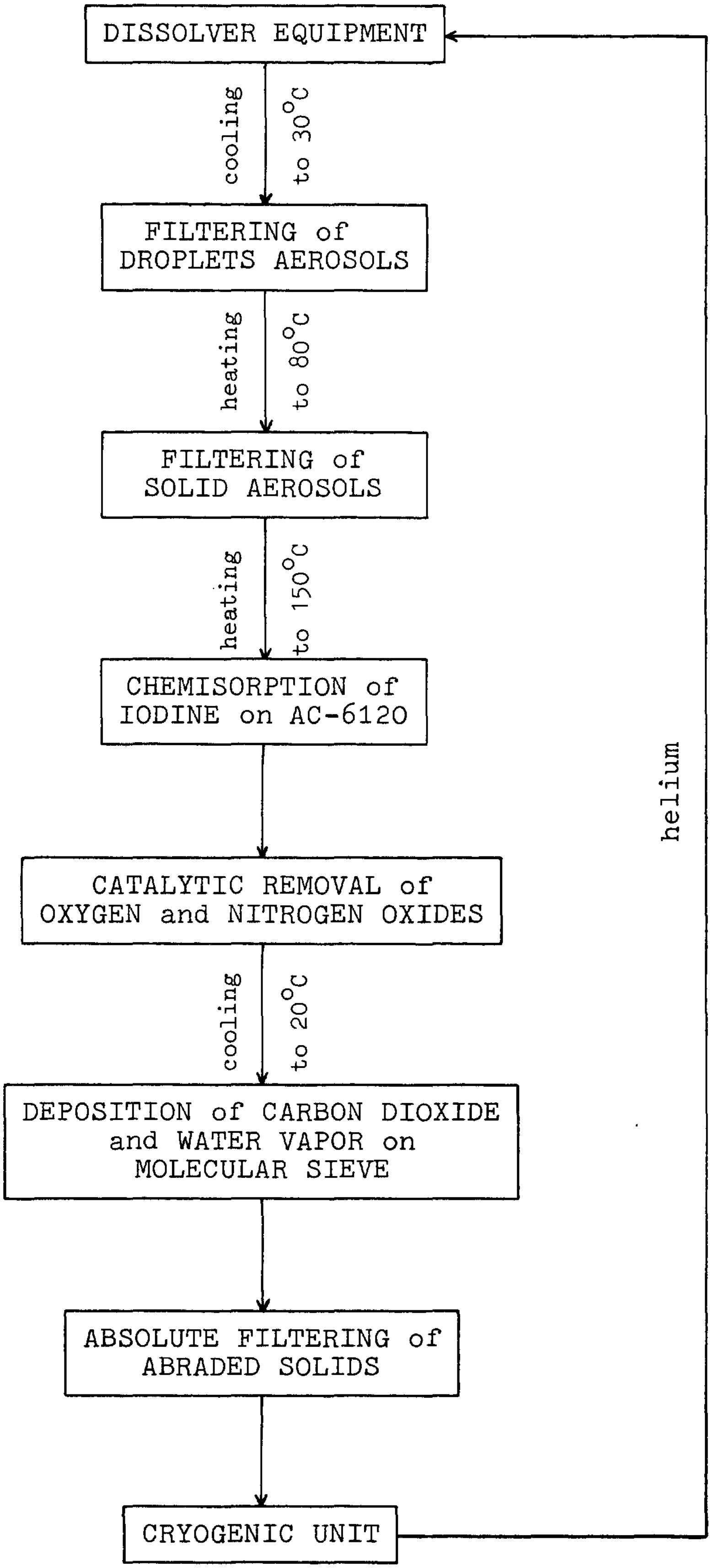

Figure 1: Block-diagram of the gas clean-up system

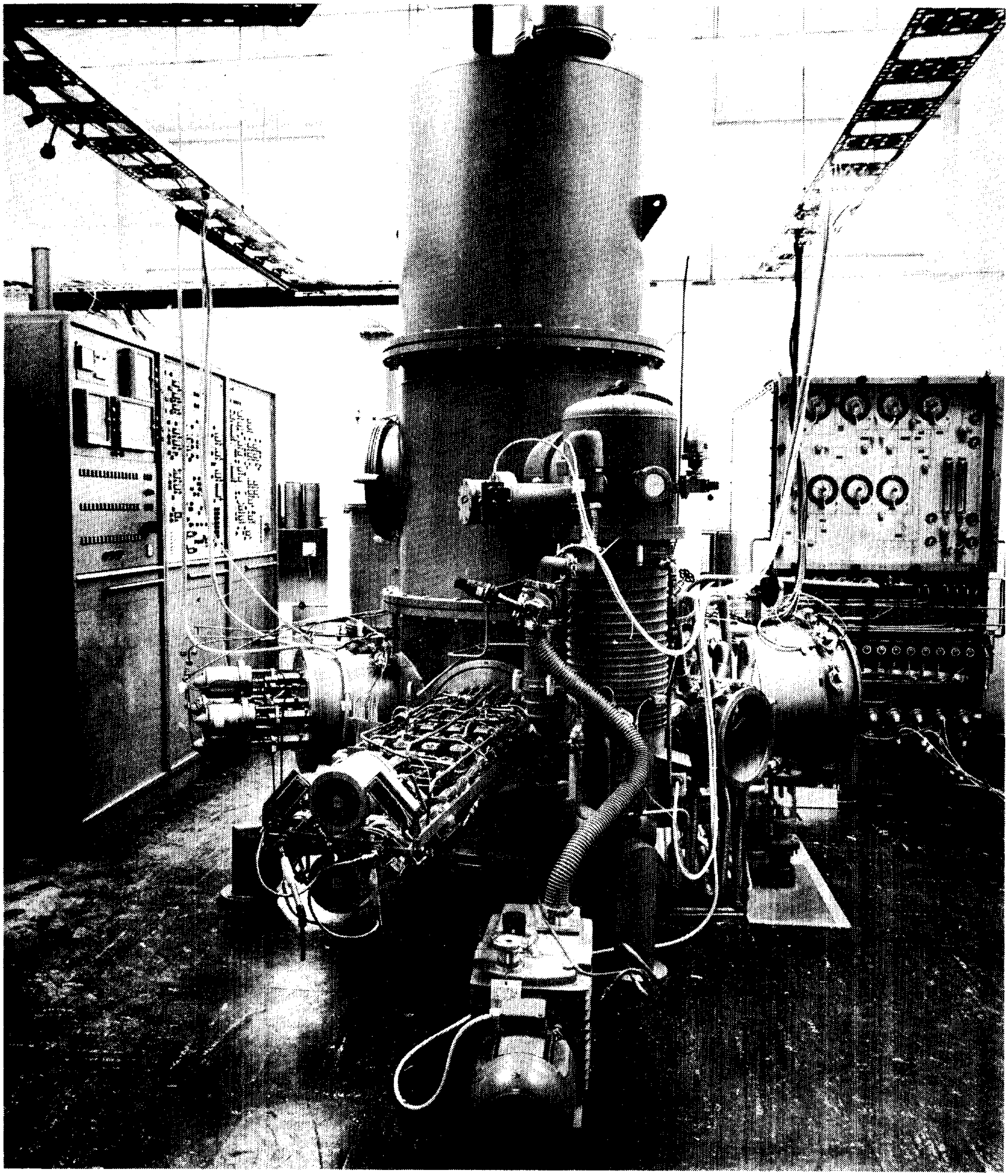

Figure 2: Full-view illustration of the complete plant
left: Instrument and control board
central: Cryogenic unit
right: Safety system

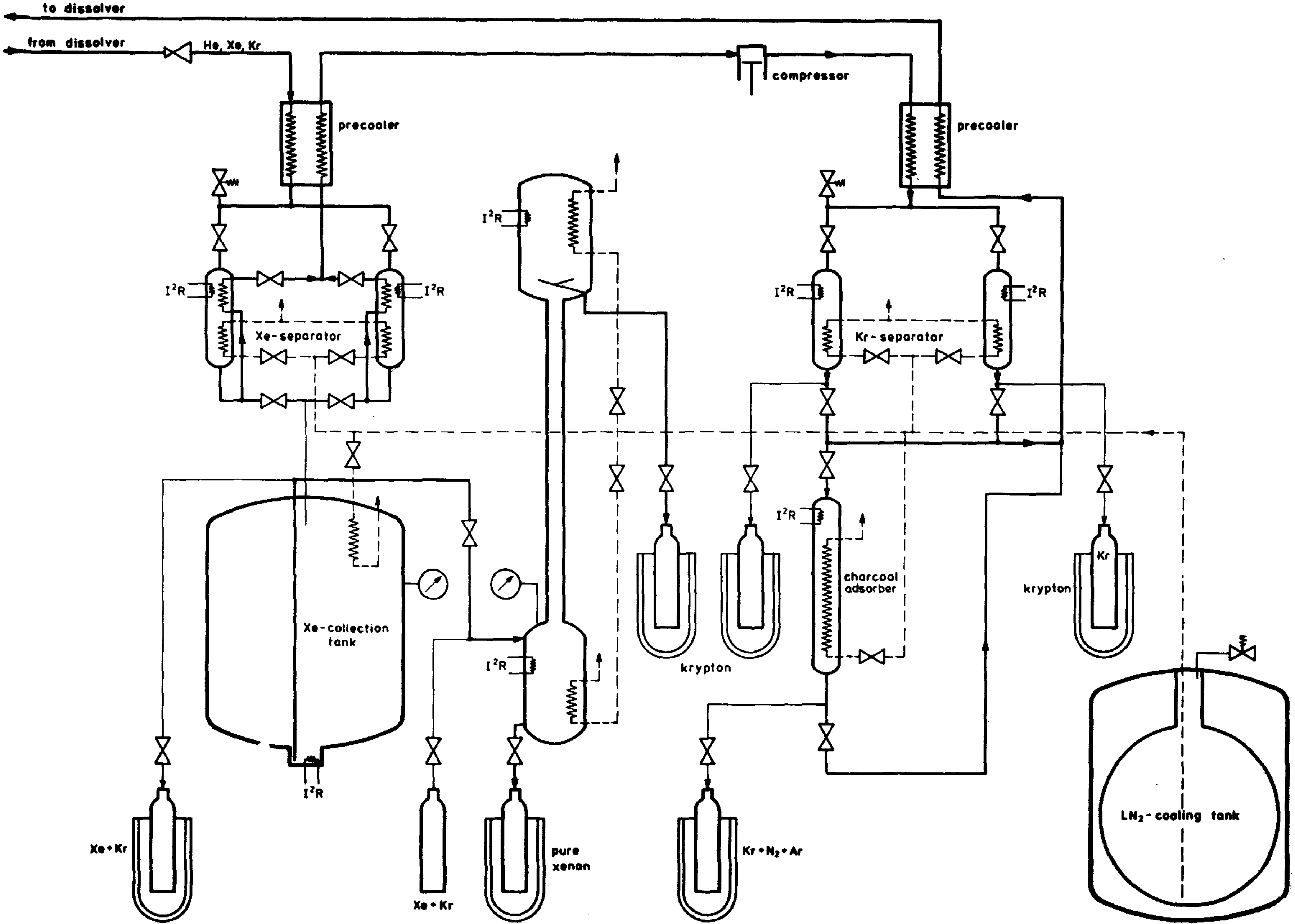

Figure 3: Flow-sheet of the cryogenic part of the helium purge-gas cycle

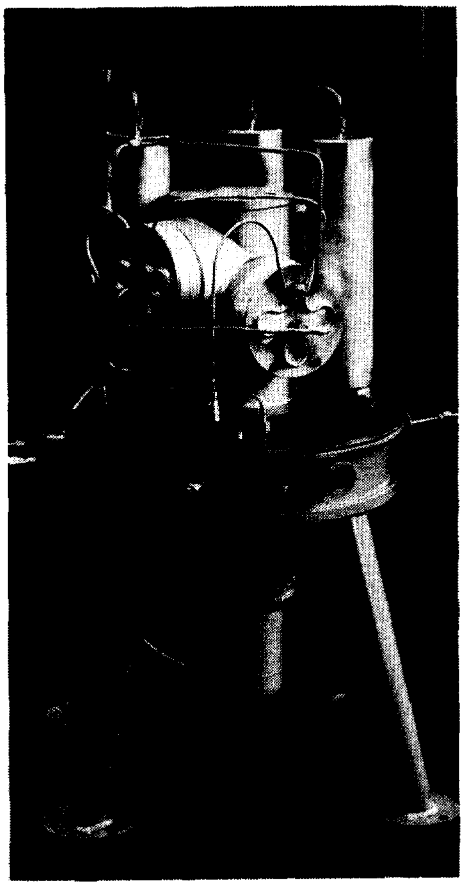

Figure 4:

Pumping station of the helium purge-gas cycle

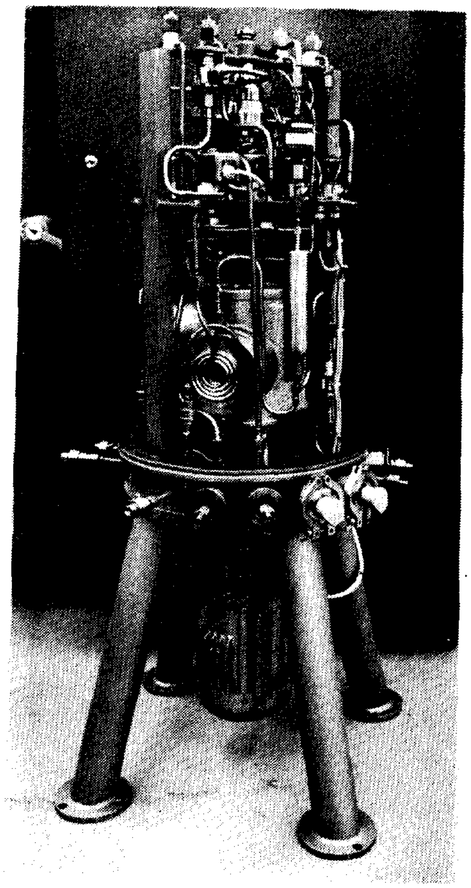

Figure 5:

Compressor station of the helium purge-gas cycle