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## CALCULATION OF FISSION PRODUCT RADIOACTIVITY IN OFF-GASES FROM A BURN-LEACH PROCESS FOR GRAPHITE-BASE FUELS

H. O. Witte<sup>a</sup>

### ABSTRACT

Equilibrium concentrations of fission product oxides in oxygen were calculated from thermochemical data. The calculations showed that, at high temperatures, an appreciable amount of fission product oxides can be expected in the off-gas from a burn-leach process for HTGR fuel. Cooling the off-gas to room temperature should condense practically all the volatile oxides since the equilibrium constants are highly temperature dependent. If the condensed oxides can be removed from the off-gas by efficient filtration or scrubbing, the remaining radioactivity in the gas would be due predominantly to <sup>85</sup>Kr. Stack-dilution calculations showed that, even under adverse conditions, the off-gas can probably be released by a 100-m stack without further dilution.

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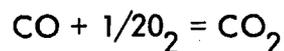
## 1. INTRODUCTION

In the burn-leach process, crushed graphite fuel elements containing pyrolytic carbon-coated carbide or oxide particles will be burned in a fluidized bed of alumina at about 750°C. The behavior of the fission products during actual fluidized-bed combustion has not been studied, but some data were obtained in laboratory-scale tube-furnace experiments.<sup>1</sup> Prototype Peach Bottom fuel irradiated to about 10,000 Mwd/metric ton (Th + U) was burned with a large excess of oxygen. Up to 35% of the cesium and 96% of the ruthenium were volatilized from the high-temperature zone during 6-hr combustions at 800°C. Practically all the fission products condensed and were trapped in the cool end of the reaction tube, and nearly all remaining activity was removed by filtering the off-gas through a 40-μ-porosity sintered-metal filter. The overall decontamination factor was greater than 10<sup>4</sup> in all experiments.

The purpose of this memo is to predict from thermochemical data the qualitative behavior of fission products during combustion. The results of these calculations will serve as a guide in planning fluidized-bed combustion experiments with irradiated fuel and in interpreting the results.

## 2. CONSIDERATION OF GAS PHASE EQUILIBRIA

Combustion in a fluidized-bed burner is achieved by using excess oxygen. Experimental data<sup>1</sup> show a typical steady-state off-gas composition of 90% CO<sub>2</sub>, 5% CO, and 5% O<sub>2</sub>, analyzed at about 25°C and 1 atm pressure. According to the equilibrium

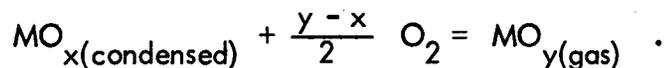


the  $\text{CO}_2/\text{CO}$  ratio found in the burning experiments should have had equilibrium oxygen pressures of about  $10^{-87}$  atm at  $300^\circ\text{K}$  and  $10^{-18}$  atm at  $1000^\circ\text{K}$ . On the other hand, with an actual oxygen pressure of about 0.05 atm, the CO pressure should have been very low. In actual burning, we have relatively high pressures of both  $\text{O}_2$  and CO; so, from the standpoint of thermochemical equilibrium, one cannot predict whether reduction by CO or oxidation by  $\text{O}_2$  will be the predominating reaction.

The formation of volatile fission product oxides in general increases with increasing oxygen pressure. For example, under the actual oxygen pressure (0.05 atm), the stable ruthenium compound in the condensed phase is  $\text{RuO}_2$ , which oxidizes to volatile  $\text{RuO}_4$ . Under the actual CO pressure, the  $\text{RuO}_2$  should be reduced to elemental Ru, but this was not noted in the previously mentioned experiments. As to cesium, the stable condensed compound under the actual oxygen pressure is  $\text{Cs}_2\text{O}$  ( $\text{CsO}_2$ ) at  $1000^\circ\text{K}$  and  $\text{CsO}_2$  at  $500^\circ\text{K}$ . Under reducing conditions, the condensed phase is  $\text{CsO}$ , which sublimates. In this case, cesium volatilization should be independent of the oxygen pressure and, because of the fairly high vapor pressure of gaseous  $\text{CsO}$  above condensed  $\text{CsO}$ , should be markedly higher than the ruthenium volatilization. In the actual burning experiments, ruthenium volatilization was greater, and cesium volatilization was strongly dependent on the oxygen pressure. This indicates the predominating influence of the oxygen pressure on fission product volatilization. Hence, in the following calculations of fission product volatilization it was assumed that all reactions were predictable by the actual oxygen pressure. It was further assumed that the condensed phases of the fission products consisted of the oxides which are stable under the actual oxygen pressure and that each condensed phase was a pure phase with a chemical activity of unity.

### 3. THEORETICAL BACKGROUND

Fission product volatilization is expressed by a reaction of the general type:



The vapor pressure of the gaseous species is calculated from the equilibrium constant and the oxygen pressure:

$$P_{\text{MO}_y} = K \left( P_{\text{O}_2} \right)^{\frac{y-x}{2}}$$

For elements having several gaseous oxides,  $\text{M}_{x_i}\text{O}_{y_i}$ , we calculated the equivalent pressure of the element in the gas phase as follows:

$$P_e = \sum_i x_i P_{\text{M}_{x_i}\text{O}_{y_i}}$$

assuming that the element was present as a monatomic gas. From this pressure, we derived the total vapor concentration by the ideal-gas law:

$$\frac{n}{V} = \frac{P_e}{RT} \left( \frac{\text{g-atoms}}{\text{unit volume}} \right)$$

where  $n$  is the number of g-atoms of the fission product element.

### 4. FISSION PRODUCT VOLATILITIES

By use of the formulas in Sect. 3, the equilibrium vapor concentrations of Cs, Ru, Te, Tc, and Se were calculated at 300, 500, and 1000°K at oxygen pressures of  $10^{-2}$  atm and 1 atm (Table 1).

The equilibrium data and the data for the stability of the condensed compounds at 500°K and higher were taken from the compilation of Bedford and Jackson,<sup>2</sup> while the data at 300°K were taken either from Kubaschewski<sup>3</sup> or were estimated.

Table 1. Equilibrium Concentrations of Volatile Fission Products in Oxygen

Element	Concentration of Element in Gas (mg/liter) when					
	$P_{O_2} = 1 \text{ atm}$			$P_{O_2} = 10^{-2} \text{ atm}$		
	300°K (27°C)	500°K (227°C)	1000°K (727°C)	300°K	500°K	1000°K
Cs	$1.00 \times 10^{-22}$	$1.35 \times 10^{-15}$	3.55	$1.33 \times 10^{-22}$	$1.35 \times 10^{-14}$	1.12
Ru	$2.06 \times 10^{-14}$	$1.47 \times 10^{-7}$	$1.49 \times 10^{-2}$	$2.06 \times 10^{-16}$	$1.47 \times 10^{-9}$	$1.49 \times 10^{-4}$
Te	$2.08 \times 10^{-31}$	$3.41 \times 10^{-14}$	$2.50 \times 10^{-1}$	$2.08 \times 10^{-31}$	$3.41 \times 10^{-14}$	$2.50 \times 10^{-1}$
Tc	$1.71 \times 10^{-6}$	$1.59 \times 10^3$	$1.70 \times 10^4$	$1.71 \times 10^{-6}$	$1.60 \times 10^3$	$5.36 \times 10^4$
Se	$1.05 \times 10^{-6}$	$7.7 \times 10^1$	a	$1.05 \times 10^{-6}$	$7.7 \times 10^1$	a

<sup>a</sup> No stable condensed compound.

Actual  $P_{O_2} = 5 \times 10^{-2} \text{ atm}$

Effect of  
 $P_{O_2}$

Variable

$\times 10^5$  at all  
temp.

none

$\times 3$  @ 1000°K

none

## 5. FISSION PRODUCT YIELD

The reference fuel for the fission product yields was a graphite fuel in which the C/Th ratio was 200 and the C/U ratio was 2750. The initial  $^{235}\text{U}/^{232}\text{Th}$  ratio was  $6.8 \times 10^{-2}$ . The calculation was made for a <sup>6 years</sup> 2100-day irradiation and a burnup of 84,000 Mwd/metric ton.<sup>4</sup> Table 2 shows the fission product concentrations in the fuel after 250 days cooling time.<sup>5</sup>

Table 2. Fission Product Content of Reference Fuel After 250 Days of Cooling

Element	<u>Grams of fission product</u> Grams of fuel
$^{85}\text{Kr}$	$5.83 \times 10^{-6}$
$^{103}\text{Ru}$	$2.68 \times 10^{-8}$
$^{106}\text{Ru}$	$1.79 \times 10^{-6}$
$^{127}\text{Te}$	$2.34 \times 10^{-8}$
$^{129}\text{Te}$	$1.78 \times 10^{-3}$
$^{137}\text{Cs}$	$3.27 \times 10^{-4}$
$^{79}\text{Se}$	$3.15 \times 10^{-6}$
$^{99}\text{Tc}$	$2.08 \times 10^{-4}$

Can't both be right.  $^{129}\text{Te}$  must be greater than  $^{137}\text{Cs}$ .  $\therefore$  Fig 1 maybe OK

## 6. OFF-GAS ACTIVITY

Combustion of the reference fuel (Table 2) in pure oxygen to give an assumed off-gas composition of 90%  $\text{CO}_2$ , 5%  $\text{CO}$ , and a remainder of oxygen and volatile fission product oxides would yield 1.956 liters (at  $300^\circ\text{K}$ ) of off-gas per gram of burned fuel. Figure 1 shows the amounts of volatile fission products that can be present in this off-gas in equilibrium with 1 atm of oxygen. The data from Table 1

??

$$1.956 \left( \frac{1000}{300} \right) = 6.53 \text{ L @ } 1000^\circ\text{K}$$

$$(3.26 \text{ L @ } 500^\circ\text{K})$$

500°K

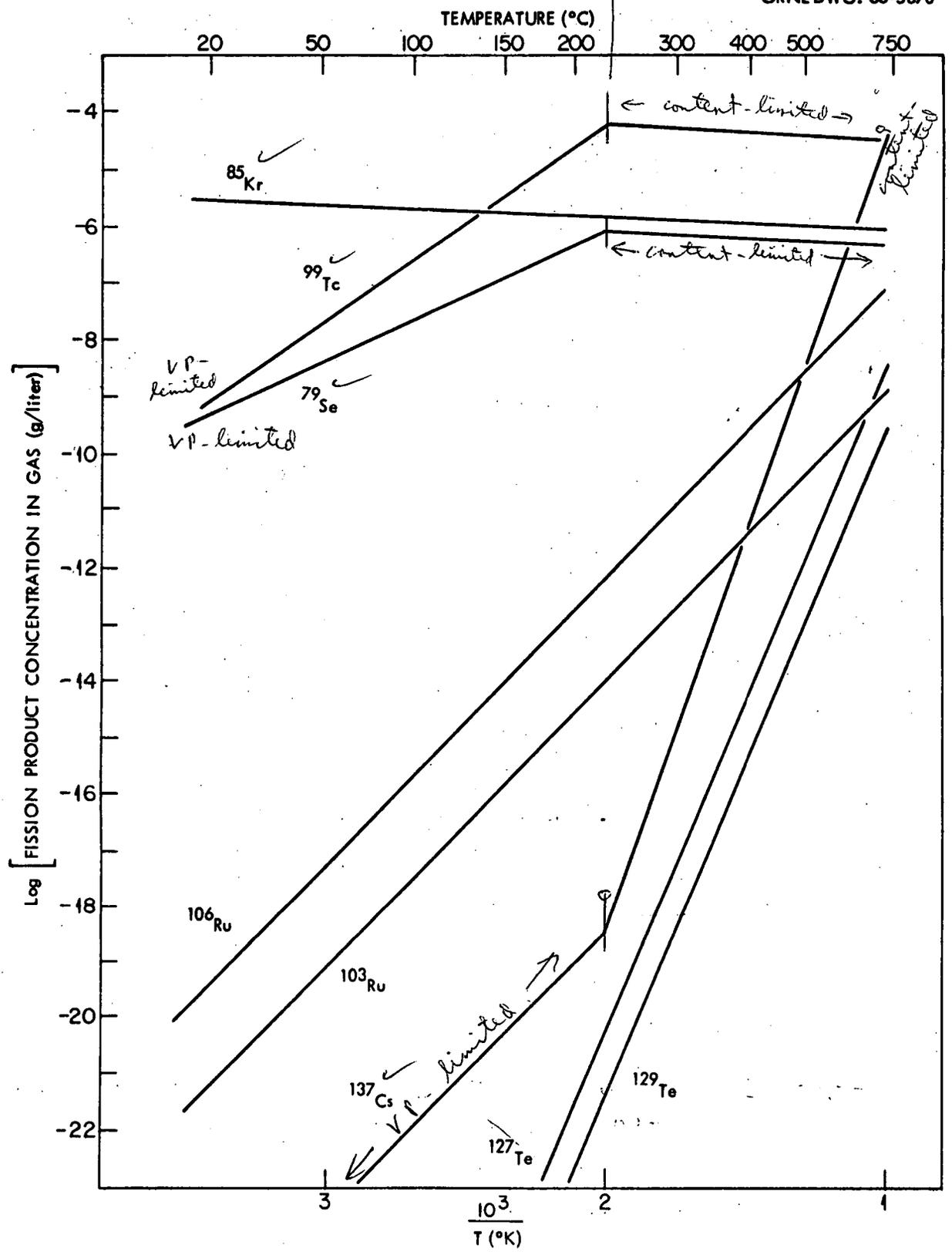


Fig. 1. Equilibrium Fission Product Concentration in Burner Off-Gas When Oxygen Pressure Is 1 atm.

for  $10^{-2}$  atm of oxygen are not shown in Fig. 1 because reduction of the oxygen pressure to  $10^{-2}$  atm would cause no important change. Figure 2 shows the activity of the off-gas in curies of fission product per liter of off-gas when the oxygen pressure is 1 atm. At room temperature, the off-gas activity is dominated by the  $^{85}\text{Kr}$  activity, but the technetium activity is also higher than the maximum permissible concentration in air.<sup>6</sup> Table 3 shows the off-gas activity in curies/liter at  $300^\circ\text{K}$ .

Table 3. Equilibrium Fission Product Activities in Burner Off-Gas at  $300^\circ\text{K}$   
When Oxygen Pressure is 1 atm.

Isotope	Curies/liter
$^{85}\text{Kr}$	$1.23 \times 10^{-3}$
$^{103}\text{Ru}$	$4.63 \times 10^{-17}$
$^{106}\text{Ru}$	$4.42 \times 10^{-16}$
$^{127}\text{Te}$	$4.08 \times 10^{-34}$
$^{129}\text{Te}$	$8.26 \times 10^{-35}$
$^{137}\text{Cs}$	$3.57 \times 10^{-24}$
$^{79}\text{Se}$	$9.01 \times 10^{-11}$
$^{99}\text{Tc}$	$3.06 \times 10^{-11}$

## 7. STACK DILUTION

The above calculations indicate that cooling the burner off-gas to room temperature should result in condensation of very nearly all the volatile oxides. If the bulk of these oxides can be removed by efficient filters, the predominant remaining radionuclide would be  $^{85}\text{Kr}$ . Since its contribution to the off-gas would be 1.23 mc/liter (Table 3), and since the maximum permissible concentration in air is,

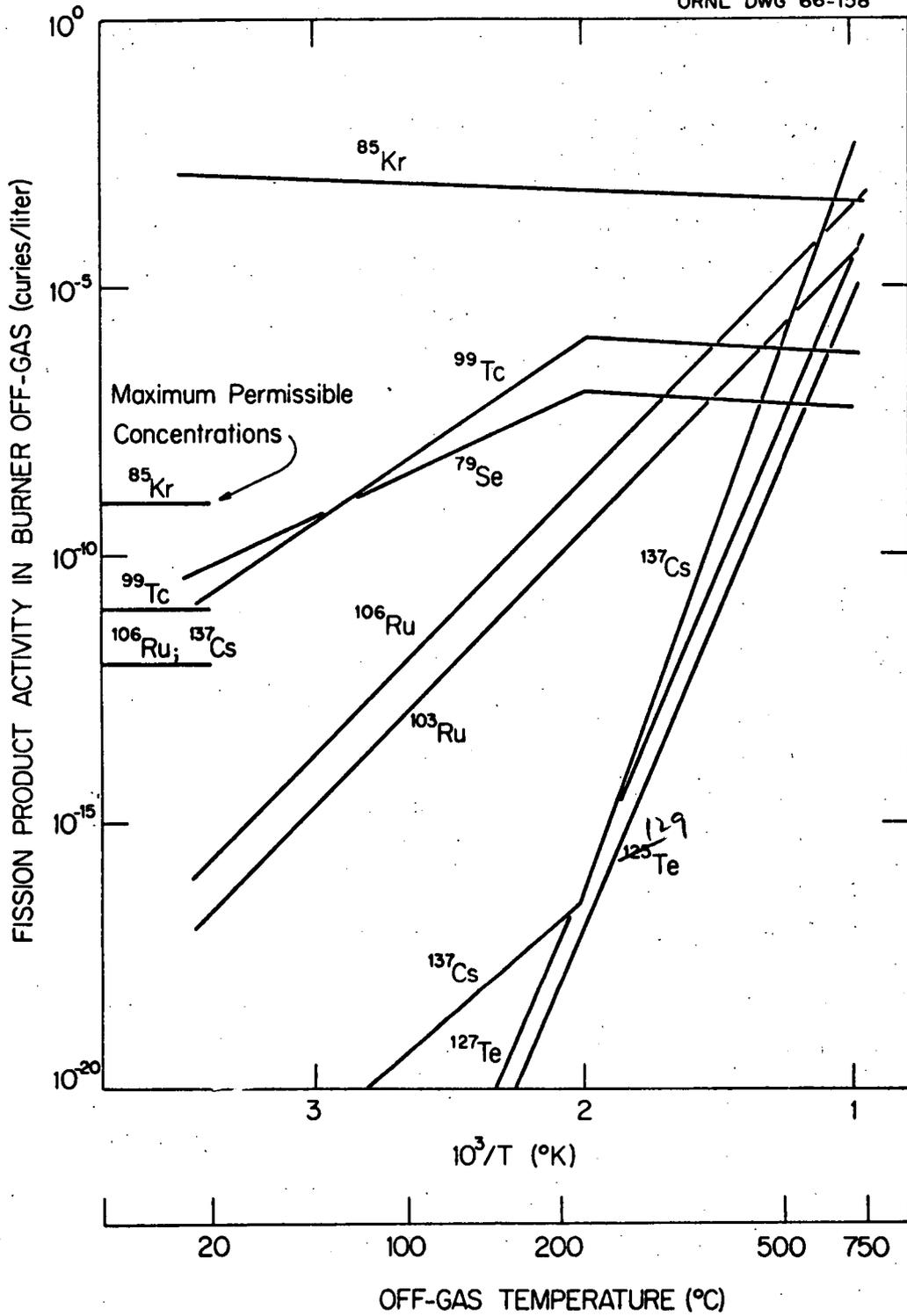


Fig. 2. Equilibrium Fission Product Activities in Burner Off-Gas When Oxygen Pressure Is 1 atm.

according to Ref. 6,  $10^{-6}$  mc/liter, a minimum dilution factor of about  $10^6$  would be necessary before this off-gas could be released to the atmosphere. The reprocessing of the reference fuel specified above at a rate of 150 kg (Th + U) per day would result in an off-gas release of about 36 liters/sec. Since the  $^{85}\text{Kr}$  activity is 1.23 mc per liter, there would be a release of about 44.2 mc/sec, but release through a 100-m tall exhaust stack might be sufficient to provide the necessary millionfold dilution. For calculation of stack-to-ground dilution of this activity we used the data given by Nichols and Guthrie.<sup>7</sup> They describe the concentration of an effluent, assuming no depletion by deposition or washout, by the Gaussian formula:

$$X = \frac{Q}{\pi G_i G_k \bar{u}} \exp \left[ -1/2 \left( \frac{y^2}{G_i^2} + \frac{k^2}{G_k^2} \right) \right]$$

where

X = concentration in curies per cubic meter,

Q = source strength in curies per second,

$\bar{u}$  = mean wind speed in meters per second,

y = cross wind distance in meters from the plume axis, which is assumed to coincide with the mean wind direction,

k = source height in meters,

$G_i^2, G_k^2$  = dispersion coefficients in square meters.

Figure 3 shows the  $^{85}\text{Kr}$  concentration in curies per cubic meter as a function of downwind distance, assuming the worst meteorological category of "extremely unstable conditions," a mean wind speed of 0.5 m/sec, and a 100-m stack. As seen from Fig. 3, the maximum krypton activity under the worst conditions is only slightly above the maximum permissible concentration. So, there is a possibility that the burner off-gas can actually be released into the atmosphere by a 100-m high stack.

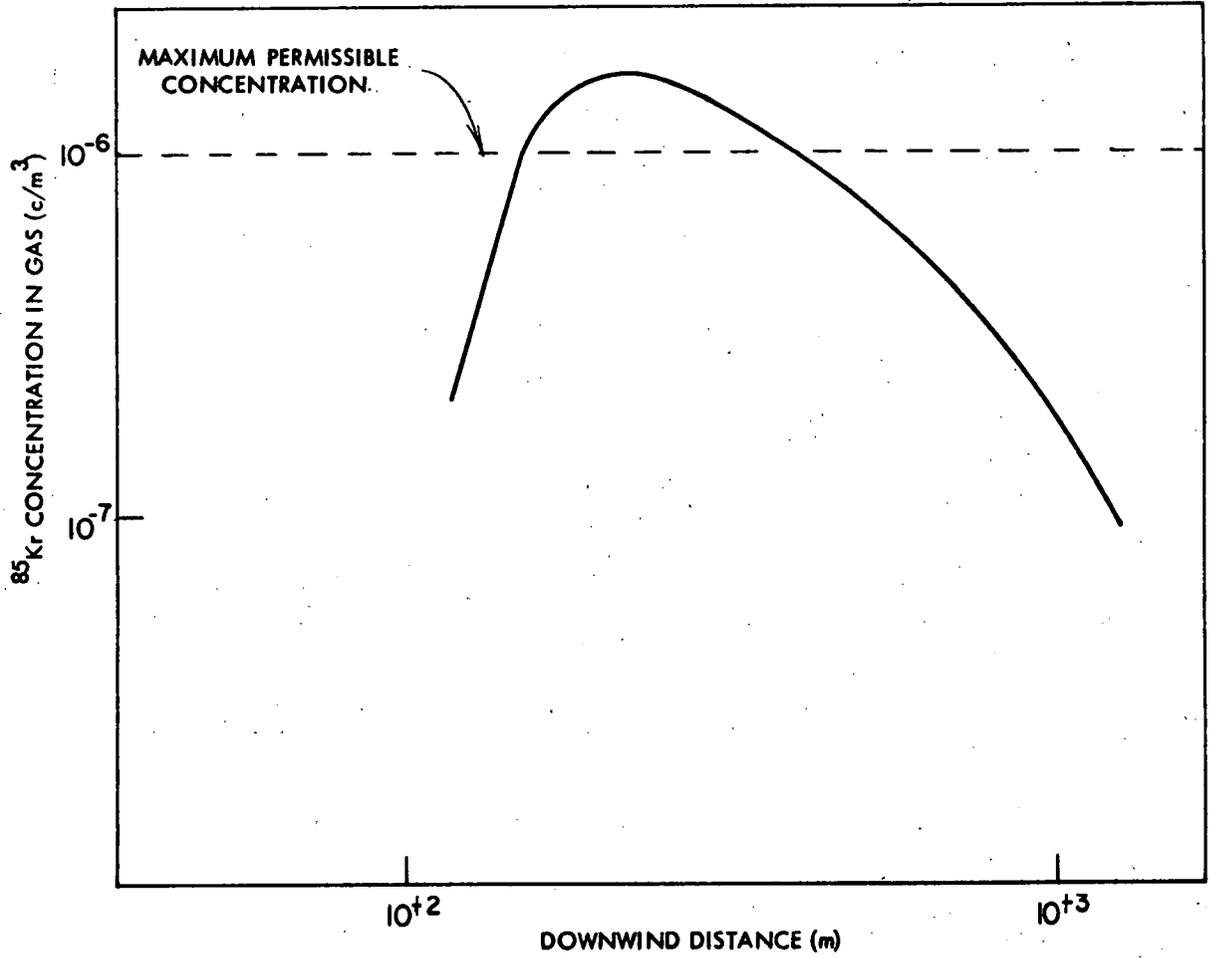


Fig. 3. <sup>85</sup>Kr Concentration in Plume-Diluted Gas As a Function of Downwind Distance.

## 8. CONCLUSION

Calculations of fission product oxide—O<sub>2</sub> equilibria showed, that at elevated temperature an appreciable amount of fission products will be present as volatile oxides in the off-gas from the combustion of graphite fuel. Cooling the off-gas to room temperature is accompanied by condensation of practically all of the oxides. If the condensed oxides can be trapped by efficient filters, the remaining off-gas activity is limited by its <sup>85</sup>Kr content. This off-gas can possibly be released by a 100-m stack without further dilution.

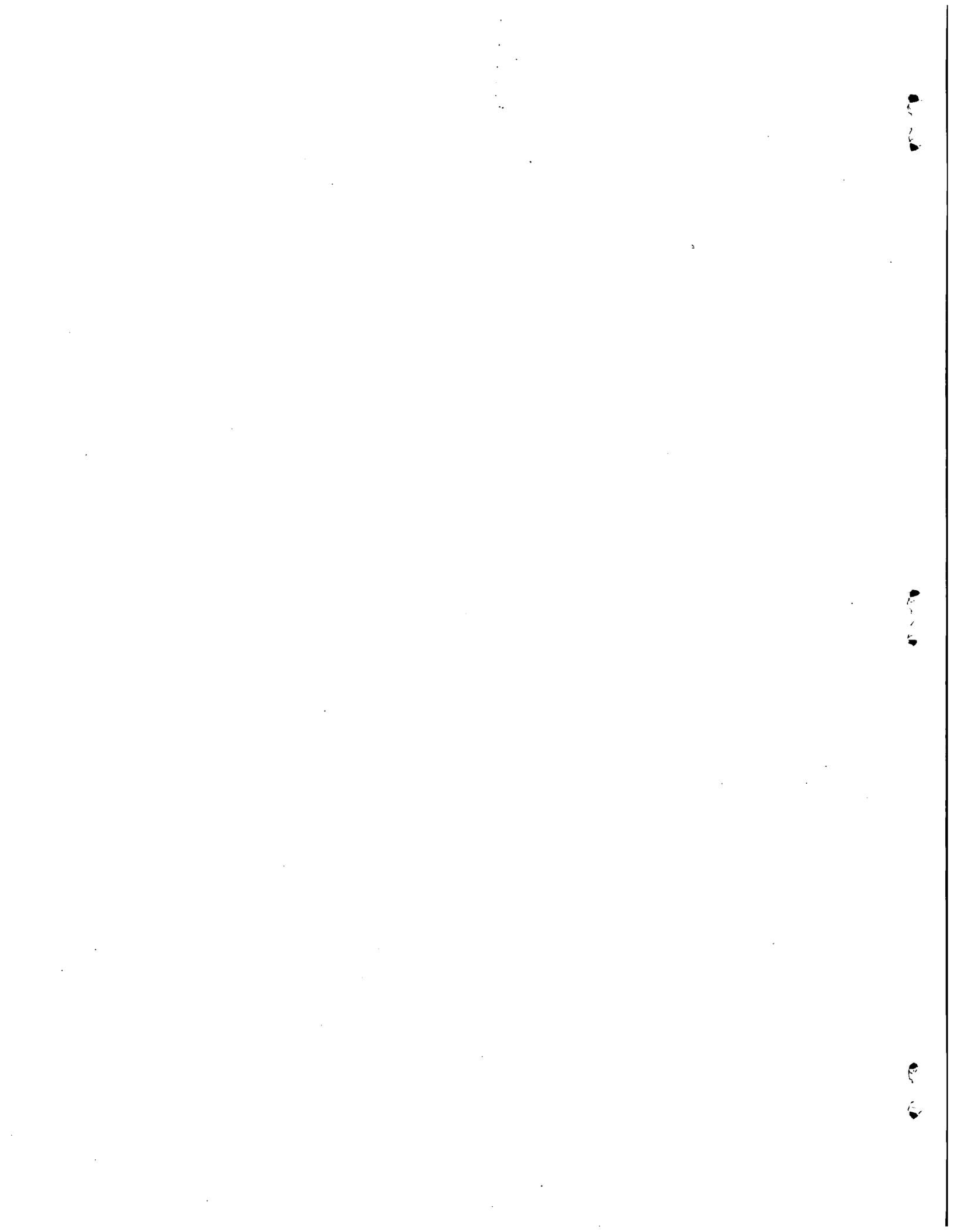
## 9. ACKNOWLEDGMENT

The author thanks L. M. Ferris and E. L. Nicholson for many helpful discussions, and E. D. Arnold for calculation of the fission product yields.

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