D. P. Report 136
(DW (62) 35)

O.E.C.D. HIGH TEMPERATURE REACTOR PROJECT

DRAGON

Dragon Project Report

[redacted]

POST-IRRADIATION RADIOCHEMICAL ANALYTICAL STUDIES ON DRAGON LOOPS AT A.E.R. HARWELL

DECEMBER, 1962

by

P. E. BROWN, R. H. FLOWERS and D. F. M. LUPTON

(A.E.R.E., HARWELL)

Dragon Project Fuel Element Symposium
Bournemouth 28th and 29th January, 1963

Winfrith, Dorchester, Dorset, England

January, 1963

POST-IRRADIATION RADIOCHEMICAL ANALYTICAL STUDIES ON DRAGON LOOPS AT A.E.R.E., HARWELL

December, 1962

by

P. E. Brown, R. H. Flowers and D. F. M. Lupton

(A.E.R.E., Harwell)

CONTENTS

LIST OF TABLES

POST-IRRADIATION RADIOCHEMICAL ANALYTICAL STUDIES ON DRAGON LOOPS AT A.E.R.E., HARWELL

by

P. E. Brown, R. H. Flowers and D. F. M. Lupton

1. INTRODUCTION

During the past three years the DIDO loop and, more recently, the PLUTO loop have provided information on the fission product release from the particular type of fuel originally chosen for HTR design studies. This is a cold pressed mixture of graphite dust and finely powered uranium which happens to stick together firmly and which is remarkably stable during pile irradiation and heating to temperatures around 1000°C. The atomic ratio of heavy metal to carbon is usually about 1:100, and in the PLUTO loop, which has a fuel element closely resembling a possible HTR fuel rod, the metal content comprises a 10:1 mixture of Th-232 and U-235.

The granule sizes of metal and graphite in the fuel have not been closely controlled; the metal is up to 25μ diameter and the graphite up to 2μ diameter, the former having a very wide spread of sizes within this limit. The extent to which the granules retain their form during pressing and subsequent heating is not known, although it is clear that the metals react to form carbides.

All the loop irradiations have indicated the pattern of fission-product escape, but in addition the PLUTO loop has provided information on the distribution of the fission-products around a gas circuit which is essentially a model reactor coolant system.

The current PLUTO loop charge (III) comprises carbon-coated UC_2 fuel particles embedded in a carbon matrix. No results are yet available on this loop. This note attempts to summarise the main features of all the experiments. Fuller accounts are given in references [1], [2], [5] and [6].

2. RELEASE OF Kr AND Xe ISOTOPES

In Table 1 the steady state release fractions for some Kr and Xe isotopes are given for each of four loop experiments completed at Harwell. All fuels were the same, within the limits of our control of fabrication pressure, impurity content and particle size, except that the PLUTO 1A fuel contained thorium. Several points may be noticed:

(a) Temperature has a small effect on release rate, but this is insignificant compared with the effects of unknown variations in the fuel itself.

(b) None of the isotopes is released at more than 50% of its rate of formation, and the majority are released at less than 10%.

(c) There is a pronounced dependence of fractional release upon decay constant, the shorter lived gases being released less than longer lived isotopes of the same gas.

(d) Xe isotopes are released less than Kr isotopes of similar decay constant, by a factor of between 2 and 10.

TABLE 1

Comparison of Gas Releases from Compacted Fuel

Nuclide	Fractional Release				$\frac{1}{\sqrt{\lambda}}$
	DIDO 1A 800°C	DIDO 1B 1130°C	DIDO 1B 1360°C	PLUTO 1A 1150°C	
Kr-89	0.16	0.039	0.079	0.020	16.6
Kr-90	-	0.009	0.012	0.00090	6.90
Kr-91	0.041	0.0019	0.0032	0.011	3.73
Xe-137	0.092	0.012	0.018	0.0024	18.3
Xe-140	0.016	0.00057	0.00038	10^{-5}	
Xe-141	0.0061	-	-	-	1.56
Kr-88	-	0.4	0.2	0.28	120
$Xe\text{-}131_m$	-	-	-	-	
Xe-133	-	0.07	0.1	0.120	810
Xe-135	-	-	-	0.050	217
$Kr\text{-}85_m$	-	-	-	0.23	150

The data from the DIDO 1B and PLUTO 1A experiments show that an interpretation of gas release based upon the simple model of diffusion from uniform spherical graphite granules is inadequate. On that model the steady-state fractional release of an isotope of a single gas should be inversely proportional to the square root of its decay constant, a relationship which holds reasonably well for the DIDO 1A results [1, 2]

It now appears that the dependence of fractional release of gases upon half-life can be much more pronounced than the simple model predicts. Such an effect could be produced by a significant delay time in the compact itself, since this would lead to overall release proportional to something between $\frac{1}{\sqrt{\lambda}}$ and $\frac{1}{\lambda}$. The possibility of Kr and Xe adsorption on the pipes between fuel and sampling traps in the loops, a phenomenon which also would increase the half-life dependence, has been studied in the particular case of the DIDO 1B loop and it is concluded that this adsorption is insignificant.

In this connection it is interesting to refer to the Kr and Xe release data obtained from the similar loop in BRI, Mol [3]. In this loop a fuel compact made from UO_2 and carbon powders, which on heating must react to UC_2 yielded almost equal releases of five rare gases ($Kr\text{-}85_m$, Kr-87, Kr-88, Xe-133, Xe-135). The release increased with rising temperature, but no half-life dependence was observed at any temperature.

These nuclides are all of relatively long half-life, but nevertheless the spherical granule diffusion model would predict a factor of two in release between $Kr\text{-}85_m$ and Kr-87, and of four between Xe-135 and Xe-133.

The method of measurement for these longer lived gases, as in the PLUTO 1A loop, is by gas sampling from a well mixed circulating gas stream.

The theory advanced by the German authors to explain the independence of release fraction and half-life is similar to that proposed by other authors to explain the so-called "burst effect" in out-of-pile annealing experiments. Briefly this theory requires the presence of active sites in the graphite, which can trap diffusing atoms and release them again only when a relatively large activation energy is provided. Thus those atoms which do not meet such a site at all constitute the observed in-pile release, and having escaped very quickly they show no half-life dependence. In an out-of-pile thermal anneal the same atoms constitute the "burst", and the ensuing slow process is the release of the "trapped" atoms.

If this mechanism is operating in the Harwell loops it should be detectable by a careful analysis of daughter products over the entire pipe-work. In the PLUTO 1A loop for instance we would expect to find at least 10-20% of Cs-137, Ba-140 and Sr-90 outside the fuel rings. That which is not in the charcoal trap should be found adsorbed on the pipe walls. Moreover a careful analysis of the fuel itself should reveal an equal loss of all Kr daughter products and of all Xe daughter products, a result which would be noticeable if the losses were of the order of 30% or more.

Such an analysis of the radiochemical results from the DIDO loops has proved that this model is incorrect. PLUTO 1A and 2A are still being analysed.

3. RELEASE OF NON-GASEOUS FISSION PRODUCTS

The behaviour of solid fission products in these loops is rather difficult to elucidate, because ambiguity arises where a nuclide could have diffused as

its gaseous precursor. Moreover it is not possible to gather escaped solids conveniently into a trap for analysis, so that an attempt has to be made to estimate the total amounts of these fission-products on all the complex surfaces of the loops from analyses of a few selected specimens.

At the present time only the DIDO 1A and 1B loop results have been thoroughly analysed in this way [5, 2]; the work is in progress on PLUTO experiments. However since the PLUTO 1A loop was a close copy of a real HTR circuit it is interesting to make some preliminary comments on contamination levels on pipe surfaces at the end of the two month run.

(a) The DIDO 1A and 1B Loops

After 75 days at around 1000°C, an analysis of components from this experiment showed that in addition to the rare gas daughter products deposited in pipes and traps some fission products had escaped into the graphite fuel box and spine. At the time of writing the DIDO 1A report [2] no firm conclusions were drawn from this result because it was considered that the unknown residence time of Kr and Xe could account for most of the observed activities. On reconsidering the results in conjunction with the more recent results from the DIDO 1B loop it seems most unlikely that any significant fraction of the solid fission products found in the graphite arose from deposition of rare gas decay products on the surfaces. The reasons for this assertion are:-

(i) The order of increasing rare gas fractional release is different from the order of increasing fractional release of daughter products, which would not occur if a fixed fraction of each Kr and Xe isotope diffused into the graphite during the passage through the fuel capsule.

(ii) The quantities of the daughter products found in the graphite are much larger than would be expected from the decay of the gaseous precursors during their few seconds of travel through the capsule, and since the graphite surfaces are too hot to allow adsorption of Kr and Xe these gases must move at the same rate as the helium carrier.

It follows that certain metallic fission-products escape from the fuel compacts at a rate comparable with the rare gases. There is probably a dependence of release on half-life, as for the gases, but since only solids of half-life greater than one week are of importance in practice this dependence is of no great significance. Table 11 [2], in which the "maximum" fractional release column is pertinent, and Table 15 [5] show the order of releases of some long-lived metals during operation of loops in DIDO. They should be compared with the steady-state values for the longer-lived gases in Table 1, which are in the range 0.1-1. It is clear that temperature has only a minor influence within the region 1000-1400°C, and that Cs and Sr escape from the compacted fuel about as rapidly as Kr and Xe, giving apparent D' values of around 10^{-7} sec^{-1}. The heavier rare-earth fission-products, Sm, Eu and Gd, probably escape at a very similar rate. Ba, Y and the other rare-earths follow, with D'

of the order of 10^{-9} sec^{-1}. Zr and Ru are well retained, giving D′ of about 10^{-12} sec^{-1}; this could be entirely due to recoil and sputtering effects. The release of I is small compared with the rare gases, but there is considerable discrepancy between the two DIDO loops regarding D′ for I-131; this could be a temperature effect. D′ appears to lie between 10^{-11} and 4×10^{-10} sec^{-1}.

It is interesting to note that of the fission-products which escaped from the fuel rings in the DIDO loops only I-131, Cs-137, Ba-140, Y-91 and Sr-89, (apart from Kr and Xe), were transported into the cold purge pipe. Only 1% or less of the released material reached the pipe, with the exception of I-131, of which 10% entered the pipe. Deposition in the pipe was very rapid, so that no solids migrated more than 20 cm along it.

(b) The PLUTO 1A Loop

Although all radiochemical analysis of components from the 1A loop was completed in October, 1962, the interpretation of the results is still incomplete. A full report will be made in February 1963; preliminary results are given in [6].

The main operational parameters of the loop are reported in full [4] by Mr. F. Sterry and co-workers; the most important point to remember when studying the analytical results is that this experiment used compacted fuel, at a centre temperature of 1150°C, enclosed in a purged graphite tube. The outer surface of the tube was cooled by helium, circulating in a system which contained the essential features of a reactor coolant circuit. Thus the cleanliness or otherwise of this circuit is a measure of the extent to which fission products in a very hot fuel may be kept out of the coolant, at least over a period of 50 days.

(i) The Main Coolant Pipes

The 15.5 cc/sec helium stream, which purges fission gases from inside the fuel tube, passes through a 5 litre charcoal bed at 30°C before rejoining the main helium coolant circuit. Hence all rare gases which decay to radioactive daughter products are reduced to unmeasurable levels of activity before entering the main circuit by this route. The other possible mechanisms of transport of solid fission products to the main helium circuit are:-

1. By solid diffusion through the graphite fuel-tube and subsequent movement over the metal surfaces.

2. By diffusion of short-lived Kr and Xe into the main helium coolant, either through the fuel tube or through leaking seals at the end of the fuel rod.

3. By transport of contaminated graphite dust from the outer surface of the fuel tube.

Samples cut from these pipes (PA 1 and 2) were relatively inactive and therefore susceptible to contamination during the

cutting operations in the high activity handling cells. Assuming the extreme case that all the Zr-95 found was in this category it is still certain that Sr-89 has arrived in the pipes during loop operation. All other nuclides are of the same order of magnitude as expected to be associated with the Zr-95 in fuel dust.

Since the pieces analysed represent about 10^{-2}-10^{-3} of the total main circuit surface area it follows that between 50 and 500 mC of Sr-89 was plated out in the circuit at shutdown, out of a total of 400 curies in the fuel. Up to 20 mC each of Zr-95, Te-129_m, Ce-141 Ce-144, Y-91 and the rare earths would also be present if we assume that all activity analysed arrived before the cutting operations.

Thus it seems that even with this type of fuel the main circuit remains sufficiently clean to permit repair work.

(ii) The Trombone, Halogen Trap and Fission Product Pipe

These three units, which in this order make up the passage of the purge gas between fuel and charcoal delay bed, will be the subject of some detailed calculations to decide whether they contain anything other than rare gas daughter products and fuel dust, but some preliminary observations are made here:-

1. All the units contain those nuclides expected from decay of short-lived Kr and Xe, but the trombone and halogen trap contain in addition significant quantities of fuel dust. Although thorium has not been extracted for actual assay, it is obvious that Pa-233, Zr-95, Ru-103, Te-129_m, Ce-144 and I-131, which do not have gaseous precursors, are present in about the same ratios as in the fuel. A rough estimate puts the fraction of the whole fuel in these units at not less than 10^{-4}. In view of the unstable nature of the fuel in the presence of water or oxygen it may be that some powdering occurred before or during operation.

2. The various forms of charcoal employed in the halogen trap are equally efficient in trapping the fuel dust. There is no evidence of any iodine migration other than that associated with such dust.

(iii) The Stainless-Steel Radiation-Shield and Graphite Heat-Shield

These components, which were at only a few hundred degrees at the hottest point, contain only a few μC per cm^2 of Sr-89, Ce-141 and Y-91. Being situated just outside the graphite carrier tube they would collect any solid fission products capable of diffusing through a centimetre or two of graphite in which the temperature dropped from 1000°C to about 300°C. They are immersed in main circuit helium and appear to carry no more deposited material than the pipes and pressure vessel. This suggests that the activity found in the main circuit does not result from diffusion of fission-products over surfaces.

(iv) Fuel Tube, Carrier Tube and Spine

These pieces of graphite, in close contact with the fuel rings, contain appreciable amounts of rare gas daughter products, recoiled fission products, diffused metals and fuel contamination. No details can yet be stated regarding the most prominent mechanisms for the arrival of specific nuclides but the situation must presumably be very similar to the DIDO loops.

4. REFERENCES

[1] AERE-R.3222 and AERE-R.3223.

[2] AERE-R.3912.

[3] Personal communication. Dr. C. B. Von der Decken, Brown-Boveri/Krupp Reaktorbau, Düsseldorf.

[4] AERE-R.4036.

[5] AERE-R.3913.

[6] DW(62)21.