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To O. C. Simpson

Date October 22, 1948

From J. E. Wilson

In Re: Prevention of Fission Product Diffusion

The favorable consideration now being given to graphite as a fuel rod material calls attention to the need for preventing diffusion of fission products from the fuel rods. There is a good possibility that diffusion of fission products from graphite will take place on a much larger scale than the diffusion from beryllia. The measurement of the helium density of graphite shows that approximately 21% of the graphite volume consists of holes "readily available" to the helium, and another 8% of the volume is filled by the helium on standing.⁽¹⁾ In all probability these same holes are filled when the graphite is impregnated with solution of uranium salts as in Dismore's experiments.⁽²⁾ By reverse diffusion fission products formed in these holes could readily reach the surface. To combat this situation it might be possible to prevent diffusion from either graphite or beryllia rods by one of several methods. These include painting the surface of the rod with an impermeable organic synthetic composition, enclosing the rods in metal cans, electroplating the rods with a suitable metal, or covering the surface with some type of inorganic ceramic glaze.

The first method, coating with an organic synthetic composition, seems the least feasible. No carbonaceous plastic or silicone plastic has yet been developed that can withstand continuous operation at 1000°C. Some of the so-called cold molding plastics approach this performance, but they are made principally of inorganic materials and will be considered under inorganic glazes. Furthermore, carbonaceous plastics have been shown to be decomposed by pile radiation⁽³⁾ and the same is probably true of the silicones since their chemical bond strength is of the same order of magnitude as that of the carbon base plastics. Unless new plastics having unusual properties are developed, further consideration of this type of coating is not worthwhile.

The next method, enclosure in metal cans, seems to offer a possibility of success. Two properties that can rule out a metal are its low melting point or its high neutron absorption cross section. These properties are given for a number of metals in the following table⁽⁴⁾:

Table 1. Neutron Absorption Cross Section & Melting Points of Some Metals

<u>Metal</u>	<u>M.P., °C</u>	<u>Cross Section, Barns</u>
Cb	2415	.00099
Ta	2996	25.
Ni	1452	5.0
Fe	1535	2.5
Al	660	0.24
Cu	1083	3.5
Pt	1756	15.
Cr	1615	2.0

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Aluminum is ruled out because of its low melting point, and tantalum and platinum may be objectionable because of their high cross section. Also tantalum reduces FeO at high temperatures. The others, Cb , Ni , Fe , Cu , or Cr might be successful in the application. Structural strength would not be important since most of the strain would be carried by the graphite. Corrosion by water or oxygen would not enter the picture presumably.

In considering the structural strength necessary, it can easily be shown that fission gases would not accumulate sufficiently to exert an appreciable pressure inside the can. The fission yield of stable Xe and Kr isotopes is about 12%. Given a power of 4000 KW, a uranium oxide content of fuel rod 4.5% of 30% enriched oxide, a volume of fuel rod material of about 800 liters, and 30% voids in the graphite, there will result 0.05 atmospheres pressure accumulated after 1 year of pile operation. It can also easily be shown that the steady state pressure due to less stable isotopes of Xe and Kr would be about 0.01 atmospheres.

Although I , Te , etc. would diffuse through the can to a limited extent, the diffusion would be far less than that from an open graphite surface. There would be no diffusion of Xe or Kr through the metal cans because these gases are not adsorbed by metal. Only those gases which undergo activated adsorption by a metal can diffuse through it. Rare gases are not adsorbed by any metal; hence, all attempts to measure their diffusion through various metals have given negative results. Ryder⁽⁵⁾ failed to detect any diffusion of argon through iron, and Baukloh and Kayser⁽⁶⁾ found that nickel was impervious to helium, neon, argon, and krypton. If He does diffuse through Cu , Ni , or Mo , Smithells found that the rate must be at least 10^5 times smaller than for the common gases⁽⁷⁾. Nitrogen diffuses through Fe and Mo but not through Cu ⁽⁸⁾. This can be related to the fact that it is actively adsorbed by Fe and Mo but not by Cu above room temperature. Activated adsorption, with strong binding forces, is a necessary preliminary to diffusion; it cannot occur as a result of a purely physical adsorption. Nitrogen will diffuse through metals which are capable of forming nitrides, but not through copper or silver to which it is chemically inert. It should be noted that diffusion through glass and silica is of an entirely different type. Diffusion occurs in the molecular state, it is not specific, and the rare gases diffuse readily⁽⁹⁾. This is the type of diffusion which occurs when Xe diffuses through graphite or beryllia fuel rod material or through a ceramic glaze.

Electroplating is the next method of diffusion prevention listed above. Electroplating the surface of a fuel rod with a suitable metal might be more convenient and economical than enclosing each rod in a separate can. References to electroplating of carbon are scarce, but it is quite feasible since the method of coating non-conducting materials with a conducting carbon preparation and then electroplating is well known.^(10,11) Beryllia fuel rods could be electroplated by a similar procedure. One point that should be considered is the fact that electroplated coatings are porous to a greater or less degree, and might be more permeable to fission products than metal cans.

The method of coating fuel rods with an inorganic ceramic glaze offers some promise of success. Glazes can probably be found that are much more impermeable to the passage of gas than graphite. Barrer⁽¹²⁾ gives

the permeability of porcelain at 1000°C as only 0.0161×10^{-9} cc of air diffusion through per second per square centimeter for 1 millimeter thickness when a pressure difference of one centimeter of mercury is maintained across the wall.

The possibility of a reaction between the glaze and the graphite must be taken into account. In the enameling of iron the presence of over 3.7% carbon in the iron was found to cause the enamel to become "transparent, uneven, and otherwise defective".⁽¹⁵⁾ Oxides of zinc are particularly affected by the presence of carbon in the iron. The raw materials from which glazes are made are nearly always oxides or combinations of oxides. Several oxides commonly used in the compounding of glazes⁽¹⁴⁾ and the lowest temperature at which they react appreciably with carbon are listed in the following table:

Table 2. Reactivity of Some "Glazing Oxides" with Carbon

<u>Oxide</u>	<u>Reaction Temperature, °C.</u>	<u>Reference</u>
Na ₂ O(D)	460 (decomposes)	(15)
K ₂ O(D)	(similar to Na ₂ O)	(15)
CaO	1755	(16)
BaO	(similar to CaO)	(17)
MgO	1950	(18)
FeO(R)	450	(16)
MnO(R)	900-950	(19)
PbO(R)	415-435	(16)
ZnO(R)	800	(20)
CdO(RX)	(similar to ZnO)	(20)
Al ₂ O ₃	2125	(21)
B ₂ O ₃ (X)	2400	(22)
Fe ₂ O ₃ (R)	400	(23)
Cr ₂ O ₃	1180	(24)
SiO ₂	1450	(16)
TiO ₂	white heat	(24)
ZrO ₂	1400	(16)

Those oxides which are reduced by carbon below 1000°C are marked "R" and those which are decomposed below 1000°C are marked "D". In addition,

the oxides of metals having very high neutron absorption cross sections are marked "X" since they could not be tolerated in appreciable amounts. The remaining oxides are CaO, BaO, MgO, Al₂O₃, Cr₂O₃, SiO₂, TiO₂, and ZrO₂. Perhaps it will be possible to formulate a suitable glaze from these oxides. Other less common oxides to which there is no objection would increase the usable list. It should be remembered that pile radiation deteriorates some kinds of glasses, however, which are also combinations of oxides similar to ceramic glazes.⁽²⁵⁾ High silicon glass especially is known to discolor rapidly under β bombardment⁽²⁶⁾, so that SiO₂ should perhaps be removed from the list of suitable oxides.

The above list of restrictions on the composition of a ceramic glaze might be sent to ceramic companies and their help solicited in formulating trial glazes. Some of the firms that might be of help in this connection are Ferro Enamel Supply Company, Illinois Clay Products Company, Norton Company, Atlas Lumnite Cement Company, and Johns Manville Company.

It is suggested that as many tests as possible be performed on the glazes before actual pile irradiation and fission product diffusion experiments are started because experience has shown that these experiments are tedious and time consuming. The following program of tests should be carried out to eliminate most of the trial glazes before fission product diffusion experiments are begun. This program could be applied to both inorganic glazes and metal plated fuel rod coatings:

1. Coating Adhesion. Dropping and handling tests on the coated graphite to make sure the coating would adhere sufficiently well to stand operational wear and tear.
2. Temperature Effect. Heating of the coated graphite to above pile temperature to find whether the coating was heat sensitive and whether difference in thermal expansion between coating and rod caused the coating to peel off.
3. Irradiation Effect. Irradiation of coated rod samples that passed the first two tests. Effect of irradiation followed by high temperature and mechanical handling should be tried.
4. Room Temperature Diffusion. Glazes not weeded out by the first three tests should be tested for relative impermeability at room temperature. This could be simply and quickly done by waxing the coated side of a graphite slab to an evacuated chamber and measuring the rate of pressure increase in the chamber with a McLeod gauge. Since the graphite is physically weak it would probably have to be supported against the atmospheric pressure by a suitably placed porous structure. This test would quickly show which of the experimental coatings were of no help in decreasing the permeability of the graphite. Samples which survived this test would be passed on to the final test.
5. Fission Product Diffusion. Small cubes of uranium impregnated graphite would be coated with the formulations found best in the above series of tests, irradiated, and rate of fission product diffusion measured at 1000°C (or whatever pile temperature is decided upon).

It is suggested that the above program should be started as soon as possible if graphite is seriously considered as a fuel rod material. To carry out the program, an increase in the personnel working on fission product diffusion will be necessary.

J. E. Wilson

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