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ACCURATE NUCLEAR FUEL BURNUP ANALYSES

FOURTH QUARTERLY PROGRESS REPORT

September - November, 1962

by

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INTRODUCTION

Accurate fuel burnup analysis is a requirement to aid in reactor design for high burnup fuels and to aid in evaluation of nuclear fuel costs. Current radiochemical methods are limited in usefulness by limited availability of long lived isotopes among fission products, the accuracy with which they can be measured due to errors in their physical constants and the volatile nature of the few available isotopes. Mass spectrometric techniques are being explored as a solution to accurate burnup analysis by seeking to measure non-radioactive refractory fission products. The use of accurate isotope dilution technique on stable fission products does not rely on the knowledge of experimental quantities such as counting efficiencies, decay schemes, decay constants, and in-pile and out-of-pile decay corrections.

SUMMARY

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The first, second and third quarterly progress reports on this project agreement are GEAP-4053-1, GEAP-4053-2, and GEAP-4082.

Work has continued on the Development of Accurate Nuclear Fuel Burnup Analysis. The work performed during the fourth quarter is summarized as follows:

1. Fission Product Migration

The analysis of three fuel samples as a function of radius has clearly established that fission products including cesium, strontium, cerium, and zirconium can migrate in an oxide fuel. This could be a source of error in any burnup analysis based on a highly localized fission product to uranium ratio unless the fission product selected does not migrate. Each of the four fission products measured has a gaseous precursor. Upon completion of the Nd separation scheme development, the same samples will be analyzed for Nd to determine whether the lack of gaseous precursors in the heavy Nd fission product isotopes will help overcome this fission product migration problem.

2. Chemical Separation of Neodymium

A chemical separation scheme for neodymium has been developed. It consists of three major steps. The first step is the removal of bulk uranium from 12<u>M</u> HCl solution on a Dowex-2 column. The second involves the separation of neodymium from rare and alkaline earths by extraction with di(2-ethylhexyl)phosphoric acid in hexane. The final step is the removal of anionic impurities and soluble organic residues on a Dowex-50 column.

Parallel work on reversed phase partition chromatography of Nd on columns of di(2-ethylhexyl)phosphoric acid supported on VYNS is

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very promising and it is planned to incorporate this tech into the separations scheme in place of the solvent extra step resulting in an all-column process.

ULA

PROCRAM PROGRESS

Progress has been made on developing nuclear fuel burnup analysis during this quarter in two main areas. These include studies on fission product migration in oxide fuels, and development of a chemical separation scheme for separation of fission product neodymium from irradiated fuels in preparation for mass analysis.

1. Fission Product Migration

One of the requirements of a fission product which is to be used as a burnup indicator is that it remain immobile in the fuel at the site of its formation, i.e., there is no change in the fission product to fuel ratio due to migration of the fission product. It is obvious that migration effects could lead to erroneous burnup results where burnup is based on a localized fission product to uranium ratio measurement. Therefore, an investigation of fission product migration in irradiated fuel has been undertaken in order to determine the extent and nature of fission product migration.

Up to the present time there have been several studies of fission product migration including work done at Hanford^[1,2] and Chalk River^[3]. The Hanford work included study of Zr-95, Ru-103, Cs-137, Ce-144 and Pu concentration relative to uranium as a function of radius in cylindrical UO₂ fuel. They appeared to have observed rings of depletion in regions near the outer edge of those samples having columnar grain structure. In most cases the effects were relatively small (10-20%) which was within their experimental error. Cs-137 and Ru-103 did appear to exhibit a real migration effect. The Chalk River report indicates that besides migration of the Xe (which is known to occur), Cs-137 and Pu migration appeared to have occurred in particular in those specimens having marked grain growth where the temperature was estimated to be about 1500°C. However, the plutonium data on migration were very scanty since a depletion band near the outer edge of grain growth was observed only one time in one sample.

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This is a limited survey of the field but does serve to point out that (a) migration of volatile species such as Xe or Cs does occur in irradiated fuel, and (b) migration of other species may occur under the influence of grain growth.

Data on fission product migration applicable to the Burnup program is very limited. In an effort to obtain a more complete picture, some fission product and plutonium migration studies are being conducted. The problem of migration has been encountered in the AEC-sponsored Fast Ceramic Reactor Program^[7]. Presented below is a survey of prior work in the subject at this laboratory followed by new work performed on the Burnup Program during the present quarter.

a. Prior Work. Under the Fast Ceramic Reactor Program fuel specimens were prepared, encapsulated and irradiated to high exposure in the General Electric Test Reactor. The fuel consisted of swaged and pelleted fuel having the composition of 20% PuO2, 80% UO2 of which half was U-235. The fuel was encapsulated in rods 150 mil in diameter. The fission product and plutonium distribution relative to uranium has been investigated in three of these specimens. The first specimen V-1 was a swaged fuel specimen with a density of about 75% (of theoretical) with an exposure of 1.06 x 10[°] MWD/T. The second specimen V-2 was a pelleted fuel specimen with a density of 96% and had an exposure of 6.4 x 104 MWD/T. Figures 1 and 2 show a transverse cross section through the fuel and cladding. Besides the central void observed, both specimens showed extensive grain growth, although it is greater in the V-1 specimen. Radial samples which consisted of annular rings, were taken with a diamond bonded abrasive wheel. The dust generated by the wheel was collected on a filter paper with this technique. Annular rings were obtained from 2 mils in width at the periphery to 10 mils in thickness near the center. These samples were dissolved and used for the analysis of the Cs-137, Ce-144, Zr-95 distribution and Pu-239 distribution relative to U-238. The uranium and plutonium isotopic composition was determined

Figure 1. SPECIMEN T-1 TRANSVERSE CROSS

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Figure 2. SPECIMEN V-2 TRANSVERSE CROSS SECTION THROUGH FUEL AND CLADDING

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for each sample. The fission product data obtained are plotted as a function of radius (distance from the periphery in mils) in Figures 3 and 4. For the fission products, the radial flux dependence, which varies by about a factor of two, has been removed and corrections due to variation of fission yield with fissioning nuclide have been made. The data were then normalized to the value obtained for a cross-sectional cut across the whole radius of the fuel.

If no migration occurs the ordinate value for each radial sample should be one. The migration of the Cs-137 from the high temperature of the center to the relative cool periphery is striking in both specimens, and is expected on the basis of its high vapor pressure at these temperatures. There appears to be little migration of the Ce-144 and Zr-95. In the V-1 specimen there does appear to be an increase at the wall of the central void, which seems to be reflected in the increase in the Cs-137 value. It is difficult to determine whether or not this increase occurred from a migration through the fuel or condensation on the wall of the void from a vapor phase which probably exists in the center void. In the V-2 specimen, even though there is a decrease in the value toward the center of the fuel, this probably does not indicate migration but reflects uncertainties in the fission yield due to Pu-239 fission.

In Figure 5, the ratio of the observed to the calculated Pu-239/U-238 ratio normalized to the cross-sectional samples have been plotted. In the V-2 specimen there appears to be no migration of the plutonium However, for the V-1 specimen, there appears to be a plutonium excess around the wall of the central void. This seems to correlate with the fission product distribution. It is of interest that although an excess does occur in this location there seems to be no corresponding ring of depletion within experimental error. However, since the volume of these annular specimens vary as the square of the radius, the amount of material contained in this central region is less than at other radial locations. Therefore, this amount of

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excess would be much less obvious as a depletion band at larger radii. The region of depletion, if it exists, would be below the level of detection. Although a region of excess occurs in the V-1 specimen it is not established whether it was migration through the fuel or condensate on the wall of the void.

The third specimen investigated was a pelleted fuel with two natural UO, pellets adjacent to the fuel. A small reservoir existed adjacent to the UO, pellets. This system provided a very large temperature gradient at the fuel to natural UO2 interface. The specimen was irradiated to 3.5 x 104 MWD/T. The fission products Cs-133, 137, Ce-144, Zr-95 and Sr-90 were measured at various longitudinal locations from samples taken with an abrasive wheel moved in 20 mil increments in a longitudinal direction. A photograph of the specimen after sampling appears in Figure 6, which also contains the location of the samples analyzed. The PuO2-UO2 fuel is in the right half of the picture with the UO, insulator pellets to the left. The columnar grain growth can be seen in the vicinity of the central voids in the fuel region. The spaces occurring in the natural UO, region were caused during the sampling operations. The results of the analyses are plotted in Figure 7. The values were obtained by means of the following equation.

Atom % Fission = Fission product atoms × initial U-238 content × 100 U-238 atoms × fission yield

This is really a method of normalization which should cancel out the dependence of the fission product on fission yield. If no migration occurs, the points for all fission products should fall on the same curve. A glance at Figure 7 shows they do not. However, this is not all due to migration. In the fuel region, the difference in the Zr-95, Sr-90, and Ce-144 is probably due to uncertainties in the fission yield. This uncertainty cannot be used to explain the difference of the Cs-133 and Cs-137 contents and is actually due to migration. The migration of the Cs-133 into the natural UO₂ region

Sample Numbers 31 33 34 58 57 () (10)(1) 20 (21) (22) (23) -Natural UO2-

Figure 6. SPECIMEN IX-1, AXIAL SAMPLE LOCATIONS

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is most extensive and shows a large excess in the region between the two natural UO₂ pellets (\approx 250 mils). The migration of the Cs-137 is also apparent but much less than that of the Cs-133. The difference in behavior can be attributed to the difference in half lives of the gaseous precursors Xe-133 (5.37 day) and Xe-137 (3.9 mins.). There is a slight migration of the Sr-90 at a position 20 mils from the fuel to insulator interface in the natural UO₂ region. At the 60 mil position, the Sr-90 value is the same as that of Ce-144 or Zr-95. The peaking of the Ce-144, Zr-95 and Sr-90 at the fuel interface is due to the higher flux at this point and not to migration.

The system under consideration provides a very sensitive indicator for migration into the natural UO₂ region because of the large difference in fission rates. The sharpness of the interface for Zr-95 and Ce-144 indicates a migration of these nuclides of less than 1% which is about the limit of detection.

The Ce-144 behavior can probably be extended to include the rare earth group of elements. The slight movement of the Sr-90 and the appreciable movement of the Cs-137 is probably a function of their vapor pressures. The fact that Cs-133 and Cs-137 differ gives some information about the diffusion rate of Xe in this system by virtue of the different half lives of the two isotopes.

b. <u>New Work</u>. Under the present contract for Development of Accurate Burnup Analysis, radial samples have been analyzed from a centrally melted fuel rod of 1.24" diameter pellets clad with 304 stainless steel with an enrichment of 4.00% U-235. It was irradiated in the Vallecitos Boiling Water Reactor for about 22 days at two different heat fluxes, the first 18 days at approximately 233,000 BTU/hr-ft² which did not cause melting or appreciably affect the fuel, the second 6 days at 490,000-533,000 BTU/hr-ft² during which the center of the fuel melted and some of the fuel in the upper regions flowed into the lower part of the rod. The total burnup of the fuel was about 300 MWD/Ton.

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Figure 8 shows a cross sectional cut of fuel rod in a region where a central void was formed. The matching autoradiograph is shown in Figure 9. The photograph of the sample (Figure 8) shows a large central void which is about 39% of the radius and 15.5% of the total volume. The inner dark ring is the region of columnar grain growth. At the boundary of the columnar grains, a region of equi-axial grain growth is seen to gradate out into the original sintered material. The remainder of the pellet is a region of original sintered material. The central void and the cracks in the fuel have been filled with a potting compound (epoxy resin) in order to provide a surface which can be polished and etched for metallographic examination.

Significant points in the radioautograph of the sample are the 30 mil wide bright band (concentration of activity) bordering on the central void and the very narrow band about 90 mils from the void. The cracks in the fuel also appear to have high concentrations of activity. The bright spots in the autoradiograph are the sample holes and are quite helpful in locating the exact sample location in relationship to the activity gradient. It can be seen that about 3 samples were taken in the 30 mil inner bright ring. The narrow bright band is approximately 10-20 mils from the end of the columnar grain growth and corresponds to a region of lower density (concentration of voids). This bright band may be due to shine from the activity below the surface, however, 2-3 samples were taken in this region and showed no significant difference from adjacent samples. It is postulated that the apparent activity in the cracks is also due to the shine from below the surface. This section of the fuel rod was placed in a microstage. The surface of the specimen was etched in order to remove any surface contamination. The sample was then positioned under a small drill press. A 20 or 60 mil diameter dental burr was used to drill out material to a depth of 1/8". During the drilling a vacuum line containing filter collected the sample. At the end of drilling, a sample

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Figure 8. CENTER MELT SPECIMEN A. TRANSVERSE CROSS SECTION THROUGH FUEL AND CLADDING.



container was placed under the tube and vacuum closed off. The filter then dropped into the sample container, the vacuum line was loaded with a new filter, and a new sample drilled.

The samples were dissolved and diluted to a constant volume and aliquots were removed for Zr and Ce, U and Pu, Cs and Sr. Mass spectrometer analyses were made for total uranium by isotopic dilution and the U-234 to Pu-239 ratio determined on a Frisch gridded alpha spectrometer. The Zr, Ce, and Cs were isolated and counted on a gamma spectrometer and the Sr isolated and beta counted. From these counts and from the mass analyses, atom ratios of fission product and Pu to U ratios were calculated. In order to remove the flux depression which would occur as a function of distance into the fuel, a computer code was run to calculate relative flux at each sample point on the radius of the fuel. The ratios of fission product atoms or Pu atoms to the U atoms in the fuel were calculated. The flux and the ratio were normalized to the sample closest to the cladding. It was expected that this point had the least effect from migration.

Figure 10 shows the results of analysis of the various samples for Zr-95, Ce-144, Cs-137, and Sr-89, as normalized. The number of atoms for the various fission products have an error of \pm 10%, the uranium an error of \pm 2%, and the calculated value of flux an error of about \pm 10%. Therefore, the overall error is about \pm 15%. It appears in Figure 10 that the Zr and Ce, at least, have moved from mid-radius to the edge of the inner void, however, because of the error in the points and the error in the normalizing point this cannot be certain.

The Pu-239/U-234 ratio were corrected by the calculated production of Pu-239 by both epithermal and thermal neutrons. Due to a possible error of \pm 10% in this calculation and an error of \pm 5% in the counting, the plotted values are probably not better than \pm 15%. The same conclusion is reached in Figure 11 as Figure 10,

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Figure 10. VARIATION OF FISSION PRODUCT DISTRIBUTION WITH RADIUS IN CENTER MELT SPECIMEN A.





namely that the Pu-239 may have migrated from mid-radius but it cannot positively be concluded.

On the basis of the foregoing data from FCR Program as well as the center melt fuel specimens, it is apparent that a movement of even non-volatile fission products can occur relative to uranium. This is dramatically shown in the center melt fuel specimen.

The mechanism by which this transport occurs is not yet apparent. It is obvious that it cannot be one of Zr vaporization, for example, since Zr or ZrO₂ has a vapor pressure less than UO₂ at these temperatures. A comparison of the fission product distribution with the theoretical curve seems to show a region of depletion indicating the inward migration of the species measured. But this is still open to some question because the difference is relatively small and could possibly be explained by errors in the theoretical and calculated curves. An equally plausible mechanism is the transport of the volatile precursors of the Zr-95 and Ce-144 before their decay.

Further work will be done during the next quarter to try to distinguish between these two mechanisms. The Pu-240 content will be determined at a variety of points. Since this is formed essentially by thermal capture on Pu-239, it should be proportional to the thermal flux if no transport through the fuel occurs. The Nd content will also be determined. Since the half-lives of the volatile precursor in this case is extremely short, the Nd can probably be considered as formed directly. This will then be used to distinguish between volatile precursor migration or migration of the actual fission product of interest.

Further work will also be performed on another center melt fuel sample taken at a different axial location of the same fuel rod. In this sample, grain growth outward from the center occurred to within 70 mils of the periphery and there was no central void.

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2. Chemical Separation of Neodymium from Irradiated Fuel

A chemical separation for fission product neodymium from solutions of irradiated uranium was proposed by Fudge^[4] involving the removal by solvent extraction of the bulk of uranium into 30% tributyl phosphate in CCl, followed by a series of extractions and back extractions from di(2-ethylhexyl)phosphoric acid (HDEHP) in heptane. In this laboratory, however, column separations have been favored for the processing of highly radioactive samples because of ease in shielding and remote manipulations. Accordingly, a column of Dowex-2 an ion exchange resin (5 mm dia. x 60 mm, 200-400 mesh, 8% cross-linked) is used to remove the bulk of the U and Pu from a 12M HCl solution of the irradiated fuel. The rare earths including neodymium as well as the alkalis and alkaline earths pass through the column, leaving behind a number of elements [5] including elements present in fuel such as U. Pu, Zr, Nb, Mo, Tc, Ru, Rb, Pd, Cd, Sn, Sb, Te and other impurities which may or may not be present such as Ti, V, Fe, Co, Cu, Zn, Ga. Ge, As, Se, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Bi, Po, and Pa.

The eluate is evaporated to dryness and converted to the nitrate by dissolution in concentrated nitric acid and evaporated to dryness. The residue is taken up in 10M HNO₃ with a small amount of KBrO₃, warmed to oxidize cerium to the tetravalent state and extracted with 0.75M HDEHP in hexane to remove cerium. The aqueous phase is evaporated to dryness. This step is repeated by evaporation to dryness and dissolving in 10M HNO₃ with KBrO₃ and extracting with 0.75M HDEHP a second time.

After evaporating the aqueous phase to dryness, the residue is dissolved in 0.01 MNO₃ and extracted with 2M HDEHP to extract Nd and the remaining rare earths from the alkali salts. The organic phase is diluted to 0.75M HDEHP and the Nd is back extracted into 10M HNO₃. After scrubbing with hexane, the aqueous phase is evaporated to dryness.

Attempts to transfer the visible residue to a rhenium mass spectrometer filament with dilute HCl resulted in poor emission of Nd⁺ ions. This

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was attributed to traces of organic phosphates remaining since filaments outgassed excessively in the mass spectrometer.

In order to eliminate the interfering residue, a small one drop (50 µliter) column of Dowex-50 (2.5 mm dia. x 10 mm, 200-400 mesh, 8% crosslinked) was used. The residue was dissolved in 1M HCl and loaded onto the column. The column was washed with 50 column volumes of 1M HCl to wash through any anionic impurities as halides, bromates, phosphates, and any sulfates, perchlorates and nitrates introduced by the dissolution procedure as well as such cationic impurities as U, Pu, Np, alkali salts and any soluble organic compounds. The Nd is recovered in 6 drops of constant boiling HCl (6M purified by distillation) leaving behind Th and other tightly held cations. The interfering residue was eliminated by this column and 50 nanogram samples of Nd ran sa isfactorily without outgassing.

Initially, some difficulty was experienced in the cerium removal step. It is felt that conversion to the nitrate may have been incomplete and traces of chloride reduced some of the Ce(IV). When filaments contained Ce along with the Nd, the Nd⁺ intensity fell off rapidly and gave way to a long lasting Ce⁺ emission. Introduction of the second evaporation with nitric acid and reoxidation and extraction of Ce, removed this Ce interference and improved Nd emission.

Work was begun on reversed phase chromatographic separation of Nd by di(2-ethylhexyl)phosphoric acid supported on VYNS resin as a result of encouraging reports from Harwell^[6]. Results have been very promising. It is, therefore, planned to incorporate this technique into the separation scheme in place of the solvent extraction step. As presently visualized, the resulting procedure will be a three column process. The first column consisting of Dowex-2 anion resin to remove bulk uranium and other cations. The second column will be of HDEHP on VYNS to isolate Nd from other rare and alkaline earths and alkalis. The final column of Dowex-50 cation resin will serve as a volume reduction

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step and will also remove anionic impurities and soluble organic residues.

When the separation scheme is completed and demonstrated to be effective on small samples, the radial distribution samples from the center melt fuel specimen "A" will be analyzed for Nd to study the migration behavior of fission product Nd in UO₂ fuel in comparison to conventional radioisotopes.

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