MEASUREMENT OF KRYPTON GRAIN-BOUNDARY INVENTORIES IN CANDU FUEL

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ABSTRACT

A technique for measuring the Kr-85 grain-boundary inventory in irradiated fuel based on the conversion of UO_2 to U_3O_8 at low temperatures has been improved. The improvements include: 1) the use of a tracer isotope to account for release from the matrix during measurement of the grain-boundary inventory and 2) the cutting of samples from known locations. With these improvements it is possible to measure radial variations in the grain-boundary inventory. The measurements of the Kr-85 grain-boundary inventory can be combined with gamma mapping and ceramography to allow investigation of the connection between microstructure and fission-product distribution.

INTRODUCTION

Fission product release experiments have been conducted at Chalk River Laboratories (CRL) for a number of years[1,2]. This work has been part of the CANDU®* Owners Group (COG) program on fission-product source term research. The principal objective of this program was to provide a data base of fission-product release from CANDU fuel, from which rate equations and fission-product release models can be developed. Single-effect fission-product release

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*   CANDU: Canada Deuterium Uranium is a registered trademark.

experiments are conducted by post-irradiation annealing of UO_2 samples. Some of these experiments have investigated the distribution of fission products in irradiated nuclear fuel[3].

The fission-product inventory in irradiated UO_2 fuel can be divided into three major components: the inventory in the fuel-to-sheath gap, the inventory on the grain boundaries, and the inventory in the UO_2 matrix. The distribution of fission products is generally a function of the fuel-irradiation history (peak linear power and burnup) and fission product chemistry.

The distribution of the fission products within the fuel is important to fuel safety analysis because the components of the inventory can be released differently and at different times in postulated accident scenarios. To predict how the inventory is released during an accident it is necessary to know the distribution of the fission products prior to the onset of accident conditions. Experimental measurements are required to quantify the distribution and to help in the development and validation of fuel performance codes which are used by safety analysts to calculate distributions of fission products. These measurements can also be used in fuel waste management studies to help calculate instant release fractions[4].

METHODOLOGY

The migration and segregation of fission products during irradiation is a process that is largely controlled by diffusion in the matrix and hence the fuel operating temperature. Fission products that are in the UO_2 will diffuse to grain boundaries given high enough temperatures. Once on the grain-boundaries, the fission products may form metallic particles (Ru, Pd, Mo, Tc, Rh) or become trapped in bubbles (Xe, Kr, Cs, I). Since volatile fission products, such as Cs and I, are only in the vapour phase at high temperatures and low pressures, it is possible that they may condense on the grain boundaries. As the concentration of these fission products increases the grain-boundary bubbles expand and can inter-connect. Once inter-connection has occurred, the gaseous fission products in the bubbles can be vented to the fuel-to-sheath gap.

The technique used to release the volatile and noble gas grain-boundary inventory was developed at CRL out of studies on the oxidation of UO_2 in air[5]. In these studies it was observed that preferential oxygen penetration along grain boundaries occurs during oxidation of UO_2 to U_3O_8 at temperatures between 400 and 600°C[6,7]. The process is shown schematically in Figure 1. At the beginning of air oxidation, the grain boundaries are oxidized preferentially and the corresponding volume expansion separates the grains, releasing the grain-boundary inventory of fission gases. The exposed grains begin to swell due to U_3O_8 formation and, as the oxidation to U_3O_8 continues, the grains crack due to volume expansion. Finally, complete conversion to U_3O_8 creates powder fragments that are smaller than the original grain size. The conversion to U_3O_8 and the fragmentation of the grains allows some of the matrix inventory to be released, in addition to the grain-boundary inventory.

In a typical test, a small section (0.2 to 1 g) of irradiated fuel is oxidized in air at about 500°C. The fuel sample is fractured along the grain boundaries releasing the grain boundary inventory of noble gases which can be quantified by gamma-spectroscopy. After the grain boundary inventory has been released the sample is heated to higher temperatures (above 1050°C) to drive

off all the noble gases in the fuel. These gases are measured to determine the total inventory in the fuel sample.

In past work at CRL[3] on grain-boundary inventories, it was assumed that all the release observed at 500°C came from the grain boundary. Any release from the fuel matrix during the oxidation was interpreted as grain-boundary release. As well, in the early experiments the radial location of the samples could only be estimated using the Cs/Zr ratio in the fuel. However, this method is only useful in cases where there has been significant Cs migration during irradiation. In the more recent work reported here, the matrix release is accounted for using a tracer technique described below and the samples have been cut from precisely measured locations.

To account for release from the fuel matrix a short-lived "tracer" isotope is introduced by low-power re-irradiation following a long (> 6 month) decay period after the original irradiation. Since the re-irradiation is at low power (and hence low fuel temperatures), the tracer fission product can not migrate to the grain boundaries during the irradiation and is predominantly located within the matrix where it is created. During the annealing at 500°C the long-lived fission products (which were produced predominantly during the power reactor irradiation) are released from both the grain boundary and the matrix while the tracer isotope is only released from the matrix. By comparing the releases of the tracer and the long-lived fission products, the matrix release of the long-lived fission products at 500°C can be accounted for. In the tests described here, the Kr-85 ($t_{1/2}$ = 10.73 years) grain-boundary inventory was measured by comparing Kr-85 releases to those of the tracer Xe-133 ($t_{1/2}$ = 5.24 days).

EXPERIMENTAL

For these experiments, sections of fuel elements were re-irradiated in a special facility in the National Research Universal (NRU) Reactor at CRL. The re-irradiation was at low power (fuel temperature < 300°C) and varied between 4 and 14 days in duration. After irradiation, test samples were cut from known radial locations. Typically, the cutting pattern gave five samples of roughly the same size. One sample was from the central region, two were from the mid-radius region and two were from the peripheral region.

The annealing experiments were conducted in a hot-cell in the Universal Cell Facility at CRL. A crucible furnace, capable of a maximum temperature of 1200°C, was used to heat the samples. Figure 2 shows a schematic diagram of the test equipment. The test sample was placed in a quartz basket that fitted near the bottom of the quartz reaction vessel. The vessel was sealed with an aluminum end-cap using an O-ring seal. A type-K thermocouple inside the quartz vessel monitored the sample temperature and was also used to control the furnace temperature. The side-arms of the quartz vessel provided inlet and outlet gas flow. The inlet side-arm was attached to a quartz tube that ran down to the bottom of the vessel so that the gas was introduced below the sample.

The atmosphere in the system was either $Ar/2\%H_2$ or air, supplied from commercial grade gas cylinders. The gas flow rate was controlled by out-cell rotameters. After passing through the reaction vessel, the gas flowed to a fission-product scrubbing system to remove volatile fission

products (eg., Cs, I). After scrubbing, the gas was routed to an out-cell gamma-counting station where the noble gas activity in the flow stream was measured.

In a typical test the sample was heated to 500°C in flowing $Ar/2\%H_2$. Once the furnace temperature was stable at 500°C, the gas was switched from $Ar/2\%H_2$ to air which was used for the rest of the test. The temperature was held at 500°C until the sample was completely oxidized. The temperature was increased to about 1100°C and held at this temperature for about 30 minutes to allow for complete release of the noble gases from the sample.

The releases of the noble gases were measured with a gamma spectrometer at an out-cell gamma-counting station. The detector used was calibrated in this geometry, so that the total activity (Bq) observed in each spectra can be calculated. Another gamma spectrometer was sighted on the fuel during the tests to measure the evolution of total activity during the test. The data measured with this spectrometer is not directly used in determining the noble gas grain-boundary inventory.

RESULTS AND DISCUSSION

The results presented are on samples from an element irradiated to high burnup (over 500 MWh/kg U). These samples were selected as an example of the information that can be obtained with this technique, especially when it is combined with other post-irradiation measurements. Ceramography and two-dimensional gamma mapping (with 0.8 mm resolution) had been conducted on a section of the fuel element prior to the annealing tests. These techniques give information on grain growth and cesium migration during irradiation. The measured radial variation in grain size is given in Table 1. Figure 3 shows a gamma-map of Cs-137 showing cesium distribution for the same element. These measurements shows there has been considerable equiaxed grain growth (> 30 μm) in the central region of the fuel and that cesium has migrated from the centre to the periphery of the element during the power-reactor irradiation. Figure 4 compares the radial variation in cesium activity and grain size.

Figure 5 shows typical release curves for Kr-85 and Xe-133 along with the thermal cycle during the tests. The measured cumulative activities have been normalized so that the releases of the two isotopes can be compared. In Figure 5, it can be clearly seen that a larger fraction of the Kr-85 than Xe-133 was released by the end of the 500°C anneal. The releases are similar for the rest of the test. Since the Kr-85 was produced during the power reactor irradiation while the Xe-133 was generated during the low temperature re-irradiation, the difference between the fractional releases at 500°C represents the grain-boundary inventory. By this method, the grain-boundary inventory can be determined as a fraction of the total inventory in the sample.

The total amount of Kr-85 released from each sample can give some information on the radial distribution of the noble gas in the element. Figure 6 shows the variation in total Kr-85 measured (in Bq/g) with diametral position; for comparison the Cs-137 variation from Figure 3 is also included. The horizontal bars on the Kr-85 measurements indicate the size of the sample. There is good agreement between the distribution of the two isotopes indicating that the migration of cesium and krypton in the fuel is similar.

Figure 7 shows the measured radial variation of the Kr-85 grain-boundary inventory along with the radial variation in grain growth from Table 1. The grain-boundary inventories are shown on an arbitrary scale. As before, the horizontal bars indicate the width-of-the sample, while the vertical bars indicate the uncertainty in the measurements. The uncertainties in the grain-boundary inventory measurements largely arises from the statistical uncertainty in the gamma spectrometer measurements of Kr-85.

CONCLUSIONS

An improved technique for measuring the grain-boundary inventory of noble gas fission products has been applied to CANDU power reactor fuels. The results presented here on an element with high burnup and high power show there can be a significant radial variation in grain-boundary inventory. The present technique takes into account some matrix release that was not accounted for in past experiments.

Measurements of grain-boundary inventories can be combined with other post-irradiation measurements like gap release, ceramography and gamma mapping to give a more information on the relationship between microstructure and fission product distribution. The grain-boundary inventory measurements are also useful for validation of fuel performance codes. In the future, it is planned to extend the technique to volatile fission products (cesium and iodine).

ACKNOWLEDGEMENTS

REFERENCES

(1)   COX, D.S., Z. LIU, R.S. DICKSON and P.H. ELDER, "Fission-Product Releases during Post-Irradiation Annealing of High-Burnup CANDU Fuel," Proceedings of the Third International Conference on CANDU Fuel, Pembroke, Ontario, Canada, 1992 October.

(2)   DICKSON, R.S., Z. LIU, D.S. COX, N.A. KELLER, R.F. O'CONNOR and R.D. BARRAND, "Cesium Release from CANDU Fuel in Argon, Steam and Air: The UCE12 Experiment," Presented at the 15th CNS Conference, Montreal, Quebec, Canada, 1994 June.

(3)   HUNT, C.E.L., F.C. IGLESIAS, D.S. COX, N.A. KELLER, R.D. BARRAND, R.F. O'CONNOR, J.R. MITCHELL, G.W. WOOD and R. MIKUCH, "Fission Product Grain-Boundary Inventory," Proceedings of the 10th CNS Conference, Ottawa, 1989.

(4)   STROES-GASCOYNE, S., J.C. TAIT, R.J. PORTH, J.L. McCONNELL, T.R. BARNSDALE, and S. WATSON, "Measurements of Grain-Boundary Inventories of ^{137}Cs, ^{90}Sr and ^{99}Tc in Used CANDU Fuel," Mat. Res. Soc. Symp. Proc. Vol. 294, (1992) 41-46.

(5)   LIU, Z., R.D. BARRAND, C.E.L. HUNT AND D.S. COX, "Particle Size Distributions of U_3O_8 Produced by Oxidation in Air at 300-900°C," Proceedings of the 13th CNS Conference, St. John, NB, 1992 June.

(6)   COX, D.S., F.C. IGLESIAS, C.E.L. HUNT, N.A. KELLER, R.D. BARRAND, J.R. MITCHELL and R.F. O'CONNOR, "Oxidation of UO_2 in Air and Steam with Relevance to Fission Product Release," Presented at the American Chemical Society Symposium on Chemical Phenomena Associated with Radioactivity Releases During Severe Nuclear Plant Accidents, Anaheim, CA, 1986 September.

(7)   COX, D.S., F.C. IGLESIAS, C.E.L. HUNT and R.F. O'CONNOR, "UO_2 Oxidation Behaviour in Air and Steam with Relevance to Fission Product Releases," Proceedings of the International Conference on CANDU Fuel, Chalk River, Ontario, Canada, October 6-8, 1986, page 527.

TABLE 1: Measured radial distribution of grain sizes (mean intercept length).

Fractional Radius		Mean Intercept Length μm
0.00	Centre	40
0.09		38
0.18		38
0.27		24
0.36		18
0.45		11
0.55		9
0.64		7
0.73		7
0.82		7
0.91		6
1.00	Edge	6
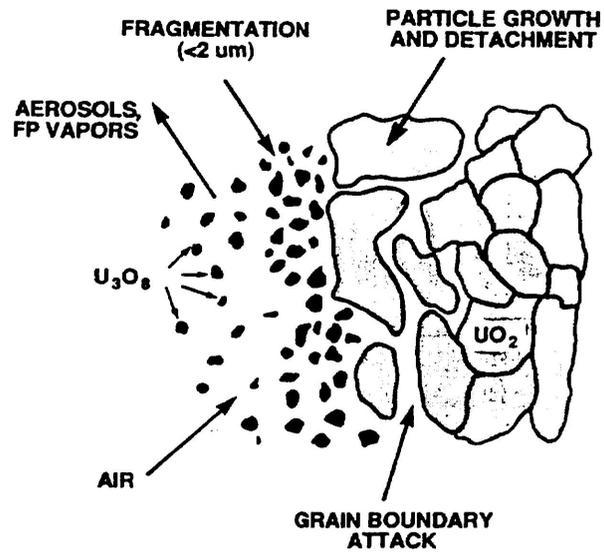
FIGURE 1: Schematic representation of low temperature oxidation of UO_2.

OUT-CELL

Gamma
Spectrometer
#1

IN-CELL

Gas
Control
Panel

Ar/2%H2

Ar

Data
Acquistion
System

Furnace
Controller

Pressure
Transducer

Gamma
Spectrometer
#2

Vent to
Cell

T/C

Furnace

Sample

Fission
Product
Scrubbing
System
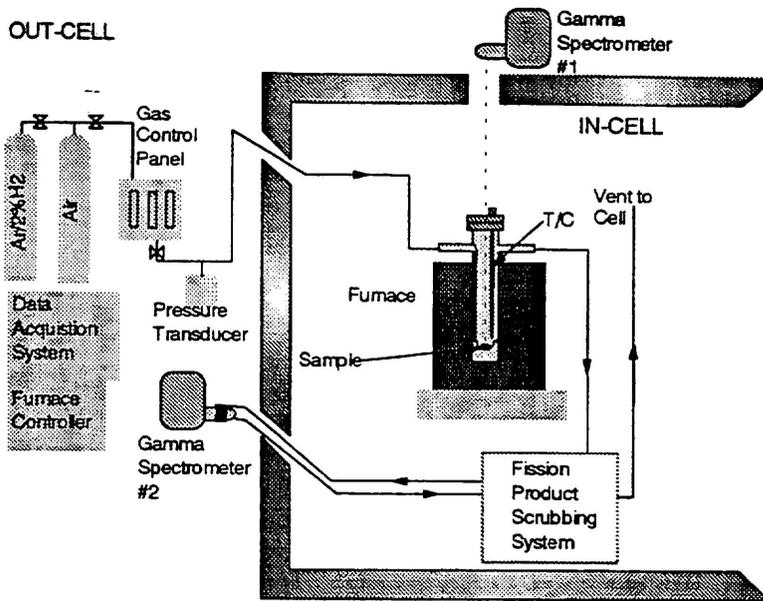
FIGURE 2: Schematic diagram of the hot-cell apparatus.
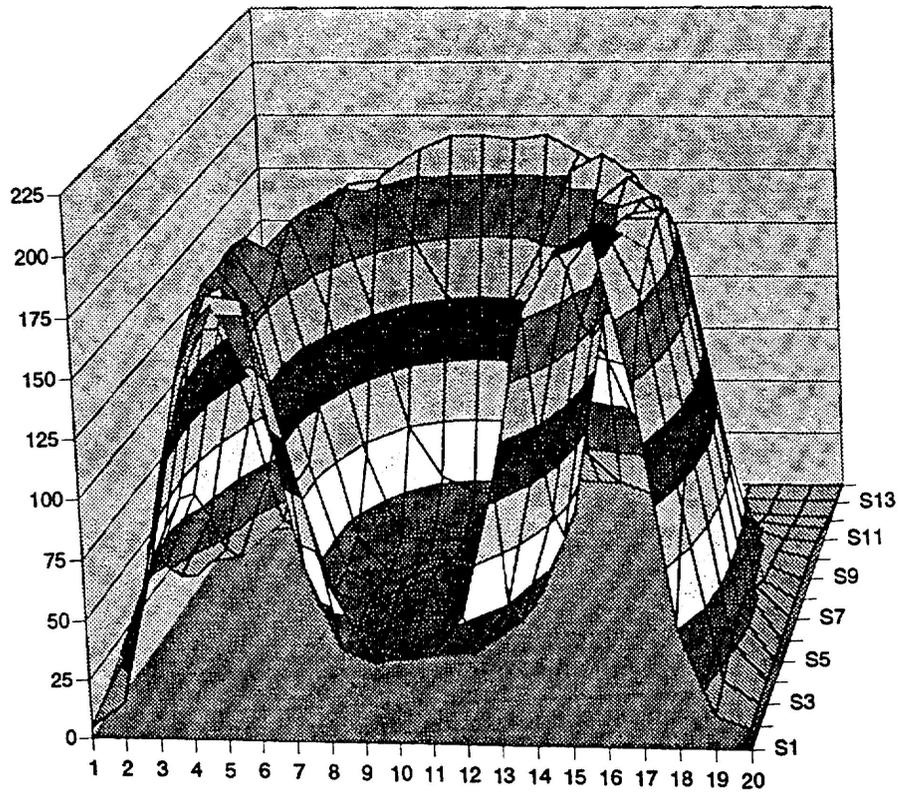
FIGURE 3: Cutaway of a gamma map showing the Cs-137 distribution in the element. Arbitrary Units.
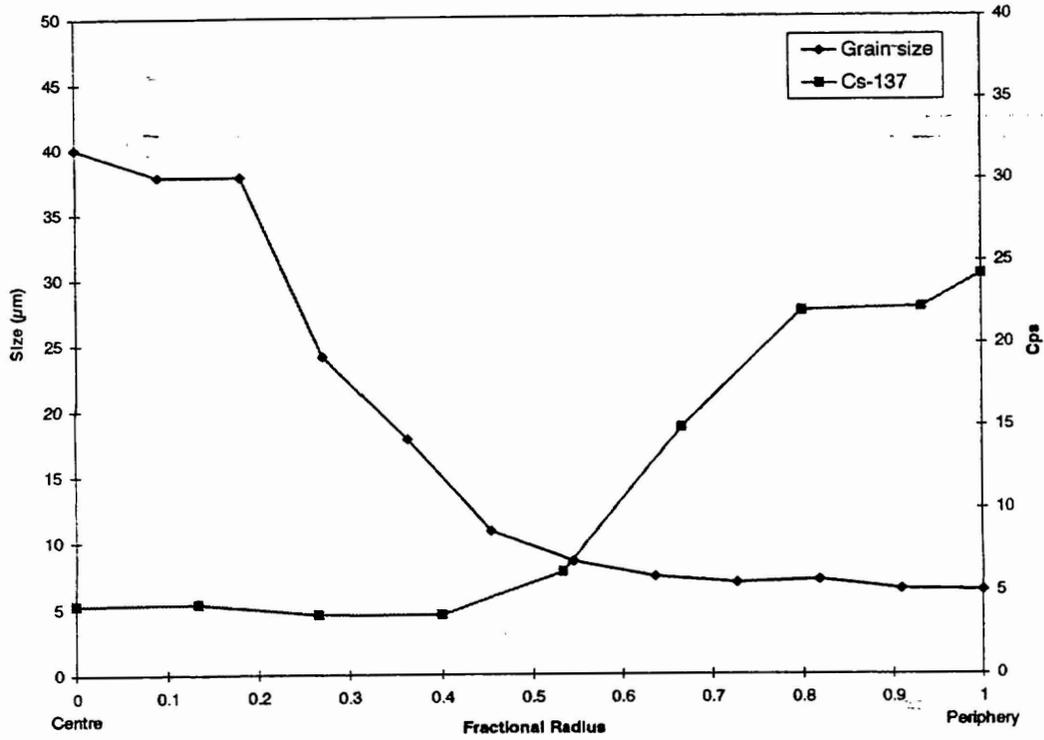
FIGURE 4: Comparison of the radial distribution of Cs-137 and grain size.
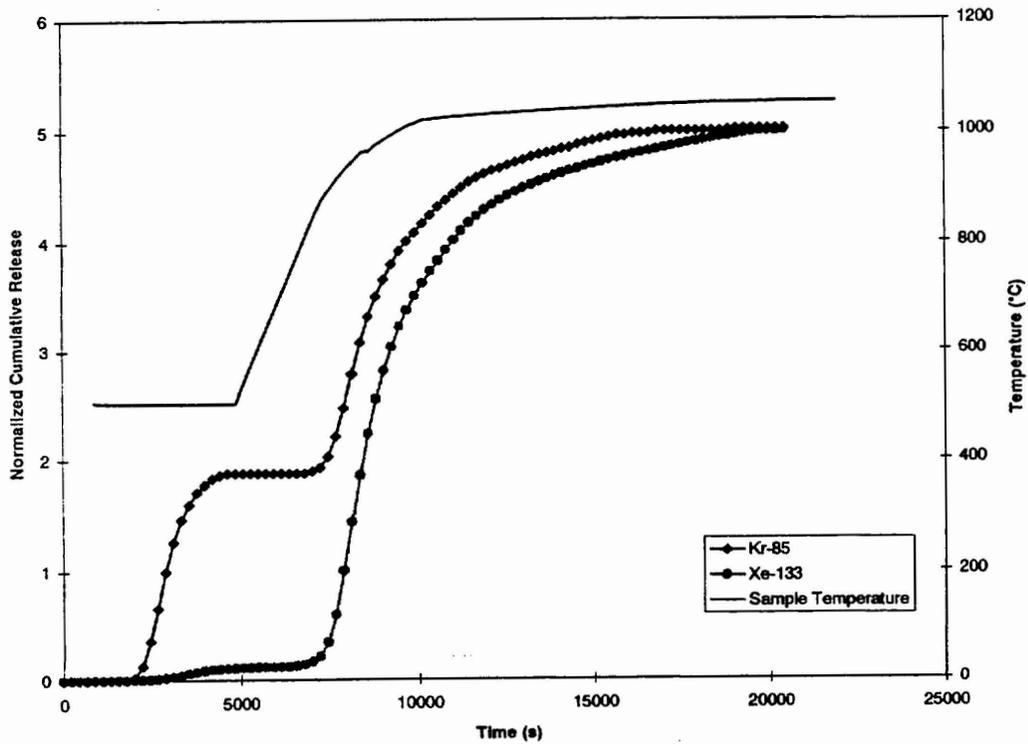
FIGURE 5: Cumulative measured Kr-85 and Xe-133 for one sample with the typical temperature profile.
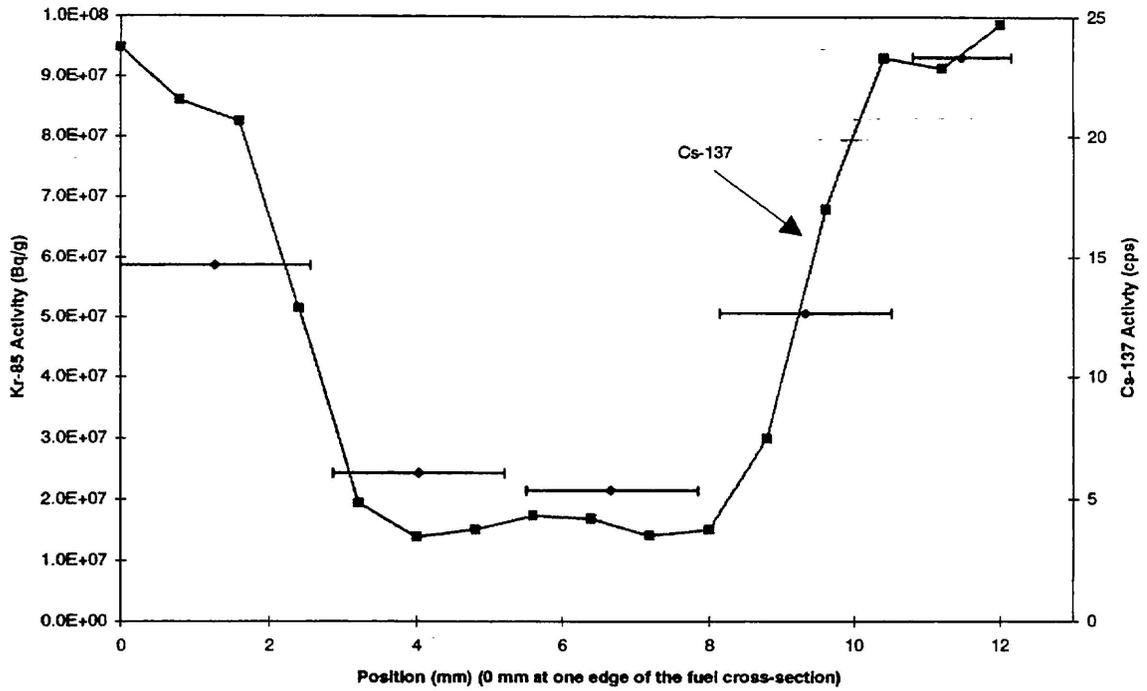
FIGURE 6: Variation of total sample inventory of Kr-85 along with the variation in Cs-137 concentration (from the gamma map). The horizontal bars indicate the width of the sample.
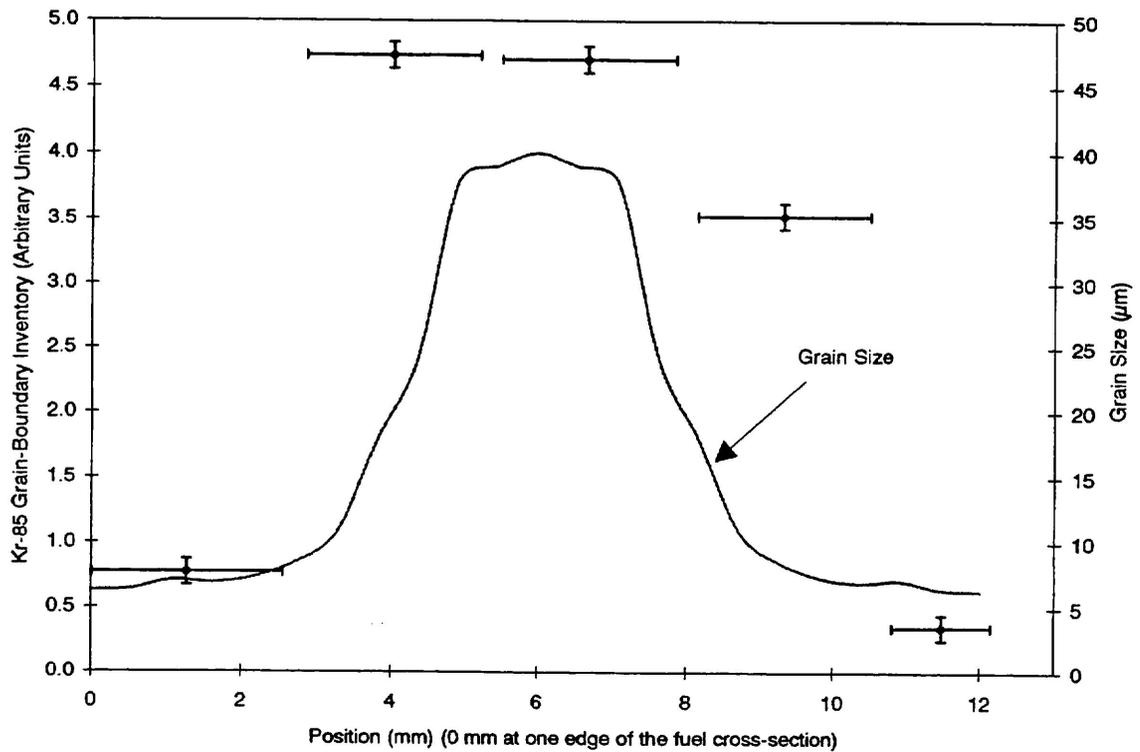
FIGURE 7: Variation in grain size and the Kr-85 grain-boundary inventory (arbitrary units). The horizontal bars indicate the width of the sample.