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Joint U.S. -Euratom
UC-25, Metals, Ceramics
and Materials
TID-4500, 45th Edition

PROGRESS REPORT
BURNABLE POISON ADDITIONS TO UO_2

For Period
July 1 to September 30, 1965

Prepared By:

R. C. Brayer
S. S. Christopher

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BURNABLE POISON ADDITIONS TO UO_2

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BURNABLE POISON ADDITIONS TO UO_2

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FOREWORD

The United States and the European Atomic Energy Community (EURATOM) on May 29 and June 18, 1958, signed an agreement which provides a basis for cooperation in programs for the advancement of the peaceful applications of atomic energy. This agreement, in part, provides for the establishment of a Joint U.S. -Euratom research and development program which is aimed at reactors to be constructed in Europe under the Joint Program.

The work described in this report represents the Joint U.S. -Euratom effort which is in keeping with the spirit of cooperation in contributing to the common good by the sharing of scientific and technical information and minimizing the duplication of effort by the limited pool of technical talent available in Western Europe and the United States.

BURNABLE POISON ADDITIONS TO UO_2

By

R. C. Brayer and S. S. Christopher

ABSTRACT

Two 6% enriched UO_2 fuel elements containing 500 ppm B_4C were fabricated at Combustion Engineering and irradiated in the Saxton Reactor to a peak burnup of 1070 MWD/MTU at a peak specific power of 17.2 kw/ft. A post-irradiation evaluation process flow chart and a sampling scheme have been finalized in preparation for the hot cell evaluation of the first element. This evaluation is being initiated. The second element will be reinserted into the reactor and will be irradiated to a total peak burnup in excess of 5000 MWD/MTU.

Sampling techniques to be used for the evaluation of the irradiated elements have been developed and tested inside Westinghouse Waltz Mill hot cells using a full length dummy element identical to the irradiated elements.

Analytical techniques for boron are being upgraded. Statistical data indicate that pyrohydrolysis of the fuel mixtures followed by NaOH titration or 1-1' dianthrimide colorimetric evaluation seems to be superior to the techniques previously used.

I. SUMMARY

Two 6% enriched UO_2 fuel elements containing 0.05 wt% B_4C were fabricated using the process described in CEND-3107-238⁽¹⁾. These elements were irradiated in the Saxton Reactor between July 12 and August 16. In-pile flux wire measurements indicated that the elements have been irradiated to 1070 MWD/MTU at a peak power of 17.2 kw/ft. One element (E-1) from the 2 x 2 assembly was removed and shipped to the Westinghouse Waltz Mill Site for post-irradiation evaluation. Underwater periscopic examination at Saxton had indicated that the element was in good condition. The second element (E-4) will be reinserted in the reactor and irradiated to a total peak burnup in excess of 5000 MWD/MTU.

A post-irradiation process flow chart and a sampling scheme have been finalized in preparation for hot cell evaluation of the first element. This process includes nondestructive testing with visual and dimensional evaluation, gamma scanning of the fuel section, and radiography of the plenum. An analysis of the gases contained in the plenum will follow. The destructive testing of the element will include evaluation of axial and radial distribution of boron and lithium (from boron transmutation); evaluation of cesium-137 for burnup determination and metallography.

An analytical program was undertaken during this reporting period to upgrade and review the boron analytical techniques being used and to carry out an evaluation of other methods. Techniques that were evaluated included emission spectrography, NaOH titrations, quinalizarin colorimetry and 1-1' dianthrimide colorimetry. Other methods were reviewed but were discarded due to low sensitivity. Three techniques have been developed which appear to be equally attractive from the point of view of precision and accuracy. Of these

(1) Brayer, R. C. and W. P. Chernock, "Burnable Poison Additions to UO_2 ", CEND-3107-238, May 1965

pyrohydrolysis followed by NaOH titration was selected for the boron analysis on the irradiated $\text{UO}_2\text{-B}_4\text{C}$ mixtures since color complexes may not be stable under irradiation. The 1-1' dianthrimide technique will be used out-of-pile as a continuous check on the in-pile methods. Duplicate samples will be prepared and periodically checked throughout the program.

II. INTRODUCTION

This program is aimed at evaluating the concept of fuel elements containing burnable poisons dispersed in UO_2 .

The principal objectives of the program are:

1. To evaluate the boron redistribution as a function of axial and radial position in irradiated vibratory compacted UO_2 fuel elements containing a homogeneous distribution of B_4C .
2. To evaluate the compatibility of UO_2 - B_4C mixtures in open and closed systems.

Irradiation testing of two full length vibratory compacted UO_2 fuel rods containing 0.05 wt% B_4C is in progress at Saxton. Post-irradiation evaluation of these rods will concentrate on the measurement of boron burnup and boron distribution as a function of axial and radial position in the rod. The reference basis for comparison will be the analysis of three rods fabricated with a process identical to that used for the fabrication of the irradiation test rods. In addition, gases generated by transmutation as well as gases produced by chemical reaction inside the fuel will be collected from the irradiated fuel element plenums for analytical evaluation. The rods will be further evaluated for cladding and fuel dimensional stability.

Data previously generated on this program concerning UO_2 - B_4C compatibility have shown that in an open system, UO_2 and B_4C will react to produce UB_2 and UB_4 . On the basis of thermodynamic evaluations of the system, it was postulated that this reaction will proceed in an open system and be inhibited in a closed system.

Recent data have indicated that B_2O_3 is also a product of the UO_2+B_4C reaction. Since B_2O_3 was not predicted by the previous thermodynamic calculations, the models will be reviewed with the object of providing for the formation of B_2O_3 .

A review of our reference analytical technique and other methods was undertaken during this reporting period to upgrade our precision and accuracy for boron determinations. Various analytical methods were evaluated and a selection was made of three techniques to be used during this program. The selection of the methods of boron analysis is described and the results of boron analyses that were performed are presented.

III. FABRICATION OF THE IRRADIATION TEST ELEMENTS AND IRRADIATION TESTING

A. Introduction

Two 6% enriched UO_2 fuel elements containing 0.05 wt% B_4C were vibratory compacted and fabricated using the techniques described in CEND-3107-238⁽¹⁾. The elements were compacted to densities of 86.4 and 86.2% of theoretical with the B_4C distributed homogeneously throughout the fuel column.

The two elements were subjected to a thorough nondestructive evaluation which included, dye penetrant and dimensional evaluations, radiography and helium leak check. Radiography and dye penetrant inspection revealed sound quality welds of the end caps. Helium leak testing indicated that the maximum leak rate of 10^{-6} atm-cm³/sec was not exceeded. The dimensions and the densities of the two rods are given in Table I. The two elements were forwarded to the reactor site and reinspected prior to insertion into the reactor. The site inspection concurred with the CEND evaluations and the elements were inserted in early July.

B. Irradiation

The irradiation program was modified to permit a preliminary irradiation of the 2 x 2 subassembly in the center position of Saxton prior to insertion of the UO_2 - B_4C fuel elements. The insertion of the poison elements into the subassembly meant the loss of the flux thimble previously present. The preliminary irradiation of the subassembly with the flux thimble in-place permitted a more precise evaluation of the thermal power output to be expected from the elements.

The two elements were inserted into the reactor on July 7 and the reactor

(1) Brayer, R. C. and W. P. Chernock, "Burnable Poison Additions to UO_2 ", CEND-3107-238, May 1965

TABLE I
DIMENSIONS OF COMPLETED FUEL ELEMENTS

<u>Identification</u>		<u>E-1</u>	<u>E-4</u>
Rod Length (in.)		40.960	40.998
UO ₂ Density (% TD)		86.4	86.2
Outside Diameter (in.)			
Top	0°	0.5991	0.5994
	90°	0.5994	0.5993
Center	0°	0.5992	0.5990
	90°	0.5993	0.5993
Bottom	0°	0.5990	0.5992
	90°	0.5990	0.5989

The wall thickness on the rods measured 0.0225 to 0.0228 in.

went to power July 12, 1965. The elements were irradiated from July 12 to August 16, 1965. The total reactor output during this period was 572 MWD thermal with 448 MWD at a power level of 23.5 MWt, 57 MWD at 20 MWt and 67 MWD at 10 MWt. The fuel operated at a peak specific power of 17.2 kw/ft and a peak burnup of 1070 MWD/MTU was achieved. One fuel element, designated E-1, has been discharged from the reactor and shipped to the hot cells for post-irradiation evaluation. The remaining fuel element E-4 will be re-inserted into the reactor and irradiated to a total peak burnup in excess of 5000 MWD/MTU.

C. Post-Irradiation Evaluation

Visual examination of fuel element E-1 irradiated to a burnup of 1070 MWD/MTU, was conducted at the reactor site prior to shipment to the hot cells. The underwater periscopic examination indicated a good surface condition with no abnormalities; a slight spotted appearance was observed in the region of maximum linear heat rating and a few longitudinal scratches produced by the clips during insertion and removal of the rod were visible. Standard cleaning procedures should remove these slight surface markings.

A dummy fuel element containing depleted UO_2 is being destructively evaluated at the hot cells in order to develop optimum remote handling procedures for element E-1. The dummy element has been sectioned in the hot cell into one inch increments, which are needed for typical axial boron analyses. The cutting was performed using a tube cutter with the rod in the vertical position. A polyethylene cup was located below the section to be cut in order to catch any falling fuel. In preparation for radial sampling, sections of the element, about one and one-half inches long, have been impregnated using "Loctite AA" which contains less than one part per

million boron. The radial sample is impregnated by depositing a small amount of Loctite on the top surface of the fuel; the Loctite is forced into the fuel to a depth of approximately one and one-half inches through the use of a pressurized gas blanket. The samples which have been impregnated are then removed from the cladding and radial samples are taken by concentric drilling with drill bits of increasing diameters. (Spark analyses have indicated that the boron content of the drill material is less than ten parts per million.) The size of the drill bits have been selected to produce equal volumes of fuel for the analyses. The length of the radial sample will be .75 in., yielding approximately four 7-grams samples of fuel. The remaining portion of the sample will be used for metallographic evaluation.

Separation equipment has been set up in the hot cells to perform the boron analyses on the irradiated fuel. A pyrohydrolysis separation followed by NaOH titration is the method being considered for determination of the boron content.

Based on the destructive analysis of the dummy fuel element and discussion with personnel at the hot cells, a sampling scheme was agreed upon for the irradiated fuel. A preliminary chart and diagram, Figures 1 and 2, indicate the operations and positions of various samples that will be evaluated. The preliminary diagram will be finalized when the results of gamma scanning and radiography of the element plenum are evaluated.

FIG. 1. POST-IRRADIATION EVALUATION PROCESS
FLOW CHART

SYMBOLS	SAMPLE TYPE	ANALYSIS TYPE	NUMBER OF ANALYSES	
			FUEL	CLAD SURFACE
I	AXIAL	Cs	3	
II	AXIAL	B Li	7 3	7
III	A RADIAL	B Li	8 4	2
	B AXIAL	Metallography	2	
Plenum	--	B	--	1

FIG. 2. ENRICHED ELEMENT SAMPLE POSITIONS

IV. ANALYTICAL PROGRAM

A. Introduction

The program requires the determination of boron in irradiated UO_2 in the presence of fission products and in the form of deposits on the stainless steel cladding. Further, thermodynamic studies aimed at determining the stability of $\text{UO}_2\text{-B}_4\text{C}$ mixtures will require analyses of various boron compounds such as B_4C , UB_2 , UB_4 , B_2O_3 , WB and other metal borides. In order to assure that the best possible techniques for both the hot cell and laboratory boron analysis are being used, a review of experimental analyses were performed to upgrade and optimize our analytical methods.

B. Discussion and Experimental Evaluation

Although many techniques such as titrimetry, colorimetry, spectrography and flame photometry have been used to analyze for the presence and concentration of boron, titrimetry and colorimetry have received the most attention and deserve further evaluation. Spectrography has also been included for evaluation due to the simplicity of the analysis. The following is a discussion of the most promising techniques for boron analysis; separation methods are also discussed as they are required for both the colorimetry and titrimetry analysis.

1) Colorimetry

Colorimetry depends on the formation of colored boron complexes with various reagents such as quinalizarin, 1-1' dianthrimide, carminic acid, chromotype 2B, curcumin, chromotropic acid, Victoria violet and methylene blue.

The color developed should have good reproducibility, high sensitivity and little overlap between the spectra of the reagent and boron complex formed.

A review was performed to determine the most promising reagents for further experimental evaluation. Based on the criteria of reproducibility of the color, sensitivity, overlap between the spectra of the reagent and the boron complex, quinalizarin and 1-1' dianthrimide were chosen for further evaluation.

An experimental evaluation of the quinalizarin and 1-1' dianthrimide colorimetric methods of analysis was conducted using boric acid standard solutions. Calibration curves were established for each reagent using solutions containing 0.0, 1.0, 3.0, 5.0, 8.0, and 10.0 μ grams of boron. Three analyses were made for each level of concentration and three spectrophotometric readings were taken per analysis. The calibration curve for each method of analysis was drawn using the least square technique. The curves obtained are shown in Figure 3. The slope of the curve for 1-1' dianthrimide indicates better precision than that obtained with quinalizarin. A precision study was subsequently conducted for each method of analysis.

A reference solution containing about 4.0 μ grams of boron per 50 ml of solution was analyzed for a period of 8 days. Eighteen sets of three samples were withdrawn from the stock solution. Nine sets were analyzed by each method of analysis at the rate of one set per day for 7 days, and two sets per day for one day. Three absorbance readings were taken per analysis. The experimental program yielded, for each method, 81 absorbance readings representing 27 analyses grouped into nine sets. The scatter of the results and the coefficient of variation

FIG. 3. CALIBRATION CURVES FOR BORON IN B_2O_3 SOLUTIONS

calculated from the data is presented in Table II. The results indicate that 1-1' dianthrimide method of analysis has better reproducibility than the quinalizarin method. In addition, for quinalizarin a decrease of 2.7% is noted between the average of all 27 readings taken last for each analysis. A similar computation for the 1-1' dianthrimide method resulted in a decrease of only 0.4%; thus pointing out the stability of 1-1' dianthrimide compared to quinalizarin.

All quinalizarin analyses were performed without noticeable incident. However, one set of the 1-1' dianthrimide analyses included in the precision study could have been rejected on the basis that the oven used for color development went out of control and the temperature increased from 110 to 130°C during sample processing. All absorbence readings for this set were much lower than any of the other samples indicating a loss of boron. The set was included in the precision study for comparison's sake, however, to obtain a better value for the potential of 1-1' dianthrimide, the statistical values were recalculated after rejecting the above set and the new values are shown in Table III. The Coefficient of Variation has been reduced for one analysis per sample from $\pm 7\%$ to $\pm 5.5\%$ and for an average of three analyses per sample from $\pm 6.3\%$ to $\pm 4.4\%$. This means that for a boron content of 500 ppm, the variation in the value for an average of three analyses per sample is ± 44 ppm for the 1-1' dianthrimide and ± 85 ppm for quinalizarin at a 95% confidence level.

As a result of this study, the quinalizarin method of analyses was discontinued and the 1-1' dianthrimide analysis is being used for subsequent studies involving boron separation.

TABLE II
STATISTICAL COMPARISON OF QUINALIZARIN AND
1-1' DIANTHRIMIDE METHODS OF ANALYSIS FOR BORON

(27 Analyses per Group)

	<u>Quinalizarin</u>	<u>1-1' Dianthrimide</u>
Maximum Value for the Scatter of Absorbance Readings (% of Mean Value)		
a) For the 81 absorbance readings	49%	28%
b) For the 27 average of three absorbance readings (Each average representing one analysis per sample)	47%	28%
c) For the averages of nine absorbance readings (Each average representing one set of three analyses per sample)	30%	24%
Maximum Scatter of Absorbance Readings Within One Analysis	8.3%	5%
Coefficient of Variation =		

$$\sqrt{\frac{\sum d^2}{n - 1}} \times \frac{100}{\text{mean value}}$$

a) One analysis per sample	<u>+10.8%</u>	<u>+7%</u>
b) Average of three analyses per sample	<u>+ 8.5%</u>	<u>+6.3%</u>

TABLE III

STATISTICAL EVALUATION OF 1-1' DIANTHRIMIDE
METHOD OF ANALYSIS FOR BORON

(72 Absorbance Readings - 24 Analyses - 8 Sets)

Maximum Value for the Scatter of
Absorbance Readings (% of Mean
Value)

a)	For the 72 Absorbance Readings	22%
b)	For the 24 Averages of Three
Absorbance Readings (Each
average representing one analysis)	20%
c)	For the 8 Averages of Nine
Absorbance Readings (Each
average representing one set
of three analyses)	13.5%

Coefficient of Variation =

$$\sqrt{\frac{\sum d^2}{n - 1}} \times \frac{100}{\text{mean value}}$$

a)	One analysis per sample	<u>+5.5%</u>
b)	Average of three analyses per
sample	<u>+4.4%</u>

2) Titrimetry

Titrimetric methods require the conversion of boron compounds to boric acid followed by the formation of a boron complex with a polyhydroxy alcohol such as mannitol. The boron content is obtained by visual or potentiometric titration. The titration method of analysis is sensitive to interference effects from other chemicals and CO_2 contamination. The titration method of analysis, however, was selected over the colorimetric method of analysis due to the effect of irradiation on the color complexes.

A Sargent motor driven constant rate burette with a digital readout system is being used to titrate the solutions. This system is able to detect 0.2 micrograms of boron using 0.1 normal NaOH for the titration. The titration is conducted to a pH of 8.3 and, to avoid CO_2 contamination, the NaOH solution is contained in a collapsible polyethylene container. The solution being titrated is blanketed with an inert gas during the titration. The accuracy of the analysis is ± 5.0 μ grams at a 250 μ grams boron level (± 10 ppm at a 500 ppm level). The precision of the analysis is $\pm 1.0\%$ at two standard deviation (± 5 ppm for 500 ppm level and a 95% confidence level).

3) Spectrography

Due to the interference of iron on the boron lines, standard spectrographic methods to determine low levels of boron in the presence of iron are extremely difficult. Further, the nature of the boron compounds being analyzed can influence the analytical results when the compounds to be analyzed have greatly different boiling points, which is the case with B_2O_3 and B_4C .

Initially, the emission spectrograph, due to the relative simplicity, was selected for use in determining boron in B_4C - UO_2 mixtures. The two

problems mentioned above were solved by using electrodes in which all the boron was converted to boron carbide in the electrode during a pre-arcing cycle. The boron spectra is then due only to the vaporization of the B_4C previously introduced. The resolution of the boron and iron lines was accomplished by using second order spectra produced by a high dispersion grating. The precision of the analysis is estimated to be 5 to 8% relative (± 50 to 80 ppm for a 500 ppm boron sample and 95% confidence level) for homogeneous dispersions of boron in UO_2 . However, when the boron particle size exceeds 80 microns, the precision approaches 30% relative (± 300 ppm at a 500 ppm level).

An evaluation of the potential for using this method on the program indicated that it should be restricted to analyzing non-irradiated UO_2 - B_4C mixtures, since irradiated fuel is normally too radioactive to be handled in the spectrographic laboratory.

Thus, the method has been dropped for hot cell analyses and the NaOH titration method was adopted for the irradiated material.

4) Separation Techniques

Since both colorimetric and titrimetric methods of analysis require boron separations, methods of isolating boron from the fuel mixture were investigated. Although many separation techniques are available, the following techniques were considered: methyl borate distillation and pyrohydrolysis.

Methylborate distillation consists of adding methanol to a slightly acid solution of the sample and distilling the ester and excess methanol into an absorbing solution. The distillate is caught in either a lime suspension or a dilute sodium hydroxide solution which hydrolyzes the ester. Although the separation is simple, results are frequently erratic and low recoveries are experienced in the presence of such elements as tungsten, aluminum, chromium, iron and silicon.

Pyrohydrolysis has been used successfully with boron in metals and compounds such as Zircaloy, uranium, stainless steel, boron carbide and UO_2 . The technique is readily applicable to remote operation and separation results in high recoveries of the boron. Pyrohydrolysis was selected as the primary method of separation for this program.

The evaluation of pyrohydrolysis as a separation method is currently in progress. Three synthetic samples of a variety of mixtures of UO_2 and boron compounds (containing 400 to 800 ppm boron) are being evaluated. Each sample is being pyrohydrolyzed in a flow of moist oxygen and the collected boric acid is being analyzed by the 1-1' dianthrimide colorimetric method and NaOH titrimetry. Preliminary results indicate a 70 to 100% recovery for B_4C and H_3BO_3 for temperatures in the range of 1200 to 1300°C and time at temperature ranging from 1-3/4 to 2 1/2 hours. Further separations are being performed and the following mixtures will be separated and analyzed; $\text{UO}_2\text{-B}_2\text{O}_3$, $\text{UO}_2\text{-UB}_2\text{-UB}_4$, $(\text{UO}_2\text{-B}_2\text{O}_3) + 50 \text{ wt\% } 304$ stainless steel chips and samples of $\text{UO}_2\text{-B}_4\text{C-UB}_2\text{-UB}_4$ impregnated in "Loctite". The results of these studies will be available during the next reporting period.

V. FUTURE WORK

During the next reporting period, element E-4 will be reinserted in the reactor for additional irradiation. Element E-1 will be nondestructively, then destructively tested at Westinghouse Waltz Mill Site in presence of Combustion Engineering personnel. The upgrading of the boron analytical technique will be completed at Combustion Engineering and the destructive testing of the depleted dummy elements will be completed. The thermodynamic study of $\text{UO}_2\text{-B}_4\text{C}$ compatibility will be initiated.