ANL-6168
Metallurgy, Ceramics,
and Materials
(TID-4500, 16th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois

THE ZrO_2-CaO-UO_2 CERAMIC FUEL FABRICATION FOR THE EBWR SPIKED CORE ELEMENTS

by

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Metallurgy Division

Final Report - Metallurgy Program 7.9.5

May 1961

Operated by The University of Chicago
under
Contract W-31-109-eng-38

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ABSTRACT

A series of experiments has been proposed in which the thermal output of the EBWR will be increased to 100 megawatts. This increase in thermal energy will be accomplished by inserting 32 spike elements in the initial fuel core. The fuel selected for these spike elements was a cubic solid solution in the system ZrO_2-CaO-UO_2.

The ceramic fuel was fabricated in the form of pellets by compacting a mixture of U_3O_8, $CaCO_3$, and ZrO_2. These pressed pellets were sintered in air at 1675°C ± 25°C to form a cubic solid solution having a composition of 9.01 w/o UO_2 (93% enriched), 9.07 w/o CaO, and 81.92 w/o ZrO_2. The procedures used in forming the fuel pellets are described in detail. Following fabrication, the pellets were loosely inserted into Zircaloy-2 tubes for subsequent assembly into fuel elements.

INTRODUCTION

The Experimental Boiling Water Reactor (EBWR) located at Argonne, Illinois, is a complete, direct-cycle, boiling-water reactor power plant.(1) This reactor is a light water-cooled-and-moderated reactor designed to operate at water temperatures up to 254°C and a pressure of 600 psig, and is designed to generate 5000 kw of electricity from 20,000 kw of heat.

The initial fuel in this reactor was a mixture of natural and slightly enriched (1.44% U^{235}) uranium alloyed with 5 w/o zirconium and 1.5 w/o niobium. This fuel was clad with Zircaloy-2 and fabricated into plates 54 in. in length, $3\frac{5}{8}$ in. in width, and either 0.212 in. or 0.280 in. in thickness. Six of these plates were assembled with side plates and top and bottom fittings to form an element assembly approximately $3\frac{3}{4}$ in. square.

The reference core in the EBWR was 4 ft in diameter, and designed to hold 76 fuel element assemblies containing 1.44% U^{235}, and 36 fuel element assemblies of natural uranium. Provision, however, was made in the structure to increase the core diameter to 5 ft, and to accommodate 148 fuel element assemblies.

The initial fuel loading has been in operation since December 1956. During operation of the reactor, a series of experiments have been initiated to increase the thermal power output above 20,000 kw, and eventually to 100,000 kw. For some of these experiments it was necessary to spike the initial core loading with 32 fuel element assemblies in which the fuel portion contained approximately 10 w/o U^{235}.

These spike fuel element assemblies were in the form of a square array containing 49 Zircaloy-2 tubes assembled with top and bottom fittings. The tubes contained 48 in. of a stabilized zirconia-urania ceramic fuel in the form of pellets loosely inserted in the tubes. These spike elements were fabricated by the ANL Metallurgy Division through its Ceramic Engineering, Coating and Jacketing, and Foundry and Fabrication groups. These groups were responsible for the manufacture of the ceramic fuel, and the procurement, inspection, loading and assembly of the fuel tubes. This report, however, will be confined to the manufacture and loading into tubes of the ceramic fuel. The inspection, fabrication and assembly of the tubes will be described in ANL-6283, Fabrication of the Spiked Core Fuel Elements for the EBWR.(2)

PRIOR DEVELOPMENT

The development and use of thoria-urania(3) compositions for use as nuclear fuels have stimulated research in other oxide systems in which urania is one component. These systems are of interest as a means of improving the high-temperature stability of urania in oxidizing environments or as a means of diluting enriched urania for fuel spike applications.

Zirconia has long been of interest in nuclear studies because of its refractoriness, chemical inertness, and resistance to either oxidizing or reducing atmospheres. Zirconia also has a low capture cross section for thermal neutrons, and would appear to be a suitable diluent for enriched urania. Pure zirconia undergoes a reversible phase transformation at approximately 1000°C, and this phase transformation is accompanied by a disruptive volume change which tends to limit the usefulness of pure zirconia. Zirconia, however, has been reported to form tetragonal solid solutions with CeO_2 and UO_2,(4) and to form cubic solid solutions having a fluorite-type structure with CaO, Y_2O_3, and MgO.(5,6) Solid solutions of CaO in UO_2 have also been shown to exist at elevated temperatures,(7) and, on the basis of structure and interatomic distances, calcia-stabilized cubic zirconia should form solid solutions with UO_2 provided there is no interference from the CaO.

The ternary system ZrO_2-CaO-UO_2 has been investigated,(8) and cubic solid solutions were found to be formed by reacting mixtures of U_3O_8 and CaO-stabilized ZrO_2 in either air or hydrogen. Zirconia which had been stabilized with 8 to 15 w/o CaO was found to form a continuous series of cubic solid solutions with UO_2 when mixtures were reacted in hydrogen, and a limited region of solid solutions when these mixtures were reacted in air. This investigation indicated that specimens formed from the powdered solid solutions could be sintered, but the sintered densities of the specimens were quite low. However, higher densities could be obtained by sintering mixtures of U_3O_8, $CaCO_3$, and ZrO_2. Specimens prepared by sintering a mixture of U_3O_8, $CaCO_3$, and ZrO_2 having a composition corresponding to 10 w/o UO_2, 9 w/o CaO, and 81 w/o ZrO_2 were found to have negligible weight changes during water corrosion at 260°C. These specimens also exhibited good stability as indicated by small weight losses when heated in air at temperatures up to 1400°C for periods as long as five days. These investigations indicated that the solid solutions in the ternary system ZrO_2-CaO-UO_2 would be suitable for a refractory, high-burnup fuel. Based on this work, the fuel selected for the spike elements was stabilized zirconia-urania solid solution.

RAW MATERIALS

The raw materials selected for the fuel manufacture were ZrO_2, $CaCO_3$, and U_3O_8. These materials as received would all pass a 325 mesh screen (44-micron opening) and were used without additional comminution. The ZrO_2* was a material with low hafnium, as is shown by the typical spectrochemical analysis in Table I. Samples of this material did not change weight when calcined in air at 1000°C, and this material was deemed suitable for use as received. However, the material necessary to complete the fuel fabrication was received in three shipping containers, and in order to minimize potential processing variables, each mixed fuel batch was made by blending equal portions of the zirconia from the three containers.

The $CaCO_3$** was reagent grade and was used as received. The enriched uranium oxide was supplied as U_3O_8, and since this material did not appear to change weight when samples were calcined at 1000°C in air, this material was used as received. The use of U_3O_8 was possible since the indicated uranium content of approximately 10 w/o, from reactor calculations, was within the compositional range of solid solutions formed by air sintering U_3O_8-stabilized zirconia compacts.

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*Carborundum Company, Niagara Falls, New York

**Baker Chemical Company, Pillipsburg, New Jersey

Table I

SPECTROCHEMICAL ANALYSIS OF REACTOR GRADE ZrO_2

Element	Concentration, ppm		
	Maximum	Minimum	Average*
Hf	140	78	102
Al	<20	<20	<20
B	ND	ND	ND
Ca	1500	1100	1275
Cr	310	140	262
Fe	2150	780	1390
Mg	190	180	188
Mn	< 20	< 20	< 20
Ni	110	50	76
Pb	<20	<20	<20
Si	370	190	293
Ti	<20	<20	<20
V	<20	<20	<20

*Average of 4 separate lots of material.

FUEL FABRICATION

Reactor calculations indicated that each of the thirty-two spike elements should contain 864 grams net of U^{235}. This uranium was to be uniformly distributed throughout the 49 fuel tubes in the subassembly, and thus each of the 4-ft lengths of fuel would contain 17.63 grams net of U^{235}. This fuel was to be in the form of sintered ceramic pellets, 0.813 cm in diameter, and with an average pellet length of 1.27 cm; approximately 150,000 pellets would be required for the loading.

The preliminary investigations had indicated that urania would enter into solid solutions with completely stabilized zirconia, and that 10 w/o CaO was sufficient to completely stabilize the zirconia. Thus, the composition of the ceramic fuel was calculated on the basis of the two components - urania and CaO-stabilized zirconia - in which the calcia content of the stabilized zirconia was held constant at 10 w/o. The urania content required was determined from bulk densities achieved in pelletizing solid solutions containing normal uranium oxide. The sintered fuel composition calculated to meet reactor requirements was 9.01 w/o UO_2, 9.07 w/o CaO and 81.92 w/o ZrO_2. Since sintering in air was more convenient than sintering in a protective atmosphere, U_3O_8 was substituted for the UO_2, and $CaCO_3$ was substituted for the CaO. The oxide mixture to be fabricated was calculated to be 8.72 w/o U_3O_8, 15.07 w/o $CaCO_3$, and 76.21 w/o ZrO_2.

The ceramic fuel pellets were fabricated by the procedure shown in Figure 1. As a criticality precaution, the enriched uranium oxide was moved to the manufacturing floor in quantities sufficient for one day's production. To simplify accountability of the enriched U_3O_8, and to ease the problem of weighing, the U_3O_8 was supplied to the manufacturing floor in individually tared bottles, each containing approximately 420 grams, or enough material for one batch. The weight of the U_3O_8 transferred was determined to within 0.01 gram, and this weight was used as the basis for calculating the weights of the remaining batch materials. The required amounts of ZrO_2 and $CaCO_3$ plus a 3 w/o addition of polyvinyl alcohol were weighed to within 0.1 gram. These materials (approximately 5,000 grams in amount) were transferred to a glove box where they were carefully charged to a two-gallon porcelain-lined pebble mill which was about one-quarter full of porcelain pebbles. The mill was sealed, and then decontaminated on the outside by wiping all exterior surfaces with Kleenex dampened with acetone. The pebble mill was wrapped in a polyethylene sheet to insure against leakage, and the mill was transferred to a mill rack where the batch was mixed for three hours. The mill was then removed and returned to the glove box.

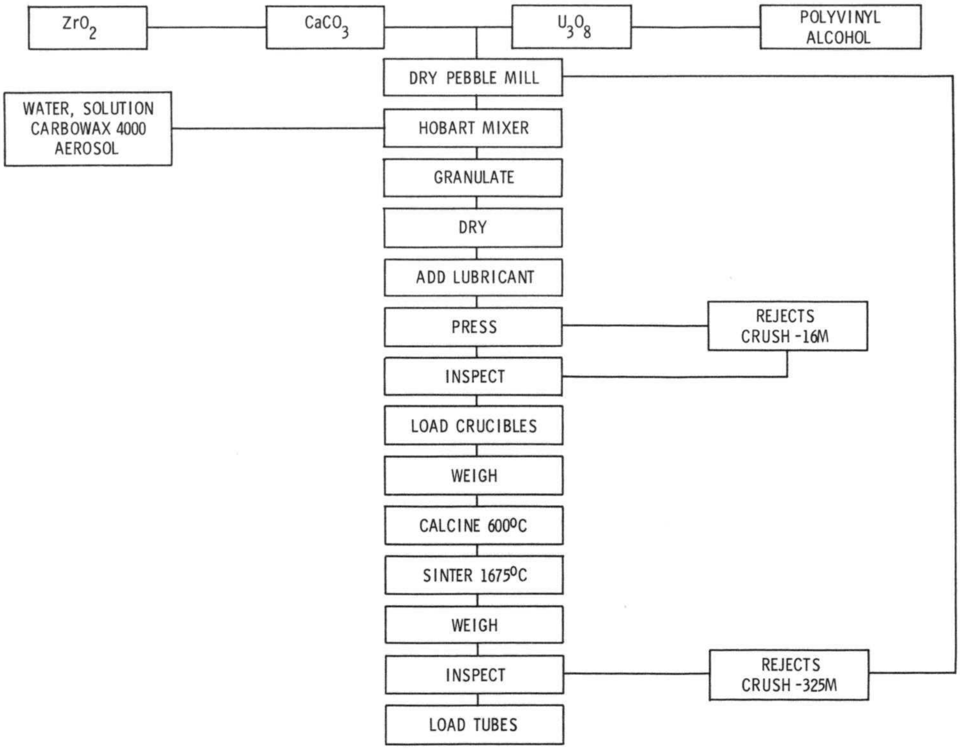


Figure 1. Flow Diagram of Material Fabrication.

The mixed, dry, powdered material was not free flowing, and would not be suitable as a feed material for an automatic press. In order to develop a free-flowing material, the mixed oxides were granulated. The mixed oxides were transferred to a small Hobart mixer, and were moistened with 28 to 30 w/o of a water solution containing 0.5 w/o Carbowax 4000 (polyethylene glycol) and 0.5 w/o Aerosol. The water solution was added slowly during mixing until the material appeared uniformly moistened. The damp material was granulated by forcing it through a 16 mesh screen. The granulator consisted of a 16 mesh screen rigidly mounted in a frame, with a motor-driven shaft extending through the center of the screen. A stainless steel blade mounted on the shaft just above the screen forced the damp mixed oxides through the screen, and a similar blade located just below the screen chopped the strings of material into granules. The damp granulated material was spread in trays and transferred to an electric dryer, where it was dried at 90°C for four hours. This procedure produced a free-flowing material in which the granules were soft enough to be crushed during pressing.

The dry granulated material was transferred to a glovebox where, prior to pressing, 100 ml of an equal volume of kerosene and oleic acid was added to each 5,000 grams of batch as pressing lubricant. The lubricating mixture was added by spraying from an atomizer while the dry granules were tumbled in the tray. This mixture was then charged into the press hopper. From the hopper, the material flowed into the press where it was compacted into right cylinders under a pressure of 14,000 to 16,000 psi at a rate of ten pellets per minute.

The press (Figure 2) was a single-cavity modification of the one used by Bach *et al.*,(9) and was designed for totally enclosed operation. It is essentially a small horizontal press with the die block mounted between two opposing air cylinders which actuate the die punches. For ease of alignment and replacement, the female die was designed as a small, hardened steel insert held in the die block by set screws. The air cylinders were controlled by solenoid valves actuated through a series of cam-activated microswitches.

In operation, the back-up air cylinder moved forward to close the exit side of the die while the pressing cylinder was withdrawn to allow material to flow into the die cavity. The pressing punch closed, forcing the material from the die cavity into the die, where it was compressed under full pressure by both cyclinders. The back-up punch was withdrawn, and the pressing punch moved through the die to eject the pressed pellet. Since all pellets were pressed under full pressure, the length of each individual pellet was contingent on the amount of material which dropped into the die cavity. This in turn was dependent on the granulation of the material. This variation in fill resulted in pressed pellets having lengths of 1.27 cm ± 0.16 cm.

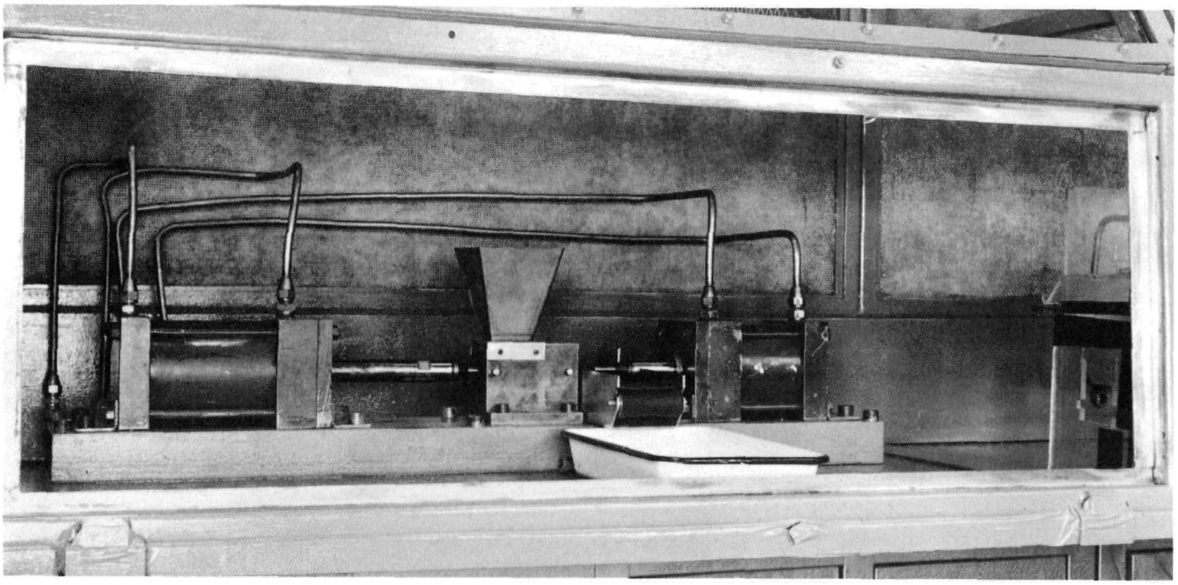


Figure 2. Single-cavity Air Press

Upon ejection from the press, the pellets were visually inspected for cracks and chips. Pellets which were free of visual defects were randomly loaded into tared, stabilized zirconia crucibles. Defective pellets were crushed to pass a 16 mesh screen and returned to the press. The loaded crucibles were weighed and transferred to an electric furnace where they were slowly heated (overnight) in air to 600°C. The peak temperature was held for four hours to insure removal of binder and lubricant. The furnace was turned off and the pellets were allowed to cool in the furnace to room temperature.

The crucibles containing the pellets were transferred to a gas-fired furnace and sintered to 1675 ± 25°C in approximately 12 hours. The peak temperature was held for 2 hours, after which the furnace was turned off and allowed to cool to room temperature. The crucibles containing the pellets were weighed (Figure 3) and the net loss in weight determined. The pellets were visually inspected for chips, cracks, or other defects, and were measured diametrically by means of ring gauges. The pellets which passed inspection were transferred to tared bottles and stored pending loading into tubes. Defective pellets were transferred to a one-gallon pebble mill, where they were crushed in alcohol to pass a 325 mesh screen. Following grinding, the alcohol slurry was poured into a tray and transferred to an electric dryer where the alcohol was evaporated. The dry calcined material was passed through a 200 mesh screen to break up the soft cake formed on drying, and returned to the weighing station for blending with the raw batch.

In order to use this crushed calcined material, several batches were mixed in which 5 w/o of the batch was calcined crushed pellets. This calcined material addition did not change the processing characteristics of the

Figure 3. Crucible Containing Sintered Pellets

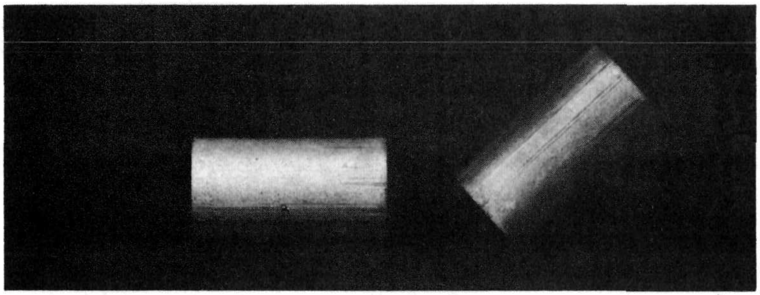
mixed oxides, but did result in a lower sintering shrinkage. This reduction in sintering shrinkage necessitated a smaller pressing die in order that the finished pellets have a uniform diameter. In practice, however, all new dies were made undersize, and as these dies wore, the 5 w/o of calcined material was eliminated. Thus only one die size was necessary, and the defective sintered pellets were reprocessed with a minimum of effort.

Approximately 470 kg of raw materials were fabricated into pellets by means of this procedure. During the fabrication, periodic measurements were made on production samples to determine pressed geometric density, sintered geometric density, and sintering shrinkage. The results of these measurements are summarized in Table II. The pressed-pellet diameters were found to be within the range of 0.953 cm ± 0.008 cm, and the sintered pellet diameters were found to be 0.810 cm ± 0.008 cm. From this, the average diametral shrinkage as calculated from the average pressed diameter was found to be 14.9%. This shrinkage was almost the same as the longitudinal shrinkage of 15.0% as calculated from the pressed and sintered lengths of the pellets. The average pressed density of the pellets as determined from dimensional measurements was found to be 2.75 g/cc, whereas the average sintered density was found to be 3.97 g/cc. These changes in size and density are shown by the appearance of typical pressed and typical sintered pellets (see Figure 4).

Table II

PROPERTIES OF CaO-ZrO_2-UO_2 SPIKE FUEL

Pressed Diameter	0.953 cm ± 0.008 cm
Sintered Diameter	0.810 cm ± 0.008 cm
Sintering Shrinkage (Longitudinal)	15% Average
Pressed Density (Geometric)	2.75 gm/cc Average
Sintered Density (Geometric)	3.97 gm/cc Average
U Content of Sintered Pellet	0.316 gm/cc Average



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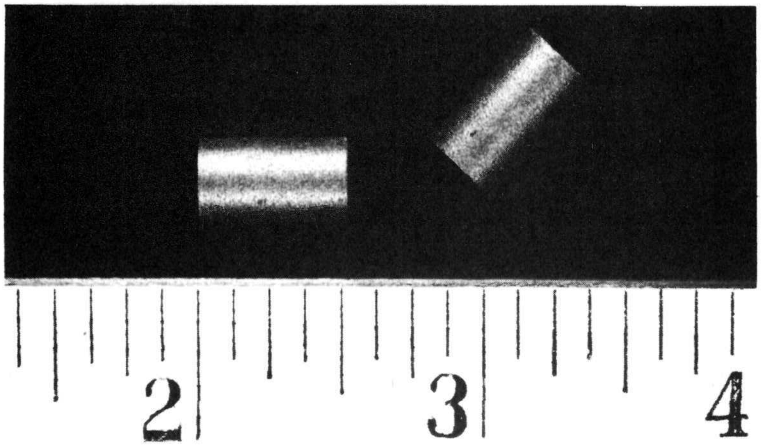

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Figure 4. Typical As-pressed (Upper) and Sintered (Lower) Pellets

Chemical analyses were made on one sample taken from each production batch. The average uranium content as indicated by these analyses was found to be 7.96 w/o. This average value for uranium compared very favorably with the average calculated value of 7.95 w/o uranium.

Several randomly selected sintered pellets were centerless ground and the thermal expansion of these specimens was measured by means of a dilatometer. The coefficients of thermal expansion as calculated are shown in Table III, and are plotted in Figure 5. The expansion of the stabilized zirconia-urania fuel was found to be essentially linear, with an average coefficient of thermal expansion from 30°C to 900°C calculated as 7.13×10^{-6} cm/cm-°C. X-ray diffraction patterns obtained from several randomly selected samples indicated that the sintered fuel material was essentially a single phase having a face-centered cubic structure (a_0 = 5.14 Å).

Table III

THERMAL EXPANSION COEFFICIENTS FOR EBWR SPIKE FUEL COMPOSITION

Temperature Range (°C)	Linear Expansion Coefficient (10^{-6} cm/cm-°C)
30-300	6.39
30-400	6.68
30-500	6.83
30-600	6.95
30-700	7.01
30-800	7.06
30-900	7.13

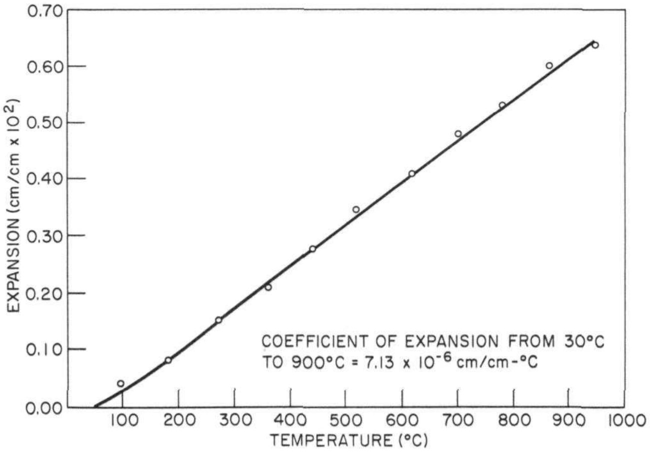

Figure 5. Linear Thermal Expansion of EBWR Spike Fuel

FUEL LOADING

The Zircaloy-2 tubes as received for loading had been numbered, and had one end closure welded in place. These tubes were also gauged on the inside diameter, and the size of the inside diameter was stenciled on the exterior surface. The tubes as received were sorted into groups according to their inside diameters, and weighed to within 0.1 gm.

The loading of the ceramic fuel pellets into the tubes was accomplished by means of the loading device shown in Figure 6. This device is essentially a flat plate of aluminum, approximately 6 feet long, mounted at an angle of 30° on an electric vibrator. The upper portion of the plate contains four grooves to accommodate the ceramic pellets, and the lower portion of the plate contains four grooves to accommodate the Zircaloy-2 tubes. At the junction these grooves are offset by the wall thickness of the tubing. A clamping device at the junction of these grooves holds the tubes in the fixture, and in line with the pellet columns.

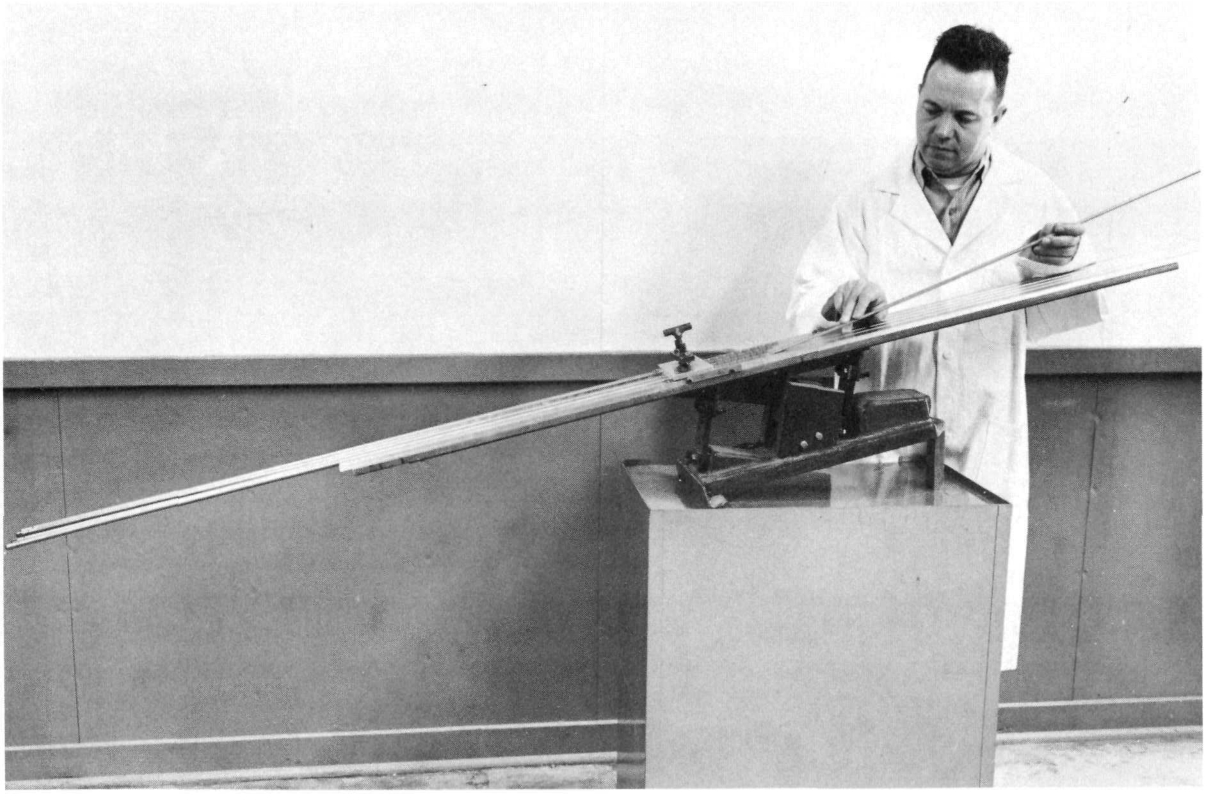

Figure 6. Fixture for Loading Fuel Pellets

In loading, four tubes were clamped in the loading fixture, and a flat sheet-metal plate was placed across the open ends of the tubes to prevent the ceramic pellets from entering the tubes. Four columns of fuel pellets, 47 ± $\frac{1}{16}$ in. long, were assembled in the upper grooves of the base plate. During this assembling operation the pellets were again visually inspected, and chipped or defective pellets were removed. The gate was removed and the pellets were pushed by means of rods into the tubes. Occasionally a pellet would stick in the tube. This in some instances could be freed by turning on the vibrator. However, if this did not free the pellet, the tube was removed from the fixture, and the pellet was tapped in place by means of an aluminum rod. These two methods of freeing jammed pellets usually were effective; however, during the fuel loading five rods were scrapped because of jammed pellets.

Following loading, the loaded tubes were weighed to within 0.1 gm, and the tube number, the tube weight before and after loading, and the weight of the fuel contained were recorded. Plastic plugs were inserted in the open ends of the loaded tubes to prevent fuel loss, and the loaded tubes were transferred to the Coating and Jacketing Group for final closure and final leak testing.

PRODUCTION SUMMARY

In fabricating the ceramic fuel for the EBWR Spiked Core Elements, sufficient pellets were manufactured to load 1568 fuel tubes. These loaded tubes contained 379,755.6 grams of ZrO_2-CaO-UO_2. In addition to this quantity 19,957.1 grams of pellets were manufactured as an overage and for irradiation test specimens. Ceramic scrap produced during the fabrication amounted to 17,693.2 grams. This scrap was generated from unprocessed batch (1,138.9 gms), defective pellets not reprocessed (12,267.1 gms), and pellets recovered from unloading 17 defective tubes (4,287.2 gms). Unaccounted material losses amounted to 1,931.3 gms. This material, while reported as a loss, was in the form of dust in the filters, on the plastic sheeting in the gloveboxes, and in material contamination on the fabrication equipment. This material is in the trash generated by the decontamination of the production facilities. A complete breakdown of materials used in production is tabulated in Appendix A.

Detailed production data, including fuel weights in individual rods, have been compiled into an unpublished Appendix B.

ACKNOWLEDGMENT

The authors wish to acknowledge Messrs. D. C. Hill, D. R. Lankard, R. E. Mailhiot, D. C. O'Rourke, P. D. Shalek, and D. E. White for their assistance in the manufacture of the fuel loading.

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APPENDIX A

RÉSUMÉ OF MATERIAL PROCESSED

(All Weights in Grams)

Number of Batches - 93

			%
U_3O_8*		39,309.45	8.43
$CaCO_3$		67,943.00	14.58
ZrO_2		343,489.80	73.68
Polyvinyl Alcohol		12,776.10	2.74
Carbowax 4000		2,668.80	.57
	Total	466,187.15	100.00

CALCULATED SINTERED COMPOSITION

			%	U%
UO_2		37,799.36	9.014	7.95
CaO		38,048.08	9.073	-
ZrO_2		343,489.80	81.913	-
	Total	419,337.24	100.00	

DISBURSEMENTS OF SINTERED MATERIAL

Loaded in 1568 Tubes		379,755.6
Irradiation Samples and Overage from Fabrication		19,957.1
Scrap Pellets Recovered from Defective Tubes		4,287.2
Scrap Pellets		4,490.9
Calcined Scrap		7,776.2
Unprocessed Batch Calcined (Scrap)		1,138.9
	Total	417,405.9
Unaccounted Material (In Crucibles, Kleenex, Plastic Sheeting, Filters)		1,931.34

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*U content 33,344.47

U^{235} content 31,073.86

w/o Oxide 96.687

w/o Binder 3.313