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GEL-ADDITION PROCESS CHEMICAL STUDIES

— Quarterly Progress Report No. 10 —

November 1968 - January 1969

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ABSTRACT

The development of the sol-gel process and related processes for preparing (U,Pu)O₂ fast reactor fuels has continued in Babcock & Wilcox's laboratories. Progress for the tenth quarter, ending January 31, 1969, is reported. The program is sponsored by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3714.

The preparation of (U, 20% Pu)O₂ sol-gel spherical fuel in two size ranges for thermal reactor testing is complete. Two uranium enrichments—depleted UO₂ and 20% enriched ²³⁵UO₂—were used to prepare materials that will yield two different heat rates with fuel of the same U/Pu ratios. Also completed is the first irradiation capsule test in a series that will show differences in the restructuring kinetics of pellets and vibratory compacted spheres and shards; the heat rate was 16.7 kW/ft, and the capsule received 9.3 EFPD. The capsule is cooling pending hot cell examination. The second capsule in the series is complete and is scheduled for exposure in February 1969.

The procedure checkout for moisture determination and oxygen stoichiometry in mixed oxide fuels is complete, and the procedures are summarized. Measurements of the gas contents and densities of irradiation specimens are complete.

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1. INTRODUCTION

This is the tenth progress report on a continuing program of experimental work on sol-gel and related methods for preparing mixed uranium-plutonium oxide fuels for fast reactor application. The program is sponsored by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-3714. This report covers the period November 1, 1968, to January 31, 1969.

The work program for this contract establishes several technical tasks including fuel preparation and characterization, reactor testing in both thermal and fast neutron fields, and analytical support. For fiscal year 1969 more limited objectives were set on a schedule that was delayed at AEC request; specifically, sol-gel pilot plant construction was delayed, along with fast reactor testing. The examination of reactor-exposed fuels has also been delayed.

During this report period work continued on the preparation of sol-gel fuels enriched in ^{235}U and on the fabrication of pins for thermal reactor exposure. Fuels of three different classes—pellets, shards (crushed pellets), and sol-gel spheres—are being fabricated for reactor exposures which will show the restructuring characteristics of all three materials under virtually identical conditions. One capsule exposure has been completed, and a second is scheduled for February 1969.

Progress on all the technical areas of the program are reviewed in the following sections. Appendix A summarizes the preparations being made in B&W's hot cells for the examination of plutonium-bearing fuels.

2. RESULTS AND CONCLUSIONS

2.1. Fuel Preparation

Sol-gel (U,Pu)O₂ fuel in spherical form has been prepared in three uranium enrichments (depleted, 20% ²³⁵U, and fully enriched). The two lower enrichments were prepared for thermal reactor testing and are now available in sufficient quantity for the total BAWTR program scheduled under this contract. The fully enriched material was prepared to bring to light any chemical flow sheet problems that may occur in preparing large quantities of fuel for fast reactor testing.

UO₂ sol preparation involving enriched material requires starting with a more dilute uranyl nitrate solution than that for depleted material. Plutonia sol preparation studies were extended to include some suggestions made by R. G. Haire of ORNL. He suggests reducing the nitrate level during the peptization step, which also increases the total plutonium concentration. His suggestions led to a decrease in sol preparation time and to a sol that could be concentrated to about 2M without apparent chemical changes. The sols prepared according to the standard flow sheet have tended to become unstable at concentrations above 1M.

Using the present laboratory equipment, up to 150 g of mixed (U, Pu)O₂ microspheres can be prepared in an 8-hour day.

2.2. Oxide Characterization

Coprecipitated powders used in this program for preparing irradiation specimens gave tap densities near 2.4 g/cm³ and subsieve sizes between 1 and 2 microns. The sorbed gas content of all materials measured about 0.03 cc/g, except for shards (crushed pellets), in which it was about four times greater—0.14 cc/g. Pellet densities were measured at 93.53 ± 0.76% of theoretical.

2.3. Irradiation Testing

Irradiation testing in the BAWTR is confined by budget limitations to studies of the restructuring characteristics of three fuel forms—pellets, shards, and spherical sol-gel. The first exposure in the restructuring series (capsule GA-2) has been completed and is cooling pending hot cell examination. A second capsule is scheduled for exposure in February 1969, and three more will follow in April 1969.

2.4. Analytical Support

A commercial moisture analyzer has been rebuilt for glove box operation with high-level alpha emitters. The furnace unit has been equipped with a heavy-walled furnace tube and a modified gas flow system; the control unit is mounted outside the box for convenient maintenance. The moisture release from UO_2 pellets was found to be virtually complete at 600 C. Mixed oxide $(\text{U,Pu})\text{O}_2$ pellets at 93% TD showed a very low water content ($\sim 1.0 \mu\text{g}$), near the detection limit of the instrument.

Thermogravimetric analysis (TGA) is being used to measure oxygen stoichiometry. This procedure requires ignition in air followed by hydrogen reduction to stoichiometric $(\text{U,Pu})\text{O}_2$, and the oxygen-to-metal ratio (O/M) is derived from the observed weight changes. The instrumentation is basically a Fisher Model 10-560-100 TGA system; the optimum temperature has been set at 800 C for oxidation and at 850 C for reduction. Pellet grinding before O/M measurement is not recommended, since observable oxidation accompanies the grinding. Crushing in a mortar and pestle, which increases the reaction rates without noticeably increasing the oxygen level, is recommended.

3. FUEL PREPARATION (E. J. Kosiancic)

3.1. Introduction

All of the fuel required for the gel-addition irradiation program in the BAWTR has been prepared. The fuel order includes 2570 g of coprecipitated powder containing 20% PuO_2 in depleted UO_2 ,^{1,2} 1288 g of coprecipitated powder containing 20% PuO_2 in UO_2 enriched to 20% ^{235}U ,³ and 1108 g of sol-gel microspheres containing 20% PuO_2 in natural UO_2 .^{3,4} The preparation of all of these has already been reported. In addition, 746 g of sol-gel microspheres containing 20% PuO_2 in UO_2 enriched to 20% ^{235}U and one small test batch of sol-gel microspheres containing 20% PuO_2 in UO_2 enriched to 93% ^{235}U were prepared during this reporting period.

3.2. Preparation of Microspheres Containing 20% PuO_2 in UO_2 Enriched to 20% ^{235}U (R. V. Carlson)

3.2.1. Preparation of UO_2 Sol Containing 20% ^{235}U

The ORNL formate flow sheet was used to convert uranyl nitrate into stable UO_2 sols.⁵ Most of the data from the preparation of these sols were reported previously.³ Laboratory work during this period centered on measurements of the uranium isotopic distribution. The analyses are now complete, and the data are shown in Table 3-1.

The measurement of uranium isotopes took on more than its usual importance in this work, because some inconsistencies were observed between calculated and observed ^{235}U levels. The 20% enriched material was prepared by isotopic dilution of fully enriched uranium. The dilution was made by mixing weighed quantities of enriched material as uranyl nitrate solution with weighed solutions of reagent-grade uranyl nitrate. The concentrations of both solutions were determined by coulometric analysis, using the standard analytical procedures available in

our laboratories. The solutions were mixed with unusual care to guarantee uniformity. Despite these precautions, the final isotopic analysis showed closer to 19.7% ^{235}U than the calculated 20.0%. The difference was much larger than the expected errors in the work.

The experiment was essentially an isotopic dilution analysis check against coulometric titration, and the discrepancy indicated that there were unsuspected errors somewhere in the procedure. Because coulometric analysis has become an accepted standard, it was necessary to determine the origin of the errors. A careful recheck showed that the reagent grade uranyl nitrate was not natural uranium as the supplier claimed, but actually depleted uranium (0.25% ^{235}U). The material had been taken as 0.7% ^{235}U for the isotopic dilution. A recalculation based on the correct isotopic analysis of the diluent uranium gave excellent correlation between the computed and measured ^{235}U content.

20%-enriched uranium was required for the finished fuel to produce an in-pile heat rate near 20 kW/ft, rather than the 15 kW/ft rate available with natural uranium-20% plutonium mixtures. The small difference in isotopic analysis between the target (20%) and actual (19.7%) is of no importance in reactor performance, so the question of isotopic analysis is of interest only because of the analytical chemistry involved. No attempt was made to readjust the isotopic level.

Table 3-1. Mass Spectrometric Analyses of Input Uranyl Nitrate Solutions

Type of solution	Uranium isotope content, wt %			
	^{234}U	^{235}U	^{236}U	^{238}U
Non-enriched stock	0.0024 ± 0.0004	0.2582 ± 0.0009	0.00452 ± 0.00039	99.735 ± 0.0001
Fully enriched stock	--	93.16 ± 0.08	--	--
First enriched feed	0.1164 ± 0.0019	19.701 ± 0.025	0.05686 ± 0.00014	80.126 ± 0.025
Second enriched feed	0.1145 ± 0.0010	19.662 ± 0.025	0.05422 ± 0.00048	80.169 ± 0.025
Third enriched feed	0.1157 ± 0.0012	19.679 ± 0.015	0.05244 ± 0.00024	80.153 ± 0.015

Table 3-2. Comparison of PuO₂ Sol Preparations

	New flow sheet	Old flow sheet ^(a)
Pu concentration in stock solution, g/l	25.3 ^(b)	29 - 56
Acid concentration in stock solution, M	1.0	1.0
Pu input, g	101.0	76 - 131
4M NH ₄ OH used for precipitation, l	3.0	1.9 - 3.1
Number of deionized H ₂ O washes	5	3 - 5
Volume of deionized H ₂ O per wash, l	2.0	1.0 - 2.0
NO ₃ /Pu mole ratio to peptize	1.2	1.8 - 2.7
Pu concentration after peptization, g/l	~70	10 - 20
Baking time, h	4.5 ^(c)	0.5 - 3.0
Final NO ₃ /Pu mole ratio	0.07	0.07 - 0.19
Pu recovered as sol, %	98 ^(d)	>91 ^(d)

(a) The nominal range of values is listed.

(b) The acid concentration of as-received Pu(IV) solution was higher than usual; therefore, it was necessary to dilute more than usual to obtain 1.0M H⁺.

(c) Baking time is a function of temperature; in this case, the temperature was held somewhat lower than usual to ensure that the powder was not overbaked by a new operator.

(d) Assuming that denitrated powder is 85 wt % Pu.

3.2.2. Preparation of PuO₂ Sol

All of the PuO₂ sol incorporated in the test fuels was prepared during previous report periods and has already been reported.^{3,4} One additional PuO₂ sol was prepared during this report period to test a flow sheet change suggested by R. G. Haire of ORNL.⁶ With the standard flow sheet,^{4,7} sufficient HNO₃ and H₂O are added to the digested oxide to adjust the NO₃/Pu mole ratio to about 2 and the plutonium concentration to about 0.06M. However, in the new run, the adjusted NO₃/Pu mole ratio was 1.2 and the plutonium concentration was about 70 g/l (≈ 0.3 M). There are at least two advantages in this flow sheet change:

1. The volume of water that must be removed before thermal denitration is reduced by a factor of about 5; thus, there is a substantial time saving at this step.
2. The total HNO₃ content is reduced by a factor of about 2; thus, there is less tendency for the PuO₂ to dissolve and convert to Pu(VI) during the drying operation.

In addition, the resultant sol could be concentrated to about 2M in plutonium. Previously prepared sols changed from dark to light green at plutonium concentrations near 1M, and then were somewhat unstable (i.e., solids settled to the bottom). It is not known whether the improved sol stability in the new run resulted from the flow sheet changes or from some other factor. Table 3-2 compares the run conditions for the new flow sheet with values from previous runs. These data indicate that, except for the changes noted above, this run proceeded in the normal manner. Thus, the flow sheet changes suggested by Dr. Haire appear to result in an excellent sol and substantial time savings.

3.2.3. Sphere Formation

A laboratory-scale sphere-forming system was used in the preparation of 20% ²³⁵UO₂-PuO₂ microspheres; the operating procedure previously outlined was followed during the new campaign.³ In order to minimize changes in the required 2-EH surfactant levels, all of the UO₂ sol was blended into one master batch. It was found that 0.4 vol % Span-80 and 0.2 vol % Ethomeen S/15 were adequate for the 12 days of column operation required to gel the material.

3.2.4. Sintering and Classification

The dried gel was handled as three sintering batches. Each was fired under the following conditions:

1. Under CO₂ atmosphere:
Heat to 450 C at 50 C/h
Heat to 600 C at 25 C/h
Heat to 900 C at 50 C/h
Hold at 900 C about 2 h
2. Under N₂-6% H₂ atmosphere:
Heat to 1250 C at 200 C/h
Hold at 1250 C for 4 h
Cool to room temperature

The final classification of the large spheres included screening and separation of the fragmented material. Only the 420 - 590-micron-diameter range was accepted, and this was passed over a roundometer* five times. The small-diameter spheres were screened, and only the material of less than 44-micron diameter was accepted. The quantities of material recovered from each batch are summarized in Table 3-3.

A total of 41% of the input plutonium and uranium was recovered as usable product. This is significantly better than the 31% recovery reported for the last campaign, mainly because of less severe startup problems.³

Table 3-3. Sol-Gel Material Recovered From Sintering Runs

Batch	420 - 590 μ rounded product, g	Coarse product scrap, g ^(a)	<44 μ product, g	Fine product waste, g
1	72	90	--	--
2	221	179	120	16
3	243	270	90	2
Total	536	539	210	18

(a) All off-sized material and rejects from the roundometer are included as scrap. Some of this material could probably be used in the sphere-pac process, since the necessary degree of roundness is not rigidly defined.

* T. M. Wald Industries, Inc.

3.3. Preparation of Microspheres Containing 20% PuO₂ in Fully Enriched UO₂

A 53.7-gram batch of fully enriched UO₂ (93.16% ²³⁵U) sol was prepared by the standard technique,⁵ except that the uranium content of the initial feed was reduced to 0.54M. Reduction was complete in 1.2 hours, and a very stable sol was obtained. One test batch of spheres containing about 25 grams of UO₂-20% PuO₂ was run. The gel spheres were generally "crinkled"—typical of excess Span-80. This test batch was sintered and no degradation of the product occurred.

3.4. Conclusion

Up to 150 grams of mixed UO₂-PuO₂ sol-gel microspheres can be prepared routinely in an 8-hour day with the present laboratory system. The routine process efficiency with this system is about 40 to 45%; the principal losses of product can be attributed to the lack of positive controls on the glove box atmosphere, moisture content, feed rates, and injection system. These problems will be greatly reduced when a unit operation system is brought on line.

4. OXIDE CHARACTERIZATION (J. M. Kerr)

4.1. Material Characterization

All of the oxide characterization work completed during this quarter was on the material used for BAWTR irradiation specimens (see section 5). Ceramography, alpha autoradiography, particle density, and sorbed gas content measurements were carried out on fuel in its finished form; tap density and Fisher subsieve sizing (FSS) measurements were taken on ceramic grade powders. All fuel material was nominally 20% PuO_2 -80% UO_2 . Part of the fuel material contained UO_2 depleted in ^{235}U , and part contained UO_2 enriched to 20% ^{235}U . The tabulation below shows the average values for tap density and FSS for the depleted and 20% ^{235}U ceramic grade powders.

	Tap density, g/cc	FSS, μ
Natural UO_2 -20 PuO_2	2.39	1.71
Enriched UO_2 -20 PuO_2	2.45	1.42

Sorbed gas contents for the pellet, shard, and sphere fuels are shown below. These were determined at 1600 C under an initial chamber pressure of about 100 microns of mercury. The shard and sphere samples were mixtures of particle sizes in the same proportion as was used in the irradiation specimens.

Fuel form	Sorbed gas release, cc/g
Pellet, enriched	0.030
Shard, enriched	0.140
Sphere, enriched	0.030 - 0.080
Sphere, normal	0.036

The particle density of the coarse fraction of the spheres (-30 + 40 mesh or 420 to 590 μ diameter) was determined by vibrating a bed of spheres to the minimum fill depth and assuming that any deviation from 63.5% of theoretical density was due to a deviation of sphere density from 100% of theoretical. Apparent sphere densities in the range of 95 to 96% TD were obtained in this fashion.

Ceramographic results all showed essentially single-phase material with a few pores near 0.002 inch in diameter in pellets and shards. Most of the observed pores were less than 0.002 inch in diameter, although some isolated pores as large as 0.005 inch in diameter were observed. There was no observable difference in microstructure between batches of spheres, batches of shards, lots of pellets, or enrichments of material. Figures 4-1 and 4-2 show typical microstructures of pellets and spheres. Shard and pellet microstructures were the same. No grain structure could be resolved in etched spheres at 800X magnification.

Alpha autoradiographic results showed no gross inhomogeneity within pellets, shards, or spheres. Figures 4-3 and 4-4 are alpha autoradiographs of enriched spheres and an enriched pellet, respectively. There was no identifiable difference in plutonium distribution between shards and pellets nor between different enrichments.

4.2. Fabrication Studies

Twenty-one fuel pins have been fabricated for assembly into seven irradiation capsules to be irradiated in the BAWTR (see section 5). Each capsule is designed to hold three pins: one pin each containing spheres, shards, and pellet fuel. All the fuel material is nominally 20% PuO_2 and 80% UO_2 . Of the seven pins each of pellet, shard, and sphere fuel, all contained 20% enriched ^{235}U . Ten more pins will be fabricated; these will be made up of five each of shard and pellet fuel containing depleted uranium. The cladding on all pins is type 304 stainless steel, and the outside and inside diameters are 0.250 inch and 0.220 inch. The end caps are also type 304 stainless steel.

All of the pins were fabricated to a smeared density of $82 \pm 2\%$ TD. It was established that this range included the maximum density to be expected from sphere-packing a system containing two different

sphere sizes. The smeared density in the pellet pins, which was maintained within a smaller range ($82.5 \pm 1\%$), was obtained by using relatively large pellet-to-cladding gaps. In the shard pins the desired density was obtained by using low-energy vipac with a weight ratio of particle sizes that will not pack to a high density.

The synthesis of spherical material is described in the fuel preparation sections of the quarterly reports in this series.^{3,4,7} Pellets were prepared from ceramic-grade coprecipitated powders; preparation of the ²³⁵U enriched material is described in the ninth Gel-Addition Process quarterly report.³ Similarly, the depleted material was prepared under a B&W-sponsored program. Shards were prepared by crushing and sizing pellet material.

Pellets were cold-pressed and sintered. Figure 4-6 is a descriptive flow sheet for pellet fuel using enriched powders. The coprecipitated powder containing depleted uranium had been in storage for more than a year; it showed differing sintering properties both when compared with its properties when it was fresh and with the sinterability of the freshly prepared enriched material. Steps are being taken to provide a more highly reducing atmosphere and a slower heating cycle to obtain pellets with the proper densities, diameters, and O/M ratios when using stored depleted powder. Table 4-1 shows the average and the range of pellet diameters, lengths, weights, and the average pellet density, as well as one standard deviation from the density. A tradeoff between density and diameter was possible in these pellet pins, because a smeared density was desired, rather than a given density and given diameter. Figure 4-5 shows the acceptable relationship between pellet diameter and density; this relationship was used to accept or reject pellets.

Vipac pins were prepared by following the descriptive flow sheet shown in Figure 4-7, and sphere-pac pins were prepared by following the flow sheet shown in Figure 4-8. The conclusion of this fabrication work will complete the objectives under this task for this fiscal year.

Table 4-1. Enriched Pellet Property Data

Diameter, in.		
Average		0.206
Range		0.205 - 0.208
Length, in.		
Average		0.250
Range		0.225 - 0.259
Weight, grams		
Average		1.4081
Density, % TD		
Average		93.53
One standard deviation		0.76

Figure 4-1. Microstructure of Pelletized UO_2 -20PuO₂
Enriched to 20% ^{235}U (80X, Bright Field,
Unetched)

Figure 4-2. Microstructure of Spherical UO_2 -20PuO₂
Enriched to 20% ^{235}U (80X, Bright Field,
Unetched)

Figure 4-3. Alpha Autoradiograph of UO_2 -20 PuO_2 Spheres Enriched to 20% ^{235}U (80 $\times$, Transmitted Light)

Figure 4-4. Alpha Autoradiograph of UO_2 -20 PuO_2 Pellet Enriched to 20% ^{235}U (80 $\times$, Transmitted Light)

Figure 4-5. Pellet Diameter Vs Percent Theoretical Density for Required Smeared Density

Figure 4-6. Pelletizing Process Flow Sheet

Figure 4-7. Vipac Process Flow Sheet

Figure 4-8. Sphere-Pac Process Flow Sheet

5. IRRADIATION TESTING (C. J. Baroch)

5.1. Introduction

The irradiation task, as described in a previous quarterly report² is divided into three subtasks:

1. Time Required for In-Pile Restructuring.
2. Sorbed Gas Behavior.
3. EBR-II Irradiations.

The scope and progress for each of these subtasks are described below.

5.2. Time Required for In-Pile Restructuring

In this subtask, the effect of heat rate and time on the restructuring characteristics of sol-gel $\text{UO}_2\text{-PuO}_2$ spheres and on angular particles and pellets prepared from coprecipitated $\text{UO}_2\text{-PuO}_2$ will be evaluated. Seventeen capsules will be irradiated in the BAWTR. The time required for restructuring at linear heat rates of about 6, 10, 15, and 20 kW/ft will be determined. The program will include a comparison of the irradiation behavior of spherical sol-gel particles prepared by ORNL and B&W.

The irradiation of one capsule (GA-2) for 9 days at 15 kW/ft has been completed. The details of this irradiation have been reported.³ Six additional capsules are scheduled for irradiation by June 30, 1969. A brief description of these six capsules is given in Table 5-1. The fabrication of capsule GA-11 is essentially complete, and the irradiation should be performed during cycle 35 of the BAWTR, which begins on February 16, 1969. Fabrication of the fuel pins and capsule components for the other capsules to be irradiated in FY 1969 has begun. The preparation of the safety analysis report for the 6, 10, and 20 kW/ft capsules has been completed and the report is in reproduction.

**Table 5-1. BAWTR Capsule Exposure Schedule,
Fuel Restructuring Series**

<u>Capsule No.</u>	<u>Linear heat rate, kW/ft</u>	<u>Exposure time, days</u>	<u>Date of insertion</u>
GA-11	15	1	February 1969
GA-15 ^(a)	6	3	April 1969
GA-14 ^(a)	10	3	April 1969
GA-13 ^(a)	15	3	April 1969
GA-8 ^(a)	20	3	April 1969
GA-4	20	1	May 1969

^(a)Capsules GA-8, GA-13, GA-14, and GA-15 are to be irradiated simultaneously.

5.3. Sorbed Gas Behavior

In this subtask the pressure created by the sorbed gas released from particulate fuel during irradiation will be determined. If practical, each capsule will contain two pins in which the gas pressure is continuously monitored. One pin will contain spherical sol-gel particles, and the other will contain angular coprecipitated particles. The gas-release characteristics of spherical sol-gel particles prepared by ORNL and B&W will be determined. By varying the linear heat rate, it should be possible to determine the amount of gas released as a function of average fuel temperature. The fuel pins will be irradiated at linear heat rates of 6, 10, 15, and 20 kW/ft.

No work was performed on this subtask because of funding limitations.

5.4. EBR-II Irradiations

The irradiations in EBR-II will provide performance data on particulate fuels under the fast reactor conditions obtainable in EBR-II. In this task the effect of heat rate and burnup on the overall performance of pellets, spherical particles, and angular particles will be evaluated.

The smeared density for all three materials will be about 85%. The irradiation of one 19-pin encapsulated subassembly in row 7 of the EBR-II and the irradiation of 18 unencapsulated pins in a subassembly to be shared with ORNL are included in this subtask. The scope of the EBR-II irradiations is described in BAW-3714-9.³ Because of funding limitations, no work was performed on this subtask during this report period.

6. ANALYTICAL SUPPORT (D. H. Schmitt)

6.1. Moisture Analysis

6.1.1. Introduction

The operational procedure checkout on the moisture determination method, as described previously,⁹ has continued. The moisture analysis instrumentation includes a Type 23-321 AMA Moisture Analyzer built by Consolidated Electrodynamics Corporation. It consists of an electrically heated tube furnace coupled to an electrolytic cell, plus the associated electrical circuitry. The sample is placed in the furnace tube and heated to a predetermined temperature. Moisture evolves and is swept into the electrolytic cell, where it is trapped in a phosphorus pentoxide electrolyte. Electrolysis converts the moisture into hydrogen and oxygen gases; the total number of coulombs passed is a measure of the amount of moisture.

The B&W instrument has been modified in several ways to improve the general performance level, lower the background correction, increase the furnace operating temperature for use with refractory samples, and facilitate glove box operation with plutonium-bearing materials. Some of these features have been discussed in previous progress reports, but the present status is reviewed in its entirety here, along with information on standards selection and analytical procedures. The instrument in its present form is shown in Figures 6-1 and 6-2.

6.1.2. Instrument Modifications

The furnace tube provided with the instrument was replaced earlier with a heavier-walled Pyrex tube for safer box operation. The new tube performed well and allowed sample heating up to 400 C. A third tube made of heavy wall Vitreosil clear fused quartz has recently

been installed, raising the maximum permissible operating temperature to 900 C. For routine work with nuclear fuels, 600 C is considered adequate, as discussed in section 6.1.4.

The tube cap (see Figure 6-1) for use with the quartz furnace tube is similar to one described earlier for use with the heavy-walled Pyrex tube.⁹ The quartz tube cap was partly filled with epoxy resin to reduce the interior gas dead space, and the surface of the epoxy bed was capped with a machined Teflon disc pressed over a layer of Teflon thread-sealing tape. The cap thus presents a solid Teflon surface to the interior of the tube.

A flow meter has been installed on the outlet of the electrolysis cell to monitor the gas flow rate during operation. The meter was installed because an automatic valve in the sweep gas line occasionally fails to close, even though the servo controlling it functions correctly. The servo responds to the moisture electrolysis rate and opens or closes the valve to control the rate at which gas enters the electrolysis cell. If the valve stem is opened one or more full turns beyond its correct operating position, the servo cannot close the valve completely. The flow meter warns the operator of such malfunctions.

A filter has been installed between the furnace tube and the electrolytic cell to prevent the mechanical carryover of finely divided material from the furnace. The filter is made from an O-ring joint^{*} containing an O-ring seal and a Teflon filter cloth of 10 micron porosity. The cloth is held in place by the O-ring when the flange joint is tightened, and the flange joint is held in place by O-rings inserted inside the inlet and outlet leads to the joint. The tubulatures from the furnace and electrolytic cells form a tight fit with the two smaller O-rings in the O-ring joint leads and keep the assembly gas-tight.

6.1.3. Standard Selection

The satisfactory performance of any analytical instrument must be demonstrated frequently by checks against known standards. Unfortunately, there are no suitable standard materials available for microgram amounts of water. Consequently, it was necessary

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* Corning No. 6780 Joint, O-Ring, plain.

to develop a suitable secondary standard for the routine checking of the instrument. Powdered silica was used for this purpose during the early stages of method development. More recently, 60-80 mesh granulated Alundum^{*} has been found to serve equally well. The material used is Norton Blue Label Alundum for carbon analysis. To establish its water content, weighed portions of Alundum were analyzed with the instrument calibrated against sodium tartrate dihydrate and sodium citrate dihydrate. A volumetric scoop was prepared; it holds a reproducible quantity of Alundum and can be used to place a standard sample in the analyzer rapidly without having to carry out a weighing operation in the glove box. The scoop holds 521.3 mg of Alundum, an amount which evolves $54.3 \pm 4.7^{**}$ micrograms of H_2O at 600 C or 34.4 ± 2.4 micrograms at 170 C.

6.1.4. Kinetics of Moisture Release

There is little agreement among various laboratories on the temperature required for quantitative evolution of water from mixed oxide fuel materials. After the quartz furnace tube was installed, the evolution of moisture was followed for three UO_2 pellets stored at ambient humidity conditions. In each case the pellet was placed in the furnace, heated to 150 C, and held at that temperature until no further moisture release was observable. The temperature was increased in 150 C intervals to 900 C, and the measurement of moisture evolved was repeated. At each step electrolysis rates in the cell dropped to background in a few minutes' time. Figures 6-3 and 6-4 summarize the results in differential and integral form, respectively.

The moisture release from UO_2 is nearly complete at 600 C. The cause of the rise in release rate at 450 C is not known, but it can be ascribed to more rapid release of chemisorbed water, or water contained in deep cracks or pores combined with higher diffusion rates. Other workers report similar results.¹⁰

* T.M. The Norton Company.

** One standard deviation.

Mixed oxide pellets analyzed in the B&W laboratories have all shown densities near 93% TD, and the moisture content has been found to be much lower than that of the UO_2 analyzed previously. This is in accord with an inverse relation between pellet density and moisture content. The results for a typical mixed oxide pellet gave 1.0 micrograms of H_2O at 600 C and 0.5 micrograms more at 900 C. These values are near the limit for the instrument and make it extremely difficult to obtain data for high-density mixed oxides comparable to those shown for UO_2 in Figures 6-3 and 6-4. The need for the information is also doubtful, since the total amount of moisture found is well within the usual requirements for nuclear fuels. Curves for mixed oxides will be established as lower-density samples are available.

At a given temperature the rate at which water appears in the electrolytic cell, as measured by the integrator readout, is determined at least by two processes—evolution from the sample surface and transport by the sweep gas into the electrolyte. The latter includes the processes of dilution and mixing in the furnace tube. Since most of the moisture evolved from high-fired pellets must arise from readsorption during low-temperature storage, it is presumed that actual release at analysis temperatures is rapid; the integrator signal will asymptotically approach a first-order rate law determined by the dilution-transport phenomena in the sweep gas. The integrator current should approach a straight line on a semi-log plot. Theoretically infinite time is required to complete the water measurement. A practical procedure requires carrying out the evolution to an acceptable degree as rapidly as possible, which, in turn, means that the operating temperature must be set high enough to ensure moisture evolution at the maximum suitable rate. The measurement is continued until the electrolytic current falls to some preselected value and the process is terminated arbitrarily. The termination point is selected so that the moisture remaining in the system is small compared to the total. By terminating a "blank" result at the same point, a sufficiently accurate correction for the undetermined water content follows automatically. The procedure amounts to an assumption that the residual water in a sample and a blank are approximately equal.

Figure 6-5 shows the results of a series of release rate measurements taken at 175 and 600 C. Curves A and B are blanks (no sample) representing the amount of moisture observed when only moist air is admitted to the apparatus. Curve A was run under standard operating conditions, and curve B shows the amount of moisture trapped when the furnace tube cap is closed rapidly. In both cases the moisture release rate fell to 0.5 micrograms/minute over background within six minutes, indicating that the furnace assembly, electrolytic cell, and associated tubing do not trap appreciable amounts of water for later slow release. Curves C and D show the moisture release at 175 C from 521 mg of 60-80 mesh Alundum and from sodium citrate dihydrate, respectively. Note the similarity in shape, even though water is (presumably) sorbed in the first case and chemically combined in the second case. Curve E (Figures 6-5 and 6-6) shows the water release from Alundum at 600 C. Comparing curves C and E indicates that Alundum seems to contain some very tightly bound water or possibly some sub-surface water which is released only slowly in spite of the increased temperature. Figure 6-6 compares moisture released from Alundum powder and from a UO_2 pellet. Furnace temperatures were 600 C in both cases; the pellet had been kept in air under ambient conditions. The curves have similar shapes near the beginning of the measurement and both approach straight lines (semi-log plot) after about 7 minutes. Curve G is a blank obtained at 600 C; it is similar to the 175 C blank shown in Figure 6-5.

By terminating a moisture determination when the moisture collection rate falls to 1.2 micrograms/minute (0.6 on these graphs, since the continuous background has been subtracted), an error of approximately -3 micrograms might be made in a moisture determination carried out on a UO_2 pellet. An error this small is of little practical consequence, and it is better to accept this possible error than to try to eliminate it by prolonging the determination time.

The limited high-temperature studies on mixed oxide materials mentioned in the preceding section of this report show that little additional moisture is expected from high density pellets at temperatures above 600 C. When lower-density materials are available,

a study of evolution rate as a function of temperature may be required to determine whether or not recovery is adequate at 600 C.

6.2. Oxygen-to-Metal Analysis

6.2.1. Introduction

The Fisher Scientific Company Thermogravimetric Analysis (TGA) System, Model 10-560-100, has been adapted for use in the determination of oxygen-to-metal (O/M) ratios in uranium oxide, plutonium oxide, and mixed uranium and plutonium oxide. The method is based on oxidation-reduction reactions of the oxides by a flowing gas stream and measurement of the accompanying weight changes. The procedure is adapted from a method developed by W. L. Lyon.¹¹ For a mixed oxide, the sample is dried in an argon atmosphere at 110 C, oxidized in air at 850 C, and then reduced at 850 C in a 6% hydrogen, 94% nitrogen atmosphere.

In the following paragraphs, the problems of the TGA procedure are reviewed, the experimental progress is summarized, and the final procedure is outlined in principle. Figure 6-7 is a diagram of the apparatus.

6.2.2. Weighing Instabilities

Unstable balance conditions are a chronic TGA problem. At the outset of this work, recorder shifts representing a few tenths of a milligram were observed with a 20-mg calibration weight on the balance pan. The instability was traceable to a combination of several effects, including a static charge on the balance, aerodynamic effects generated by gap flow past the sample, and the electronic instability of the electrobalance controller. Static charge effects have been minimized by substituting a quartz filament for a Nichrome hangdown wire supporting the weighing pan and by avoiding direct handling of the hangdown and concentric flow tubes. Aerodynamic forces were minimized by shortening the concentric flow tube by about 1 inch, thereby allowing the sample pan to hang just below the lower opening of this tube where gas flow velocities are lower and, therefore, less troublesome. Instability in the electrobalance controller was eliminated by replacing some defective components in the unit.

After the modifications listed were complete, some minor noise and instability were still apparent in an actual thermogram. The residual noise introduces errors that prevent working with weight changes at the sensitivity limits of the electrobalance. However, the thermograms obtained serve as a useful guide for detecting oxidation and reduction reactions and for estimating their degree of completion. To reduce the noise level further, actual weighings are made with the gas flow past the sample cut off.

6.2.3. Gas System

It was quickly observed that little or no reduction of U_3O_8 took place in the apparatus as originally designed, even at a gas (6% H_2 —94% N_2) flow of 200 cc/min at temperatures to 800 C. A check of the system soon showed gross gas leaks around the balance chamber door; the gas system was rerouted to put the inlet in the hangdown tube. At the same time a copper tube furnace was installed on the inlet line to remove trace amounts of oxygen, and a new furnace and thermocouple were installed.

6.2.4. Uranium Oxide Reduction

Equipment tests have been carried out using National Bureau of Standards (NBS) Chemical Standard No. 950a— U_3O_8 . The material was heated at 850 C in air for 1 hour to ensure its initial oxygen stoichiometry. When the apparatus modifications described in sections 6.2.3. and 6.2.4. were complete, a sample analyzed in quadruplicate at 1050 C and 300 cc/min gas flow showed O/M ratios of 2.008, 1.995, 2.005, and 2.004. The experiment was repeated at a gas flow of 200 cc/min with the same results. These data were taken as proof that the equipment is functional. The temperature was chosen experimentally and is the lowest value that gives essentially quantitative reduction of U_3O_8 .

6.2.5. Plutonium Oxide Reduction

Lyon's procedure¹¹ calls for air oxidation of the mixed oxide and subsequent reduction to $(U,Pu)O_2$. Pure PuO_2 has a tendency to over-reduce in hydrogen gas mixtures to give a hypostoichiometric oxide.¹² The use of the Lyon method, therefore, depends on establishing

conditions which will reduce the uranium to stoichiometric UO_2 without over-reducing the PuO_2 .

At 950 C in 6% H_2 -94% N_2 for 1 hour, pure PuO_2 showed no tendency to over-reduce. Evidence for the appearance of hypostoichiometric material was found at 1050 C, however. Further work on pure oxides was dropped at this point, and studies were initiated with mixed oxides.

6.2.6. Mixed Oxide Materials

Stoichiometric standards for mixed oxides are not available, but in 1968 an interlaboratory comparison of data was made on a single batch of prototype FFTF pellets. The results for this well-characterized material have been reported by the participating laboratories.¹³ B&W participated in this program, and, since there were several unused pellets still available in our laboratories, permission was sought and received to continue procedure checkout work with these FFTF materials.

From the 1968 studies it was found that the rate of reduction of mixed oxides is quite different from that of the pure oxides individually. Therefore, recommended furnace temperatures may vary from those used with pure materials. The oxidation rates compare closely with those of the individual components, but the reduction appears to be quantitative at temperatures as low as 800 C (versus 1050 C for a pure U-O system).

Figure 6-8 summarizes the apparent oxygen stoichiometry of a series of determinations carried out at reduction temperatures between 700 and 1000 C. Incomplete reduction is obtained below 800 C, and overreduction occurs above 900 C; 850 C has been selected as the optimum reduction temperature.

Grinding of the pellets to speed up reaction rates is not recommended because the B&W data indicate that grinding increases the apparent oxygen stoichiometry. Pellet samples may be crushed with a mortar and pestle, however, with little effect. The moisture content of pellets is generally too low to affect the stoichiometric analysis. Powders generally require drying, however, before analysis, but the drying operations must be carried out under conditions that do not affect the oxygen content. Table 6-1 shows the O/M values obtained on pellets treated in several ways.

Table 6-1. Results of O/M Analysis of
LMFBR/FFTF Pellets

<u>Pellet No.</u>	<u>O/M</u>
54 (pellet ground to powder)	2.000 2.000 1.997
56 (pellet crushed)	1.992 1.997 1.990 1.997
17 (pellet crushed)	1.992 1.990 1.995 1.993
18 (pellet crushed)	1.995 1.995 1.992 1.990
Overall avg of these 15 results:	1.994
Round Robin Avg:	1.995

6.2.7. Procedure Summary

The current procedure for O/M ratios on mixed oxides includes the following steps:

1. Calibrate the electrobalance using a known weight.
2. Add a 10-20 mg sample to the sample pan.
3. Record the sample weight (if a sample is thought to contain interfering amounts of moisture, it is dried in argon at 110 C for 30 minutes before weighing).
4. Purge the system with about 200 cm³/min for 5 minutes.
5. Heat the sample to 800 C by raising the tube furnace to surround the hangdown tube.
6. When oxidation is complete, change the atmosphere to 6% hydrogen, 94% nitrogen and reduce the sample at a flow rate of 200 cm³/min and a temperature of 850 C.

7. When reduction is complete, lower the furnace and cool the sample, leaving reducing gas on.
8. When the sample has cooled to below 50 C, turn off the reducing gas and purge the system using air.
9. Record the final weight of the sample.
10. Calculate the O/M using the following equation:

$$O/M = 2.000 - \frac{M}{16} \left(\frac{W_2 - W_1}{W_1} \right)$$

where   M = average molecular weight of mixed oxide
               W₁ = dry (starting) weight
               W₂ = final (reduced) weight

6.3. Powder Characterization

6-3.1. Sol-Gel Microspheres

Analyses of sol-gel microspheres for plutonium, uranium, O/M, and moisture are complete, and the data are summarized below. In addition, mass spectrometric data are given for the analysis of samples of uranyl nitrate used as input material.

6.3.1.1. Description of Samples

- 4-E-87 Coarse sphere fraction for Pu, U, O/M, and moisture (depleted U).
- 4-E-88 Fine sphere fraction for Pu, U, O/M, and moisture (depleted U).
- 4-E-91 Coarse sphere fraction for Pu, U, O/M, and moisture (20% ²³⁵U).
- 4-E-92 Fine sphere fraction for Pu, U, O/M, and moisture (20% ²³⁵U).
- MS-2, -4, -6 Identical samples of uranyl nitrate for mass spectrometric analysis from first batch of downgraded material.
- MS-7 Sample of uranyl nitrate for mass spectrometric analysis from second batch of downgraded material.
- MS-10 Sample of uranyl nitrate for mass spectrometric analysis from third batch of downgraded material.

6.3.1.2. Plutonium and Uranium Assay

The analyses for plutonium and uranium were performed using controlled-potential coulometry following sample dissolution in 13 M HNO₃ and 0.01 M HF. The analyses were performed in quadruplicate, on a weight basis.

Table 6-2. Total Metal in Sample

<u>Sample</u>	<u>U, mg/g</u>	<u>Pu, mg/g</u>	<u>$\frac{\text{Pu}}{\text{U+Pu}}, \%$ (a)</u>
4-E-87	706.0, 700.0, 699.5, 710.3 (<u>704.0</u>)	172.7, 169.6, 169.8, 171.0 (<u>170.8</u>)	19.52
4-E-88	705.0, 709.6, 705.8, 707.9 (<u>707.1</u>)	172.3, 174.0, 174.1, 173.9 (<u>173.6</u>)	19.71
4-E-91	719.3, 715.4, 714.9, 718.8 (<u>717.1</u>)	168.3, 168.7, 167.8, 167.9 (<u>168.2</u>)	19.00
4-E-92	705.7, 712.7, 710.1, 713.1 (<u>710.4</u>)	167.5, 169.3, 169.4, 168.9 (<u>168.8</u>)	19.20

(a) Calculated on the averages.

6.3.1.3. Oxygen-to-Metal Ratio (O/M)

The analyses for O/M were done by micro-thermogravimetry based on a modification of the method given by Lyons.¹¹ The analyses were performed in quadruplicate.

Table 6-3. Oxygen Stoichiometry

<u>Sample</u>	<u>O/M atom ratio</u>	<u>Avg</u>
4-E-87	1.973, 1.975, 1.975, 1.980	(1.976)
4-E-88	1.988, 1.986, 1.988, 1.985	(1.987)
4-E-91	1.975, 1.971, 1.975, 1.973	(1.974)
4-E-92	1.981, 1.981, 1.985, 1.985	(1.983)

6.3.1.4. Moisture Content

Moisture analyses were run in quadruplicate, and, since no attempt was made to control the storage conditions for these samples, analyses were made at both 100 and 600 C on the same portions of sphere material. This procedure was adopted to show whether or not there is a relationship between the surface area of the sphere material and the water content. Data accumulated over several weeks indicate that a part of the moisture present in mixed oxide samples is held quite strongly on the surface, while the balance is relatively easy to remove. Thus, the total moisture content of the samples reflects the conditions of storage (temperature, humidity, age), and the more strongly held water reflects the amount of surface area of the sample material. The latter is a fairly constant quantity, and the former is not. Since humidity conditions were not controlled during preparation of the material, storage, and analysis of the samples, it is impossible to average the data given in Table 6-4.

Table 6-4. Moisture Content of Microsphere Material (ppm)

<u>4-E-87</u>	<u>31 Dec 68</u>	<u>2 Jan 69</u>		<u>3 Jan 69</u>	
600 C	15.9	11.5		18.0	11.2
100 C	9.1	5.5		8.1	4.9
Difference	6.8	6.0		9.9	6.3
<u>4-E-91</u>					
600 C	10.8	9.1		10.1	16.7
100 C	5.4	4.6		3.5	6.4
Difference	5.4	4.5		6.6	10.3
<u>4-E-88</u>					
600 C	156.7	69.6	66.7	50.5	49.1
100 C	74.0	33.0	28.0	22.1	20.7
Difference	82.7	36.6	38.7	28.4	28.4
<u>4-E-92</u>					
600 C	87.9	57.3	56.8	46.8	41.1
100 C	44.4	28.3	26.4	16.0	10.2
Difference	43.5	29.0	30.4	30.8	30.9

6.3.1.5. Uranium Isotopic Analysis

Twenty-percent-enriched uranium as uranyl nitrate was prepared by isotopic dilution of fully enriched material. Samples from each of the three batches prepared were analyzed using mass spectrometry for uranium isotopic distribution. The results are summarized in Table 6-5.

Table 6-5. Uranium Isotopic Analyses

Sample		Isotope, atom %			
		²³⁴ U	²³⁵ U	²³⁶ U	²³⁸ U
1st batch	MS-2	0.12	19.71	0.06	80.11
	MS-4	--	19.71	--	80.11
	MS-6	--	19.68	--	80.15
2nd batch	MS-7	0.11	19.66	0.05	80.17
3rd batch	MS-10	0.12	19.68	0.05	80.15

6.3.2. Mixed Oxide Pellets

Analyses of (U,Pu)O₂ pellets for plutonium, uranium, O/M, and moisture are complete and the data are summarized below.

6.3.2.1. Description of Samples

Pellet No.

66	Analyzed for Pu and U (20% ²³⁵ U).
78	Analyzed for Pu and U (natural U).
25	Analyzed for O/M (20% ²³⁵ U).
39	Analyzed for O/M (natural U).
60	
67	Analyzed for moisture (20% ²³⁵ U).
68	
85	
9	
32	Analyzed for moisture (natural U).
36	
78	

6.3.2.2. Plutonium and Uranium Assay

The analyses for plutonium and uranium were performed by controlled-potential coulometry following sample dissolution of the entire unground pellet. The analyses were performed on a weight basis, using six aliquots each for plutonium and uranium determinations.

Table 6-6. Total Metal in Pellet Sample

Pellet No.	U, mg/g	Pu, mg/g	$\frac{\text{Pu}}{\text{U+Pu}}, \%$ (a)
66	709.9, 706.8, 709.3, 705.1, 710.9, 711.2 (708.9)	172.8, 173.9, 174.1, 173.1, 171.2, 173.4 (173.1)	19.63
78	716.1, 718.1, 708.8, 722.0, 716.9, 709.7 (715.3)	174.6, 174.4, 171.0, 173.3, 172.1, 174.8 (173.4)	19.51

(a) Calculated on the averages.

6.3.2.3. O/M Analyses

The analyses for O/M were done by micro-thermogravimetry based on a modification of Lyons' method.¹¹ The analyses were performed in quadruplicate, and the results are shown below.

Pellet No.	O/M, atom. ratios	Avg
25	1.973, 1.968, 1.968, 1.975	1.971
39	1.976, 1.981, 1.975, 1.976	1.977

6.3.2.4. Moisture Analyses

Moisture was determined using the CEC type 321 AMA Solids moisture analyzer. An unground pellet was used for moisture determinations at 100 and 600 C.

Table 6-7. Moisture Determinations at 100 and 600 C

<u>Pellet No.</u>	<u>100 C</u>	<u>600 C</u>	<u>Difference</u>
60	0.6	1.7	
67	0.4	1.6	
68	0.6	1.7	
85	0.8	2.1	
Average	0.6	1.8	1.2
9	1.4	3.1	
32	1.4	2.9	
36	1.1	2.7	
78	1.6	3.1	
Average	1.4	3.0	1.6

6.4. Analytical Sample Load

During this quarter, 39 samples were analyzed, representing a total of approximately 182 analyses. The analyses included total uranium, total plutonium, moisture, oxygen-to-metal ratio (O/M), and isotopic composition of uranium.

Figure 6-1. Moisture Analyzer, Furnace and Electrolytic Unit Installed in Glove Box

Figure 6-2. Moisture Analyzer, Glove Box Arrangement

Figure 6-3. Moisture Released by Three Uranium Dioxide Pellets

Figure 6-4. Integral Moisture Released by Three Uranium Dioxide Pellets

Figure 6-5. Moisture Evolution From Standard Materials

Figure 6-6. Moisture Evolution at Elevated Temperatures

Figure 6-7. TGA Apparatus for O/M Determination,
Gas Flow per Original Design

Figure 6-8. Oxygen-to-Metal Ratios at Reduction Temperatures Between 700 and 1000 C

APPENDIX A
Hot Cell Modifications for Plutonium Fuels

— A Special Progress Report on B&W-Sponsored Work —

by
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ABSTRACT

A stainless steel and Homalite box is under construction for use within the B&W hot cells. When it is complete, the auxiliary box will permit the safe examination of sub-kilo quantities of reactor-exposed plutonium-bearing fuels. Facilities will be provided for capsule opening, NaK removal, pin sectioning and polishing, microstructure studies, fission gas determinations, and sampling for burnup analysis.

At the present time the box and most of its internal fittings are on site. The schedule for completing the installation will be established by the requirements of AEC Contract AT(30-1)-3714. Currently the Company expects to complete the unit by January 1, 1970. The cell modifications are being carried out as part of the B&W capital expansion program, and no public funds are involved.

1. Introduction

For the past five years Babcock & Wilcox has tested irradiated core materials in the beta-gamma hot cell facility in its Nuclear Development Center. Continuing efforts with thermal reactor fuels, as well as an immediate need for work with plutonium-bearing materials, require the Company to add equipment for examining high-level alpha emitters in its hot cell complex. The development of a system for working with sub-kilogram quantities of plutonium is underway and will be installed with a minimum of interference with work in progress on conventional fuels. This progress report describes the planned hot cell modifications, summarizes the current status, and outlines the schedule for completing the work. It is a summary of B&W-sponsored activities involving no public funds and has been prepared as a matter of information to those using B&W hot cell facilities.

2. Present Hot Cells

B&W completed the first NDC hot cell unit early in 1964 and since then has added three smaller support cells. The present floor plan is shown in Figure A-1, and some of the construction details are shown in Table A-1.

The 4-cell complex is served by a common isolation area which provides secondary containment when any of the cell access doors are open. The cells are interconnected by transfer ports, making it unnecessary to open the main doors for sample transfers. Irradiation capsules enter Cell 1 for disassembly; the exposed samples are transferred to the appropriate operating stations for testing.

The present complex has a projected work load that will require it as an operating entity for several years. Thus, any modifications for work with large quantities of alpha emitters must minimize disruptions of current experimental work. Constructing separate cells for alpha work is not feasible, either from a lead time or cost standpoint; therefore, a portion of the existing facility will be adapted for plutonium work.

Table A-1. Construction Details of the NDC Hot Cell

Cell	Use	Internal dimensions L x W x H, ft	Shielding copy E - 1 MeV	Shield wall	Op. sta	Containment
1	Non-destr tests, disassembly	16 x 8 x 15	1 MCi	42" Ilmenite	3	Negative pressure
2	Metallography	18 x 4 x 9	10 KCi	13" Lead shot	3	Negative pressure
3	Mechanical test	9 x 4 x 9	1 KCi	11" Lead shot	1	Negative pressure
4	Encapsulation, remote welding	6 x 6 x 9	10 KCi	Composite: 13" lead shot 24" ferrophosphous	1	Negative pressure

3. Alpha Handling Specifications

The following guidelines and specifications have been established for work with high-level alpha fuels:

1. Destructive tests on plutonium-bearing materials will meet the same contamination control criteria used in the Plutonium Development Laboratory.
2. An inert atmosphere will not be required.
3. Useful life will be four years.
4. Heat dissipation will be limited to 1 kW decay heat plus that generated by the equipment.
5. Test objects will be limited to $3 \times 3 \times 40$ inches external dimensions and 100 pounds in weight.
6. Radiation levels will be limited to 10^6 RHM (mixed fission products).
7. The following basic operations will be provided:

Capsule disassembly.
Na/NaK removal.
Sample visual examination.
Sample macrophotography.
Sample dimensional measurements.
Clad puncture and fission gas analysis.
Void volume determination.
Fuel sectioning and sampling.
Sample mounting and polishing.
Microstructure examination.
Autoradiography.

The specifications will be met by installing an alpha box inside Cell 1.

4. Alpha Containment Design

4.1. Materials

The box is made of stainless steel and Homalite-CR-39 and is gasketed with neoprene.

4.2. Dimensions

The box is designed to fit into one corner of Cell 1 (see shaded area, Figure A-1). It is $6 \times 6 \times 8$ feet high and will be served by two

operating stations. The support frame places the glove box floor 38 inches above the hot cell floor, permitting transfer of materials between cells to continue. Work with conventional samples may continue at the remaining station.

4.3. Construction Details

The box is designed as a series of modular panels bolted to the box frame. The frame members are channels designed so that the gasket bolts do not penetrate into the contaminated zone, eliminating many sealing problems. The modular concept was chosen to permit the maximum flexibility in arrangement of bag-out ports, manipulator seals, ventilation ducts and filter changers. Some of these locations are still under consideration, but the modular construction has allowed B&W to contract for box fabrication. The modular construction will reduce considerably the time required to complete the installation.

5. Box Operation

5.1. Capsule Disassembly

A slow-speed abrasive wheel which can be used as a slitter or cutoff saw has been fabricated for capsule disassembly. The design was adapted from one suggested by Doe.¹⁴

5.2. NaK Removal

NaK is completely removed from an exposed capsule by reacting the last traces with butyl alcohol. Figure A-2 shows the specialized equipment used.

5.3. Visual Examination and Macrophotography

These operations will be carried out using a Kollmorgen 301 periscope already installed in the hot cells.

5.4. Fission Gas Analysis

Fission gases are analyzed by placing the irradiated pin in an evacuated chamber and puncturing the cladding. The escaping gases are trapped and can be analyzed in any of three ways. A small quadrupole mass spectrometer is installed directly on the gas manifold. The sample can be analyzed without removing it from the hot cells. Sample

bombs are also available, into which gas samples can be pumped and sealed off for analysis in the most sensitive equipment available at NDC—either the magnetic focusing mass spectrometer or a gas chromatograph. The gas handling equipment is shown in Figures A-3 and A-4. The latter is the in-cell portion of the equipment which will be installed directly with the alpha box.

5.5. Microstructure

Commercially available grinding and polishing equipment has been adapted for use inside the box. Two remote metallographs are available. A Unitron instrument has been modified so that its stage and microscope head can be installed inside the box. The controls are outside the shielding wall. A B&L Remote Research Metallograph installed in Cell 2 is available for detailed examinations.

5.6. Dimensions

A scanning profilometer has been developed and is currently being tested. It is illustrated in Figure A-5.

6. Box Maintenance

All contemplated operating procedures are based on the assumption that direct operation or maintenance inside the box will be impossible once the box has been in service. Equipment maintenance or replacement and material transfers must be handled remotely.

Bag-out procedures are based on work done at Los Alamos Scientific Laboratory.¹⁵ A modification of the standard high-level waste container used on this site (see Figure A-6) is designed to mate with a 5-inch-diameter port for high-level bag-out operations. A similar 18-inch port accommodates equipment, low-level wastes, or other materials to be removed in alpha-tight containers.

7. Operational Safety

The most severe safety problem is control of alpha contamination; it is adequately dealt with by the sealed-box arrangement. Fire and criticality hazards are equally important and have been treated by the following considerations:

7.1. Fire

Infrared detectors and high-temperature sensors are both being included in an automatic fire control system. The overall system is still in the design stage.

7.2. Criticality

Mass limits will be imposed on the system to allow for control of masses within the alpha box and for interactions with materials in adjacent operating positions.

8. Present Status and Schedule

At the present time most of the hardware has been ordered for the alpha box installation, and much of it is on hand. The box frame is on site and has been assembled and leak tested. Some of the equipment panels which are still under design were replaced by blank modules for these tests. Of a total of seven panels, five are completely designed and one of these has been fabricated and is on hand. The remaining two panels are still under design. All remaining design work is scheduled for completion during the third quarter of 1969.

Before any major changes in NDC operating procedures involving radioactive materials are initiated, a formal safety review is required by B&W management and by the terms of our isotope license. The review is carried out by the NDC Isotopes Committee; the alpha box installation is scheduled for review in late summer 1969. Following committee review, the actual installation can begin.

The first samples to be examined will originate from the AEC sol-gel contract, and that contract schedule will be the determining factor in bringing B&W alpha hot cell capabilities into full operational status. At the present time five (U,Pu)O₂ fuel capsules are proposed for hot cell examination during FY 1970. If this schedule is retained, installation of the alpha box will be completed during the fourth quarter of 1969. The equipment will be fully operational by the end of 1969.

Figure A-1. Hot Cell Floor Plan Showing Location of Alpha Box

Figure A-2. NaK Removal Equipment

Figure A-3. Fission Gas Collection and Analysis System,
Instrumentation and Controls

Figure A-4. Fission Gas Collection and Analysis System,
In-Cell Puncture Unit

Figure A-5. Fuel Pin Profilometer

Figure A-6. High-Level Waste Storage Tube

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