IRRADIATION PERFORMANCE OF
THORIA-URANIA FUEL MATERIALS

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ABSTRACT

The work accomplished during the period January 1, 1965, to March 31, 1965, on the irradiation performance of thoria-urania fuel materials is described. The objectives of this program are as follows:

1. To establish, experimentally, particular physical properties of thoria-urania that are of interest to the reactor designer.
2. To present such physical property data in a form suitable for engineering application.

The following experimental results were obtained during the quarter:

1. The permeability coefficient of compacted UO_2 was measured.
2. The gas flow was identified as a combination of Knudsen and viscous flows.
3. Thermal transpiration occurred at atmospheric pressure but decreased at higher pressures.
4. Thoria-urania fuel was produced from pure thoria and normal uranium in an application of the sol-gel method.
5. The sorbed gas release indicated that the gas content of the sol-gel thoria urania is generally less than 0.1 cm^3 per gm. Gas content tended to increase when the urania content was increased.

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CONTENTS

	Page
1. INTRODUCTION	1-1
2. GAS PERMEABILITY OF THORIA-URANIA — TASK 02...	2-1
2.1. Task Objective	2-1
2.2. Task Description	2-1
2.3. Work Accomplished During This Report Period	2-2
2.4. Planned Work for Next Report Period	2-6
3. SORBED GAS RELEASE DETERMINATIONS — TASK 03 ..	3-1
3.1. Task Objective	3-1
3.2. Task Description	3-1
3.3. Work Accomplished During This Report Period	3-1
3.4. Planned Work for Next Report Period	3-10
4. UNIRRADIATED FUEL THERMAL CONDUCTIVITY — TASK 04	4-1
4.1. Task Objective	4-1
4.2. Task Description	4-1
4.3. Work Accomplished During This Report Period	4-1
4.4. Planned Work for Next Report Period	4-4

List of Tables

Table

3-1. NO ₃ /Th Mole Ratios of Denitrated TNT	3-4
3-2. NO ₃ /Th Mole Ratios of Denitrated Materials Used in Preparing Various U/Th Sol-Gel Fuels	3-4
3-3. Data on Sol-Gel Fuel	3-6
3-4. Sizing of Sol-Gel	3-7
3-5. Gas Release From Sol-Gel Fuels	3-8
3-6. Weight Loss Upon Calcination of Sol-Gel Fuel	3-9

List of Figures

Figure	Page
2-1. Assembled High Pressure Gas Permeability Apparatus. .	2-7
2-2. High Pressure Gas Permeability Apparatus	2-7
2-3. Effect of Temperature on Permeability of Vibratory Compacted Fuel.	2-8
2-4. Effect of Uniform Fuel Temperature Runs on Room Temperature Permeability.	2-9
2-5. Effect of Fuel Outgassing at Elevated Temperature on Room Temperature Permeability.	2-10
2-6. Thermal Transpiration Fuel Specimen.	2-11
2-7. Low Pressure Apparatus Modified for Thermal Transpiration Experiment.	2-12
2-8. Temperature Profile From Thermal Transpiration Experiment.	2-13
2-9. Permeability of Specimen V-3 After Thermal Transpiration Experiment.	2-14
2-10. Permeability of Pellet Fuel	2-15
3-1. Generalized Flowsheet of Sol-Gel Process	3-11
3-2. U/Th Ratio of Sol-Gel Fuel Vs Gas Released.	3-12
3-3. Weight Loss of Sol-Gel Upon Calcination Vs Gas Released.	3-13
3-4. Input Thoria NO_3 /Th Mole Ratio Vs Gas Released	3-14
3-5. Percentage of Oxide Greater Than 10 Mesh Vs Gas Released.	3-15
3-6. Idealized Spectrum of Argon, Oxygen, and Nitrogen Mixture	3-16
3-7. Isotopic Spectrum of Commercial Grade Argon	3-17
4-1. Thermal Simulation Device	4-5
4-2. Cooling Jacket With a Clad Specimen in Place, Showing Sight Pipe Holes at the Top and the Thermocouple Lead- Through at the Side.	4-6
4-3. Heat Gradient Vs Sight Pipe Location for Various Temperatures	4-7

1. INTRODUCTION

Complete exploitation of the advantages of thorium as a fertile material in thermal and particular resonant spectrum reactors has been inhibited by the lack of quantitative physical property data for thoria and thoria-urania fuels. Thoria and thoria-urania solid solutions have not been investigated as thoroughly as pure urania has. The meager information available has been deduced from extrapolation of urania data to thoria data or produced from the few isolated programs dealing with thoria itself. No reliable performance information on thoria-urania fuel is available, especially in the higher performance areas, and there is no knowledge of the material's ultimate performance limits.

This contract provides for a series of experiments directed toward establishing certain physical properties of thoria-urania fuel materials that are necessary for improved reactor core design. The program is divided into six experimental tasks and an additional task providing supervision, reports, and technical support. The experimental tasks are as follows:

<u>Task No.</u>	<u>Supporting Measurements</u>
02	Gas Permeability of Irradiated Fuel
03	Sorbed Gas Release Determinations
<u>Thermal Conductivity</u>	
04	Unirradiated Fuel Thermal Conductivity
05	Irradiated Fuel Thermal Conductivity
<u>Gas Release</u>	
06	Dynamic Inpile Fission Gas Release Experiment
07	Static Gas Release Experiment

The program has progressed to the point where some experimental results are available. Under the gas permeability task, the permeability coefficient of compacted UO_2 was measured, and the gas flow was identified as a combination of both Knudsen and viscous flows. As the temperature of the specimen is raised, structural changes within the specimen are indicated by an appreciable reduction in permeability. Thermal transpiration was also examined in a compacted fuel specimen. At atmospheric pressure, a temperature gradient of about 600 C produced a pressure difference of 14%. At higher pressures, the change was less. These results indicate that thermal transpiration is effective in a fuel rod operating in a thermal gradient, but that the significance of thermal transpiration decreases as pressure increases.

In the sorbed gas release determinations, thoria-urania fuel (up to 10 wt % urania in thoria) was produced from pure thoria and normal uranium using the sol-gel method. Initial sorbed gas release determinations indicated that the gas content of the sol-gel thoria-urania is low (generally less than 0.1 cm^3 per gm). There is a tendency for the gas content to increase with increasing urania concentrations. Other production parameters also have been investigated.

For Task 04 (unirradiated fuel thermal conductivity) the thermal simulation device has been fabricated and tested without fuel. The thermal gradient axially along the length of the heater rod is lower than was originally expected. It now seems that an axial thermal gradient of less than 200 C can be easily obtained in a fuel specimen. Comparison measurements and calorimetric measurements have indicated that end losses from the specimen probably will not exceed 7% of the total power input.

Toward the end of this report period, the Atomic Energy Commission notified B&W that the program for the irradiation performance of thoria-urania fuel materials should be brought to an orderly close by June 30, 1965. Consequently, all work on Tasks 05, 06, and 07 (irradiated fuel thermal conductivity, dynamic inpile fission gas release experiment, and static gas release experiment) has been concluded since no results from these tasks could be expected by this date. The irradiated fuel thermal conductivity task and the static gas release experiment had been completely designed and were awaiting receipt of materials and fuel for specimen and capsule fabrication prior to insertion in the reactor.

During this report period no progress was made on either of these tasks, but some of the materials were received.

The design of the dynamic inpile fission gas release experiment was completed. Additionally, a bench test apparatus was set up to evaluate the effectiveness of the proposed instrumentation for this inpile fission gas release experiment. The practicability of the planned experiment was demonstrated in the laboratory.

No further discussion of Tasks 05, 06, and 07 will be included in this report. A summary of the work on these tasks will be included in the final report.

2. GAS PERMEABILITY OF THORIA-URANIA — TASK 02 (A. C. Batten, Task Leader)

2.1. Task Objective

The principal objective is to obtain information on the gas permeability of thoria-urania at both room and elevated temperatures. Also, the occurrence of thermal transpiration and its effect on permeability will be investigated.

2.2. Task Description

Fuel rods are normally designed with a void volume in which gases released from the fuel can accumulate. The rate at which locally released gases permeate to expansion voids is of interest in predicting gas movement and pressure buildup within fuel rods. The accuracy of fission gas analyses of irradiated fuel specimens depends on the complete removal of all gases within the open pores of the fuel. Fission gases have been observed to emanate from fuel specimens long after the analysis has been completed, indicating that not all of the gas was initially released to the sampling system.

During core operation it is anticipated that thermal excursions will cause variations in fission gas pressures, resulting in large variations of driving force for movement of the gas through the structure. The magnitude of the local pressure buildup due to a pulse of fission gases released to open porosity depends on the restriction to gas flow offered by the fuel.

When a temperature difference exists within the fuel specimen, gas flow may occur as a result of thermal transpiration. Under conditions of Knudsen flow, gas flows from the cold zone to the hot zone until the function $P/\sqrt{T}$ is the same at both ends. Since flow through a porous medium of nonuniform pore size is expected to consist of both Knudsen and viscous flows, the extent of thermal transpiration and its resultant effect on gas permeability of nuclear fuels should be determined.

The initial program effort concerns the design and construction of an apparatus to test the permeability of thoria-urania fuel specimens to various gases. The magnitude of the variables involved will be determined by preliminary bench tests on both pellet and vibratory compacted fuels. Information from these tests will then be used in designing an apparatus to make precision measurements for permeability calculations. The existence of thermal transpiration and its resultant effects on permeability may influence the conditions of testing and the final design of the apparatus.

2.3. Work Accomplished During This Report Period

2.3.1. Summary

1. The effects of uniform temperature on a vibratory compacted fuel specimen were determined.
2. The existence and extent of thermal transpiration at essentially atmospheric pressure conditions were determined on a vibratory compacted fuel rod.
3. The bench test apparatus for high pressure measurements was assembled and checked for satisfactory operation.

2.3.2. Bench Test Design

It was anticipated that the permeability of the pressed and sintered fuel pellet would differ greatly from that of the more porous vibratory compacted fuel. In an effort to establish a range of expected gas flow through both fuel types, two sets of bench apparatus were constructed for low and high pressures. It was also considered necessary to establish a relationship between low- and high-pressure flow measurements to determine the need for a more complex final apparatus.

2.3.2.1. Low Pressure Apparatus

This apparatus was previously described and illustrated in the last quarterly technical report (BAW-3376-2, page 2-2).

2.3.2.2. High Pressure Apparatus

Figure 2-1 shows the assembled high pressure apparatus, and Figure 2-2 is a schematic diagram of the apparatus. After the specimen is attached to the apparatus with bite-type pressure fittings,

the upstream (right) side is pressurized to a desired constant gas pressure, which is measured by a precision test gage. The flow of gas passing through the specimen is measured by the rate of water displacement into the burette at atmospheric pressure. Normally, the downstream side of the specimen is maintained at atmospheric pressure. However, the metering valve and precision test gage at the left may be used to increase the downstream pressure as desired.

2.3.3. Test Results

2.3.3.1. Permeability of Powder Fuel

Figure 2-3 shows the effects of uniform fuel temperature on the permeability to helium of a vibratory compacted fuel specimen. The theoretical values for the permeability coefficient K were calculated from the relationship,

$$K = \frac{B_o}{\eta} \bar{p} + \frac{4}{3} K_o \sqrt{\frac{8 RT}{\pi M}}$$

where

B_o = viscous flow permeability coefficient

η = viscosity of the gas

$\bar{p}$ = mean pressure of the gas in the porous medium

K_o = Knudsen flow permeability coefficient

R = universal gas constant

T = temperature of the gas

M = molecular weight of the gas

B_o and K_o were determined experimentally from the room temperature permeability coefficient K . Since B_o and K_o are independent of temperature, the slight decrease in K is a combined effect of temperature on the viscosity η and the mean thermal molecular velocity $\bar{v}$, since

$$\bar{v} = \sqrt{\frac{8 RT}{\pi M}}$$

The large decrease in the observed permeability during heating indicates a structure change (compaction of the oxide fuel), or improved sealing of the fuel at the tube wall, or possibly both. The inverse hysteresis effect during cooling indicates relaxation of the seal at the tube wall. Calculations indicate that an interference of 0.0007 inch

at 580 C should have occurred between the tube wall and the oxide fuel. Inside diameter measurements of the tube after the temperature runs showed a possible permanent increase of 0.0003 inch.

Figure 2-4 shows the change in the room temperature permeability of the same vibratory compacted fuel specimen after the uniform fuel temperature runs. Initially, the fuel specimen was outgassed under vacuum at 580 C for 2 hours. The approximate twofold increase in room temperature permeability after the temperature runs indicates the importance of making all comparison permeability runs at elevated temperatures. Even outgassing of the fuel at elevated temperatures for 2 hours appears to appreciably change the permeability at room temperature. Figure 2-5 shows the observed difference in permeability between specimen V-3 prior to outgassing and specimen V-1 after outgassing at 580 C. Since the bulk densities of both specimens were very nearly the same (86.5 and 86.7% theoretical for specimen V-1 and specimen V-3, respectively), these specimens may be compared in considering temperature effect. Also shown is the change in permeability of specimen V-3 after outgassing at 500 C and after the thermal transpiration run, which will be discussed next.

2.3.3.2. Thermal Transpiration in Powder Fuel

To investigate thermal transpiration, a special vibratory compacted fuel specimen, Figure 2-6, with thermocouples placed on each face of the fuel was prepared. In addition, thermocouples were placed along the outside surface of the tube to record the temperature gradient along the fuel length. A short heater cord covered with thermal insulation was placed over one end of the fuel, while the other end was exposed to room temperature. The specimen (V-3) was attached to the low pressure apparatus (Figure 2-7) which was slightly modified to provide smaller chamber volumes for rapid pressure change response.

The surface temperature profile obtained along the fuel length is shown in Figure 2-8. At the hot end, the temperature of the face of the fuel at the center was 621 C, or 9 C lower than the outside surface temperature. At the cold end, the fuel face temperature and the surface temperature were identical. The starting pressure in both chambers was atmospheric (750 mm Hg). The equilibrium pressures reached as a result of thermal transpiration were 826 mm Hg at

the hot end and 725 mm Hg at the cold end. The ratio of pressures obtained was 1.14, compared with the theoretical ratio of 1.73 calculated from the relationship

$$\frac{P_1}{P_2} = \sqrt{\frac{T_1}{T_2}}$$

where

p_1 = pressure at T_1 end

p_2 = pressure at T_2 end

T_1 = higher temperature in K

T_2 = lower temperature in K

The results indicate that only 19% of the expected transpiration effect was achieved for the conditions of test. However, this result is not surprising since the theoretical value can only be obtained under entire Knudsen flow conditions. The permeability plots show that a combination of Knudsen and viscous flow was obtained with the vibratory compacted fuel under pressure conditions similar to those used for the thermal transpiration experiment. (See Appendix A, BAW-3376-1.) Part of the reverse flow from thermal transpiration may be returned by the pressure buildup through capillaries in the fuel which are sufficiently large for viscous flow. The net result is that complete transpiration cannot be achieved.

After the thermal transpiration experiment, room temperature permeability runs were made on the same specimen (V-3), using the modified low pressure apparatus. The average pressure ($\bar{p}$) was extended to 11 atmospheres determined by a test gage instead of the manometer, which was previously used. The measured gas flow varied from 0.18 to 4.23 cm³-atm/sec for pressure drops of 298 to 1622 cm Hg. Figure 2-9 shows the results compared with those obtained in the low range using a manometer. The displacement in the plot is caused by inaccuracies between the manometer and the test gage. The significance of this test is that the straight line plot indicates that, up to 11 atmospheres pressure, turbulent flow in the fuel was not reached.

2.3.3.3. Permeability of Pelletized Fuel

The operation of the high pressure apparatus was tested using a fuel pellet which had the peripheral surface coated

with copper. The pellet was sealed into a fixture by a series of rubber O-rings. For pressure drops of 1.90 to 20.4 atmospheres, the gas flow varied from 0.004 to 0.145 cm³-atm/sec. The permeability based on 12 initial test runs with helium gas is shown in Figure 2-10. All points fell on or very close to the line, which indicates that accurate gas flows were measured by the water displacement technique. The lower permeability of pellet fuel compared to powder fuel is readily apparent by comparing the plot with Figure 2-9.

2.4. Planned Work for Next Report Period

During the next report period, the effect of a temperature gradient on the flow of gas through nuclear fuel will be investigated. The extent of thermal transpiration at elevated pressures will be determined, and gas flow under both temperature and pressure gradients will be obtained. By comparison with gas flow obtained under a pressure gradient at uniform elevated temperatures, the effect of thermal transpiration on gas permeability may be evaluated.

Figure 2-1. Assembled High Pressure Gas Permeability Apparatus (WAS-65-490)

Figure 2-2. High Pressure Gas Permeability Apparatus (NDC-1184 C)

Figure 2-3. Effect of Temperature on Permeability of Vibratory Compacted Fuel

Figure 2-4. Effect of Uniform Fuel Temperature Runs on Room Temperature Permeability

Figure 2-5. Effect of Fuel Outgassing at Elevated Temperature on Room Temperature Permeability

Figure 2-6. Thermal Transpiration Fuel Specimen
(NDC-1220 C)

Figure 2-7. Low Pressure Apparatus Modified for Thermal Transpiration Experiment (WAS-65-491)

Figure 2-8. Temperature Profile From Thermal Transpiration Experiment

Figure 2-9. Permeability of Specimen V-3 After Thermal Transpiration Experiment

Figure 2-10. Permeability of Pellet Fuel

3. SORBED GAS RELEASE DETERMINATIONS — TASK 03 (C. J. Halva, Task Leader)

3.1. Task Objective

Absorbed and adsorbed gases released from unirradiated sol-gel fuel will be determined, qualitatively and quantitatively, as a function of temperature.

3.2. Task Description

Samples of sol-gel fuels of varying composition, size, and preparation history will be pyrolyzed at different temperatures under vacuum. The amount of sorbed gases evolved will be measured and collected. The collected gases will be analyzed using gas chromatographic and/or mass spectrometric methods. The amount and nature of these gases will be studied to determine whether changes in production methods are necessary to improve sol-gel thorium.

3.3. Work Accomplished During This Report Period

3.3.1. Summary

Modifications have been made in the overall experimental approach to this program in order to obtain as much information as possible about the nature of sorbed gases in sol-gel fuels before the close out of the program on June 30, 1965. The original experimental approaches to the program have been altered to accomplish this.

Nine batches of thorium nitrate tetrahydrate (TNT) have been denitrated for the thorium utilization program. Eight batches of Th-U oxide sol-gel fuel have been produced for this program. The analyses of both the denitrated material and the oxide product have been completed.

The oxide product has been partially screened into +10 mesh and -10 mesh size fractions. Samples of the +10 material have been degassed, and the quantity of the gas released has been measured.

The mass spectrometer has been operating in the gaseous mode. Samples of various gases and mixtures of gases have been identified using this unit. Very little additional work has been done with the gas chromatograph.

3.3.2. Progress on Sorbed Gas Studies

3.3.2.1. Modifications of Overall Program

Due to the phase out of the contract for this program, the original experimental approach to this task, described in BAW-3376-1, has been materially modified. All the fuel originally scheduled for production has been made. Experiments to determine the effects of storing the fuel in different environments have been cancelled, and all fuel studies will be made on sol-gel fuel stored in air. Experiments to determine the effect of pulverizing the sol-gel oxide in different gaseous environments have also been terminated, and the fuel will be pulverized only in air. Gas release experiments will employ only sol-gel fuels instead of a wide variety of nuclear fuels originally proposed.

Samples of the larger size fraction of the sol-gel fuel and pulverized samples of the same fuel will be degassed at various temperatures to determine the gas release and makeup. The values obtained will be used as indicators of the maximum and minimum sorbed gas content. An average value will be calculated from these.

The effect of the uranium content and temperature on the amount and species of sorbed gas released will still be studied.

3.3.2.2. Sol-Gel Method of Producing Oxide Fuels

The sol-gel method for the preparation of mixed urania-thoria consists of several chemical steps. Each of these steps is critical in the preparation of a good final oxide. Thorium nitrate tetrahydrate (TNT) is denitrated at about 450 C in a steam atmosphere in the first step of the overall process. If the denitration is carefully carried out under controlled conditions, a finely divided product consisting of $\text{ThO}_2 \cdot \text{NO}_3$ is produced. This product forms a colloidal suspension known as a sol on mixing with water and diluted nitric acid at a pH of

about 3 to 4. Experiments have shown that the best sols are formed when the NO_3 -to-Th mole ratio in the denitrated product is between 0.03 and 0.06.

Uranyl nitrate is then added to the sol, and conditions are adjusted to give a final NO_3/Th mole ratio of 0.12. Uranium is absorbed on the thorium sol in a recirculating blend tank at a temperature of 70 to 80 C. The thorium-uranium sol is then pumped into evaporator trays and dried to a gel over an 8-hour period at a maximum temperature of 130 C.

The dried gel is transferred to a calcining oven. The gel is converted to an oxide by firing at 1150 C in an argon-hydrogen atmosphere (reducing) for 4 hours. The uranyl (+6) ions are converted to uranous (+4) ions in this step because of the calcining conditions. The final product ($\text{ThO}_2\text{-UO}_2$) is cooled to room temperature in an argon atmosphere. The resultant product is a dense (98 to 99% theoretical density is very common) particulate oxide which is not easily oxidized. Figure 3-1 is a generalized flowsheet of the overall sol-gel process.

The sol-gel method described above is very useful for producing fuels in which UO_2 varies from 0 to 6%. Above this range the uranium should be added to the sol as ammonium diuranate (ADU) or uranium trioxide in order to obtain a final NO_3/Th mole ratio of 0.12.

3.3.2.3. Denitration of Thorium Nitrate Tetrahydrate (TNT)

Five hundred pounds of TNT were denitrated in this program for use in the first step of the sol-gel process, the formation of a stable sol. This amount of TNT is equivalent to approximately 90 kg of final oxide. Nine batches of the material were denitrated in 20 to 25 kg (TNT) lots. Table 3-1 shows the NO_3/Th mole ratios for this series of denitration.

Table 3-1. NO₃/Th Mole Ratios of Denitrated TNT

<u>Batch No.</u>	<u>NO₃/Th (mole)</u>	<u>Weight of denitrated material, kg</u>
1	0.040	10
2	.048	10
3	.075	10
4	.043	10
5	.067	10
6	.061	10
7	.051	10
8	.049	10
9	0.079	10

As mentioned previously, experience with denitrated thoria has demonstrated that a NO₃/Th mole ratio of 0.030 to 0.060 is very suitable for the formation of stable urania-thoria sols. Denitrated thoria with a higher NO₃/Th mole ratio could be used for batches with a low percentage of UO₂. NO₃/Th mole ratios of less than 0.030 do not generally give good colloidal suspensions, probably due to the presence of excess ThO₂. The various batches of sol-gel fuel were made from the denitrated material, keeping the foregoing factors in mind. Table 3-2 shows the ratios applicable to each UO₂ production point.

Table 3-2. NO₃/Th Mole Ratios of Denitrated Materials Used in Preparing Various U/Th Sol-Gel Fuels

<u>Batch No.</u>	<u>U/Th ratio in fuel, %</u>	<u>NO₃/Th (mole) of denitrated materials</u>
1	0	0.075
2	1	.061
3	2	.067
4	3	.051
5	4	.043
6	5	.040
7	7.5	.049
8	10.5(a)	0.048

(a) Uranium added as ADU to the sol.

3.3.2.4. Production of Sol-Gel Fuel

Eight batches of sol-gel fuel with varying U/Th ratio were produced during the last quarter. In each of the sol-gel batches, certain procedures were followed. The total NO_3 -to-Th mole ratio was adjusted to 0.12 in the sol in all cases. The sols were circulated for 4 to 6 hours before transfer to the drier. The sols were dried overnight at a temperature of 130 C. The dried gels were then calcined at 1150 C in an argon-hydrogen atmosphere. The weight loss during this calcining operation was recorded.

Table 3-3 lists the analytical data for the fuel produced. All of the fuel was produced without difficulty with the exception of the 10.5% batch. This batch was made by the addition of ammonium diuranate instead of uranyl nitrate to the thorium sol. ADU addition was necessary to maintain a total nitrate-to-thorium mole ratio of 0.12 in the sol. In this batch the sol separated into a semi-precipitate phase (solids phase) and a liquid phase. The combined phases had a U/Th ratio of about 10.5%. The solids phase had a U/Th ratio of 8.8%, while the liquid phase had a U/Th ratio of 12.75%. The solids phase represented about 11% of the total weight of the combined sol. This data indicates a settling out of the ThO_2 in the solids phase.

After drying the sol to a gel, it was noted that instead of the usual gel size distribution, in which most of the particles are 40 mesh or larger, about 50% of the particles appeared to be -100 mesh. The fine fraction had a U/Th ratio of 10.25%. The remaining coarse fraction had a U/Th ratio of 13.04%. The coarse fraction probably represents the liquid phase of the sol.

The oxide also consisted of fine and coarse fractions with about the same distribution that the gel had. The fine fraction had a U/Th ratio of 9.56%, while the coarse fraction had a ratio of 12.22%. From this data it is very difficult to analyze the whole problem involved. It is not certain that the ADU addition to the sol caused the erratic conditions. A more thorough study of the data and more analyses may be necessary in order to understand all the parameters involved in this run.

Table 3-3. Data on Sol-Gel Fuel

Sample No.	Weight, kg	Uranium-to-thorium ratio ^(a) , %			Desired ratio	Density of fired oxide ^(b) , gm/cc
		Sol	Gel	Oxide		
TU-26	10	4.95	4.95	5.03	5 ± 0.5	9.91
TU-27	10	4.00	4.03	3.93	4 ± 0.4	9.87
TU-28	10	3.08	3.08	3.09	3 ± 0.3	9.92
TU-29	10	2.01	1.98	1.98	2 ± 0.2	9.89
TU-30	10	1.03	1.02	1.02	1 ± 0.1	9.74
TU-31	10	7.52	7.30	7.28	7.5 ± 0.75	9.74
T-8	10	ThO ₂	ThO ₂	ThO ₂	ThO ₂	9.77
TU-32	6	10.51	13.04 ^(c)	12.22 ^(c)	10.5 ± 1.0	9.98 ^(c)
			10.22 ^(d)	9.56 ^(d)		9.55 ^(d)

(a) Average accuracy of each U/Th ratio is $\pm 2\%$.

(b) Accuracy of density is approximately $\pm 0.5\%$.

(c) Coarse.

(d) Fine.

3.3.2.5. Degassing Studies of Fuels

The sol-gel oxide fuel produced for this program has been partially sieved into +10 mesh and -10 mesh size fractions. Table 3-4 lists the size distributions found for the oxide samples submitted for analysis. Table 3-4 indicates that most of the material produced is +10 mesh.

Table 3-4. Sizing of Sol-Gel

<u>Sample No.</u>	<u>U/Th ratio, %</u>	<u>Weight of +10 mesh, %</u>	<u>Weight of -10 mesh, %</u>
TU-26	5	77.9	22.1
TU-27	4	82.0	18.0
TU-28	3	74.9	25.1
TU-29	2	87.8	12.2
TU-30	1	65.9	34.1
TU-31	7.3	76.4	23.6
TU-32 (coarse)	10.5	69.0	31.0
T-8	0	88.0	12.0

Weighed individual samples of the +10 mesh material were degassed in a Leco vacuum extraction unit at 1390 C. Studies indicated that equilibrium conditions for the amount of gas removed from the fuel were reached after 3 to 4 minutes in this unit. All samples of sol-gel fuel were degassed for 5 minutes. Table 3-5 lists the amounts of gas removed from the specimens in terms of cubic centimeters per gram of fuel. This table indicates that in fuels with higher U/Th ratios the amount of gas released is generally greater. There is no direct linear correlation between the U/Th ratio and gas release, however. For instance, sample TU-31 (7.28% U/Th) released less gas than did either sample TU-26 (5.03% U/Th) or sample TU-27 (3.93% U/Th). Sample TU-32, which had the maximum U/Th ratio of 10.5%, released less gas than did sample TU-26 (5.03% U/Th). It should be

kept in mind, however, that the maximum batch was prepared by the ammonium diuranate route, rather than by the conventional uranyl nitrate method. Consequently, this maximum batch is not directly comparable to the other batches. Figure 3-2 is a plot of the U/Th ratio of the sol-gel fuel versus the gas released at 1390 C. All the points with the exception of those for the 7.3% and 10% U/Th ratio batches fit the curve. Since the sol-gel route is conventionally designed to go only to a U/Th ratio of 6% by uranyl nitrate addition, our data points for U/Th ratios of 5% and below are very interesting. This data indicates a direct correlation between uranium content and gas release. Further studies are needed to verify this correlation.

Table 3-5. Gas Release From Sol-Gel Fuels

<u>Sample No.</u>	<u>U/Th ratio, %</u>	<u>Gas released, cm³/gm</u>
TU-26		0.24
TU-26	5.03	0.30
TU-26		0.34 (avg, 0.31)
TU-26		0.35
TU-27		0.13
TU-27	3.93	0.09
TU-27		0.27 (avg, 0.16)
TU-27		0.16
TU-28		0.062
TU-28	3.09	0.073 (avg, 0.068)
TU-28		0.068
TU-29		0.050
TU-29	1.98	0.013
TU-29		0.068 (avg, 0.038)
TU-29		0.021
TU-30		0.005
TU-30	≈1.00	0.000
TU-30		0.000 (avg, 0.002)
TU-30		0.004
TU-31		0.081
TU-31	7.28	0.070 (avg, 0.077)
TU-31		0.079

Table 3-5. (Cont'd)

<u>Sample No.</u>	<u>U/Th ratio, %</u>	<u>Gas released, cm³/gm</u>
TU-32	≈ 10.5	0.19
TU-32		0.24
TU-32		0.23 (avg, 0.20)
TU-32		0.14
T-8	0	0.004
T-8		0.003
T-8		0.009 (avg, 0.006)
T-8		0.007

Other parameters were also investigated for correlation with the amount of gas released. Table 3-6 lists the percentage of weight loss for each batch of fuel upon calcination. It was postulated that the fuel batches with more weight loss upon calcination could be the batches with less gas release. Figure 3-3 shows that there is a correlation between the 1, 2, 3, 4, and 5% U/Th ratio batches, but that the 0, 7.3, and 10.5% U/Th ratio batches do not fall into any pattern.

The NO₃/Th mole ratio of the starting denitrated thorium was also compared with the gas release. Figure 3-4 is a plot of this data.

Table 3-6. Weight Loss Upon Calcination of Sol-Gel Fuel

<u>U/Th ratio, %</u>	<u>Weight loss, %</u>
0	6.6
1	7.4
2	6.9
3	6.6
4	6.1
5	5.1
7.5	6.7
10.5	7.7

The motive that prompted these correlations was the possibility that we were not removing all the nitrate upon calcination. The nitrate bound to the thorium is much harder to remove than

that added to the system. This idea is contrary to the plan that the fuels with the lower U/Th ratios are made from the denitrated thorium with the higher NO_3/Th mole ratios. Figure 3-4 indicates that there is an almost inverse correlation between input thorium NO_3/Th mole ratios and the gas released. All points except that for the batch having a U/Th ratio of 10%, made by the ADU route, fall near a curve. Since the points for the batches having U/Th ratios of 0, 1, and 2% are not completely in line, the data may lack accuracy because the small specimens released small quantities of gas. Pyrolysis of 10-gram batches in the future may help solve this problem.

Another parameter investigated was the particle size distribution of the fuel. From our crude sieve analysis the percentage of the oxide of the various batches of fuel above +10 mesh was plotted against the gas released. Figure 3-5 is the resultant plot. No correlation is apparent. This parameter was investigated to rule out the possibility that the fuels with the higher gas releases were composed mostly of either the large sieve fraction or the small sieve fraction. As the -10 sieve fraction and the pulverized composite samples are analyzed, more data will be available and a correlation may become apparent. When larger 10-gram samples are degassed, in the vacuum extraction system designed for this program, the overall average values for gas release will be more meaningful.

3.3.2.6. Mass Spectrometer Modifications

The mass spectrometer has been completely converted to the gas analysis mode. Samples of H_2 , He, N_2 , O_2 , CH_4 , C_2H_6 , CO_2 , and Ar have been injected and identified on this unit. Figure 3-6 is an idealized spectrum of a spiked sample of Ar, N_2 , and O_2 . Figure 3-7 is an isotopic spectrum of commercial grade argon. Calibration of the spectrometer to give semi-quantitative analyses will be accomplished in the near future. Analyses of some released gases will probably proceed within the next month.

3.4. Planned Work for Next Report Period

The finer sieve fraction (-10 mesh) and the pulverized composite samples of the sol-gel fuels will be analyzed for total gas content. Temperature release data will be studied on selected specimens. Calibration

of the mass spectrometer and analyses of the eluted gases will be measured. A report covering this entire program will be issued at the termination of the project.

Figure 3-1. Generalized Flowsheet of Sol-Gel Process

Figure 3-2. U/Th Ratio of Sol-Gel Fuel Vs Gas Released

Figure 3-3. Weight Loss of Sol-Gel Upon Calcination Vs Gas Released

Figure 3-4. Input Thoria NO_3/Th Mole Ratio Vs Gas Released

Figure 3-5. Percentage of Oxide Greater Than 10 Mesh Vs Gas Released

Figure 3-6. Idealized Spectrum of Argon, Oxygen, and Nitrogen Mixture

Figure 3-7. Isotopic Spectrum of Commercial Grade Argon

4. UNIRRADIATED FUEL THERMAL CONDUCTIVITY — TASK 04

(J. M. Kerr, Task Leader; E. N. Harbinson)

4.1. Task Objective

The primary objective is to establish a correlation between fuel structure and temperature in thoria-urania. This correlation can then be used in estimating the temperatures at which fuel operated during irradiation. The secondary objective is the determination of the thermal conductivity of unirradiated thoria-urania to about 2500 C. These data are expected to provide a useful comparison with inreactor thermal conductivity information.

4.2. Task Description

An apparatus will be constructed which will be capable of (1) establishing microstructures, similar to structures obtained in pile, in both pellet and compacted powder specimens, (2) measuring temperatures associated with structural changes of interest, and (3) performing reliable and accurate calorimetry for thermal conductivity determinations. Initially, existing technology will be studied in an effort to establish a basis for the conceptual design of the apparatus and to examine the experimental factors influencing structural changes.

An initial test will be made on UO_2 pellets so that the performance of the apparatus can be judged against existing UO_2 structure-temperature correlations and thermal conductivity. After this initial UO_2 test, ThO_2 - UO_2 pellets will be tested. Study of two different U/Th ratios is planned.

4.3. Work Accomplished During This Report Period

4.3.1. Summary

During this report period the fabrication and systems check-out of the thermal simulation device were completed. Procurement

of materials and equipment has been completed except that not all of the materials have been received.

4.3.2. Apparatus Fabrication and Check-Out

The thermal simulation device has been completed and is shown in Figure 4-1. On the right is the control panel, which contains the primary system water pump switch and a power control for the heater. Also located here is the multipoint recorder, which monitors thermocouples located on the outside diameter of the clad specimen, at the upper and lower electrode clamps, and in the upper and lower portions of the inert gas chamber. The vacuum system is immediately behind the control panel. The inert gas chamber with the specimen tube, heater, and cooling jacket inside is near the front of the table. The micro-optical pyrometer is in front of the inert gas chamber. A photograph of the cooling jacket with a specimen clad tube in place is shown in Figure 4-2. Behind the inert gas chamber is the gas cleanup train consisting of a Zircaloy chip furnace (on the table) and a cold trap (on the wall). The furnace is operated at 1000 F (540 C), and the cold trap is filled with either liquid nitrogen or a mixture of dry ice and acetone. The primary coolant line enters and exits at the rear of the inert gas chamber. The heat exchanger for this system is on the left behind the laboratory cart. The demineralized water is pumped from the heat exchanger through a water flowmeter and one leg of a differential temperature transducer before entering the cooling jacket. The flow from the cooling jacket goes through the second leg of the differential temperature transducer, through a flow switch, and into the heat exchanger. A small demineralizer bed is attached to the cooling jacket outlet water line, and a small portion of the water is constantly put through the ion exchange bed.

The secondary water system is fed from the pipe on the floor and feeds the chill plate, electrode clamps, chip furnace, and heat exchanger. The water supply is from a building tap. All drains are sight drains.

The readout for the differential temperature transducer is in millivolts. Presently, this is measured on a potentiometer located on the laboratory cart in the left foreground.

Initial heating runs were made with empty clad tubes in place. These runs determined the efficiency of cooling, temperature

gradient along the heater, approximate power requirements to obtain given temperatures, and general operational characteristics of the device. The maximum heater temperature in these runs was about 2200 C. The power calculated by calorimetry was compared with the power indicated by electrical measurements. The clad temperature was monitored by three Chromel-Alumel thermocouples soft-soldered to locations at each end and in the middle. No detectable temperature difference could be noted between the thermocouples, nor did they show any significant increase over the temperature of the coolant water. During some of the early runs, it was noted that the apparent "chimney" effect was quite large. The gradient was very lopsided up the heater: the upper electrode clamp was much hotter than the lower clamp. By inserting radiation shields inside the heater and inserting an asbestos washer around the heater and between the clad and the top electrode clamp, this chimney effect was greatly reduced. It was obvious that, as the temperature increased from approximately 1500 to 2200 C, the thermal gradient along the length of the heater tended to flatten out. This can be seen in Figure 4-3. All temperatures have been corrected for the emissivity of tungsten at these temperatures and for the absorption caused by the sight glass. The calibration chart provided with the pyrometer is based on a Bureau of Standards bulb. At the temperatures used to date, the pyrometer is less than one degree centigrade out of calibration. On receipt of the sheathed W-5% Re/W-26% Re thermocouples, a more accurate temperature profile along the heater length can be determined.

To obtain the power output of the heater, the temperature rise in the coolant water is measured to ± 0.039 C with the differential temperature transducer, and the quantity of water flowing past the specimen is measured by the water meter. If the end losses are low, power output calculated by using these values should agree with the power output measured by using the voltage drop across the heater and the resistivity of the tungsten heater at the particular temperature. By measuring the voltage drop from electrode clamp to electrode clamp and by integrating the resistivity with respect to temperature along the heater length, the linear power output of the heater was determined. For the steady-state condition in which the heater was maintained at approximately 2250 C, the power output based on electrical measurements was

5.36 kw/ft. Linear power output determined by the calorimetry technique was 4.89 kw/ft. The two methods of determining the power output gave reasonable agreement. Because of the uncertainties in the temperature of the heating element between the last measured temperature and the electrode clamp, the power output determined by calorimetry is probably more accurate.

4.4. Planned Work for Next Report Period

In the next report period one run with insulated UO_2 pellets and at least one run with insulated $\text{ThO}_2\text{-UO}_2$ pellets will be performed. In addition, several isothermal runs will be performed in a high temperature furnace to obtain a correlation between equiaxed grain size and temperature.

Figure 4-1. Thermal Simulation Device (WAS-65-492)

Figure 4-2. Cooling Jacket With a Clad Specimen in Place,
Showing Sight Pipe Holes at the Top and the
Thermocouple Lead-Through at the Side
(WAS-65-493)

Figure 4-3. Heat Gradient Vs Sight Pipe Location for Various Temperatures

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