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***Mound Laboratory Isotopic
Power Fuels Programs:
April-September 1971***

January 14, 1972

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DATE 2/17/72

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MOUND LABORATORY

Miamisburg, Ohio
operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company
for the

U. S. ATOMIC ENERGY COMMISSION

U S Government Contract No. AT-33-1-GEN-53

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MONSANTO RESEARCH CORPORATION

A Subsidiary of Monsanto Company

MOUND LABORATORY

Miamisburg, Ohio 45342

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UNITED STATES ATOMIC ENERGY COMMISSION

U S Government Contract No AT 33-1-GEN-53

Foreword

This report presents the technological achievements of Mound Laboratory in its isotopic fuels programs during the past three months. The separate reports compiled here represent the work of the following sections of the Nuclear Operations Department (Director W. T. Cave): Nonweapons Programs (Manager R. E. Vallée), and Quality and Reliability (Manager D. P. Kelly).

This work is supported by the AEC Division of Space Nuclear Systems, Division of Isotopes Development, and Division of Reactor Development and Technology.

Summaries of all sections are compiled at the front of this report. Brief introductions to the work are included with each section.

Previous reports in this series are:

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The production of PMC fuel discs was continued and Pioneer Capsules 6, 7, 8, 9, and 10 were fueled. All of the molybdenum-coated $^{238}\text{PuO}_2$ particles used in the PMC fabrication were coated exclusively by the MoCl process.

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A study was undertaken to ascertain the feasibility of loading 5.5 W of ²³⁸PuO₂ shards into a milliwatt capsule strength member. The ThO₂ shards were used in this study because of their similarities in bulk and packing densities to those of ²³⁸PuO₂. Various experiments indicated the fuel would have to be pressed into the available volume if the required weld clearance of 125 mils were to be met.

A loading fixture was fabricated which allows the fuel to be compacted until the weld clearance was obtained without any apparent distortion to the strength member.

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All of the materials yielded organic offgas products. In addition to the organic materials, the Min-K 1301 also released large quantities of water vapor relative to the other offgas products.

The tests indicated that more rigorous outgassing procedures and controlled atmosphere handling of Min-K 1301 are needed to prevent contamination by water vapor. The organic material released from the Min-K 1301 seems to be residual organic material that remained after the Min-K was outgassed. The organic material released by

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both the POCO and pyrolytic graphite was probably the result of storage in plastic bags and a different storage method is recommended. However, more organic outgassing products were released from ZrO_2 than from both types of graphite. In addition to the contamination picked up from the plastic bags, it appears that there is some organic residual remaining in the ZrO_2 , possibly the binder used during the pressing operation.

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A sample of Min-K 1301 that had undergone several outgassing processes was put under long term test in a quadrupole mass spectrometer. The sample was on test for 31 days during which time it was subjected to various thermal cycles up to a maximum temperature of 1250°F under a vacuum atmosphere. The sample suffered a weight loss of approximately 3.2% during this period; most of this weight loss could be attributed to hydrogen and water vapor, the primary offgassing constituent detected by the mass spectrometer. After this experiment, a portion of the primary sample was used for a TGA study during which further weight loss occurred.

Samples of Min-K 1301 that had never been subjected to any prior outgassing treatment at Teledyne Isotopes or Mound Laboratory were studied by TGA and x-ray analysis. The results of these studies indicate that Min-K 1301 is primarily silicon metal with asbestos fiber running through the material. The data also indicate that the bulk material readily absorbs moisture from the air. In addition, there is an indication that a greater weight loss occurs from the fibrous material.

THE EFFECTS OF Min-K 1301 AND HYDROGEN ON PMC-TANTALUM INTERACTION 75

As part of the investigation of the accelerated attack of the tantalum components of the Pioneer capsule, a series of tests was made to study the effects of Min-K and hydrogen on PMC-tantalum interaction. Under the conditions of the test (168 hr at 825°C) it appears that hydrogen and Min-K accelerate the interaction between PMC fuel and the Ta-10 wt % W liner.

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Plutonium-238 Fuels

FUEL PREPARATION

PMC Fuel Discs The production of PMC (plutonia-molybdenum cermet) fuel discs was continued during this report period. Feed batches of 105 - 177 μm and 177 - 250 μm $^{238}\text{PuO}_2$ particles, exchanged with $^{18}\text{O}_2$, were coated with molybdenum metal by the hydrogen reduction of MoCl_5 . The molybdenum-coated $^{238}\text{PuO}_2$ particles were vacuum hot pressed at 1650 - 1700°C and 13,500 psi for 15 min. The hot-pressed discs were machined to dimension, outgassed at 1000°C, gaged, and sent for calorimetry and neutron emission rate measurements. The pertinent data for Pioneer Capsules 6, 7, 8, 9, and 10 are given in Tables 1-5.

Three standard discs were shipped to LASL. The pertinent information is included in Table 6. (T. C. Elswick and B. R. Kokenge)

Multi-Hundred Watt Development Five plutonium oxide (PPO) spheres and one plutonia-molybdenum cermet (PMC) sphere were fabricated for the Multi-Hundred Watt (MHW) program.

The PMC sphere, SPM-3, was prepared with production-grade, molybdenum-coated, $^{238}\text{PuO}_2$ particles having a 17.9 wt % molybdenum content. The sphere was pressed at 10,000 psi for 10 min at 1660°C in POCO-AXF graphite. The concave punches were plasma sprayed with tantalum to 0.001 in. and lined with 0.001 in. of tantalum foil. Upon cooling at the nominal rate for PMC disc fabrication, the punches tapped free of the graphite body. The diameter of the as-pressed sphere ranged from 1.701 to 1.728 in. The sphere was transferred for machining on the in-line lathe installed for machining spherical fuel forms. The machined sphere was outgassed at 1400°C under $<10^{-4}$ torr vacuum and transferred for optical gaging. The gaging data, corrected to 20°C, showed the sphere to have a diameter range of 1.5849 to 1.5961 in. The average skin temperature of SPM-3 in helium was 190°C. The specific property data on SPM-3 are given in Table 7, and Figure 1 shows the machined and outgassed sphere during gaging.

Five PPO spheres were fabricated at Mound Laboratory during this report period. Various types of $^{238}\text{PuO}_2$ feed were used to test the fabricability of PPO spheres.

The first two PPO spheres, SPO-1 and SPO-2, were prepared from $^{238}\text{PuO}_2$ particles prepared by the hydroxide process and sintered at 1600°C. (Portions of this material were sent to LASL for pressing.) This material

Table 1

FUEL STACK DATA FOR PIONEER CAPSULE 6

Disc Number	Type	Total Weight (g)	Total Power (W)	% Mo	Power Density (W/cc)	Specific Power (W/g)	Impurities		Neutron Emission (n/sec/g ^{238}Pu) ($\times 10^3$)
							0.31 wt% (ppm)	Total (ppm)	
PM-90T	-2	66.9	21.20	17.9	3.26	0.317	663	729	5881
PM-91T	-3	99.5	32.60	17.4	3.41	0.328	707	806	4383
PM-92T	-4	117.0	37.22	17.4	3.32	0.318	788	888	6749
PM-93T	-5	120.8	38.61	17.8	3.33	0.320	672	751	5598
PM-94T	-5	122.4	39.34	17.6	3.34	0.321	799	899	4905
PM-94B	-6	131.6	41.68	17.6	3.32	0.317	799	899	4859
PM-95T	-6	132.1	42.30	17.0	3.36	0.320	968	1068	4508
PM-95B	-6	130.2	41.43	17.0	3.32	0.318	968	1068	4438
PM-96B	-6	129.3	41.83	16.6	3.40	0.324	643	743	4167
PM-97T	-6	138.0	43.98	17.0	3.36	0.319	933	997	4635
PM-97B	-6	137.0	43.57	17.0	3.36	0.318	933	997	4543
PM-98T	-6	138.6	44.83	16.2	3.43	0.323	844	939	4192
PM-98B	-6	139.2	44.93	16.2	3.43	0.323	844	939	4193
PM-93B	-5	121.4	38.75	17.8	3.32	0.319	672	751	5461
PM-92B	-4	117.3	37.50	17.4	3.36	0.320	788	888	6953
PM-91B	-3	99.4	32.51	17.4	3.42	0.327	707	806	4381
PM-90B	-7	70.0	22.31	17.9	3.27	0.319	663	729	5976

Table 2

FUEL STACK DATA FOR PIONEER CAPSULE 7

Disc Number	Type	Total Weight (g)	Total Power (W)	Mo (%)	Power Density (W/cc)	Specific Power (W/g)	Impurities		Neutron Emission (n/sec/g ²³⁸ Pu) (x 10 ³)
							0.31 wt% ^a (ppm)	Total (ppm)	
104B	-7(-017)	67.1	21.75	16.4	3.46	0.324	712	786	4.895
106T	-3(-021)	97.6	31.17	17.3	3.41	0.319	783	867	4.744
108T	-4(-023)	115.3	36.84	17.0	3.34	0.320	962	1024	6.324
93B	-5(-025)	115.7	36.79	17.8	3.33	0.318	672	751	5.504
131B	-6(-035)	136.7	44.51	16.8	3.53	0.326	1199	1327	4.366
131T	-6(-035)	137.6	44.89	16.8	3.53	0.326	1199	1327	4.278
132T	-6(-035)	137.3	45.50	16.7	3.60	0.331	965	1052	7.121
132B	-6(-035)	138.9	46.04	16.7	3.62	0.331	965	1052	6.920
114T	-6(-035)	129.8	42.35	17.8	3.38	0.326	1185	1331	3.686
121T	-6(-035)	124.5	41.25	17.4	3.56	0.331	1070	1136	3.541
121B	-6(-035)	125.0	41.46	17.4	3.56	0.332	1070	1136	3.513
112T	-6(-035)	126.8	41.70	17.5	3.38	0.329	1378	1463	4.103
111T	-5(-031)	126.2	41.65	17.0	3.50	0.330	791	857	4.152
87T	-5(-025)	112.6	36.10	18.3	3.31	0.321	1220	1316	24.204
107T	-4(-023)	118.1	38.55	16.4	3.47	0.326	662	716	4.592
105B	-3(-021)	97.4	31.24	17.3	3.43	0.321	865	969	4.253
104T	-2(-027)	58.8	19.02	16.4	3.41	0.323	712	786	6.627
Weight of fuel		1965.4	640.81						5.962
Weight of shims		145.6							
Total weight		2111.0							

^a Specification of listed impurities.

Table 3

FUEL STACK DATA FOR PIONEER CAPSULE 8

Disc Number	Type	Total Weight (g)	Total Power (W)	Mo (%)	Power Density (W/cc)	Specific Power (W/g)	Impurities		Neutron Emission (n/sec/g ²³⁸ Pu) (x 10 ³)
							0.31 wt% ^a (ppm)	Total (ppm)	
103B	-7(-017)	66.8	21.46	17.4	3.43	0.321	930	1045	4.326
115T	-3(-021)	96.4	31.02	18.3	3.39	0.322	1300	1428	4.167
108B	-4(-023)	113.9	37.00	17.0	3.39	0.325	962	1024	5.954
93T	-5(-025)	116.1	36.89	17.8	3.32	0.318	672	751	5.489
101T	-6(-035)	130.1	42.29	16.1	3.45	0.325	976	1077	13.127
129T	-6(-035)	137.6	44.68	18.5	3.52	0.325	1038	1119	5.907
133B	-6(-035)	137.9	45.06	17.4	3.53	0.327	906	987	4.302
133T	-6(-035)	135.4	44.42	17.4	3.51	0.328	906	987	4.375
122T	-6(-035)	124.4	41.26	17.7	3.55	0.332	1065	1115	4.136
113B	-6(-035)	127.9	42.43	16.7	3.44	0.332	915	972	4.205
130B	-6(-035)	127.5	42.39	16.5	3.60	0.332	1026	1118	4.166
130T	-6(-035)	135.7	45.15	16.5	3.59	0.333	1026	1118	4.274
111B	-5(-031	125.4	41.58	17.0	3.51	0.332	791	857	3.940
109T	-5(-025)	122.2	39.87	16.7	3.43	0.326	485	539	4.566
107B	-4(-023)	117.9	38.53	16.4	3.47	0.326	662	716	4.617
106B	-3(-021)	97.6	31.38	17.3	3.41	0.322	783	867	4.611
103T	-2(-027)	59.2	18.82	17.4	3.37	0.318	930	1045	4.352
		1972.0	644.23						5.138
Weight of shims		137.1							
Total Weight		2109.1							

^aSpecification of listed impurities.

Table 4

FUEL STACK DATA FOR PIONEER CAPSULE 9

Disc Number	Type	Total Weight (g)	Total Power (W)	Mo (%)	Power Density (W/cc)	Specific Power (W/g)	Impurities		Neutron Emission (n/sec/g ²³⁸ Pu) (x 10 ³)
							0.31 wt% ^a (ppm)	Total (ppm)	
PM-123B	017	66.4	22.02	17.3	3.51	0.332	742	857	4.009
PM-125B	021	100.7	33.11	17.2	3.58	0.329	1204	1280	3.889
PM-127B	023	119.5	39.17	17.2	3.57	0.328	1015	1110	3.985
PM-117T	025	118.6	38.18	18.2	3.37	0.322	1032	1145	3.790
PM-136B	033	136.8	44.72	17.7	3.53	0.327	874	984	5.312
PM-136T	033	135.1	44.14	17.7	3.56	0.327	874	984	5.165
PM-135T	033	136.1	43.40	17.2	3.44	0.319	1156	1255	6.637
PM-134B	033	136.9	44.63	17.2	3.52	0.326	858	930	5.700
PM-134T	033	137.7	44.72	17.2	3.54	0.325	858	930	5.556
PM-117B	033	128.0	41.39	18.2	3.36	0.325	1032	1145	3.739
PM-114B	033	127.1	41.63	17.8	3.38	0.328	1185	1331	3.597
PM-120T	033	128.6	42.30	17.2	3.54	0.329	1074	1160	3.583
PM-110T	031	119.1	39.02	17.1	3.48	0.328	566	628	3.615
PM-94T	025	116.9	37.52	17.6	3.34	0.321	799	899	4.718
PM-127T	023	121.0	39.67	17.2	3.57	0.328	1015	1110	4.027
PM-125T	021	98.8	32.50	17.2	3.54	0.329	1204	1280	3.976
PM-123T	027	59.8	19.85	17.3	3.50	0.332	742	857	3.829
Total disc		1987.10	647.97	Aug.	3.49				4.496
Shims		134.12							
Total weight stack		2121.22							

^aSpecification of listed impurities.

Table 5

FUEL STACK DATA FOR PIONEER CAPSULE 10

Disc Number	Type	Total Weight (g)	Total Power (W)	Mo (%)	Power Density (W/cc)	Specific Power (W/g)	Impurities		Neutron Emission (n/sec/g ^{238}Pu) ($\times 10^3$)
							0.31 wt% ^a (ppm)	Total (ppm)	
PM-124B	017	66.8	21.84	18.3	3.47	0.327	994	1053	3.709
PM-126B	021	97.5	31.69	18.1	3.42	0.325	1002	1086	4.193
PM-128B	023	119.2	38.93	17.2	3.54	0.327	1130	1233	6.616
PM-80B	025	114.5	37.67	17.1	3.31	0.329	1070	1131	30.442
PM-140B	033	136.3	43.84	18.3	3.44	0.322	1095	1153	4.494
PM-141B	033	137.0	43.67	18.5	3.43	0.319	939	1022	6.961
PM-141T	033	136.6	43.56	18.5	3.44	0.319	939	1022	6.780
PM-140T	033	136.8	44.07	18.3	3.43	0.322	1095	1153	4.575
PM-139B	033	136.8	44.23	18.7	3.47	0.323	1236	1356	5.813
PM-137T	033	137.5	45.47	16.5	3.60	0.331	727	815	4.223
PM-120B	033	126.4	41.73	17.2	3.50	0.330	1074	1160	3.501
PM-137B	033	138.2	45.80	16.5	3.61	0.331	727	815	4.372
PM-110B	031	119.0	39.14	17.1	3.46	0.329	566	628	3.488
L-PMC-131	025	115.9	37.68	18.2	3.29	0.325			29.106
PM-128T	023	120.2	39.33	17.2	3.54	0.327	1130	1233	6.757
PM-80T	021	93.8	30.72	17.1	3.35	0.328	1070	1131	28.440
PM-124T	027	58.6	19.15	18.3	3.41	0.327	994	1053	3.874
Total disc weight		1991.10	648.52		3.45				9.024
Shims		121.57							
Total Weight Stack		2112.67							

^a Specifications of listed impurities.

Table 6

DATA FOR LASL DISCS

<u>Disc and Type</u>	<u>Mo (wt%)</u>	<u>Impurities (ppm)</u>	<u>Physical Density (g/cc)</u>	<u>Power Density (W/cc)</u>	<u>Total Weight (g)</u>	<u>Power Density (W/cc)</u>	<u>Neutron Emission (n/sec/g ²³⁸ Pu)</u>	<u>Weight ²³⁸ Pu (g)</u>	<u>Diameter at 20°C (in.)</u>	<u>Thickness at 20°C (in.)</u>
PM-102B(-6)	17.9 ^a	977 ^b (1101) ^c	10.71	43.68	136.3	3.43	4584	76.8	2.1432	0.2170
PM-102T(-6)	17.9 ^c	977 ^b (1101) ^c	10.76	43.96	137.4	3.44	4762	77.3	2.1421	0.2180
PM-113T(-6)	16.7 ^c	915 ^b (972) ^c	10.4	43.39	131.4	3.43	4300	76.3	2.1431	0.2155

^aWeighted average.

^bThese are the impurities (cationic) with respect to the
PMC cationic Impurity Specifications.

^cThese are the impurities (cationic) reported as a total.

^dPM-102T and PM 102B did not have standard chamfers.

Table 7

SPM-3 PROPERTY DATA

Total Power (W)	Total Analyzed Cationic Impurities (wt %)	Power Density ^a (W/cc)	Specific Neutron Emission (n/sec/g-Pu)	Range of Diameters (in.)
104.5	0.11	2.99-3.06	12.1×10^3	1.5849 - 1.5961

^a Power density range based on maximum-minimum diameters observed in gaging and corrected to 20°C.

had a nominal size range of 0 to 105 μm . The graphite punches and die body were fabricated from POCO grade AXF graphite. The concave portions of the punch faces and the interior of the die body were sprayed with colloidal graphite and polished with a soft cloth. The graphitic material and its treatment were the same for all PPO pressings described in this report. SPO-1 was pressed at 1466°C and ~2500-lb load on the 1.43 in. graphite punch. However, the graphite punches did not completely close. The charge was held at 1466°C and ~2500-lb load for 50 min and then cooled at ~3°C/min even though no closure occurred. SPO-1 was removed from the graphite punch and die assembly by cutting with a hacksaw. An attempt

FIGURE 1 - SPM-3 sphere after machining and outgassing. (Darkened area on lower section of sphere resulted from discoloration on glovebox front.)

FIGURE 2 - SPO-1 after removal from graphite punch and die.

to remove the punches manually was unsuccessful. The as-pressed sphere showed no visible surface cracks. Figure 2 shows SPO-1 after removal from the graphite punch and die. SPO-1 was held on a ceramic insulator for 22 days, after which time, there were no observable cracks on the sphere's surface. SPO-1 was transferred to the gaging area. The sphere was placed on a 3/4 in. concave metal pedestal for the gaging. Over a 45 min period this crack propagated to the opposite pole. After gaging, SPO-1 was transferred to another glovebox for drop-testing. The sphere was dropped a distance of 8 in. onto tantalum foil placed on the glovebox floor. The sphere did not fracture or break up. SPO-1 was then dropped from a height of 14 in. Upon impact the PPO sphere broke into three major sections and one chip which was $\sim 1/4 \times 1/8 \times 1/16$ in. No powder was observed on the tantalum foil where the impact occurred. Figure 3 shows the fragments from SPO-1. At this point, SPO-1 was sampled for impurities; the data collected on SPO-1 are presented in Table 8. It should be noted that the carbon content of SPO-1 was <100 ppm; however, it was out-of-round by 0.034 in. This large out-of-roundness value was due to the non-closure of the punches during the hot pressing. The gaging data on SPO-1 showed this sphere expanded from the 1.43 in. die size, a phenomenon that was later observed on SPO-2.

FIGURE 3 - Fragments of SPO-1 after dropping from 14 in. onto stainless steel glovebox floor.

SPO-2, the second MRC sphere, was prepared with the same feed as was used in the SPO-1 pressing. This sphere was pressed at 1488°C for 52 min at a total load of 9000 lb on the 1.43 in. punch. The much higher load was used in order to ensure closure of the graphite punches, since in the first pressing it was difficult to close the punches. After

pressing, the punch and die assembly was cooled to ambient temperature at 3°C/min. The graphite die body was cut to remove the PPO sphere. The PPO sphere was easily removed from the punches and showed no visible cracks on the surface. After 62 hr of storage on a ceramic insulator, one crack appeared running from the pole to the equator. The sphere was packaged and transferred to gaging, calorimetry, and neutron counting. After these analyses were run, SPO-2 was returned to the glovebox line and stored on a ceramic insulator. At this time the original crack had propagated from pole to pole. Approximately five days after the fabrication of SPO-2, the sphere fractured into two pieces, one piece being nearly twice the size of the other. The larger of the two pieces was dropped from an 8 in. height whereupon it fractured into five pieces. The original remaining piece, along with the five fractured pieces, is shown in Figure 4. The broken sections of SPO-2 were sampled for impurity analysis. The pertinent data on SPO-2 appear in Table 8. SPO-2 was out-of-round by 0.009 in. and exhibited a density of 83-84% of theoretical. The carbon content of SPO-2 was <100 ppm.

FIGURE 4 - Five fragments from SPO-2 after drop testing from 8 in. and original fractured section.

SPO-3 was fabricated from hydroxide feed prepared by forcing the uncalcined hydroxide through a 63 μm screen. The material was then calcined and sintered according to the normal production cycle except the sintering temperature was held to $<1400^\circ\text{C}$. SPO-3 was vacuum hot pressed in a 1.43 in. graphite punch and die assembly at a 2500-lb load and 1510°C . These conditions were held until the ram travel on the hot press had stopped. Forty minutes after the above-stated conditions were achieved, the ram travel stopped. The punch and die assembly was cooled at $3^\circ\text{C}/\text{min}$ to ambient temperature and removed from the hot press. When the assembly was removed from the hot zone, it was discovered that a piece of the graphite insulating felt had become wedged between the moving press ram and the top of the die body, thus preventing total closure of the die. As a result no definite physical measurements of the product sphere could be made. SPO-3 exhibited a 0.050 in. out-of-roundness due to the non-closure of the punches within the die cavity. The pertinent data on SPO-3 are given in Table 8. Figure 5 shows the as-pressed SPO-3 after removal (by cutting the die) from the punch and die assembly.

SPO-4 and SPO-5 were both prepared from feed prepared by ball-milling Mound hydroxide-prepared $^{238}\text{PuO}_2$. Feed particles, the same as described for SPO-1 and SPO-2, were sent to LASL. These particles were broken up, outgassed at 1400°C for 2 hr in $\text{H}_2^{16}\text{O}-\text{Ar}$, ball-milled for 42 hr, and returned to Mound Laboratory.

SPO-4 was pressed in a 1.50 in. graphite punch and die assembly at 1480°C and a 2500-lb load for 11 min. Closure of the punches occurred just prior to achieving the 1480°C pressing temperature. (It should be noted that due to the design of the current hot-pressing facility, pressing loads of $<2500\text{-lb}$ are difficult to read and control because of the pressure gage readout system and the size of the hydraulic lines. Therefore, 2500-lb load is stated for pressings at MRC instead of the 500-lb used at LASL.) SPO-4 was cooled at $10^\circ\text{C}/\text{min}$ to ambient temperature. The lower punch was removed from the graphite die body by tapping. The sphere rolled free from the punches. A lip was observed at the equator on the sphere. This lip was attributed to the difference in punch travel between the upper and lower punches. This difference resulted from allowing too great a volume for the powder charge inside the punch and die assembly coupled with the single moving ram of the hot press. Otherwise, SPO-4 had an excellent appearance with a smooth surface. The gaging data indicated this sphere to be 0.019 in. out-of-round (1.448 to 1.467 in. on the diameters); however, part of this was due to the above-described lip. Fifteen days after fabrication slight hairline cracks were noted on the polar areas of this sphere; however, they do not appear to be detrimental to its integrity. SPO-4 will be held for further observation. Table 8 gives the pertinent data collected on SPO-4.

SPO-5 was pressed in a 1.47 in. graphite punch and die assembly at 1480°C and a 2500-lb load for 11 min. Closure of the punches occurred just as the 1480°C temperature was reached. The sphere was cooled at $10^\circ\text{C}/\text{min}$ and removed from the graphite punch and die assembly by cutting the die body. (The punches did not release in this case.) The body had very

Table 8

PPO SPHERE DATA

Sphere	Impurities Total Analyzed Cationic (wt %)	Range of Diameters (20°C)(in.)	Out-Of-Round (in.)	% Theoretical Density Range ^a (g/cc)	Power (W)	Specific Neutron Emission (n/sec/g-Pu)	Comments
SPO-1	0.118	1.445-1.479	0.034	74-80	92.53	9.64×10^3	Hydroxide feed <105 μ m; pressed at 1466°C, 50 min, 2500 lb; no closure of punches; no surface cracks upon opening; survived 8 in. drop test, broke upon dropping from 14 in. Crack appeared during gaging on metal pedestal.
SPO-2	0.295	1.437-1.446	0.009	83-84	96.62	5.98×10^3	Hydroxide feed <105 μ m; pressed at 1488°C, 52 min, 9000 lb; closure of punches; no surface cracks upon opening; hairline crack pole to equator found after 62 hr.
SPO-3		1.433-1.483	0.050	76-84	96.92	4.51×10^3	Hydroxide feed green, sized <63 μ m; pressed at 1510°C, 40 min, 2500 lb; apparent closure of punches; graphite insulating felt did not allow punch closure, hence larger out-of-round value.
SPO-4		1.448-1.467	0.019	85-88	104.21	1.02×10^4	Hydroxide feed <105 μ m; ball-milled 42 hr at LASL; pressed at 1480°C, 11 min, 2500 lb; closure of punches; punches came free of die body without cutting; no surface cracks at time of opening; slight hairline cracks appeared on polar regions 15 days after fabrication; lip on equatorial band.
SPO-5		1.424-1.440 ^b	0.016 ^c	85-88 ^c	100.4		Hydroxide feed <105 μ m; ball-milled 42 hr at LASL; pressed at 1480°C, 11 min, 2500 lb; closure of punches; die body cut to remove sphere; no surface cracks at time of opening, no visible cracks 10 days after fabrication.

^aBased 11.4 g/cc theoretical density for PuO₂.^bBased on data obtained with micrometers at ambient temperature.^cBased on weight of product sphere; no calorimetry value available.

FIGURE 5 - As pressed SPO-3 PPO sphere.

smooth surfaces except for some rough areas around the equator. This sphere has not yet been transferred for optical gaging, calorimetry, or neutron counting. However, using micrometers to gage the sphere the range of diameters at ambient temperature was 1.424 (equatorial) to 1.440 in. (polar), or 0.016 in. out-of-round. Ten days after fabrication SPO-5 showed no evidence of cracks. Additional data will be obtained on this sphere. The available data on SPO-5 are given in Table 8. (W. A. Zanolli and B. R. Kokenge)

FUEL CHARACTERIZATION

Oxygen Exchange Rate Studies The preparation of a low neutron flux plutonium dioxide fuel has many applications. The normal oxygen distribution gives a neutron flux of about 17.0×10^3 n/sec/g of ^{238}Pu . Since the oxygen-17 and oxygen-18 isotopes undergo an (α, n) reaction, it has been found that by enriching the normal oxygen with oxygen-16, the neutron count can be lowered to about 3.0×10^3 n/sec/g of ^{238}Pu or just slightly higher than the spontaneous fission of plutonium-238. The preparation of $^{238}\text{Pu}^{16}\text{O}_2$ is therefore of considerable interest. For a better understanding of the exchange reaction between oxygen and $^{238}\text{PuO}_2$, kinetic data were obtained at several temperatures. The rate of reaction was also investigated as a function of particle preparation. The rate data were obtained by following the increased neutron flux associated with the reaction

The apparatus used for the exchange studies is shown in Figure 6. The counts were recorded with a Texas Nuclear 9148 series neutron counter located directly outside the box in which the exchange was conducted. The data obtained in all these experiments showed the exchange reaction to be first order in respect to oxygen-18. The rate constants were calculated from plots of $\log \{({}^{18}\text{O}_g) - ({}^{18}\text{O}_g)_\infty\}$ as a function of time.

FIGURE 6 - Apparatus for the oxygen exchange studies.

The results in Figure 7 show that the rate of exchange between oxalate-prepared and hydroxide-prepared ${}^{239}\text{PuO}_2$ to be quite different. A much faster rate was observed for the oxalate material at all temperatures used in this study. Oxalate-prepared material attained equilibrium within 5 to 15 min over the various temperatures used. With the exception of the 15-min equilibration time at 1550°C , the hydroxide-prepared material required a much longer period of time to achieve equilibrium. A curve similar to the one shown in Figure 7 has been reported in the literature and was interpreted to be a surface exchange reaction followed by a slower diffusion reaction into the interior of the oxide particle. This is obviously the case in this study and explains the large difference in exchange rate between the oxalate- and hydroxide-prepared materials. Since the oxalate-prepared particles have an average diameter of $1\ \mu\text{m}$, a surface exchange reaction is sufficient to obtain a rapid equilibration time; how-

FIGURE 7 - Exchange reaction at 700°C of hydroxide and oxalate PuO₂.

ever, the hydroxide material contained particles of 125-297 μm in diameter with a grain size of 10-20 μm ; hence diffusion plays a much larger role in the rate of exchange. Because of this difference in the material characteristics, temperature becomes an important controlling factor in the exchange rate of hydroxide material; hence explaining the very large rate increase between 700 and 1550°C.

As observed in Table 9, particle size has little effect on the rate of exchange of hydroxide-prepared PuO₂. Particles with a diameter between 10 and 125 μm undergo only slightly faster exchange than particles with a diameter of 125 to 297 μm . Apparently, even with hydroxide-prepared particles of these various diameters the diffusion exchange reaction is still an important rate-controlling factor. Since the diffusion exchange reaction is controlled by grain size and temperature, these are probably the most important characteristics to consider when attempting to describe the mode of exchange in various materials.

As would be expected, the reaction rate for the exchange of oxalate-prepared PuO₂ increases with temperature. The rate data are shown in Table 9. The effect of temperature on the exchange of hydroxide PuO₂ is

shown in Figure 8. When the exchange temperature is raised to 1550°C the diffusion exchange reaction is apparently accelerated sufficiently to allow the hydroxide material to come to a rapid equilibrium.

Sintering the sample would be expected to slow the diffusion controlled reaction, and this was found to be the case as shown in Figure 9. The exchange of oxalate-prepared PuO_2 would not be expected to be dependent upon sintering since the reaction is largely surface controlled.

Table 9 shows that sintering, indeed, has no effect on the exchange rate of oxalate-prepared PuO_2 . (R. L. Deaton and C. J. Wiedenheft)

FIGURE 8 - Exchange of hydroxide PuO_2 at 700°C and 1550°C.

FIGURE 9 - Effect of sintering on exchange of hydroxide PuO_2 at 1000°C .

Table 9

EXCHANGE PARAMETERS AND RATE CONSTANTS
FOR THE OXYGEN EXCHANGE OF PuO_2

Sample Preparation	Sintering Temperature ($^\circ\text{C}$)	Exchange Temperature ($^\circ\text{C}$)	$r^{16}\text{O}_{g-a}$ (%)	Rate Constant (min^{-1})
Oxalate	1550	1550	59.3	85.8×10^{-7}
Oxalate	1300	1300	71.7	66.3
Oxalate	1000	1000	73.3	30.7
Oxalate	700	700	71.8	27.7
Oxalate	1550	1000	73.3	36.2
Hydroxide	1550 ^a	1550	70.5	22.5
Hydroxide	1300	1300	70.8	7.2
Hydroxide	1550	1300	71.2	6.1
Hydroxide	1000	1000	70.7	6.9
Hydroxide	700	700	72.7	2.6
Hydroxide	1550 ^b	1550	72.0	26.4
Hydroxide	1550 ^c	1550	70.9	35.5
Hydroxide	1550 ^d	1550	72.6	25.1

^a 125-297 μm particles unless otherwise noted.

^b Sintered an additional 6 hr.

^c Fines (10-125 μm) sintered an additional 6 hr.

^d New batch obtained for comparison (125-297 μm).

Self-Diffusion of Oxygen in $^{239}\text{PuO}_2$. The preceding report (pp.) concerning the exchange of PuO_2 showed that dense refractory particles with a diameter larger than about 10 μm undergo oxygen exchange by an oxygen diffusion reaction. For a better understanding of the complete oxygen exchange process of these larger particles of PuO_2 , the rate of oxygen self-diffusion in PuO_2 was determined. The diffusion equation gives an insight to the rate of oxygen exchange of these particles at low temperatures where the diffusion process is the predominant mode of exchange.

The method used to determine the diffusion coefficients is that of gas-solid isotope exchange between $^{239}\text{PuO}_2$ microspheres and oxygen-18. This method is applicable for diffusion coefficient measurements when the rate of the surface exchange reaction between the gas and solid is much faster than the rate of diffusion of the exchanging ion through the lattice. Solutions to the diffusion equation for measurements of this type have been worked out by Carman and Haul¹ and by Crank².

The equation developed by Crank was used in calculating the diffusion coefficients:

$$\frac{M}{M_\infty} = 6 \left[\frac{Dt}{a^2} \right]^{\frac{1}{2}} \left\{ -\frac{1}{2} + 2 \sum_{n=1}^{\infty} \text{ierfc} \frac{na}{\sqrt{Dt}} \right\} - \frac{3Dt}{a^2} \quad (1)$$

where ierfc is the first inverse error function complement.

For the situation where the fractional exchange, $\frac{M}{M_\infty}$, is small, Equation 1 reduces to:

$$\frac{M}{M_\infty} = 6 \left(\frac{Dt}{a^2} \right)^{\frac{1}{2}}$$

where M is the amount exchanged at time t in seconds and M_∞ is the amount of oxygen-18 exchanged at equilibrium. The radius of the sphere undergoing exchange is a , and D is the diffusion coefficient.

Oxygen-18 in $^{239}\text{PuO}_2$ undergoes an (γ, n) reaction whereas oxygen-16 does not. This allows a convenient means of measuring the rate of oxygen exchange. The experimental procedure used is described in the previous report. The reaction was followed by noting the increase in the neutron flux with the increase in the oxygen-18 content in the $^{239}\text{PuO}_2$. After following the exchange reaction at the exchange temperature for several hours the temperature was increased to 1550°C where the equilibrium neutron flux is readily obtained.

The oxygen self-diffusion rate in PuO_2 was measured with microspheres of PuO_2 . These microspheres were prepared by passing hydroxide-precipitated particles of PuO_2 through a plasma torch. The spheres used in this study were generally 63-149 μm in diameter; however, the same diffusion coefficients were observed for microspheres 149-210 μm in diameter. The microstructure of these spheres show them to be nearly single grained material

From the exchange rate data at each temperature, the dimensionless plots of $\frac{Dt}{a^2}$ as a function of time were constructed. In all cases linear plots were obtained with the lines passing, within experimental error, through the origin. The plot of $\log D$ as a function of T^{-1} is shown in Figure 10. From this plot the diffusion equation is $D = 1.19 \times 10^{-3} e^{-42,200/RT}$.

The activation energy for the self-diffusion of oxygen in PuO_2 was found to be 42.2 kcal/mole. This compares favorably with 29.7 kcal/mole for UO_2 ⁴ and 56.0 kcal/mole for ZrO_2 ⁵ both of which are oxides that also have a fluorite structure. (R. L. Deaton and C. J. Wiedenheft)

Stoichiometry by TGA A study was initiated in an effort to better understand the stoichiometric characteristics of the uncoated and molybdenum coated plutonium oxide and the plutonia-molybdenum cermet (PMC) material used as heat source fuel for the Transit/Pioneer programs.

A thermogravimetric analysis apparatus capable of operation under vacuum or inert gas up to 2500°C is being employed for this investigation. Oxidation of substoichiometric material is achieved in another TGA apparatus capable of operation up to 1000°C in an oxidizing atmosphere.

Uncoated $^{238}\text{PuO}_2$ In the initial experiments $^{238}\text{PuO}_2$ fines (less than 100 μm), prepared by the hydroxide method, were heated to 1900°C on molybdenum pans under 10^{-5} torr vacuum. The results showed the start of weight loss at 1650°C. In approximately 4 min, the temperature had reached 1900°C, where it was held constant for 45 min. The weight loss was rapid and decreasing in rate up to 15 min. At this time a linear rate, which was interpreted as congruent vaporization, was observed for the remaining 30 min of heating. Stoichiometry calculations were made by subtracting the weight loss due to congruent vaporization from the total weight loss and assuming the remaining loss was oxygen. The calculated value was $\text{PuO}_{1.54}$. The reduced material was also analyzed by reoxidation in the TGA apparatus. The subsequent weight gain was used to calculate the stoichiometry. These results exhibited a stoichiometry of $\text{PuO}_{1.87}$. Several determinations were made on similar material under the same conditions, and the results continued to show the disagreement between weight loss and weight gain. A determination was made at 1700°C and holding for 30 min. The results showed a 0.86% weight loss; however, reoxidation showed no weight gain. This indicated that the weight loss was not due to oxygen. To date this anomaly cannot be explained; however, two possibilities are: 1) the material is losing entrapped gases or impurities when heated to these temperatures; 2) a reaction with the molybdenum pan forms volatile MoO_3 . Work is continuing in an effort to solve this anomaly.

Molybdenum-Coated $^{238}\text{PuO}_2$ Coated material (Batch PC1-160-L) exhibited weight loss characteristics similar to the uncoated particles when heated to 1900°C under vacuum. During these experiments, the observation was made that coated particle stoichiometry could be analyzed by heating in an air atmosphere up to 300°C. This temperature was determined

FIGURE 10 - Log D plotted as a function of T^{-1} .

to be sufficient to convert substoichiometric plutonium oxide to PuO_2 without oxidizing the molybdenum coating. The results on as-received coated material showed no measurable weight gain indicating a stoichiometry of $\text{PuO}_{2.00} \pm 0.02$. The stoichiometry of an aliquot heated in a vacuum to 1900°C , then reoxidized, calculated as $\text{PuO}_{1.92}$.

Another interesting observation was that when the coated particles were heated to 700°C , the molybdenum coating was naturally oxidized and a weight gain continued for about 10 min. At this point, the weight remained constant for several minutes. The thought occurred that the percent of molybdenum coating could be calculated provided the oxygen-molybdenum ratio was known. Therefore, the coated particles were heated to 700°C and the percent molybdenum coating was calculated using the MoO_2 ratio. The results were very close to that of the known analytical value of molybdenum. This was repeated several times with good agreement. However, a literature survey of the known oxidation characteristics of molybdenum revealed that MoO_3 should be formed under these conditions; therefore, the above calculation had no basis. The literature also revealed that MoO_3 is volatile in this temperature range. It appeared from these data that an increase in temperature should cause all the molybdenum to form MoO_3 and subsequently volatilize. This reaction and weight loss could be used to calculate the molybdenum concentration. Determinations were made and the weight loss data were used to calculate the molybdenum concentration. The values were quite low indicating that only a portion of the molybdenum was forming MoO_3 and subsequently volatilizing.

This behavior led to the metallographic examination of coated material after it had been heated to 700°C for 10 min or before any appreciable volatilization occurred. This examination revealed three phases which were then analyzed by the electron microprobe. Figures 11 and 12 exhibit a triple exposure of a line scan for plutonium and molybdenum respectively of an unheated molybdenum-coated PuO_2 particle. In contrast, Figures 13 and 14 show line scans for plutonium and molybdenum respectively of a particle from the same batch that was heated to 700°C in air for 10 min. The dark area shows the absence of plutonium, while the intermediate zone exhibits a moderate amount of plutonium, and the smooth gray area is indicative of a larger quantity of plutonium. The reverse is apparent for a molybdenum scan. These data clearly display an intermediate phase which contains both molybdenum and plutonium. This phase could be a ternary complex of Mo-Pu-O. This would explain why all the molybdenum did not convert to MoO_3 and volatilize. It is also speculated that since a portion of molybdenum oxide is tied up on the PuO_2 , the remainder is converted to MoO_3 , resulting in a composition which averages MoO_2 . This is a possible reason for the calculation of weight percent molybdenum using the MoO_2 ratio to yield good agreement with analytical results. If these speculations are true, then surface area should affect the results. Investigative efforts will be directed in this area.

The conclusion to date is that molybdenum-coated plutonium oxide stoichiometry can be determined by TGA. Also, it may be possible to determine molybdenum content by this technique with further investigation.

(D. E. Etter)

FIGURE 11 - Electron microprobe line scan for plutonium (unheated Mo-coated $^{238}\text{PuO}_2$).

FIGURE 12 - Electron microprobe line scan for molybdenum (unheated Mo-coated $^{238}\text{PuO}_2$).

FIGURE 13 - Electron microprobe line scan for plutonium (Mo-coated $^{238}\text{PuO}_2$ heated in air for 10 min at 700°C).

FIGURE 14 - Electron microprobe line scan for molybdenum (Mo-coated $^{238}\text{PuO}_2$ heated in air for 10 min at 700°C).

Table 10

AMBIENT TEMPERATURE DIMENSIONAL STABILITY TEST RESULTS

Disc Identification	Disc Measurements	Uncoated Discs		Coated Discs (in)										
		10-24-70	2-25-71	3-8-71	3-11-71	3-17-71	3-22-71	3-25-71	3-29-71	4-2-71	4-5-71	4-8-71	4-23-71	
PM-56B (BMI-12152)	Major Diameter (in)	A	1 9310	1 977	1 969	1 956	1 966	1 966	1 968	1 963	1 964	1 964	1 963	
		B	1 9305	1 977	1 977	1 977	1 972	1 971	1 977	1 974	1 969	1 971	1 968	1 967
	Minor Diameter (in)	A	1 7490	1 768	1 766	1 768	1 765	1 766	1 766	1 764	1 766	1 766	1 767	1 769
		B	1 7495	1 764	1 766	1 764	1 765	1 765	1 765	1 764	1 765	1 765	1 766	1 771
	Thickness (in)	1	0 2160 (max 0)	0 230	0 229	0 229	0 230	0 229	0 229	0 229	0 228	0 228	0 228	0 228
		2	0 2165 (max 90)	0 233	0 230	0 231	0 230	0 231	0 231	0 230	0 232	0 231	0 231	0 231
		3	0 2150 (min 90)	0 230	0 229	0 230	0 230	0 231	0 230	0 229	0 230	0 230	0 229	0 229
	Major Diameter (in)	A	1 9305	1 965	1 965	1 965	1 965	1 963	1 961	1 964	1 964	1 963	1 963	1 964
		B	1 9305	1 970	1 969	1 967	1 968	1 965	1 964	1 964	1 967	1 967	1 966	1 965
	PM-56T	Minor Diameter (in)	A	1 7468	1 75	1 752	1 757	1 753	1 753	1 750	1 751	1 753	1 755	1 753
		B	1 7473	1 756	1 754	1 760	1 753	1 753	1 752	1 753	1 754	1 755	1 753	1 756
Thickness (in)		1	0 2140 (max 0)	0 222	0 222	0 222	0 222	0 221	0 222	0 221	0 222	0 222	0 222	0 223
		2	0 2155 (max 90)	0 225	0 225	0 226	0 224	0 220	0 224	0 224	0 224	0 224	0 224	0 224
		3	0 2125 (min 0)	0 225	0 222	0 223	0 222	0 220	0 221	0 224	0 223	0 222	0 223	0 223

Table 11

DESTRUCTIVE ANALYSES OF PRODUCTION
GRADE PLUTONIA-MOLYBDENUM CERMET
ISOTOPIC FUEL

Chemical Analyses	
<u>(wt %)</u>	
Molybdenum	21.66
Thorium	0.11
Chlorine	0.02
Fluorine	0.15
Total Plutonium	66.00
Spectrographic Analyses	
<u>(ppm of Disc Weight)</u>	
Aluminum	400
Barium	<25
Boron	<25
Calcium	500
Chromium	85
Cobalt	ND
Copper	125
Iron	305
Lead	<50
Magnesium	27
Manganese	<50
Nickel	85
Silicon	250
Sodium	ND

Evaluation of Molybdenum-Coated PMC Discs Two PMC discs [PM-56B and PM-56T; Type (-3)] were coated at Battelle Memorial Institute in Columbus, Ohio, by the molybdenum hexafluoride-hydrogen CVD barrel-coating process. Subsequent examination at Mound Laboratory found the discs to be almost black to dark violet in color with dendritic needles evident on the major diameters.

The discs were marked with a Vibratool to preserve orientation for gaging purposes, wrapped with 0.001 in. (0.003 cm) tantalum foil, and stored in O-ring sealed, stainless-steel vessels in an inert-gas alpha box. The discs were periodically removed from storage and gaged to determine whether dimensional changes take place during storage. Table 10 is a summary of the ambient temperature dimensional stability tests which have been terminated. There is no indication that the discs changed in size during the test, within the limits of measurement, as was previously reported.⁶ The roughness of these discs made the uncertainty of the gage data greater than that for machined, uncoated, PMC discs.

The disc designated as PM-56B-3 (BMI-12152) was sectioned for chemical analysis and metallographic examination. The analytical data received to date are shown in Table 11. Metallographic analysis showed the thickness of the molybdenum coating varies from 0.0030 to 0.0045 in. (0.0076

to 0.0104 cm) respectively, based on representative areas, as shown in Figures 15 and 16. Figure 16 shows the needle-like fragments extending from the surface of the molybdenum coating.

The disc designated as PM-56T-3 (BMI-10752) was stored in anticipation of the performance of high temperature compatibility studies. However, due to the existence of a dark violet coloration apparent on the surface of this disc, the high temperature test was not performed. This coloration was also apparent on PM-56B-3 (BMI-12152). Therefore, PM-56B-3 was sectioned and then scanned on the electron microprobe to determine whether or not foreign impurities such as fluorine, chlorine or tantalum could be found in the molybdenum coating or at the molybdenum coating - PMC interface. The results of the electron microprobe showed no detectable quantities of fluorine, chlorine or tantalum present in the coating or at the coating interface. (G. N. Huffman)

Destructive Analyses of PMC Process Control Discs Production grade PMC discs are randomly selected from the production cycle for destructive analyses to ensure control of the process. Pie-shaped specimens are cut from the disc for metallographic, isotopic, heavy element, chemical, and spectrographic analyses. These data are listed in Table 12. Photomicrographs representative of the microstructure of the discs not previously reported⁷ are shown in Figures 17-20. The physical analyses on the two most recently submitted discs, PM-89B and PM-96T, are presented in Table 13. (G. N. Huffman)

FIGURE 15 - PM-56B-3 (BMI-12152) showing molybdenum-coating thickness of ~3 mils (125X).

Table 12

DESTRUCTIVE ANALYSES OF PRODUCTION GRADE PLUTONIA-MOLYBDENUM

Isotopic Analyses (wt % of Total Pu)		Process Control Disc Designation		
		PM-42B6	PM-60B6	PM-64T6
^{238}Pu		0.0001	0.0001	0.0001
^{238}Pu		80.3	80.2	80.1
^{239}Pu		15.7	15.9	16.3
^{240}Pu		2.76	2.84	2.72
^{241}Pu		0.980	0.791	0.704
^{242}Pu		0.340	0.182	0.172
Heavy Element Analyses (wt % of Total Pu)				
Mass No.	Assignment			
227	-	<0.01	<0.01	<0.01
231	-	<0.01	<0.01	<0.01
232	Th	0.10	0.10	0.10
233	U	<0.01	<0.01	<0.10
234	U	0.62	0.77	0.78
235	U	<0.005	<0.005	<0.005
236	U	<0.002	<0.002	<0.002
237	-	0.16	0.07	0.06
241	Am	0.0748	0.0542	0.0512
Chemical Analyses (wt % or ppm of Disc weight)				
Molybdenum, %		17.68	15.90	16.22
Thorium, %		<0.10	<0.10	<0.10
Carbon, ppm		<100	<100	<100
Chlorine, %		<<0.01	<<0.01	<<0.01
Fluorine, %		0.18	0.11	0.04
Spectrographic Analyses (ppm of Disc Weight)				
Aluminum		< 50	50	≤ 50
Barium				
Calcium		≤ 250	≤ 250	< 250
Chromium		< 50	< 50	< 50
Cobalt				
Copper		50	< 50	< 50
Iron		500	400	100

Table 12 (continued)

Spectrographic Analyses (Cont.) (ppm of Disc Weight)	Process Control Disc Designation		
	PM-42B6	PM-60B6	PM-64T6
Lead			50
Magnesium	<50	<50	<50
Manganese	<50	<50	<50
Nickel	50	50	<50
Silicon	50	<50	80
Sodium			

Isotopic Analyses (wt % of Total Pu)	Process Control Disc Designation			
	PM-73B	PM-76B	PM-89B	PM-96T
²³⁸ Pu				<0.0001
²³⁸ Pu				
²³⁹ Pu				
²⁴⁰ Pu				
²⁴¹ Pu				
²⁴² Pu				

Heavy Element Analyses
(wt % of Total Pu)

Mass No.	Assignment			
227	-			
231	-			
232	Th			
233	U			
234	U			
235	U			
236	U			
237	-			
241	Am			0.1224

Chemical Analyses

(wt % or ppm of Disc Weight)

Molybdenum, %	16.69	15.62	17.32	17.32
Thorium, %	0.04	<0.04	0.15	0.17
Carbon, ppm	<100	<100	<100	60
Chlorine, %	<<0.01	<<0.01	<<0.01	0.01
Fluorine, %	0.14	0.09	0.21	0.01

Table 12 (continued)

Spectrographic Analyses (ppm of Disc Weight)	Process Control Disc Designation			
	PM-73B	PM-76B	PM-89B	PM-96T
Aluminum	60	50	80	<50
Barium				<25
Calcium	<100	<100	<100	<250
Chromium	50	70	<50	<50
Cobalt	80	50	50	ND
Copper	50	<50	<50	<50
Iron	80	90	110	<100
Lead				
Magnesium	<50	<50	<50	<25
Manganese				<25
Nickel	<50	<50	<50	<50
Silicon	<50	<50	<50	<50
Sodium	ND	ND	ND	ND

FIGURE 16 - PM-56B-3 (BMI-12152) showing molybdenum-coating thickness of ~4.5 mils (125X).

FIGURE 17 - Cross section photomicrograph of PM-73B (125X) as polished.

FIGURE 18 - Cross section photomicrograph of PM-76B (125X) as polished.

FIGURE 19 - Cross section photomicrograph of PM-89B (125X) as polished.

FIGURE 20 - Cross section photomicrograph of PM-96T (125X) as polished.

Table 13

PHYSICAL CHARACTERISTICS OF PLUTONIA-MOLYBDENUM
CERMET PROCESS CONTROL DISCS

	Disc Designation	
	PM-89B	PM-96T
Disc Type	6	6
Weight, g	131.9	128.4
Volume, cm ³	12.68	12.36
Density, g/cm ³	10.40	10.39
Power, W	42.50	41.18
Neutron emission, n/sec	3.40×10^6	3.88×10^5
Power density, W/cm ³	3.35	3.33
Specific power, W/g	0.322	0.321
Specific neutrons, n/sec/g ²³⁸ Pu	4.6×10^4	5.36×10^3
Dimensions corrected to 20°C		
Diameter, in.	2.140	2.1430
Thickness, in.	0.214	0.2110

Preliminary Studies of the Mobility Characteristics of ThO₂ and PuO₂ Fines A series of tests was performed to determine the possible effect of molybdenum oxidation on the mobility of PuO₂ or ThO₂ fines through cracks or holes in impacted heat source capsules, fueled with either plutonia-molybdenum (PMC) or thoria-molybdenum simulant. Since an impacted fueled capsule was not available for these tests and since the time available for conducting these tests was minimal, experiments and equipment were designed to simulate post-impact conditions.

The apparatus designed for these tests consists of two quartz chambers with standard tapered joints. The reaction chamber is a simple quartz tube with a standard female joint. The collection chamber is a quartz tube containing a cold finger and fitted with a standard male joint and a 1/8 in. (0.3 cm) i.d. orifice tube. When the apparatus is assembled, the 1/8 in. tube of the collection chamber extends several inches into the reaction tube and seals the chambers from each other except for the 1/8 in. i.d. orifice tube producing a static system. This apparatus is shown in Figure 21.

In all experiments the samples to be tested were weighed and carefully placed near the rear of the reaction chamber. The collection chamber and the loaded reaction chamber were then fitted together so that the orifice tube did not come in contact with the fines. The reaction tube portion of the apparatus was then placed in the heat zone of a horizontal

FIGURE 21 - Apparatus for mobility studies.

tube furnace. The furnace was heated at approximately $14^{\circ}\text{C}/\text{min}$ to 800°C , held at this temperature for 2 hr, and then cooled to room temperature. The apparatus was removed from the furnace and carefully disassembled. The entire collection chamber, including the inside of the orifice tube, was rinsed with distilled water to collect any fines transported during the test. The wash solution was quantitatively transferred to a volumetric flask and analyzed for either thorium or plutonium by liquid scintillation techniques.

The ThO_2 and PuO_2 fine-powder samples were prepared by the reverse strike oxalate precipitation process which produces large amounts of particles less than $5\text{ }\mu\text{m}$ in diameter.

Blended material was prepared by thoroughly mixing 20 wt % of 100-mesh molybdenum powder with the appropriate fuel fines.

The cermet simulated-impact samples consisted of cermet specimens that had been crushed and broken to simulate impact debris. General Electric ThO_2 -molybdenum cold-pressed and sintered cermet and production-grade PuO_2 -molybdenum cermets were used for these tests. A typical example of this material is shown in Figure 22.

Because of the limited time available for this study, no attempt was made to determine the particle size distribution of the test samples or

FIGURE 22 - Typical example of impacted materials.

of the fines transported. However, previous work at this laboratory has shown that approximately 30% of the particles produced by the technique used in this work are less than 5 μm in diameter.

The results of both the ThO_2 and PuO_2 mobility tests are listed in Table 14.

Table 14

FINES TRANSPORT PROPERTIES OF ThO_2 AND $^{238}\text{PuO}_2$

<u>Sample Type</u>	<u>Fines Transported (wt %)</u>	
	<u>ThO_2</u>	<u>PuO_2</u>
Fine Powder	0.000	0.35
	0.000	0.89
	0.005	0.62
Blended Molybdenum Powder with Fines	0.008	0.54
	0.000	1.00
	0.000	
Simulated Impact Debris	0.004	0.45
	0.001	

After evaluation of the results and experimental methods, the following conclusions were reached.

1. Under the conditions of the experiments, the fines mobility properties of thoria and plutonia are different. In all tests, plutonia fines appeared to have a greater mobility than the thoria fines. The differences in the mobility properties between these two powders might be attributed to pressure differentials caused by the experimental procedure, particle recoil from plutonium-238 alpha radiation, surface charges, particle agglomeration, and hygroscopic behavior. It was observed during the reaction tube loading operation that the thoria powder had a greater tendency to agglomerate than did the plutonia powder.
2. Within experimental error and the experimental procedures used, the oxidation of molybdenum has no apparent effect on the fines mobility properties of the powders and impact debris samples of either ThO_2 or PuO_2 .

In conclusion, it is our opinion that these experiments have demonstrated the need for further testing; and before the mobility values of plutonia or thoria fines obtained in these experiments are extrapolated to full-scale fueled capsules, further testing should be performed.

(R. L. Deaton and W. H. Smith)

Preliminary Milliwatt Generator Loading Studies A study was undertaken to ascertain the feasibility of loading 5.5 W (th) of $^{238}\text{PuO}_2$ shards into a milliwatt capsule strength member. The program requirements were that the shards had to have a random size distribution in the 53-105 μm size range and the minimum acceptable clearance between the 10-mil shim covering the fuel and the weld zone had to be in the range of 100 to 125 mils to prevent blowout during welding.

Thorium dioxide shards were used in this study because of their similarities in bulk and packing densities to those of $^{238}\text{PuO}_2$. The apparent density of the ThO_2 shards was 10.0 g/cc. Calculations showed that 12.6 g of ThO_2 shards had the same volume as 13.7 g of PuO_2 which is the amount of PuO_2 necessary to obtain 5.5 W (th). For this study, therefore, 12.6 g of ThO_2 were used to simulate the fuel loading into two test capsules of approximately the same volume (3.22 ml).

Various loading techniques were used in an effort to obtain maximum packing density. Vibrating and tapping during loading failed to produce more than a 60-mil clearance between the weld area and a 10-mil shim positioned atop the fuel. Calculations indicated that there would be a 0.7 ml loss from the capsule volume to accommodate the required 125-mil weld clearance. In addition to this loss, another 0.05 to 0.08 ml of volume would be lost in accommodating the 10-mil shim. When these losses were subtracted from the original capsule volume, only 2.47 ml were

available for the fuel loading. Since 5.1 - 5.2 g/cc is the normal tap density for PuO_2 , it is apparent that the maximum thermal loading that can be expected under ideal packing conditions is 5.0 - 5.1 W.

It was therefore obvious that the fuel would have to be pressed into the available volume to obtain the necessary thermal loading under the imposed restrictions. A loading fixture (Figure 23) was fabricated to accomplish this task. After the ThO_2 shards were loaded with the aid of a Vibratool to improve the packing, the top punch was placed into position and the fuel particles compressed under a ram force of 100-300 lb. After compaction, no visible distortion of the shim or capsule was apparent.

Concern was expressed over the possibility of particle breakup during the compacting operation. In order to see whether this did occur, two simulant fuel loadings were made. One resulted in a weld clearance zone of 125 mils; the other produced a weld clearance zone of 180 mils. After compaction the simulant was removed and submitted for particle size analysis. The analysis showed no apparent shift in particle size distribution in either fuel loading.

If the present milliwatt capsule dimensions and thermal loading are critical, the compacting operation described above appears to be the only means of accomplishing the fuel loading. However, since $^{238}\text{PuO}_2$ and ThO_2 have slightly different pressing characteristics, it would be desirable to test this operation using $^{238}\text{PuO}_2$ to determine its feasibility prior to accepting it as an operational procedure. (R. L. Deaton)

FIGURE 23 - Milliwatt strength member loading fixture.

Capsule Design and Testing

FUEL/CAPSULE MATERIAL COMPATIBILITY TESTS

$^{238}\text{PuO}_2$ /Ta-10 wt % W at 800°C Ta-10 wt % W capsules containing $^{238}\text{PuO}_2$ were annealed at 800°C for 31, 60, and 94 days. The test capsule configuration is shown in Figure 1. Chemical analysis of the $^{238}\text{PuO}_2$ is given in Table 1.

FIGURE 1 - Capsule configuration for 800°C, Ta-10 wt % W/ $^{238}\text{PuO}_2$ compatibility study.

Figure 2 is a photomicrograph of a typical portion of the Ta-10 wt % W edge after a 94-day thermal exposure. The clean, undisturbed edge is typical of all heat treatments. Figures 3 and 4 are hardness traverses of the capsule bottoms and walls. Hardness traverses across an unfueled capsule annealed for 94 days are also included in Figures 3 and 4.

Table 1

CHEMICAL ANALYSIS OF $^{238}\text{PuO}_2$ USED IN 800°C,
Ta-10 wt % W COMPATIBILITY STUDY

<u>Element</u>	<u>Analysis</u> <u>(wt %)</u>
Ni	<0.002
Fe	0.06
Al	0.07
Ca	0.03
B	<0.01
Si	Trace
Cr	<0.03
Cu	Trace
Mg	0.01
Zn	<0.03
Na	<u>Trace</u>

Total <0.26

FIGURE 2 - Ta-10 wt % W after 94 days of exposure to $^{238}\text{PuO}_2$ at 800°C.
590X, unetched.

FIGURE 3 - Hardness traverses across Ta-10 wt % W capsule bottom after the capsules have been heat treated at 800°C. All capsules contained $^{238}\text{PuO}_2$ except the standard.

FIGURE 4 - Hardness traverses across Ta-10 wt % W capsule walls after the capsules had been heat treated at 800°C. All capsules contained $^{238}\text{PuO}_2$ except the standard.

Hardening of the Ta-10 wt % W is noted as a result of the $^{238}\text{PuO}_2$. This hardening is assumed to be due to dissolved oxygen which has been taken from the $^{238}\text{PuO}_2$.

Cracks were observed in all the capsules including the one that did not contain $^{238}\text{PuO}_2$. Figure 5 shows one of the cracks observed in the fueled specimen annealed for 94 days. The amount of cracking could not be correlated with the presence of $^{238}\text{PuO}_2$ or hardness although the number of cracks seemed to decrease with longer exposure. (D. R. Schaeffer)

FIGURE 5 - Ta-10 wt % W after 94 days of exposure to $^{238}\text{PuO}_2$ at 800°C. 590X, unetched.

$^{238}\text{PuO}_2$ /Ta-10 wt % W Inner Container and T-111 Outer Container at 1200°C

The object of this study was to evaluate the compatibility of $^{238}\text{PuO}_2$ with the combination of a Ta-10 wt % W inner container and a T-111 outer container at 1200°C. Information on the compatibility of $^{238}\text{PuO}_2$ with Ta-10 wt % W and T-111 as separate containers has been previously reported¹ and where applicable, this information will be compared with the results of the present test.

Capsules constructed as shown in Figure 6 were annealed at 1200°C for 70 and 120 days. The inner capsules were TIG welded in an argon atmosphere and then electron beam welded into a Hastelloy X outer capsule. The Hastelloy X outer capsule provides oxidation protection during heat treatment. A molybdenum intermediate capsule or tungsten foil was

FIGURE 6 - Capsule configuration for $^{238}\text{PuO}_2$ /Ta-10 wt % W/T-111 compatibility study.

placed between the T-111 and Hastelloy X as a diffusion barrier. Analysis of the fuel is given in Table 2.

Table 2

CHEMICAL ANALYSIS OF $^{238}\text{PuO}_2$ USED IN
 $^{238}\text{PuO}_2$ /Ta-10 wt % W/T-111 COMPATIBILITY TESTS

<u>Element</u>	<u>Analysis (wt %)</u>
Ni	<0.002
Fe	0.06
Al	0.07
Ca	0.03
B	<0.01
Si	Trace
Cr	<0.03
Cu	Trace
Mg	0.01
Zn	<0.03
Na	<u>Trace</u>

Total <0.26

PuO₂/Ta-10 wt % W Compatibility Figures 7 and 8 describe the two variations in the appearance of the edge of the Ta-10 wt % W. The 10 μ m thick surface reaction product seen in Figure 7 was not found on the 70-day sample and in only two places on the 120-day sample. This reaction product is made up of two layers. The x-ray strip chart analysis in Figure 7 indicates that the outer layer is an oxide containing plutonium and tantalum, and that the inner layer is composed of oxygen, plutonium, tantalum, and tungsten. The 1 to 5 μ m thick surface layer seen in Figure 8 was found on most of the capsule surface. Figure 9 contains an x-ray strip chart analysis of a similar portion of this type of surface layer. The white reaction product was found to be rich in tantalum and iron. This layer has been reported earlier¹ in a test involving ²³⁸PuO₂ of similar purity and was tentatively identified as the Ta(Fe,Cr)₂ inter-metallic compound. The detection of plutonium in the middle of this layer corresponds to a dark oxide particle embedded in the white layer. It is believed that the particles which are dispersed in the white layer are the oxygen, tantalum, plutonium, and/or oxygen, tantalum, plutonium, tungsten reaction products mentioned above. Both types of surface layers penetrated the base metal at the grain boundaries. Maximum depth of grain boundary penetration was 30 μ m after 120 days at 1200°C.

FIGURE 7 - Photomicrograph and x-ray strip chart analysis of Ta-10 wt % W after exposure to ²³⁸PuO₂ for 120 days at 1200°C.

FIGURE 8 - Ta-10 wt % W after exposure to $^{238}\text{PuO}_2$ for 120 days at 1200°C . 610X, unetched.

Hardness traverses across the Ta 10 wt % W capsule bases are given in Figure 10. The hardness increased after thermal exposure. This increase is believed due to dissolved oxygen in the Ta-10 wt % W which had been released by the $^{238}\text{PuO}_2$.

Effect on the T-111 Two effects were noted in the T-111 capsules due to the $^{238}\text{PuO}_2$. Hardening of the T-111 occurred as depicted in Figure 12. The general increase in hardness is believed due to dissolved oxygen, whereas the increase at the outer edge is believed due to the influence of outer container (molybdenum or tungsten and Hastelloy X). The second effect noted in the T-111 was the formation of the 9-10 μm thick surface layer seen in Figure 11. Electron microprobe analysis of this layer found only tantalum (approximately 98 wt % tantalum). Hardness of this surface layer was similar to that of the base metal.

Summary The Ta-10 wt % W inner capsule was hardened by dissolving oxygen released by the $^{238}\text{PuO}_2$. The Ta-10 wt % W also reacted with the $^{238}\text{PuO}_2$ and its impurities to form various reaction products at the Ta-10 wt % W/ $^{238}\text{PuO}_2$ interface. The primary reaction product found at this edge is believed to be the $\text{Ta}(\text{Fe},\text{Cr})_2$ intermetallic compound. Oxides containing tantalum and plutonium, and tantalum, plutonium, and tungsten were found rarely as a two-layer scale and are thought to be present as particles dispersed in the layer of intermetallic compound and as intergranular penetrations.

FIGURE 9 - X-ray strip chart analyses across the edge of Ta-10 wt % W in an area similar to that seen in Figure 8.

FIGURE 10 - Hardness traverse across Ta-10 wt % W capsule bases after thermal exposures to 1200°C.

FIGURE 11 - Edge of T-111 after exposure to 1200°C for 120 days. 620X, unetched.

The T-111 outer capsule was hardened by dissolved oxygen which had diffused through the Ta-10 wt % W inner capsule. The T-111 also developed a layer of tantalum on its interior surface. Since the T-111 is not in intimate contact with the Ta-10 wt % W except at portions of the capsule base, transport of the oxygen from the Ta-10 wt % W to the T-111 must occur by nonsolid diffusion. It is thought that the transport mechanism involves the formation of a volatile, tantalum oxide (e.g., TaO and/or TaO₂) at the external Ta-10 wt % W surface. This gaseous oxide then deposits on the T-111 where it decomposes allowing the oxygen to diffuse inward and forming the observed tantalum layer on the T-111.
(D. R. Schaeffer)

Impact Testing of Capsule Materials An impact tester was designed and constructed which is to perform impact tests at high temperature in a vacuum. Figure 13 is a sketch which describes the apparatus. It is basically a drop weight tester whose hammer, anvil, and impact velocity are designed to comply with the Charpy impact test criteria.

The energy absorbed during impact is measured by determining the velocity of the hammer prior to and after impact. The velocity of the hammer at impact is determined by a set of stationary reed switches which are activated by a magnet attached to the hammer. The two reed switches start and stop a timer. Thus, with the distance between the switches known, the velocity of the hammer can be determined. The velocity of the hammer after impact is obtained by the use of a piezoelectric accelerometer. Upon impact the accelerometer generates a charge whose amplitude is proportional to the acceleration it experiences. This output of the accelerometer is displayed on an oscilloscope as a function of time. Integration of the resulting acceleration as a function of time curve gives the velocity change of the hammer. The energy absorbed during impact can then be calculated from the following equation:

$$\Delta E = 1/2 MV_i^2 - 1/2 MV_f^2$$

where V_i = hammer velocity before impact,
 V_f = hammer velocity after impact, and
 M = mass of hammer

Results from a preliminary test are given in Figure 14. In this test, a subsize, V-notch, Charpy impact specimen fabricated out of T-111 (Ta, 8 wt % W, 2.4 wt % Hf alloy) was impacted at room temperature at 11.01 ft/sec. The specimen did not fracture but was bent upon impact. The area under the curve in Figure 14 corresponds to a velocity change of 6.76 ft/sec and a change in energy of the hammer of 22.66 ft-lb.

A second set of reed switches are positioned so that they are activated after completion of the impact. They are used in a manner similar to the other set of switches to determine the velocity of the hammer after impact. The purpose of these switches is to provide a check for the accuracy of the accelerometer. In the above preliminary test (Figure 14), the second set of switches determined the change in velocity of the

FIGURE 12 - Hardness traverses across T-111 capsule bases after thermal exposures to 1200°C.

FIGURE 13 - Sketch of high temperature impact tester.

A: Lower of top set of reed switches closes and triggers oscilloscope.

B: Hammer hits specimen.

C: Impact of specimen complete.

D: Hammer hits base of impact tester

*Negative acceleration is acceleration in an upward direction.
Positive acceleration is acceleration in a downward direction.

FIGURE 14 - Photograph of curve generated by a piezoelectric accelerometer attached to the hammer of an impact tester. The trace generated between points B and C records the acceleration of the hammer as it hits a subsize, V-notch, Charpy impact specimen made from T-111.

hammer to be 6.69 ft/sec which corresponds to a change in energy of 22.53 ft-lb.

No impact tests at elevated temperatures have been made. They will follow a check-out of the equipment to withstand 1316°C.

(D. R. Schaeffer)

Reference

1. J. E. Selle, J. J. English, P. E. Teaney, and J. R. McDougal, The Compatibility of $^{238}\text{PuO}_2$ with Various Refractory Metals and Alloys - Interim Report, MLM-1706 (Oct. 1970), 214 pp.

Special Studies: Pioneer Program

INVESTIGATIONS OF PIONEER CAPSULE MATERIALS

At the request of AEC/SNS a study of the various nonmetallic materials used in the Pioneer radioisotopic thermoelectric generator (RTG) was undertaken. This study was initiated because the Pioneer RTGs on life test were losing electrical power faster than predicted.

The purpose of the study was to investigate these nonmetallic materials to determine whether anything that was deleterious to the Pioneer generator system was being released by these materials at elevated temperatures. These materials were for the most part processed by Teledyne Isotopes according to their specifications as had been the materials used in the Pioneer generator. The materials consisted of Min-K 1301*, ZrO₂, pyrolytic graphite, and POCO graphite.

In addition to the studies of the generator materials, a study was also made of the Min-K 1301 that had been first processed by Teledyne Isotopes, then shipped to Mound Laboratory where it was machined, vacuum outgassed, and stored in a vacuum atmosphere for later use in the capsule shipping containers.

The primary testing method used was residual gas analysis (RGA); however, thermal gravimetric analysis (TGA), differential thermal analysis (DTA), x-ray diffraction analysis, and emission spectrographic analysis were employed in some phases of the study.

POCO and Pyrolytic Graphite Samples of unoutgassed and outgassed (according to Teledyne Isotopes Specification PS0200008) POCO and pyrolytic graphite were made available for testing. These samples were studied by residual gas analysis in approximately the same thermal environment as the RTG. The thermal environment agreed upon prior to testing by both Teledyne Isotopes and AEC/SNS consisted of the following phases: 1) 1 hr at 500°F; 2) 2 hr at 1000°F; 3) 2 hr at 1300°F; 4) 2 hr at 1800°F; 5) ~16 hr at 1300°F. The samples were maintained in a vacuum environment during the residual gas analyses. There was no programmed heating rate used.

*Min-K is an insulating material composed primarily of silicon metal with a form of asbestos fiber as a binding material.

One additional test condition was added at Mound. Since the test specimen had to be weighed and mounted on the test equipment in air, the specimens were vacuum outgassed at ambient temperatures for at least 12 hr prior to testing in order to clean the specimen.

The test results are summarized below:

A. POCO Graphite Both the unoutgassed and the outgassed specimens behaved essentially the same. Organic fractions were observed as off-gassing products from both specimens at temperatures up to 1500°F. Above 1500°F only trace amounts of masses 15 [$(\text{CH}_3)^+$] and 27 [$(\text{C}_2\text{H}_3)^+$] were observed.

Trace quantities of mass 18 [$(\text{H}_2\text{O})^+$] were observed in the unoutgassed specimen at temperatures up to ~1140°F, but no mass 18 was observed in the outgassed specimen. The relative intensity of the organic products in the unoutgassed sample was slightly greater than in the outgassed sample.

Both samples lost 0.01 wt % during test, which is not significant. Both samples outgassed mass 41 [possibly C_3H_5^+], which is the same mass number observed in the gas samples taken from RTG test generators SN-37 and -39.

On the basis of the experimental data one would conclude that there are not many contaminants present in POCO graphite even before outgassing and that the contaminants observed during testing, with the exception of water vapor, probably came from the specimens being stored in plastic bags. This is a reasonable conclusion since both the outgassed and unoutgassed samples were stored in plastic bags prior to testing and both had essentially the same offgassing products. The only difference was the relative intensities of the product, ~10% greater for each observable mass in the unoutgassed specimen. However, the unoutgassed specimen was not as carefully handled as the outgassed specimen and could have picked up more organic material from the plastic storage bag.

With the exception of masses 15 and 27, all of the products are reduced to essentially zero intensity at about 1500°F in vacuum.

B. Pyrolytic Graphite Two samples of pyrolytic graphite, one unoutgassed and the other outgassed according to the Teledyne Isotopes specification previously listed, were also tested by residual gas analysis (RGA). These samples were exposed to the same thermal environment as listed previously for the POCO graphite as well as the 12-hr vacuum environment at ambient temperature prior to the initiation of the tests.

The data gathered on the outgassed pyrolytic specimen have been disregarded since at some period during the test the bottom weld of the stainless steel sample tube developed a leak. This was indicated by the appearance of the constituents of air in the mass scan during the test and later confirmed by the appearance of the sample after test and its weight gain, ~0.56 wt %, after being taken off test.

The data gathered on the unoutgassed specimen, however, indicated that the outgassed sample should have been relatively clean. These data indicated the presence of some organic materials that were observed at temperatures up to 1800°F; however, after the final temperature soak at 1300°F for ~16 hr nothing was observed offgassing from the sample.

There were fewer organic structures observed as offgassing products from the pyrolytic sample than had been observed from the POCO samples. The relative intensities of the offgas products were essentially the same as those for the outgassed POCO sample. This tends to support the conclusion that the organic materials are appearing because of the abrasive action of the sample against the plastic storage bag. The unoutgassed pyrolytic graphite sample lost only 0.01 wt %, the same quantity as the POCO specimens.

Since the unoutgassed pyrolytic graphite sample was relatively clean, one would expect the outgassed material to be at least as clean.

ZrO₂ Only one sample of ZrO₂, outgassed according to the Teledyne Isotopes procedure, was tested. The same thermal cycle and prior vacuum outgassing were used on this sample as had been used on the graphite specimens. However, at the request of Teledyne Isotopes this sample was wrapped in 5-mil tantalum foil.

While again this sample lost only 0.01 wt %, the offgassing products were a slightly different nature from those that had been observed during the testing of the graphites. The sample and the tantalum foil were discolored after the test. The low mass organic species of the methane, ethane order were ~45% greater in relative intensity than those observed in the worst case graphite (unoutgassed POCO), and mass 41 was a significant contributor to the total outgassing products. All species had disappeared after the 16-hr thermal soak at 1300°F. The sample was cooled to ambient and reheated to 800°F. During this short term heating (~1 hr) organic offgassing species were again observed at an intensity just above background.

Since the sample and the tantalum foil were discolored they were submitted for further analyses. The discolored tantalum foil was submitted for emission spectrometric analysis and the ZrO₂ for x-ray diffraction analysis.

The emission spectrometer was unable to identify the discolored portion of the tantalum foil, thus suggesting the stain was due to an organic substance rather than a metal impurity.

The x-ray diffraction analysis was performed in two steps. The first involved the analysis of the center section of the ZrO₂ sample (this was not discolored). The results of this analysis indicated the presence of two phases of ZrO₂: monoclinic and either tetragonal or cubic. The analysis of the discolored portion indicated the presence of two phases of ZrO₂ and another pattern which could not be identified in the available

ASTM files. However, it is possible that this phase is due to some organic compound.

In comparing the data available on this sample with that available on the graphite specimens, one has to conclude that the contamination of the sample is due in part to the sample's abrasive nature in the plastic storage bag. However, there exists the possibility that some additional organic contamination from some unidentified source is present.

The data on all of the graphite specimens indicate that they are relatively free of possible contaminants and that the organic offgassing products observed are a direct result of their contact with the plastic storage bags. This problem can be eliminated by either changing to a different type of storage container or vacuum outgassing the materials immediately prior to use.

The data on the ZrO_2 specimen indicate contamination again from the plastic storage bag along with the possibility of contamination resulting from some unknown source since the relative intensity of the offgassing organic products was much greater than that observed for the graphite, and organic offgassing products were observed upon reheating the ZrO_2 samples.

The results of these studies are condensed in Table 1.

Min-K 1301 Initially, two samples of Min-K 1301 were studied by TGA, DTA, and RGA. These samples were furnished by Teledyne Isotopes and had been exposed to their outgassing treatment (Teledyne Isotopes Specification PS0200001) in addition to another outgassing immediately prior to shipment to Mound Laboratory. This additional outgassing process, while not stated in the Teledyne specification, used the same maximum temperature of the controlled outgassing; the time at temperature, however, is not known. Since that study, tests have been conducted on additional samples of Min-K 1301. These samples were obtained from material held at Mound for use in Pioneer shipping containers and from an additional sample furnished by Teledyne Isotopes.

A. Test Sample S/N 1 This sample had been sealed in a plastic bag in an argon atmosphere after being twice outgassed at Teledyne Isotopes prior to shipment to Mound Laboratory. It was used for DTA and TGA studies only. The TGA experiment in air showed less than 1% weight loss upon heating the specimen to 1240°F. The DTA experiment showed a transformation peak at 900°F with no other obvious changes (Table 4A).

B. Test Sample S/N 3 This sample was prepared for shipment to Mound Laboratory exactly as was S/N 1. It was used for TGA, DTA, and RGA experiments.

The TGA experiment in air showed less than 1% weight loss upon heating the specimen to 1240°F. The DTA experiment showed a maximum transformation peak at 680°F with another peak observed at 900°F (Table 4A).

Table 1

SUMMARY OF RGA STUDIES FOR POCO GRAPHITE,
PYROLYTIC GRAPHITE AND ZrO_2

General Test Parameters:^a

<u>Time</u> <u>(hr)</u>	<u>Temperature</u> <u>(°F)</u>	<u>Test Stage</u>
12	72	Vacuum pumping
1	500	Steady state level
2	1000	Steady state level
2	1300	Steady state level
2	1800	Steady state level
16	1300	Steady state level
2	1300 to 72	Cooling
~1 ^b	72 to 800	Heating

- Test Concluded -

^a No programmed heat up rate was observed in heating the sample from one steady state level to the other.

^b Only for the ZrO_2 sample.

1. Unoutgassed POCO Graphite:

Weight loss: 0.01%
Masses detected: 12, 14, 15, 16, 17, 18, 26, 27, 28, 29,
32, 34, 41, 42, 46, 47, 48, 58, 62.

2. Outgassed POCO Graphite:

Weight loss: 0.01%
Masses detected: 12, 14, 15, 16, 25, 26, 27, 28, 29,
32, 34, 41, 42, 43, 44, 46, 62.

3. Unoutgassed Pyrolytic Graphite:

Weight loss: 0.01%
Masses detected: 14, 15, 16, 25, 26, 27, 28, 41, 43, 46, 62.

4. Outgassed Pyrolytic Graphite:

Sample disregarded because of system air leak.

5. Outgassed ZrO_2 (in tantalum foil):

Weight loss: 0.01%
Masses detected: 15, 16, 17, 25, 26, 27, 28, 30, 36, 37,
(initial run) 38, 39, 40, 41, 43, 56, 67, 70, 72, 82,
87, 90, 94, 100, 110.
Masses detected: 15, 16, 25, 27, 28, 40, 41, 43, 82, 90,
(second run) 94, 100.

For the RGA experiment, 1.39124 g of Min-K 1301 were used. After the sample had been weighed, it was placed in a stainless steel tube which was mounted in a line of sight position to the residual gas analyzer. The weighing operation and sample tube mounting were performed in air. The entire air operation, however, was limited to ~5 min. Prior to the insertion of the sample into the sample tube, the tube had been preheated to 1200°F in order to outgas it. Once the sample tube was attached to the RGA, the system was evacuated to a pressure of 10^{-8} torr and was maintained at this pressure for ~18 hr prior to the initiation of the test in order to clean the sample after its 5-min air exposure.

Following the long period of evacuation, the sample tube was heated by a resistance furnace to the previously agreed upon test temperatures. The temperature of the sample tube was monitored by a chromel-alumel thermocouple which was attached to the exterior of the tube in the vicinity of the sample. The sample tube was then heated to 500°F and maintained at this temperature for ~1 hr; the temperature was raised to 950°F and maintained for ~2 hr. After the 2 hr at 950°F, the sample tube temperature was raised to 1250°F and maintained at this temperature for ~2 hr. Following this test period, the temperature was lowered to 950°F and maintained at this temperature for 11 hr after which the test was concluded.

During the test period, random mass scans were made with the RGA; the data from these scans were monitored with a recorder. No mass scans were made during the 11-hr soak at 950°F; however, after this period one final scan was made prior to concluding the test.

After the test, the sample was removed from the sample tube along with the residue powder (collected from the sample tube). This material weighed 1.37008 g, showing a weight loss of 1.5% during test.

A summary of the test data from the RGA study on sample S/N 3 is presented in Table 2, and a plot of the primary detectable masses (intensity at 10^{-8} torr partial pressure as a function of temperature at scan time) is shown in Figure 1 along with a scale of test time. Masses 12, 13, 14, 18, and 28 were the predominant species although the presence of several organic radicals were observed.

Since masses 12, 13, and 14 are on the low end of the mass spectrum scanned and since a broad spectrum peak was observed in the mass 12-13-14 range, it was not possible to assign a relative intensity to any of these mass peaks. However, the appearance of mass 12 suggests the presence of carbon. Mass 18, which was the primary species observed, is water vapor. This species was observed throughout the heating cycle; however, it disappeared after the 11-hr temperature soak at 950°F. Mass 28 was the other major species observed. This mass number would indicate the possible presence of nitrogen, $(C_2H_4)^+$, $(CO)^+$, silicon, or a combination of several of these species. The possibility of the presence of nitrogen is remote since this would indicate the presence of air. The

Table 2
SUMMARY OF RGA STUDY

Min-K 1301 (S/N 3)

Initial Sample Wt.: 1.39124 g
Final Sample Wt.: 1.37008 g
Weight loss: ~1.5%

Test Parameters:

<u>Time</u> <u>(hr)</u>	<u>Temperature</u> <u>(°F)</u>	<u>Test Stage</u>
18.0	72	Vacuum pumping
4.5	72-500	Initial heating
1.0	500	First steady state level
3.0	500-950	Second heating
2.0	950	Steady state level
2.5	950-1200	Third heating
2.0	1200	Steady state level
1.0	1200- 950	Start of cooling
11.0	950	Steady state level

- Test Concluded -

Primary Masses Detected: 12-13-14, 18, 28.

Other Masses Detected: 15, 16, 17, 24, 25, 26, 27, 29, 30,
32, 33, 34, 40, 41, 42, 44.

relative amount of oxygen (mass 32) present during the study is also shown in Figure 1. It can be seen that there is no correlation between the presence of mass 28 and mass 32 during the test that would indicate the presence of air.

After the RGA study, the test sample was submitted for x-ray and emission spectrographic analysis. The results of these analyses, shown in Table 3, indicate that silicon metal was the primary constituent by weight and that some modified form of asbestos was used as the binder material. They also indicate that no extensive change of the metallic element was observed after the RGA study.

Sample M/L 1 This sample consisted of Min-K 1301 that had been furnished by Teledyne Isotopes for use as insulation in Pioneer shipping containers. Prior to its arrival at Mound Laboratory, this material had been processed according to the Teledyne Isotopes specification listed previously for Min-K 1301 processing. When it was received at Mound Laboratory it was machined to its desired dimensions in air, then out-

FIGURE 1 - Mass scan for Min-K sample S/N-3.

Table 3

X-RAY AND EMISSION SPECTROMETER ANALYSIS

Sample S/N 3 As Received:

- Phase 1: Filmly lattice substance; gray particles adhering to substance; X-ray pattern: Si metal.
- Phase 2: Bundles of brownish colored rods;
X-ray pattern: $(\text{Mg,Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
- Phase 3: Pale blue chunks (imbedded in phase 1);
X-ray pattern: none detected.

Emission spectrographic
analysis:

Si - major
Fe - minor (0.3 to 0.005 wt %)
Mn - minor (0.3 to 0.005 wt %)
Mg - minor (0.3 to 0.005 wt %)
Al - minor (0.3 to 0.005 wt %)

Sample S/N 3 - After RGA Study

- Phase 1: Filmly lattice substance; gray particles adhering to substance; X-ray pattern: Si metal
- Phase 2: Bundles of reddish-brown rods;
X-ray pattern: $(\text{Mg,Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
and SiO_2 (α -quartz)
- Phase 3: Pale blue chunks;
X-ray pattern: none detected

Emission spectrographic
analysis:

Si - major
Fe - minor (0.3 to 0.005 wt %)
Mn - minor (0.3 to 0.005 wt %)
Mg - minor (0.3 to 0.005 wt %)
Al - minor (0.3 to 0.005 wt %)

Common Forms of Asbestos:

$\text{Ca}(\text{Mg,Fe})_3(\text{SiO}_3)_4$
 $\text{Al}(\text{Mg,Fe})_2(\text{AlO}_3)_2(\text{SiO}_3)_2$
 $\text{Fe}(\text{Mg,Fe})_2(\text{FeO}_3)_2(\text{SiO}_3)_2$

gassed at 1000°F for 1 hr in a vacuum of 10^{-4} torr. After outgassing, the material was stored in an open beaker in a vacuum box under a vacuum between 10^{-4} to 10^{-5} torr for ~7 weeks. During this 7-week period, the vacuum box was backfilled with argon and opened several times to remove samples, and was re-evacuated after the removal of the samples.

Portions of this material were tested using TGA and RGA measurements. Sample M/L 1-A was used for TGA study. During this study the sample lost 15.8% of its weight by heating to 1112°F in air. Sample M/L 1-B was also studied by TGA. This sample lost 14.4% of its weight by heating to 1112°F in air. Sample M/L 1-C was used in an aborted RGA study. The sample was placed in the RGA apparatus and vacuum outgassed at ambient temperature for ~5 hr prior to initiation of the test. During the initial part of the test only mass 18 was observed being offgassed from the sample. Organic fractions became obvious offgassing products above 150°F. At ~400°F, the relative intensities of the offgassed organic fractions were much greater than that of mass 18. When the sample temperature reached 700°F, a burst of gas was observed. The resulting pressure rise from this gas burst was so great that it activated the innerlock on the high vacuum portion of the RGA system which is activated at a total pressure of ~250 μ m. At that point in the test the RGA had to be throttled down in order to analyze the gas mixture. The throttling down action greatly reduced the sensitivity of the instrument. However, even at this reduced sensitivity organic fractions were observed as offgassing products, particularly masses 15, 27, and 29. No water vapor (mass 18) was observed. At the conclusion of the test the sample was removed and weighed. A weight loss of 12.6% had occurred.

A portion of the sample was then used in a TGA study. The results of this study showed a 4.12% weight loss after heating the sample in air to 1112°F approximately 0.5 hr after it had been removed from the RGA test apparatus.

D. Sample M/L-2 This sample was another piece of Min-K 1301 that had the same previous history as sample M/L-1. A TGA study of this sample showed an approximate weight loss of 11.0% on heating to 1112°F in air.

The TGA analyses of samples M/L-1 and -2 are shown in Table 4-B.

E. Samples M/L-1A, M/L-1C, M/L-2 In addition to the previous tests additional observations were made on these samples. In an attempt to study the effects of the offgassing products on Ta-10 wt % W and T-111, additional tests were performed.

In the first test a portion of M/L-1A that had not been tested by TGA was placed in a glass sidearm of an experimental setup which included metal coupons of T-111 and Ta-10 wt % W suspended in the main tube. The experimental system was a closed-glass system. The experiment consisted of pressurizing the system with ~0.66 atm of helium and heating the sidearm with the Min-K enclosed to ~1050°F and the main sample tube

(T-111 and Ta-10 wt % W) to 1400°F. These conditions were maintained for ~18 hr. After the system cooled, a simple bend test was performed on the T-111 and Ta-10 wt % W samples to test their ductility. In this case the samples were extremely brittle and broke quite easily.

In the second test a portion of M/L-2 was tested in the same manner. Once again the metal samples were embrittled. However, relatively speaking, the samples had a little more ductility than the previous metal samples.

The third test involved the use of a portion of sample M/L-1C after it had been exposed to the RGA test conditions. Once again the T-111 and Ta-10 wt % W samples had lost their ductility. However, the samples could be bent without breaking as the previous samples had, but cracks in the bend area of these specimens could be seen by the unaided eye.

To study the integrity of the system without Min-K 1301 present, specimens of Ta-10 wt % W and T-111 were heated for ~5 hr under the same conditions as stated above without Min-K 1301 present. The samples after test remained ductile and showed no signs of embrittlement, indicating the test system to be air tight.

During all these studies crystalline material deposited on the sidearm that contained the Min-K 1301. In addition, a liquid deposited on the stainless steel tubing of the RGA system after sample M/L-1C was studied. An attempt was made to identify both the crystalline material and the liquid by infrared spectrometry.

The analysis of the liquid (produced in vacuum) which was neutral to pH paper indicated the possible presence of a highly branched aliphatic hydrocarbon. However, this could not definitely be established. The crystals produced in a partial air atmosphere were acidic to pH paper and could possibly be identified by the reaction:

$R - C \begin{smallmatrix} \text{=O} \\ \text{-OH} \end{smallmatrix}$ being a solid. These data are highly speculative without additional studies.

F. Sample I² This sample of Min-K 1301 was furnished by Teledyne Isotopes. It had been outgassed according to the specification PS0200001 and packaged first in a vacuum-sealed plastic bag, then in an argon-filled plastic bag prior to shipment to Mound Laboratory.

When it was received at Mound, the package was transferred to an argon atmosphere glovebox where it was opened and the sample was cut into three pieces.

Sample I²-1 was used for an TGA study, Sample I²-2 for a RGA study, and Sample I²-3 for a TGA study after machining and vacuum outgassing.

Sample I²-1 for the TGA study was removed from the glovebox and a portion was tested immediately. This portion of the sample lost 2.5% of its weight after being heated in air to 1112°F. The remaining part of the sample (I²-1a) was deliberately left in air. Approximately 24 hr later a portion of the air-exposed material was used in a TGA study. This portion lost 3.1% of its weight under the same test conditions. Approximately 48 hr after the first sample had been studied by TGA, another portion of the air-exposed material (I²-1b) was studied by TGA under the same conditions. This portion lost 3.6% of its weight.

All of the samples studied by TGA showed the same general profile, i.e., a quick weight loss by 302°F and no further weight change. This would indicate that the majority of the offgassing product was water vapor.

The portion of sample (I²-2) that was to be used for RGA study was removed from the glovebox and weighed in air, then placed in the sample tube of a quadrupole mass spectrometer sampling system. The air exposure time was limited to ~15 min. The sample was then vacuum outgassed at ambient temperature for approximately 5 hr prior to the initiation of the test.

The sample was then heated to 1150°F and the offgassing products observed. At about 200°F, mass 18 became the predominant offgassing species. Throughout the entire run from this point on, mass 18 was the predominant species although significant quantities of masses 17, 19, and 28 were observed. The other masses observed were essentially those observed previously for sample S/N 3 (see Table 2). The significance of this test was the use of the quadrupole mass spectrometer which has a mass range of 0 to 600 amu. With this instrument it was possible to separate the masses 12, 13, and 14 that were observed previously on sample S/N 3. The information obtained from the quadrupole indicated the presence of masses 12 and 14, with mass 14 being the predominant species.

After the test the sample was again weighed and showed a weight loss of 3.24%. One-half hour later the sample was used in a TGA study; a 1.6% weight loss occurred after heating in air to 1112°F.

The third portion (I²-3) of the sample was machined to size. A sample (I²-3a) was taken from this machining and used for TGA study. It showed 2.1% weight loss after heating in air to 650°C. The balance of the sample (I²-3b) was vacuum outgassed at 1000°F in a vacuum of 10⁻⁴ torr for 1 hr. The sample was then cooled and maintained in the furnace overnight in a vacuum. The following day a portion was used for a TGA study. The sample was maintained in argon until just prior to the TGA study, and it lost 2.5% of its weight during heating to 1112°F in air. The weight loss occurred over a longer time period at higher temperatures than that observed in samples that contained primarily water. This would indicate the presence of some material other than just water.

Table 4

SUMMARY OF TEST RESULTS ON MIN-K 1301

A. DTA Study:

Maximum Temperature: 1240°F
 Sample S/N 1: Transformation Peak - 900°F
 Sample S/N 3: Transformation Peaks- 680°F (max.)
 900°F

B. TGA Study in air:

Sample	Maximum Test Temperature (°F)	Weight Loss (%)	Comments
S/N 1	1240	~ 1	Test conducted immediately upon receipt of the material from Teledyne Isotopes.
S/N 2	1240	~ 1	Same as for Sample S/N 1.
M/L 1-A	1112	15.8	Test conducted immediately upon removal from vacuum storage box.
M/L 1-B	1112	14.4	Same as for Sample M/L 1-A.
M/L 1-C	1112	4.12	Test conducted immediately after the sample had lost 12.6% of its weight during the RGA study.
M/L 2	1112	11.0	Same as for Sample M/L 1-A.
I ² - 1	1112	2.5	Same as for Sample S/N 1.
I ² - 1a	1112	3.1	Test conducted after sample was stored in air for ~24 hr.
I ² - 1b	1112	3.6	Test conducted after air storage for ~48 hr.
I ² - 2	1112	1.6	Test conducted immediately after the sample had lost 3.24% of its weight during the RGA study.
I ² - 3a	1112	2.1	Test conducted after machining in air.
I ² - 3b	1112	2.5	Test conducted after machining in air and vacuum outgassing.

The data on all the Min-K 1301 samples led to the following conclusions:

1. Min-K 1301 was by weight primarily silicon metal.
2. Min-K 1301 had a nonuniform distribution of an asbestos binder.
3. If it is assumed that the presence of organic material caused the transformation peaks observed in the DTA study of samples S/N 1 and S/N 3, and from the results of the DTA study (Table 4A), it is obvious that the organic material was not uniformly distributed in the material.
4. The TGA study of these samples (Table 4B) showed no weight loss greater than 3.6%.
5. The RGA studies did show that the tested samples had residual organic material and water vapor present even after two outgassing processes were performed on some of the Min-K 1301 material (sample S/N 3). The material appeared hygroscopic.
6. Since only small samples of Min-K 1301 were studied by the residual gas analyzer and all indications are that the material is nonuniform, the results of the RGA study cannot be considered representative of large quantities of Min-K 1301. (R. E. Zielinski and D. E. Etter)

ADDITIONAL STUDIES ON Min-K 1301

The I²-3b sample of Min-K 1301 described in the previous section was subjected to another series of tests. The sample was stored in a sealed container with an air atmosphere for ~8 days before it was retested. After this period of time, a TGA run was made on a portion of the sample; it lost 2% of its weight from heating to 1202°F. The sample was vacuum outgassed to a maximum temperature of 1300°F and then another TGA run was made. This time the material lost only 0.2% of its weight.

Twelve days later after being stored in a sealed container with an air atmosphere, a portion of the Min-K 1301 sample lost 1.5% of its weight during heating in air to 1292°F.

The sample was mounted in the quadrupole mass spectrometer sampling system. It was maintained at ambient temperature (72°F) under a vacuum atmosphere for two days before testing began. The testing cycle consisted of various thermal cycles up to a maximum temperature of 1250°F for varying periods of time under a constant vacuum. The offgassing products were monitored at various times during these cycles.

From the initiation of the test cycle through its conclusion, the primary offgassing products were hydrogen and water vapor. The cracking pattern of methane was also observed early in the test period along with an increase in the carbon intensity above the background level of the instrument. During the test the sample lost ~3.2% of its weight. Most of this weight loss was the result of hydrogen and water offgassing.

Since this test was just completed, the data have not yet been fully analyzed and the analysis is currently in progress. The results of this analysis will be reported at a later date. It is interesting to note, however, that immediately after the test, a part of the sample continued to lose weight during a two-part TGA study. Initially the sample lost an additional 0.9% of its weight upon heating it in air to 1382°F. The sample was then cooled to ambient temperature and remained at this temperature for approximately 0.5 hr prior to reheating to 1382°F. Again, the sample lost weight, ~0.85%.

Since this material has been shown to be so nonuniform, the results of this test on one portion of Min-K 1301 cannot be considered as completely representative of Min-K 1301; however, the preliminary results of this test do indicate that hydrogen and water vapor are still present in Min-K 1301 even after extensive outgassing treatments. The exact percentage of water vapor and hydrogen present in Min-K 1301 is solely dependent on the individual samples and the environment they have been exposed to.

Samples of Min-K 1301 which were received from Teledyne Isotopes, Inc., and had no prior outgassing treatment at Teledyne Isotopes were tested by TGA and x-ray analysis. Seven samples of this material were used in TGA studies. Three samples were uniform consisting of both fibrous and powder material. Two samples were composed of primarily fibrous material with some powder adhering to the fibers. The remaining two samples were composed of powdery materials only. The results of these tests are shown in Table 5.

Table 5

TGA STUDY OF MIN-K 1301

<u>Sample Number</u>	<u>Sample Composition</u>	<u>Maximum Test Temperature (°F)</u>	<u>Weight Loss (%)</u>
1	Uniform	1292	6.50
2	Uniform	1292	5.34
3	Powder	1292	0.70
4	Fiber	1292	2.96
5	Uniform	1292	8.47
6	Powder	1292	0.98
7	Fiber	1292	2.30
2A ^a	Uniform	1292	1.67

^a Sample Number 2 rerun after cooling to ambient temperature and reheating one hour later.

Two samples taken from material before TGA and one sample taken from material after TGA were submitted for x-ray analysis. These samples were taken from different areas of the primary sample; however, the results were the same for all samples and are presented in Table 6.

Table 6

X-RAY ANALYSIS OF MIN-K 1301

Powder Material: Si Metal and Trace of $(\text{Fe}, \text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$

Fibers: $(\text{Fe}, \text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$

No SiO_2 observed in either before or after TGA samples.

From these data, it is obvious that the offgassing products are nonuniformly distributed in the bulk material of Min-K 1301 since the weight loss of samples taken from the parent bulk sample are significantly different. It also appears that Min-K 1301 repeatedly loses weight during each thermal cycle to which it is exposed. Whether the weight loss is the result of the liberation of water that the material adsorbs on exposure to air or is due in part to some reaction taking place in the material cannot be determined from this study. However, it is significant to note that all the weight loss in Sample 2 had occurred prior to reaching maximum temperature and yet when the sample was reheated, it again lost weight. The weight loss profiles of two different sample runs are also different. The TGA run from Sample 2 showed that a major portion of the weight loss had occurred before the sample temperature reached 750°F ; that no further weight loss occurred until the sample temperature was 1112°F ; and that then additional weight loss occurred. The weight loss continued until the sample temperature reached 1225°F after which no further weight loss was observed. For Sample 2A, the weight loss was continuous until the sample temperature was approximately 850°F , after which no further weight loss was observed. For Sample 2A, 80% of the weight loss occurred before the sample temperature had reached 300°F , thus indicating the presence of some adsorbed material that is quickly released. For Sample 2, the sample temperature was approximately 700°F before 80% of the weight loss occurred. The data also indicate that more weight loss occurs from heating the fiber material rather than the powder material. This weight loss could be the result of the fibers adsorbing more moisture or a chemical reaction that takes place with the fibers since the weight loss in the fibers occurs over a wider temperature range (ambient to 1184°F).

These tests did indicate that Min-K 1301 repeatedly loses weight on reheating after air exposure. They also showed that the powder material appears to have fewer offgassing products present than the bulk material or the fibers. This would suggest that using just the powder material after outgassing would be much more beneficial to a system that has need of a silica insulating material and is sensitive to offgassing products such as water vapor. (R. E. Zielinski)

THE EFFECTS OF MIN-K 1301 AND HYDROGEN ON PMC-TANTALUM INTERACTION

Recent problems with cracking of tantalum components of the Pioneer heat source capsules has been the cause of considerable concern. The severity of the problem was not anticipated in view of prior compatibility data, and it appears probable that something has caused an accelerated attack of the tantalum components. A gas analysis showed considerable hydrogen and some water present inside the generator. Investigations on Min-K showed that considerable weight loss occurred during outgassing. Most of this weight loss was found to be water, suggesting that the Min-K might be a source of the capsule degradation. The effects of hydrogen or the outgassing products of Min-K 1301 on the tantalum components were, therefore, investigated in a series of tests.

Two types of tests were conducted with the same basic capsule assembly shown in Figure 2. Table 7 summarizes the test matrix. Tests 1-4 were conducted with the configuration shown in Figure 3. Dimensions of each container are summarized in Table 8. The basic capsule assembly was TIG welded into the Haynes 25 outer container in a helium atmosphere. The volume of Min-K was approximately 0.3 in.³. Tests 5 and 6, carried out

FIGURE 2 - Schematic of basic capsule assembly.

Table 7

SUMMARY OF TEST MATRIX

Test Number	PMC Fuel	Ta-10 wt % W Liner	T-111 Strength Member	Pt-20 wt % Rh Clad	Min-K 1301	Hydrogen	Haynes 25 Outer	Test Description
1		X	X	X			X	Blank
2	X	X	X	X			X	Fuel, no Min-K
3		X	X	X	X		X	Min-K, no fuel
4	X	X	X	X	X		X	Fuel, plus Min-K
5	X	X	X	X		X		Hydrogen, plus fuel
6		X	X			X		Hydrogen, no fuel

FIGURE 3 - Schematic of test configuration for tests 1-4.

Table 8

DIMENSIONS OF CONTAINERS USED IN TESTS

Container	Outside Diameter (in.)	Wall Thickness (in.)	Outside Length (in.)	Thickness of End Caps (in.)
Ta-10 wt % W	0.375	0.032	1.010	0.020
T-111	0.500	0.032	1.196	0.020
Pt-20 wt % Rh	0.6	0.020	1.54	0.020
Haynes 25	1	0.125	2.69	0.187

in hydrogen, utilized the basic capsule assembly in a tube furnace in a flowing argon-5% hydrogen mixture. Due to a shortage of material, test 6 contained no platinum-20 wt % rhodium. All tests were conducted at 825°C for 1 week (168 hr).

Prior to use the Min-K 1301 was vacuum outgassed at 704°C. (The material had previously been outgassed at Teledyne Isotopes before shipment.) This material, as received, lost 2% of its weight after heating to 650°C in air. After outgassing to a temperature of 704°C, the material lost an additional 0.2%. This was the smallest weight loss ever observed in a sample of Min-K 1301 tested at Mound.

The fuel was taken from analytical disc PM-96T. Rectangular pieces about 1/4 in. square and 1/2-3/4 in. long were cut with a rotary cutoff wheel utilizing a diamond blade. The fuel specimens were then vacuum outgassed to 1000°C. Following this the fuel samples were brushed with a stainless steel brush to remove a slight surface tarnish.

After removal from the furnace, samples were taken for metallographic analysis using a rotary cutoff wheel with a silicon-carbide wheel. The samples were pressure mounted in epoxy resin, ground on 600 grit paper, and polished on a vibratory polisher for 6 hr with 1 μ m alumina followed by 24 hr with 0.05 μ m alumina. All samples were first examined in the unetched condition. Following this, microhardness measurements were made, and the samples were then etched and re-examined.

Microhardness traverses were made across each capsule. All measurements were made on a Leitz Miniload microhardness tester, and all measurements were made by the same operator so that the possibility of errors from either of these two sources was kept to a minimum.

Since the hydrogen, no-fuel sample had no platinum-rhodium clad, extensive reaction occurred, and the capsule disintegrated as shown in Figure 4. X-ray diffraction showed the presence of tantalum oxide suggesting the presence of either water in the gas or a leak in the furnace. A helium leak check revealed no leaks in the system. The gas analysis was not sensitive to less than 500 ppm H₂O. This test is being re-run with a platinum-rhodium clad around the T-111.

FIGURE 4 - Photograph of test number 6 run in hydrogen with no Pt-20 wt % Rh clad.

Some cracks in the T-111 occurred from the hydrogen, plus-fuel test and a thin reaction layer on the inside edge of the Ta-10 wt % W was found. These are shown in Figures 5 and 6. Electron microprobe analysis of the reaction layer revealed tantalum and oxygen. The rest of the samples appeared similar to each other in both the etched and unetched condition. Typical photomicrographs are shown in Figures 7 and 8. Microhardness traverses are shown in Figures 9-11. It should be noted that Figure 11 is on a much more compressed scale than Figures 9 and 10. Average values for each of the tests are summarized in Table 9. For the hydrogen, plus-fuel test, the averages were calculated without using the highest value in each case.

All the data for the Ta-10 wt% W are consistent and indicate that Min-K 1301 and hydrogen have a pronounced effect on the microhardness of the

FIGURE 5 - Photomicrograph of T-111 from test number 5, PMC in hydrogen. Unetched - 120X.

FIGURE 6 - Photomicrograph of Ta-10 wt % W from test number 5, PMC plus hydrogen, showing thin reaction layer on inside surface. Unetched - 640X.

FIGURE 7 - Photomicrograph of Ta-10 wt % W from test number 4, PMC plus Min-K. $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-HF}$ etch - 120X.

FIGURE 8 - Photomicrograph of T-111 from test number 4, PMC plus Min-K.
HNO₃-H₂SO₄-HF etch - 120X.

Table 9

AVERAGE MICROHARDNESS VALUES^a

<u>Test Description</u>	<u>Ta-10 wt % W</u>	<u>T-111</u>
Blank	272	272
Fuel, no Min-K	297	267
Min-K, no fuel	274	375
Fuel, plus Min-K	331	290
Hydrogen, plus fuel	547	660

^aVickers Hardness Number

FIGURE 9 - Results of microhardness traverses across Ta-10 wt % W capsules from tests 1-4.

FIGURE 10 - Results of microhardness traverses across T-111 capsules from tests 1-4.

FIGURE 11 - Results of microhardness traverses on Ta-10 wt % W and T-111 from hydrogen, plus-fuel tests.

alloy. Although the effect of Min-K 1301 is less than that of hydrogen, this effect is real and greater than that of fuel alone. The fact that the Min-K did not have as great an effect as hydrogen is probably a reflection on the quality of the Min-K.

With T-111, there is one anomaly. The Min-K, no-fuel test appeared harder than the Min-K, plus-fuel sample. The reason for this is unknown. It is apparent that the source of the hardening agent was the inside of the fuel, plus-Min-K sample as evidenced by the hardness increase at the inside surface.

Under the conditions of these tests, it appears that:

- 1) some hardening occurs as a result of reaction with outgassing products of the Min-K and the hydrogen and/or impurities in the hydrogen, and

- 2) hydrogen and Min-K 1301 accelerate the interaction between the PMC fuel form and the Ta-10 wt % W liner. (W. H. Jones, B. R. Kokenge, and J. E. Selle)

DIMENSIONAL STABILITY OF PMC DISCS

PMC discs were removed from three Pioneer capsules as a part of their postmortem analyses. The three capsules thus far defueled at Mound Laboratory were PF-5, PF-6, and PF-3 in that order.

Five discs were removed from PF-5 and gaged without any treatment. After gaging, two of these discs (PM-81B-7 and PM-86B-5) were outgassed at 1000°C according to the normal production outgassing cycle. After outgassing, these two discs were regaged to see whether or not the outgassing had any effect on their dimensions. The results of these measurements are given in Table 10. Table 11 gives the dimensional changes noted for all the PMC discs. In all cases dimensional increases were found on the measured dimensions. In the case of the two PMC discs that were outgassed and regaged (PM-81B-7 and PM-86B-5), no significant dimensional changes were found as a result of the outgassing.

The PMC discs removed from PF-5 had a grayish coloration on the disc surfaces exposed to the Ta-10 wt % W liner. A sample of this gray material was scraped from the surface of PM-81B-7 and submitted for x-ray diffraction analysis. The results of the x-ray analysis showed this material to be Ta_2O_5 .

PM-86B-5, after gaging, outgassing, and regaging, was remachined to a nominal (-5) diameter of 2.070 in. (5.258 cm) from its original diameter of 2.0835 in. (5.2921 cm). In addition, approximately 0.002 in. (0.005 cm) were taken off each face of the disc and nominal 1/32 in. chamfers machined on the disc edges. The disc machined in a normal fashion and its physical appearance after the remachining was similar to that of a

Table 10

PMC DISC DIMENSIONS

<u>Identification</u>	<u>Capsule</u>	<u>Maximum Gaged Dimensions Before Loading (20°C)</u>			<u>Maximum Gaged Dimensions After Removal From Capsule (20°C)</u>			<u>Maximum Gaged Dimensions After Removal From Capsule and Outgassing at 1000°C (20°C)</u>		
		<u>Minor Diam (in.)</u>	<u>Major Diam (in.)</u>	<u>Thickness (in.)</u>	<u>Minor Diam (in.)</u>	<u>Major Diam (in.)</u>	<u>Thickness (in.)</u>	<u>Minor Diam (in.)</u>	<u>Major Diam (in.)</u>	<u>Thickness (in.)</u>
PM-81B-7	PF-5	1.3842	1.6944	0.2185	1.3910	1.7066	0.2219	1.3906	1.7063	0.2235
PM-86B-5	PF-5		2.0705	0.206		2.0850	0.2075		2.0835	0.2075
PM-84T-3	PF-5	1.7494	1.9288	0.2180	1.7572	1.9375	0.2205			
PM-87B-6	PF-5		2.1433	0.2060		2.1691	0.2100			
L-PMC-132-6	PF-5		2.1456	0.2175		2.1705	0.2220			
PM-98T-6	PF-6		2.1433	0.223		2.1490	0.224			
PM-92B-4	PF-6	1.9592	2.050	0.214	1.9643	2.0547	0.214			
PM-62T-6	PF-3		2.1444	0.2125		2.1549	0.2190			
PM-46B-4	PF-3	1.9572	2.048	0.2155	1.9628	2.0553	0.2185			

Table 11

CHANGES IN PMC DISC DIMENSIONS
(Before Capsule Loading vs Removal From Capsule)

<u>Identification</u>	<u>Capsule</u>	<u>Δ Minor Diameter (in.)</u>	<u>Δ Major Diameter (in.)</u>	<u>Δ Thickness (in.)</u>
PM-81B-7	PF-5	+0.0068	+0.0122	+0.0034
PM-86B-5	PF-5		+0.0145	+0.0015
PM-84T-3	PF-5	+0.0078	+0.0087	+0.0025
PM-87B-6	PF-5		+0.0258	+0.0040
L-PMC-132-6	PF-5		+0.0249	+0.0045
PM-98T-6	PF-6		+0.0057	+0.001
PM-92B-4	PF-6	+0.0051	+0.0047	0.000
PM-62T-6	PF-3		+0.0105	+0.0065
PM-46B-4	PF-3	+0.0056	+0.0073	+0.0030

FIGURE 12 - PM-84T-3 shown on the left as removed from PF-5. PM-86B-5 shown on the right after outgassing and remachining.

normal PMC production disc. Figure 12 shows PM-84T-3 on the left as removed from PF-5. PM-86B-5, shown on the right in Figure 12, shows its appearance after outgassing and remachining. (Note the darker surface on PM-84T-3 as compared to the remachined surface of PM-86B-5.) Based on physical appearance and machinability, it appears that at least some discs from opened capsules can be reprocessed. (T. C. Elswick and B. R. Kokenge)

PMC DISC OUTGAS EXPERIMENT

The purpose of this investigation was to identify any gases liberated from a PMC fuel disc at approximately the operating temperature (925°C) of the Pioneer heat source.

The apparatus designed and fabricated for this study is shown in Figure 13. It consisted of a resistance furnace, a stainless-steel vacuum chamber with eight sample ports and a Ta-10 wt % W inner container. The four horizontal ports, located 1 in. (2½ cm) above the hot zone, each contained a gold foil cylinder. The gold foil, which was used to collect the high temperature volatiles, was partially housed in a stainless-steel tube containing a magnetic material. The tubes were positioned so that only the gold foil was exposed to the area above the disc. They were

FIGURE 13 - Apparatus used for the PMC disc outgassing experiment.

removed, as desired, from the exposure area by magnetically withdrawing them into the water-cooled sampling port without disturbing the system atmosphere. The vertical sampling containers, used to collect ambient temperature gases, were constructed of copper and included a valve and a standard taper which was adaptable for mass spectrometric analysis.

A tantalum-sheathed chromel-alumel thermocouple, located in intimate contact with the PMC disc, was employed to monitor the temperature.

A PMC disc, with the properties shown in Table 12, was cut into three equal sections and introduced into the reaction vessel. Tantalum foil was packed around and on top of these fuel sections. The system was evacuated to 2×10^{-4} mm and closed, including all four mass spectrometer sampling containers. The system was allowed to equilibrate overnight (18 hr) and reach a temperature of 470°C . Then the furnace was turned on and the disc temperature was raised to 925°C in 30 min. At this time (t_0), the #1 gold foil was removed, and the #1 mass spectrometer gas container was opened, allowed to equilibrate for 5 min, and then closed. This sampling procedure was repeated for #2, 3, and 4 at 7, 23.5, and

Table 12

PMC FUEL DISC PROPERTIES

Identification	PM-100T
Impurities (ppm)	1303
Molybdenum (wt %)	16.1
Power Density (W/cc)	3.45
Neutron emission rate (n/sec/g-Pu)	1.51×10^4 (before test)
Neutron emission rate (n/sec/g-Pu)	1.51×10^4 (after test)
Coated Particles Feed	34.0 wt % by MoF process
	66.0 wt % by MoCl ₅ process

47.5 hr, respectively. After the final sampling, the system was allowed to cool 1 hr and removed from the furnace. The temperature of the disc was 530°C. At this time, the system was backfilled with argon, and all gold foils and mass spectrometric gas sampling containers were removed for analysis.

The gold foils were sectioned into two pieces, approximately 1/4 in. ($\frac{1}{2}$ cm) square. One section was analyzed by emission spectroscopy, while the other was examined on the electron microprobe for molybdenum, tantalum, chlorine and fluorine.

The microprobe results showed no detection of fluorine or molybdenum on any of the foils. The #1 foil indicated a slight increase over background for chlorine, while the other three were negative. Tantalum was detected in increasing amounts for Samples 2, 3, and 4. No tantalum was detected on Sample #1. Table 13 shows a comparison of chart readings for tantalum as determined by the microprobe.

Table 13

ELECTRON MICROPROBE RESULTS FOR TANTALUM

<u>Sample Number</u>	<u>Chart Reading (Ta) Au-Foil Reference</u>	<u>Chart Reading (Ta) Au-Foil Sample</u>
1	10.5	10.5
2	10.5	20
3	16	33-61 ^a
4	18	45-84 ^a

^aRange from four sampling sights.

Analysis of the gold foils was inconclusive by the neutron activation technique. The gold foil sections examined by the microprobe were also analyzed by emission spectroscopy. The results of this analysis showed

no significant impurity changes except that increasing amounts of tantalum were found on the gold foils the longer they were exposed to the hot zone area above the tantalum foil and PMC disc.

The results of mass spectrometric analysis of the ambient temperature gas samples are shown in Table 14. Both blanks were taken after 1 hr at 925°C and before the PMC disc was introduced.

After this test, a temperature measurement was made in the vicinity of the gold foil collector location by inserting a thermocouple in #1 sample port using a thermocouple vacuum passthrough. The system was evacuated identically to the original test, and the thermocouple located in the disc region read 925°C. At this time the thermocouple located in the area of the gold foil read 405°C.

The major gas species identified from the mass spectrometer was hydrogen. Since the experiment was conducted under vacuum and at elevated temperature, it is apparent that the stainless-steel apparatus outgassed hydrogen. This is apparent from the large amount shown in the blank sample. (D. E. Etter, B. R. Kokenge, C. E. Burgan, J. L. Harrison, and D. L. Hobrock)

Table 14

MASS SPECTROMETRIC ANALYSIS OF AMBIENT TEMPERATURE GAS AT VARIOUS TIMES

<u>Components</u>	<u>Blank #1</u>	<u>Blank #2</u>
2-H2	90.7	86.6
3-HD	0.2	0.2
4-D2	0.0	0.0
4-HT	0.0	0.0
5-DT	0.0	0.0
6-T2	0.0	0.0
3-He	0.0	0.0
4-He	0.0	0.0
18-	0.2	3.2
28-N2 or CO	8.2	9.3
32-O2	0.0	0.0
40-Ar	0.6	0.7
44-CO2	0.1	0.0 T
<u>Components</u>	<u>#1 t₀</u>	<u>#2 T-7 hr</u>
2-H2	1.4	25.7
3-HD	0.0	0.1
4-D2	0.0	0.1
4-HT	0.0	0.0
5-DT	0.0	0.0
6-T2	0.0	0.0
3-He	0.0	0.0
4-He	1.3	41.1
18-	0.6	3.4
28-N2 or CO	60.6	1.6
32-O2	12.7	0.0
40-Ar	23.2	28.0
44-CO2	0.2	0.1
20-HF	~50 ppm	?
<u>Components</u>	<u>#3 T-23.5 hr</u>	<u>#4 T-47.5 hr</u>
2-H2	14.9	10.1
3-HD	0.0 T	0.0 T
4-D2	0.0	0.0 T
4-HT	0.0	0.0
5-DT	0.0	0.0
6-T2	0.0	0.0
3-He	0.0	0.0
4-He	44.2	48.8
18-	5.9	1.6
28-N2 or CO	13.3	18.0
32-O2	1.3	2.4
40-Ar	20.1	18.9
44-CO2	0.1	0.1
20-HF	~100 ppm	~50 ppm

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