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***Investigation of
Supplementary Materials
Used in the Pioneer RTGs and
Capsule Shipping Containers***

R. E. Zielinski and D. E. Etter

January 12, 1972

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ABSTRACT

The program for investigating the materials used in the Pioneer radio-isotopic thermoelectric generator (RTG) and capsule shipping container was initiated when the electrical power output of the RTGs on test at Teledyne Isotopes had decreased to a level below that predicted. The program objective was to determine what material(s), if any, could be released to the internal structure of the RTG and the shipping container from the nonmetallic components of these structures as their temperatures were increased. The materials studied were POCO graphite; pyrolytic graphite; pressed, sintered, and machined ZrO_2 ; and finally Min-K 1301. Residual gas and thermalgravimetric analyses were the primary methods of investigation.

All of the materials were observed to yield organic off-gas products. In addition to the organic materials, the Min-K 1301 also released large quantities of water vapor and hydrogen relative to the other off-gas products.

The tests indicated that even a more rigorous outgassing procedure and controlled atmosphere handling of Min-K 1301 could not eliminate the off-gassing of water vapor and hydrogen. The organic material released from the Min-K 1301 seemed to be a residual that remained after the Min-K was outgassed according to specifications. The organic material released by both the POCO and pyrolytic graphite was probably due to storage in plastic bags and a different storage method is recommended. For the ZrO_2 , however, more organic outgassing products were observed than for 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 or some type of machining lubricant.

INTRODUCTION

At the request of AEC/SNS a study of the various nonmetallic materials used in the Pioneer 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 and 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, ZrO_2 , pyrolytic graphite, and POCO graphite.

In addition to the studies on the generator materials, a study was also performed on samples of Min-K 1301 that had never been outgassed by Teledyne Isotopes or Mound Laboratory and samples that had been first processed by Teledyne Isotopes, then shipped to Mound Laboratory where they were remachined, vacuum reoutgassed, and stored in a vacuum atmosphere for possible later use in the capsule shipping containers.

The primary testing methods used were residual gas and thermalgravimetric analyses; however, 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. This thermal environment was agreed upon prior to testing by both Teledyne Isotopes and AEC/SNS¹. It consisted of the following steps: 1) 1 hour at 500°F; 2) 2 hours at 1000°F; 3) 2 hours at 1300°F; 4) 2 hours at 1800°F; 5) ~16 hours at 1300°F. The samples were maintained in a vacuum environment during the residual gas analyses. There was no programmed heating rate used to heat the sample between the various steps listed above.

¹ Telecon with Mr. Vince Redmond, AEC/SNS, and Mr. Frank Russo, Teledyne Isotopes, June 11, 1971.

One additional test condition was added by MRC. Since the test specimen had to be weighed and mounted on the test equipment in air, it was decided to vacuum outgas the specimens after mounting at ambient temperatures for periods of at least 12 hours prior to testing in order to "clean" the specimens.

The test results are summarized below.

- A. POCO Graphite Both the unoutgassed and 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[(CH₃)⁺] and 27[(C₂H₃)⁺] were observed.

Trace quantities of mass 18[(H₂O)⁺] were observed in the unoutgassed specimen at temperatures up to ~1140°F, while 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[(C₃H₅)⁺-possibly], which is the same mass number observed in the gas samples taken from RTG test generators, S/N 37 and S/N 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 off-gassing 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 a vacuum of 10⁻⁶ torr.

- 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 means of 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-hour 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 observance of the constituents of air on 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 accumulated 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 hours nothing was observed off-gassing from the sample.

There were fewer organic structures observed as off-gassing products from the pyrolytic sample than had been observed from the POCO samples. The relative intensities of the off-gas products observed from the pyrolytic sample were essentially the same as those for the outgassed POCO sample. This tends to support the conclusion that the organics 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 previously referenced, was tested. The same thermal cycle and prior vacuum outgassing were used on this sample as had been stated above for use on the graphite specimens. However, as per the request of Teledyne Isotopes¹ this sample was wrapped in 5-mil tantalum foil.

While again this sample lost only 0.01 wt %, the off-gassing products were of a slightly different nature than those that had been observed during the testing of the graphite. The sample and the tantalum foil were discolored after the test. The low mass organics of the methane, ethane fractions 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-hour thermal soak at 1300°F. The sample was cooled to ambient and reheated to 800°F. During this short term heatup (~1 hour), organic off-gassing species were again observed at an intensity just above instrument background.

Since the sample and the tantalum foil were discolored they were submitted for further analyses. The discolored tantalum foil was

¹ Telecon with Mr. Vince Redmond, AEC/SNS, and Mr. Frank Russo, Teledyne Isotopes, June 11, 1971.

submitted for emission spectrometric analysis and the ZrO_2 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 ZrO_2 sample (this was not discolored). The results of this analysis indicated the presence of two phases of ZrO_2 - monoclinic and either tetragonal or cubic. The analysis of the discolored portion indicated the presence of two phases of ZrO_2 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.

Summary and Conclusion: POCO Graphite, Pyrolytic Graphite, and ZrO_2 . The data on all of the graphite specimens indicate that they are relatively free of possible contaminants and that the organic off-gassing 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 off-gassing organic products was much greater than that observed for the graphite, and organic off-gassing products were observed upon reheating the ZrO_2 sample. The results of these studies are condensed in Table 1.

Min-K 1301 Since the major portion of this study involved Min-K 1301, numerous samples of the material were tested. To avoid confusion in the text of the report, therefore, these samples are identified in Table 2 by sample number and history before the test. The test results are briefly summarized in Table 3.

Table 1

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

General Test Parameter:*

<u>Time (hr)</u>	<u>Temperature (°F)</u>	<u>Test Stage</u>
12	72	Vacuum pump down
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	Cool down
**~1	72 to 800	Heat up

- Test Concluded -

*No programmed heating rate was observed in heating the sample from one steady state level to the other.

**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, 38, 39, 40, 41, 43, 56, 67, 70, 72, 82, 87, 90, 94, 100, 110.
 (initial run)
 Masses detected: 15, 16, 25, 27, 28, 40, 41, 43, 82, 90, 94, 100.
 (second run)

Table 2

MIN-K 1301 TEST SAMPLES AND HISTORY

Sample Number	History
1A	Sample furnished by Teledyne Isotopes after being 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 used the same maximum temperature of the specification outgassing; however, time at temperature is not known. Sample was sealed in a plastic bag in an argon atmosphere prior to shipment to Mound Laboratory.
1B	As stated above for Sample 1A.
3A	As stated above for Sample 1A.
3B	As stated above for Sample 1A.
3C	As stated above for Sample 1A.
3CA	As stated above for Sample 3C.
3CAFT	As stated above for Sample 3C plus the testing period to which sample 3C was exposed.
M/L 1A	Sample consisted of Min-K 1301 that had been furnished by Teledyne Isotopes for use as insulation in Pioneer shipping containers. The material was outgassed by Teledyne Isotopes according to PS0200001 prior to shipment to Mound Laboratory. After receipt of the material at Mound Laboratory, it was machined to its desired dimensions in air, then outgassed at 1000°F for 1 hour in a vacuum atmosphere of 10^{-4} torr. After outgassing, the material was stored in an open beaker in a vacuum box under a vacuum in the range of 10^{-4} to 10^{-5} torr for a period of ~7 weeks. During this time the vacuum box was backfilled with argon and opened several times to remove material. The box was re-evacuated after the removal of the samples.
M/L 1B	As stated above for Sample M/L 1A.
M/L 1C	As stated above for Sample M/L 1A.
M/L 1D	As stated above for Sample M/L 1A.
M/L 1E	As stated above for Sample M/L 1A.
M/L 1F	As stated above for Sample M/L 1A.
M/L 1C AT	Portion of sample M/L 1C after RGA test.
M/L 1C AT-1	Portion of sample M/L 1C after RGA test.

Table 2 (continued)

Sample Number	History
I ² 1A	Min-K 1301 furnished by Teledyne Isotopes after being subjected to their outgassing process (PS0200001). This material was packaged in a vacuum-sealed plastic bag then in an argon filled plastic bag prior to shipment to Mound Laboratory. At Mound the material was stored in an argon atmosphere glovebox prior to use.
I ² 1B	As stated above for Sample I ² 1A plus 24-hour air exposure prior to testing.
I ² 1C	As stated above for Sample I ² 1A plus 48-hour air exposure prior to testing.
I ² 1D	As stated above for Sample I ² 1A.
I ² 1D-AT	As stated above for Sample I ² 1D plus the testing cycle of I ² 1D.
I ² 1E	As stated above for Sample I ² 1A plus an additional air exposure time of 24 hours during which time some machining of the sample was performed.
I ² 1F	As stated above for Sample I ² 1E plus an additional vacuum outgassing at 1000°F in a vacuum of 10 ⁻⁴ torr for 1 hour after the machining operation. The sample was maintained in a vacuum atmosphere for ~12 hours after outgassing; then it was stored in an argon atmosphere until the initiation of testing.
N-1 through N-7	Min-K 1301 furnished by Teledyne Isotopes. This material was never subjected to an outgassing process at either Teledyne Isotopes or Mound Laboratory and was stored in air until the initiation of the test period.
N-2A	Same as N-1 through N-7.
Q-1	As stated above for Sample I ² 1F plus an additional 8-day air storage period prior to test.
Q-2	As stated above for Sample Q-1 plus an additional vacuum outgassing to 1300°F prior to test.
Q-3	As stated above for Sample Q-2 plus an additional 12-day air storage period prior to test.
Q-4	As stated above for Sample Q-3.
Q-4 A-1	As stated above for Sample Q-4 plus the test cycle to which Q-4 was exposed.
Q-4 A-2	As stated above for Sample Q-4 A-1 plus the test cycle to which Q-4 A-1 was exposed.

Table 3
TEST RESULTS FOR MIN-K 1301 SAMPLES

Sample Number	Method of Testing	Test Conditions	Results
1A	Thermo-Gravimetric Analysis (TGA)	Rapid heatup in air to 1240°F	~1% weight loss
1B	Differential Thermal Analysis (DTA)	Rapid heatup in air to 1240°F	Transformation peak observed at 900°F.
3A	TGA	Rapid heatup in air to 1240°F	~1% weight loss
3B	DTA	Rapid heatup in air to 1240°F	Maximum transformation peak at 680°F, secondary peak at 900°F.
3C	Residual Gas Analysis (RGA)	Maximum temperature 1250°F (see text for further details)	1.5% weight loss, primary off-gassing products H ₂ O, C ₂ H ₄ , CH ₄ . (See Table 4 and text for further details)
3C A	X-ray and Emission Spec.	-----	See Table 5 for results.
3C AFT	X-ray and Emission Spec.	-----	See Table 5 for results.
M/L 1A	TGA	Rapid heatup in air to 1112°F	15.8% weight loss
M/L 1B	TGA	Rapid heatup in air to 1112°F	14.4% weight loss
M/L 1C	RGA	Maximum temperature 700°F (see text for details)	12.6% weight loss, see text for further details).
M/L 1C	TGA	Rapid heatup in air to 1112°F ~0.5 hour after conclusion of RGA study on M/L 1C.	4.12% weight loss
M/L 1D	TGA	Rapid heatup in air to 1112°F	11.0% weight loss
M/L 1E, Bend Studies M/L 1F, M/L 1C AT-2		See text.	See text.

Table 3 (continued)

Sample Number	Method of Testing	Test Conditions	Results
I ² 1A	TGA	Rapid heatup in air to 1112°F	2.5% weight loss
I ² 1B	TGA	Rapid heatup in air to 1112°F	3.1% weight loss
I ² 1C	TGA	Rapid heatup in air to 1112°F	3.6% weight loss
I ² 1D	RGA	Maximum temperature 1150°F (see text for further details)	3.24% weight loss, maximum off-gassing species H ₂ O and CH ₄ (see text for further details).
I ² 1D-AT	TGA	Rapid heatup in air to 1112°F	1.6% weight loss
I ² 1E	TGA	Rapid heatup in air to 1200°F	2.1% weight loss
I ² 1F	TGA	Rapid heatup in air to 1112°F	2.5% weight loss
N-1	TGA	Rapid heatup in air to 1292°F	6.5% weight loss
N-2	TGA	Same as for N-1	5.34% weight loss
N-3	TGA	Same as for N-1 (powder material from Min-K 1301)	0.7% weight loss
N-4	TGA	Same as for N-1 (fibrous material from Min-K 1301)	2.96% weight loss
N-5	TGA	Same as for N-1	8.47% weight loss
N-6	TGA	Same as for N-1 (powder material from Min-K 1301)	0.98% weight loss
N-7	TGA	Same as for N-1 (fibrous material from Min-K 1301)	2.30% weight loss
N-2A	TGA	Same as for N-1	1.67% weight loss
N-1 before TGA	X-ray	-----	See Table 6 for results
N-5 before TGA	X-ray	-----	See Table 6 for results
N-1 after TGA	X-ray	-----	See Table 6 for results
Q-1	TGA	Rapid heatup in air to 1202°F	2% weight loss
Q-2	TGA	Rapid heatup in air to 1202°F	0.2% weight loss

Table 3 (continued)

Sample Number	Method of Testing	Test Conditions	Results
Q-3	TGA	Rapid heatup in air to 1292°F	1.5% weight loss
Q-4	RGA	Maximum temperature 1250°F (see text for further details)	3.2% weight loss H ₂ and H ₂ O were the primary outgassing products. (see text for further details)
Q-4 A1	TGA	Rapid heatup in air to 1382°F	0.9% weight loss
Q-4 A1-2	TGA	Rapid heatup in air to 1382°F.	0.85% weight loss

Additional Information on Min-K Samples

Sample S/N 3C For the RGA experiment 1.39124 grams of Min-K 1301, sample S/N 3C 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 operation, however, was limited to ~5 minutes. 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 a period of ~18 hours prior to the initiation of the test. This was done in order to "clean" the sample after its 5-minute air exposure.

Following the long period of evacuation, the sample tube was heated by means of a resistance furnace to the previously agreed upon² test temperatures. The temperature of the sample tube was monitored by means of 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 hour; the temperature was raised to 950°F and maintained for ~2 hours. After the period of time at 950°F, the sample tube temperature was raised to 1250°F and maintained at this temperature for ~2 hours. Following this test period, the temperature was lowered to 950°F and maintained at this point for 11 hours 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 hours 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 grams, showing a weight loss of 1.5% during test.

A summary of the test data from the RGA study on sample S/N 3C is presented in Table 4 and a plot of the primary detectable masses (intensity at 10^{-8} torr partial pressure vs 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 was observed. Since masses 12, 13, and 14 were 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-hour temperature

² Telecon with Frank Russo, Teledyne Isotopes, May 18, 1971.

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

Table 4

SUMMARY OF RGA STUDY ON SAMPLE S/N 3C

Min-K 1301 (S/N 3C)

Initial Sample Weight: 1.39124 grams
 Final Sample Weight: 1.37008 grams
 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 pump down
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

soak at 950°F. Mass 28 was the other major species observed. This mass number would indicate the possible presence of N_2^+ , $(C_2H_4)^+$, $(CO)^+$, Si^+ , or a combination of several of these species. The possibility of the presence of N_2 is remote since this would indicate the presence of air. It can be seen by observing the relative amount of O_2 present during the study (the plot of mass 32 is also shown in Figure 1), 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, sample S/N 3C A was submitted for x-ray and emission spectrometer analysis. The results of these analyses are shown in Table 5 along with the results from sample S/N 3A which were taken before the RGA study. These results 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.

Samples M/L 1A-B-C These samples consisted of Min-K 1301 that had been furnished by Teledyne Isotopes for use as insulation in Pioneer shipping containers. Prior to their 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 outgassed at 1000°F for 1 hour in a vacuum atmosphere of 10^{-4} torr. After outgassing the material was stored in an open beaker in a vacuum box under a vacuum in the range of 10^{-4} to 10^{-5} torr for a period of ~7 weeks. During this 7-week period the vacuum box was backfilled with argon and opened several times to remove samples and reevacuated after the removal of the samples. Because of the long storage time this material would have been re-outgassed prior to actual use; however, the decision was made to test this material to determine the effects of long-term storage on "clean" Min-K.

Portions of this material were tested using TGA and RGA measurements. Sample M/L 1A was used for TGA study. During this study the sample lost 15.8% of its weight by heating it to 1112°F in air. Sample M/L 1B was also studied by TGA. This sample lost 14.4% of its weight by heating it to 1112°F in air. Sample M/L 1C was used in an abortive RGA study. The sample was placed in the RGA apparatus and vacuum outgassed at ambient temperature for ~5 hours prior to initiation of the test. During the initial part of the test only mass 18 was observed as being off-gassed from the sample. Organic fractions became obvious off-gassing products above 150°F. At ~400°F, the relative intensities of the off-gassed 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 inner-lock on the high vacuum portion of the RGA system which is activated at a total pressure of ~250 microns. 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; however, organic fractions were observed as off-gassing products,

Table 5

X-RAY AND EMISSION SPECTROMETER ANALYSES
OF SAMPLES S/N 3C A AND S/N 3C AFT

Sample S/N 3C A

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: $(\text{Mg,Fe})_7 \text{Si}_3 \text{O}_{22} (\text{OH})_2$.

Phase 3: Pale blue chunks (imbedded in Phase 1) - x-ray pattern: none detected.

Emission spec analysis: Si - major
Fe - minor (0.3 to .005 wt %)
Mn - minor (0.3 to .005 wt %)
Mg - minor (0.3 to .005 wt %)
Al - minor (0.3 to .005 wt %)

Sample S/N 3C AFT

Phase 1: Filmly lattice substance - gray particles adhering to substance - x-ray pattern: Si metal
 SiO_2 - trace quantity

Phase 2: Bundles of reddish-brown rods - x-ray pattern: $(\text{Mg,Fe})_7 \text{Si}_3 \text{O}_{22} (\text{OH})_2$ and SiO_2 (α -quartz)

Phase 3: Pale blue chunks - x-ray pattern: none detected.

Emission spec analysis: Si - major
Fe - minor (0.3 to .005 wt %)
Mn - minor (0.3 to .005 wt %)
Mg - minor (0.3 to .005 wt %)
Al - minor (0.3 to .005 wt %)

Common Forms of Asbestos: $\text{Ca}(\text{Mg,Fe})_3 (\text{SiO}_3)_4$
 $\text{Al}_2 (\text{Mg,Fe})_2 (\text{AlO}_3)_2 (\text{SiO}_3)_2$
 $\text{Fe}(\text{Mg,Fe})_2 (\text{FeO}_3)_2 (\text{SiO}_3)_2$

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% was observed.

A portion of the sample (M/L 1C AT-1) 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 ~0.5 hour after it had been removed from the RGA test apparatus.

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

Samples M/L 1E, M/L 1F, M/L 1C AT-2 In addition to the tests mentioned above additional observations were made on these samples during an attempt to study the effects of the off-gassing products on Ta-10W and T-111.

In the first test a portion of M/L 1E 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-10W suspended in the main tube. The experimental system was a closed-glass system. The experiment consisted of pressurizing the system with ~0.66 atmosphere of helium and heating the sidearm with the Min-K enclosed to ~1050°F and the main sample tube (T-111 and Ta-10W) to 1400°F. These conditions were maintained for ~18 hours. After cooling the system a simple bend test was performed on the T-111 and Ta-10W 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 1F was tested in the same manner as stated above. Once again the metal samples were embrittled. However, relatively speaking, the samples had a little more ductility than the previous samples.

The third test involved the use of a portion (M/L 1C AT-2) of sample M/L 1C after it had been exposed to the RGA test conditions. Once again the T-111 and Ta-10W samples had lost their ductility. However, the sample 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-10W and T-111 were heated for ~5 hours 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 deposits were observed on the side-arm that contained the Min-K 1301. In addition, a liquid was 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 means of 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:

These data are highly speculative without additional studies.

In a previous study³ performed by Martin Nuclear on raw Min-K 1301, a tar-like condensate was observed on pyrex sample tubes. This material was "an amber colored tar-like substance" which was assumed to be binder residue or reaction product with white crystalline material dispersed throughout the tar-like layer. The crystalline material was postulated to be hexamethylenetetramine. In the present study no evidence of this material was found.

Sample I² 1D This sample 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 minutes. The sample was then vacuum outgassed at ambient temperature for ~5 hours prior to the initiation of the test.

The sample was then heated to 1150°F and the off-gassing products observed. At about 200°F, mass 18 became the predominant off-gassing species. Throughout the entire run from this point on mass 18 was the predominant species although significant quantities of masses 2, 17, 19, and 28 were observed. The other masses observed were essentially those as observed previously for sample S/N 3C (see Table 4). The significance of this test was the use of the quadrupole mass spectrometer which has a mass range of 0 to 600 amu. Using this instrument it was possible to separate the masses 12, 13, and 14 that were observed previously on sample S/N 3C. 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 sample I² 1D-AT was used in a TGA study and showed a 1.6% weight loss after heating in air to 1112°F.

³ "Investigation of Gas Pressure Buildup in Thermoelectric SNAP Generators," MND-3143-1, January 1964.

A portion of the I² sample group was sent to the Machine Shop for machining. Sample I² 1E was taken from this after 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 1F) was sent for vacuum outgassing at 1000°F in a vacuum of 10⁻⁴ torr for one hour. The sample was then cooled and maintained in the furnace overnight in a vacuum condition. 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.

Sample Group Q This group of samples came from the parent sample designated I² 1F. Specifically this group of samples had the same history as sample I² 1F prior to testing plus an additional 8-day storage period in a sealed container with an air atmosphere.

Sample Q-1 was tested by TGA immediately following the 8-day storage period. This sample lost 2% of its weight during heatup to 1202°F in air.

The remaining material in the Q group of samples was further exposed to a vacuum outgassing at a maximum temperature of 1300°F. Immediately after this outgassing a portion of sample Q-2 was tested by TGA. It lost only 0.2% of its weight during heatup in air to 1202°F. The remaining Q-2 sample was then used in a study entitled "The Effects of Min-K 1301 and Hydrogen on PMC-Tantalum Interaction". This study⁴ was performed at Mound Laboratory. The summary of the test report states: "Under the conditions of these tests it appears that hydrogen and Min-K 1301 accelerate the interaction between the PMC fuel form and the Ta-10W liner". The test conditions were similar to those present in a Pioneer RTG and the Min-K 1301 used in the test showed the smallest weight loss observed in a sample tested by means of TGA at Mound Laboratory.

Twelve days after the vacuum outgassing, during which time the remaining portion of the Q group of samples was stored in a sealed container with an air atmosphere, sample Q-3 was tested by TGA. The sample lost 1.5% of its weight during heatup in air to 1292°F.

At the same time as sample Q-3 was being tested, sample Q-4 was being mounted in the quadruple mass spectrometer sampling system. Sample Q-4 was maintained at ambient temperature (72°F) under a vacuum atmosphere for a period of 48 hours prior to the initiation of the test. 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 off-gassing products were monitored at various times during these cycles. The test period was 31 days.

From the initiation of the test cycle through its conclusion, the primary off-gassing products were hydrogen and water vapor. The cracking

⁴"The Effects of Min-K 1301 and Hydrogen on PMC-Tantalum Interaction," submitted by W. H. Jones, B. R. Kokenge, and J. E. Selle.

pattern of CH_4 was also observed early in the test period along with an increase in the carbon intensity above the background level of the instrument. The test was concluded when the intensity levels of the off-gassing products were reduced to those of the background levels of the instrument. During the test the sample lost ~3.2% of its weight. Most of this weight loss was the result of the hydrogen and water off-gassing.

An analysis of the test data showed that very little organic material off-gassed from this sample as compared to previously tested samples.

This test was also different from the previous RGA studies of Min-K 1301 in that it was long-term and it involved several thermal cycles from ambient to peak temperature. The data indicate that Min-K 1301 tested in this manner behaved differently than during short-term testing. In this particular test approximately twice as much weight loss occurred compared to a sample (Q-3) with the same pre-test history tested on a short-term basis. Also in this test the thermal cycling had an effect on the release of the off-gassing products from the Min-K 1301. Early in the test, copious quantities of H_2 and H_2O off-gassed from the sample when the test temperature reached 150°F . This maximum intensity off-gassing continued throughout the thermal cycle until the sample again reached ambient temperature, when the intensity levels returned to the background levels. This phenomenon continued for ~5 days. After this period of time, the same phenomena occurred when the sample temperature reached 475°F ; this continued for 7 days. After 7 days a sample temperature of 810°F was necessary to initiate this occurrence. This temperature was valid for 12 days after which period a temperature of 1100°F was necessary to initiate maximum off-gassing intensity; this continued for a 4 day period. After this period of time, it was necessary for a sample temperature of 1250°F for maximum off-gassing to occur. This continued for a 24-hour period after which the intensity levels of the off-gassing product dropped to slightly above background at all temperatures.

The data indicate that the gas release from Min-K 1301 is a time-temperature phenomena. The gas release may be a product of desorption of physisorbed and chemisorbed gases; these gases once desorbed from the internal structure of the porous Min-K 1301 diffuse through the material and are then released. Desorption of physisorbed gases would account for the quick weight loss that occurred in most of the TGA studies where the samples were quickly heated to peak temperature (<8 minutes) in air then immediately cooled. Chemisorbed gases on the other hand require high temperatures and vacuum conditions to be desorbed. It is quite possible that both types of adsorbed gases exist in Min-K 1301 since this study showed long times at high temperatures in vacuum were required to "clean" this material.

The word "clean" is used in a relative sense in the above paragraph since sample Q-4 A1 was removed from sample Q-4 immediately after the RGA study and used for a TGA study. Approximately 0.5 hour after being

removed from the vacuum environment of the quadrupole mass spectrometer, sample Q-4 A1 lost 0.9% of its weight upon heating it in air to 1382°F. The sample was then cooled to ambient temperature and maintained at this temperature for ~0.5 hour prior to reheating to 1382°F in air. Again the sample now designated Q-4 A1-2 lost weight - 0.85%. Both of these weight losses were probably the result of the desorption of atmospheric moisture adsorbed by the material during its 0.5-hour air exposure. These results indicate that no matter how "clean" Min-K 1301 is, it can be quickly re-contaminated on short term exposures to air.

Sample Group N This group of samples came from material shipped to Mound Laboratory from Teledyne Isotopes, Inc. This material had no prior outgassing treatment at Teledyne Isotopes and was tested at Mound by means of TGA and x-ray analysis.

Seven samples of this material were used as TGA samples. Samples N-1, N-2, and N-5 were chunks of the parent material. Samples N-4 and N-7 were composed of primarily fibrous material with some powder adhering to the fibers. The remaining samples N-3 and N-6 were composed of just the powdery material. The results of these tests are shown in Table 3.

Two samples of before-TGA material and one sample of after-TGA material were submitted for x-ray analyses. The results from all three samples were the same and are presented in Table 6.

SUMMARY AND CONCLUSION

Min-K 1301 The data on all of the Min-K 1301 specimens indicate that the material is primarily Si metal by weight with a form of asbestos fiber used as a binding material. The asbestos binder has a very non-uniform distribution in the material. Organic material present in Min-K 1301 is probably a residual amount left over from the production process. The RGA studies indicate that the organic materials can be successfully outgassed from Min-K 1301.

The data obtained from the tests performed on the M/L samples are difficult to explain. This sample group had an abnormal amount of contamination - even more than the N sample group which was never preconditioned. One can only speculate as to the cause of this contamination. Improper outgassing or the long storage period could have been the source of this contamination. In any case, sample group M/L material was not similar to any other sample group tested. The data gathered from the studies performed on M/L samples are not entirely useless, however. These data show that Min-K 1301 can retain large amounts of organic materials which are released during temperature excursions. These organic materials, in turn, can result in marked changes in the tensile properties of refractory metal alloys at elevated temperatures.

Up until the RGA study on sample Q-4, the TGA studies were thought to be good indicators of the condition of Min-K 1301 samples. The test on sample Q-4 dispelled that idea. The present series of TGA studies at

Table 6

X-RAY ANALYSES OF GROUP N SAMPLES OF MIN-K 1301

Samples: N-1 before TGA

N-5 before TGA

N-1 after TGA

Results: Powder Material:

Si metal and trace of $(\text{Fe,Mg})_7 \text{Si}_8 \text{O}_{22} (\text{OH})_2$

Fibers:

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

No SiO_2 observed in either before or after TGA samples.

most gave a relative indication of the presence of physisorbed water and organic materials. Physisorbed water would be desorbed at the lower temperatures of the TGA run and the organic materials at the higher temperatures. Heating for short time periods in air as has been done in the TGA series cannot indicate the presence of chemisorbed gases or diffusion processes.

However, the TGA studies were valuable for tests of the sample-N group where the parent material was taken apart and the powder material ground and run as independent samples in contrast to the fibrous material. The data from these tests indicate that more weight loss occurs from heating the fibrous material rather than the powder material. This is to be expected since the powder material is primarily Si metal. The use of just the loose powder material after outgassing would be much more beneficial to a system that has need of a Si metal insulating material and is sensitive to off-gassing products from bulk Min-K 1301.

The RGA studies did indicate that in addition to organic materials, large quantities of H_2 and H_2O off-gas from Min-K 1301 (even from samples of the material that have been thoroughly out-gassed and re-out-gassed - e.g., sample Q-4). These studies show that the "cleaning up" of Min-K 1301 seems to be an impossible task which even if accomplished can be negated by exposing the material to air or the sources of moisture.

E. E. Hardy
Monsanto Research Corp.
1515 Nicholas Road
Dayton, Ohio 45418

D. W. King
U. S. Atomic Energy Commission
P. O. Box 5400
Albuquerque, New Mexico 87115

S. A. Upson
U. S. Atomic Energy Commission
P. O. Box 5400
Albuquerque, New Mexico 87115

L. E. Fellenz
Monsanto Research Corp.
1101 - 17th Street N.W.
Washington, D. C. 20036

Jules Simmons
U. S. Atomic Energy Commission
Div. of Reactor Dev. Hdq.
Washington, D. C. 20545

G. L. Rogers
U. S. Atomic Energy Commission
Division of Research
Washington, D. C. 20545

W. J. Haubach, Jr.
U. S. Atomic Energy Commission
Division of Research
Washington, D. C. 20545

V. V. Berniklau
U. S. Atomic Energy Commission
P. O. Box 5400
Albuquerque, New Mexico 87115

Dr. Charles F. Curtiss
University of Wisconsin
Theoretical Chemistry Institute
1112 West Johnson Street
Madison, Wisconsin 53715

Dr. David White
Chairman and Professor
Department of Chemistry
University of Pennsylvania
34th and Spruce Streets
Philadelphia, Pennsylvania 19104

Dr. Gordon W. Powell
Ohio State University
Department of Metallurgical
Engineering
116 West 19th Avenue
Columbus, Ohio 43210

Dr. Warren F. Stubbins
Physics Department
University of Cincinnati
Cincinnati, Ohio 45221

Miss Margaret E. Madden
Monsanto Research Corp.
Technical Information Center
Central Library
800 North Lindbergh Blvd.
St. Louis, Missouri 63141

Howard W. Mattson
Monsanto Research Corp.
Public Relations
800 N. Lindbergh Blvd.
St. Louis, Missouri 63141