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INVESTIGATION OF GAS PRESSURE
BUILDUP IN THERMOELECTRIC
SNAP GENERATORS

MND-3143-1

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FOREWORD

This report summarizes the procedures, tests and results of an investigation of gas pressure buildup in thermoelectric generator materials. It includes a description of the gas pressure increase phenomenon and its effects on thermoelectric generator performance. The program was conducted to determine the cause of internal pressure increase, and to recommend procedures for controlling outgassing of thermoelectric generator materials.

The effort was performed under Contract AT(30-1)-3143 for the U.S. Atomic Energy Commission by the Martin Company.

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SUMMARY

The program for investigating gas pressure buildup in thermoelectric generators was initiated in February 1963 and continued through December 1963. The program objectives were:

- (1) Determine the source(s) of internal gas pressure increase in SNAP thermoelectric generators.
- (2) Establish methods of alleviating or eliminating the condition.
- (3) Conduct a proof-of-principle test on an electrically heated - 60-watt thermoelectric SNAP generator* to determine the effectiveness of the procedures developed to control or eliminate the condition.

The gas pressure increase in the generators that were initially filled with dry inert gas results from:

- (1) Decomposition of the phenol-formaldehyde resin that is used as a binder in the Min-K 1301 thermal insulation.
- (2) Desorption of atmospheric gases and water vapor that adsorb on the surface of the insulation.

The degree of gas release in both cases was determined to be temperature and pressure dependent.

The recommended procedure to control gas pressure buildup for all future generators is:

- (1) Precondition the Min-K by burning off the phenolic resin binder.
- (2) Vacuum outgas the insulation at a temperature above its maximum operating temperature.
- (3) Install a gas getter** (zirconium) to absorb any gases that may be released during subsequent generator operation.

*Previously constructed under Contract AT(30-3)-217.

**Metallics that react with certain gases at elevated temperature.

The complete recommended procedure to control this pressure buildup could not be employed in the 60-watt thermoelectric SNAP generator test since the generator had been previously constructed and assembled using Min-K that had not been preconditioned by outgassing. Therefore, a modified outgassing procedure was established for the generator when the test was initiated. The procedure, in essence, specified that the generator be maintained on continuous evacuation while the thermoelement hot junction temperature was slowly increased to $\sim 525^{\circ}\text{F}$, and that the generator be subjected to frequent rapid evacuations and gas changes as the temperature was increased to 960°F^* . Two thousand, one hundred forty-three grams of zirconium sponge were inserted in the hottest region of the generator to react with getterable gases that remained after the outgassing and evacuation procedure.

The 60-watt electrically heated SNAP generator was then maintained on a stability test for two months. The generator internal gas fill pressure remained essentially constant throughout the period, demonstrating that the recommended control procedure will alleviate the internal gas pressure buildup condition.

*Lead telluride thermoelements begin to sublime in a vacuum at elevated temperatures in the 950° to 1000°F range.

I. INTRODUCTION

The program for investigating gas pressure buildup in thermo-electric generators was initiated to determine what caused the condition and to find a solution to the internal gas pressure increase. The gradual increase in generator gas fill pressure appeared to have a deleterious effect on the overall generator performance due to an increasing extraneous heat loss.

The problem was first recognized when the SNAP-7A* thermo-electric generator was returned from the U. S. Coast Guard Station, Curtis Bay, Maryland, to determine what was causing the gradual power output reduction. The generator had originally been delivered to the U. S. Coast Guard by Martin Nuclear Division on December 15, 1961. By early June of 1962, the power output had deteriorated approximately 25% to the point where system operation was marginal. The generator was removed from the Coast Guard light buoy and returned to Martin on June 20, 1963.

During the diagnostic investigation of the generator, it was discovered that the internal gas fill pressure (100% helium at time of delivery to the Coast Guard) had increased from 3 psig to ~17 psig. A gas sample was then analyzed by the gas chromatograph technique**. The analysis showed that the original 100% helium gas fill had been diluted with large quantities of hydrogen and lesser amounts of nitrogen, methane, ethane, carbon monoxide, oxygen, carbon dioxide and propane in descending order. An investigation of other SNAP 7 generators revealed the fact that other generators were also exhibiting an increase in internal pressure with time.

A study proposal was then submitted to the U. S. Atomic Energy Commission recommending an investigation of the gas pressure buildup phenomenon. The program was initiated in February 1963.

*Experimental power source for Coast Guard light buoy.

**This technique does not detect water vapor.

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II. GAS PRESSURE BUILDUP PHENOMENON

The pressure increase in thermoelectric generators was attributed to thermal or irradiation effects upon the materials within the generators. These materials are few in number. They include Min-K insulation, a silicone grease, Sauereisen cement, alumina, mica, thermoelectric elements, the heat source surfaces, the container surfaces and miscellaneous wiring. The plausible mechanisms of pressure increase are desorption, dehydration and decomposition. These three topics are discussed separately.

A. DESORPTION

One of the three recognized sources of the gases found in the test generators was the desorption of gases attached to the surfaces of all materials in the generator that were exposed to the atmosphere. As the amount of gas available for desorption is a function of the surface area, it was expected that porous materials, such as Min-K, would be a major source. Its effectiveness as an insulator is dependent upon its porosity. The other materials in the generator would contribute their apportioned fraction to the total pressure increase, but if desorption were the major cause of the pressure buildup, then Min-K was the most likely source. As there was no way to degas the Min-K and saturate its pores with a desired inert gas before inserting it into the generator, it was obvious that a considerable volume of nitrogen, oxygen and moisture would be contained mechanically by the pores. Most of this gas could easily be removed by reducing the pressure in the generator housing to perhaps 1 or 2 mm of Hg for an appropriate period of time. The time period is dependent upon the rate of flow of the gas from the pores and capillaries. At the end of the treatment, a considerable amount of gas would remain adsorbed on all the exposed surfaces in the generator.

There are two types of adsorbed gases, chemisorbed and physisorbed. The binding forces of chemisorption are very strong and are comparable to those leading to the formation of chemical compounds. It may be regarded as the formation of a surface compound. The energies involved in chemisorption range from about 10^4 to 10^5 calories per mole. Chemisorption is seldom reversible. Generally, the solid must be heated to a high temperature and the pressure reduced to a high vacuum to remove chemisorbed gases. Chemisorption is complete when the surface is covered by an adsorbed monolayer.

In contrast with chemisorption, physisorption is the result of much weaker forces between a solid surface and adsorbate molecules that are similar to the van der Waals forces between molecules. These forces

are undirected and mostly nonspecific. They are the forces which lead to condensation of a vapor into a liquid. The energies of physisorption range from a few hundred to a few thousand calories per mole. Physical adsorption is generally quite readily reversible, i.e., on decreasing the pressure the adsorbed gas is desorbed. An exception to this rule is observed when the adsorbent contains many fine pores or capillaries. Physical adsorption is also somewhat dependent upon temperature. Physisorption may lead to adsorbed layers many molecules thick. Physically adsorbed layers may form on top of an underlying chemically adsorbed layer. There are systems known which exhibit physisorption at one temperature and chemisorption at some higher temperature.

One of the obvious complicating mechanisms which must be considered along with adsorption, whether chemical or physical, is the diffusion rate of the desorbed gases from the porous mass of Min-K. This is particularly complicating along with desorption because of the very steep thermal gradient between the hot inner and cooler outer surfaces of the Min-K. In certain systems, adsorption or desorption reaction rates are even controlled by diffusion. This may or may not be the case with Min-K, however, its possibility cannot be excluded. Such a mechanism could account for the delayed pressure buildup if, in fact, outgassing or desorption were the causes of the pressure increase.

Another material which could contribute a rather large amount of desorbed atmospheric gases is mica. Mica is used as a slip and dielectric surface at the hot shoe junction with the heat source. Mica adsorbs an enormous amount of the atmospheric gases because of its platelet structure. The physisorbed gases are lost at about 300° F. The chemisorbed gases are lost at about 900° F. The desorption of the chemisorbed gases could be a cause of at least part of the pressure increase in the generators.

B. DEHYDRATION

The volume of hydrated materials inside the generator is relatively small. According to the producer, Min-K contains no hydrate materials. Sauereisen, used in some generators, contains water initially but, reportedly, this water is driven off with a low temperature (~200° F) bakeout.

There is yet another source of water in the form of a hydrate, the mica mentioned in the preceding discussion. Mica is hydrated potassium aluminum silicate, $3 \text{ Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ or variations thereof which decomposes at elevated temperature. Dehydration of mica

(crystallographic water) starts at about 900° F, so it must be considered as a source of gaseous components which cause the internal pressure increase.

It is possible that dehydration, too, can be induced by radiation. If this is true, one can expect a pressure increase after the radio-isotope heat source is placed in the generator.

C. DECOMPOSITION

The decomposable materials in the generator are limited. The most obvious one is the organic binder in Min-K insulation. The others are Sauereisen and mica. The Min-K producer claims that the phenolic binder, phenol formaldehyde, decomposes starting at 300° F and would be completely decomposed at temperatures much less than the 900° F operating temperature of the inner surface of the Min-K.

The possibility that radiation can induce decomposition is remote, simply because there are no decomposable materials remaining in the generator after the thermal treatment, which is completed prior to charging with the isotopic heat source.

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III. DESCRIPTION OF PROGRAM

Two types of manometric test devices, both variations of ordinary manometric equipment, were used to determine the source of the gas and to provide at least a partial answer to the gas buildup problem. One type of test was run in an aluminum pressure container with about 125 cubic inches of Min-K insulating material. This test series was designed to establish the environmental effects on the insulation--particularly to gamma radiation. The second test was designed to determine the effectiveness of various select metallics to act as gas getters which might react with certain of the evolved gases.

A. HEAT AND IRRADIATION TESTS

The test device used was a 5-inch diameter aluminum can, 9 inches high with a flanged cover as shown in Fig. 1. The preshaped insulation was inserted into a can, and the cover, which contained all of the penetrations, was bolted into place. A 240-watt calrod heater, capable of maintaining a temperature of 540° C, was centrally located in the insulation and was present in all tests whether used or not. (Some specimens were subjected to radiation only.) Two thermocouples were located within the can. One was on the surface of the heater and in all tests where heat was employed, it was the controlling thermocouple. The other was attached to the inside surface of the aluminum wall. All tests that required irradiation were run in a gamma irradiation facility under 12 feet of water. The test setup is shown in Fig. 2. The temperature gradient across the insulation in the underwater tests was somewhat greater than the gradient in the tests out of the radiation field that were run in air.

Test devices were fabricated so that five separate tests could be run concurrently. The gamma irradiation facility shown in Fig. 3 was arranged so that three irradiation tests could be run simultaneously as illustrated in Fig. 2. Radiation dosimetry vials, approximately 3/8 inch in diameter, were disbursed around the three containers in the radiation environment to provide periodic calibration and measurement of the total accumulated gamma dose the containers received. The containers were subjected to a total dose of approximately 10^6 R, which is roughly equivalent to the first 30 days of operation of a SNAP 7 generator.

Three parameters were measured during irradiation and/or heating: (1) container pressure (noted and recorded periodically), (2) surface temperature of heater element, and (3) inside surface temperature of the container. The temperatures were recorded continuously. Barometric pressure was recorded to correct manometer readings of the internal pressure of the containers.

Fig. 1. Sketch of Aluminum Canister for Irradiation Tests

Fig. 2. Sketch of Gamma Facility and Canister Arrangement

Fig. 3. Martin Company Gamma Irradiation Facility

The procedure used to set up the tests was established from the normal practices used when initiating tests on SNAP generators. This procedure was as follows:

- (1) Completely assemble the test devices.
- (2) Evacuate overnight at room temperature and then backfill with argon.
- (3) Re-evacuate to 200 microns of Hg (about 1/2-hour maximum) with heater temperature at 320° C and backfill with argon.
- (4) Re-evacuate to 200 microns of Hg (1/2-hour maximum) with heater temperature 510° to 540° C and backfill with argon.
- (5) Pressurize to about 1.5 psig with argon; then obtain internal gas sample. Re-adjust pressure, if necessary.
- (6) Immerse required test devices in gamma pool and conduct test.
- (7) Initiate tests early in the morning so that hourly pressure readings can be made during most of the first day.
- (8) Continue hourly pressure readings during the normal working hours only.
- (9) Sample internal gas atmosphere at conclusion of the test.

The limiting factor that controlled the minimum internal pressure and the time at minimum pressure during the setting up of the tests was in consideration of the effect upon the thermoelectric elements in an operating generator.

Two forms of the Min-K 1301 insulation were studied in these tests: (1) as received material, i. e., raw Min-K, and (2) preconditioned Min-K. The procedure used to precondition the Min-K duplicated the process used previously on a few occasions. The procedure was as follows:

- (1) Heat in air at $490^{\circ} \pm 10^{\circ} \text{C}$ for 24 hours.
- (2) Remove from furnace and cool.
- (3) Heat in hydrogen at $490^{\circ} \pm 10^{\circ} \text{C}$ for 0.5 hour.
- (4) Furnace cool.

(5) Evacuate and backfill with argon.

(6) Seal insulation in plastic bags.

Tests in the aluminum pressure cans were designed to evaluate the effects of heat, heat plus radiation and radiation only on insulating materials. Raw and preconditioned Min-K, and Corning Glass AA insulation, which has no binder, were tested.

The three canisters for irradiation testing were placed in a perforated, thin-walled aluminum basket and centered in the 12-inch diameter radiation test area at the bottom of the gamma irradiation pool. The remaining two canisters in each test series were located out of the pool near the monitoring and control equipment.

B. GAS GETTER TESTS

A second type of test device fabricated of Pyrex was intended to evaluate a potential solution to the gas buildup problem. Analytical results of the initial gas samples taken from the SNAP 7A, 7B, 7D and 7E generators indicated that the major cause of pressure buildup was hydrogen, a getterable gas. These tests were devoted to determining the efficacy of using getters. The work was done concurrently with the irradiation tests.

Five metals, zirconium, columbium, uranium (present in some generators as shield material), titanium and tantalum, were selected for the getter tests. Under ideal laboratory conditions with pure hydrogen at one atmosphere, the occlusive capacities (solubility) of the five metals were determined.* These solubilities are summarized in Table 1.

TABLE 1
Solubility of Hydrogen in Metals at Several Temperatures
(cc H₂ (STP)/gm metal)

<u>Metal</u>	<u>Temperatures (°C)</u>					
	<u>200</u>	<u>300</u>	<u>400</u>	<u>450</u>	<u>500</u>	<u>550</u>
Zirconium	238	236	234	232	230	225
Columbium	93	88	77	65	47	30

*Smith, D. P., "Hydrogen in Metals," University of Chicago Press, 1948.

TABLE 1 (continued)

<u>Metal</u>	<u>Temperatures (°C)</u>					
	<u>200</u>	<u>300</u>	<u>400</u>	<u>450</u>	<u>500</u>	<u>550</u>
Uranium*	0	0.003	0.01	0.018	0.022	0.022
Titanium	7	18	211	218	227	227
Tantalum	42	37	28	18	14	10

*Values for solubility of hydrogen in uranium at 200°, 300° and 400° C refer to true solubility. However, a stable hydride, UH_3 , begins decomposition at about 260° C and is completely decomposed at 440° C. Uranium reacts with hydrogen even at room temperature, thus can absorb large volumes of gas.

The materials selected exhibited a spectrum of hydrogen solubilities, two with high capacities, one with intermediate capacity, and two of low capacities, in the probable operating temperature range of 500° to 550° C. The choice of getter materials was based somewhat upon the availability of metals. All of the metals selected for testing are of the exothermic occlusion type. The metals that adsorb hydrogen by exothermic occlusion characteristically retain bright surfaces that are highly receptive to more hydrogen because of rapid diffusion of the adsorbed hydrogen into the interior of the adsorbing metal.

The metals generally undergo a volume expansion as hydrogen is adsorbed, although specific measurements have not been made for all of the materials selected for these studies. Sieverts, Gotta and Halberstadt** found that for tantalum containing adsorbed hydrogen in an atom ratio of $\text{H}/\text{Ta} = 0.78$, there is a volume increase of 10%. The same investigators found that for zirconium with an atom ratio of $\text{H}/\text{Zr} = 1.92$, there is a 15.4% increase in volume.

The adsorption properties of the test metals for gases other than hydrogen are variable, although all appear to react to a degree if the temperature is high enough. For example, zirconium getters oxygen at 400° C, and nitrogen, carbon monoxide and carbon dioxide at 500° to 800° C. Zirconium also getters water vapor in the 200° to 350° C range with formation of an oxide and adsorption of the hydrogen. Al-

**Sieverts, A., Gotta, A. and Halberstadt, S., Z. anorg. allgem. Chem., 187 156 to 164, 1930.

though no specific information was found concerning the reactions and gettering ability of the test materials for hydrocarbons, it was established that tungsten decomposes hydrocarbons beginning at about 1200° C with the formation of carbides. Indications are that the temperatures encountered in thermoelectric generators are not high enough to getter hydrocarbons. Specially prepared catalysts for decomposing hydrocarbons at low temperatures, even less than 100° C, are available but they are in the realm of laboratory curiosities.

All of the data in Table 1 were determined with metals in the fully annealed condition. It was not clear if the metals were outgassed in vacuum prior to test but they probably were. It is known that some metals, for example, tantalum and titanium, when used to adsorb a gaseous mixture which contains oxygen, forms a protective oxide film that reduces the absorption of other gases. Other metals, for example, zirconium and columbium, are only slightly affected.

With this background information, getter tests in Pyrex manometric equipment were undertaken concurrently with the irradiation tests in the aluminum canisters. The test setup of the Pyrex equipment is shown in Fig. 4. An effort was made to minimize the internal volume of the test devices to get the greatest response possible from the manometer, and to make the volumes nearly equal so that direct comparisons of tests could be made. The total internal volumes of the three individual test devices, designated Nos. 1, 2 and 3, were 73, 70 and 67 cc, respectively.

The test devices were checked for leaks with a mass spectrometer after assembly and were pressurized to about four inches of mercury for periods ranging from about four hours to overnight to check for leaks before and after each test. No leaks were detected during any check.

The procedure for the test setup in the Pyrex devices was about the same as for the aluminum cans.

- (1) Insert test insulation into tarred Pyrex tube and weigh.
- (2) Insert tarred test getter into Pyrex tube.
- (3) Assemble test tube to manometer and manifold.
- (4) Evacuate overnight at room temperature and backfill with argon. Close stopcock between manifold and manometer when mercury reaches the stopcock during initial evacuation and leave closed until final internal pressure adjustment.
- (5) Re-evacuate to ~50 microns of Hg and again backfill with argon.

Fig. 4. Pyrex Test Equipment for Gettering Tests

- (6) Re-evacuate to ~50 microns of Hg and again backfill with argon.
- (7) Heat the test material to $530^{\circ}\text{C} \pm 10^{\circ}$ and adjust internal pressure to one atmosphere.
- (8) Record pressure hourly during the first test day and on subsequent days if necessary.
- (9) Test life for about 100 hours.
- (10) At conclusion of the test, weigh Pyrex tube with getter and insulation still in tube.
- (11) Remove getter and reweigh.

The internal pressure was adjusted to one atmosphere instead of 1.5 psig as in the aluminum can tests to minimize the internal stress of the rubber connections of the devices and minimize any tendency to leak at these points. Heavy-walled rubber vacuum tubing which fitted very tightly was used to make all connections. A thin silicone grease seal was provided at all glass-to-rubber joints and Glyptal was used liberally at the exterior junction of all these connections. The exposed internal rubber surfaces were minimized.

Near equivalent weights of test insulation were used in all tests except the initial set of three so that direct comparisons would be possible, as the volumes of the test devices were nearly equivalent. Atmospheric pressure corrections were applied to all manometer data. No attempt was made to duplicate the exact conditions in the generator, that is, the volume ratios of the generator to the insulation, and other contained materials were not duplicated. Rather, a small amount of insulation restricted in volume to the hot zone of the split tube furnaces used in these tests assured even heating throughout the insulation.

C. PROOF-OF-PRINCIPLE TEST

The initial plans for investigating gas pressure buildup specified that the 60-watt electrically heated generator, without shield and outer housing (previously manufactured under AEC Contract AT (30-3)-217), be used in a proof-of-principle test to demonstrate effectiveness of the recommended solution. This type of generator with shield and outer housing installed is shown in Fig. 5. As the test program progressed, it became apparent that the recommended solution would be to burn off the phenolic resin binder from the insulation in air and thoroughly out-gas the insulation in an inert atmosphere prior to operation.

Fig. 5. SNAP 7B 60-Watt Generator

The 60-watt generator, however, had been assembled with Johns Manville Min-K 1301 in the as-received condition, i.e., the phenolic resin binder had not been removed. In addition, no precautions had been taken to protect the insulation from atmospheric water vapor during the assembly.

However, the decision was made to test the generator. The tests were to be conducted with a view to doing the best job possible in out-gassing the thermal insulation and protecting the generator during heat-up operation rather than conducting a complete test of the recommended conditioning procedures. Any information gained relative to gas pressure buildup was to be incidental. Accordingly, the procedure listed was specified.

- (1) Install approximately 2000 grams of zirconium sponge in the center fuel capsule hole of the fuel block (hottest region of the generator) to serve as a hydrogen and oxygen gas getter.
- (2) Leak check the generator with a helium mass spectrometer. The leakage rate was not to be greater than 10^{-6} cc/sec of STP helium.
- (3) Thoroughly evacuate the generator under room temperature conditions to remove as much adsorbed water vapor as practical prior to applying heat to the interior. The generator was evacuated until the internal pressure reached 10 to 20 microns of Hg (generator was actually evacuated to a pressure of ~4 microns).
- (4) Leak check the generator evacuation and gas backfilling manifold.
- (5) Continue evacuating the generator while raising the hot junction temperature to 500° to 550° F and the cold junction to 200° to 225° F. The generator was to be maintained at these temperature limits under continuous evacuation for a minimum of 48 hours. The evacuation was to be accomplished through a cold trap that collected any water vapor released from the generator. The evacuation was to be considered complete when the generator pressure decreased less than five microns within a 24-hour period.
- (6) Fill the generator with helium and slowly adjust the hot junction to 960° F and the cold junction to 150° to 175° F. The generator was to be subjected to three to four gas changes per day during the temperature adjustment period.

- (7) Set the power input equal to the SNAP 7B thermoelectric generator (1480 to 1485 watts) and develop performance parametric curves.
- (8) Obtain a gas sample from the generator for gas analysis, evacuate the generator and backfill with helium.
- (9) Set the generator on the fixed resistive external load that yields maximum power and conduct a two-month stability test. The power input, external load and internal gas pressure were not to be adjusted during this period.
- (10) Obtain a gas sample, evacuate the generator and backfill with helium.
- (11) Stabilize the generator on the same external load specified in Item (9) and take a new set of performance data. Compare these data with those from the stability test to determine any change in performance.
- (12) Reduce power input to the generator and slowly cool to room temperature. Evacuate the generator and backfill with argon.
- (13) Remove the zirconium sponge gas getter from the generator and weigh.
- (14) Secure the thermoelectric generator and store for future use.

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IV. RESULTS OF INVESTIGATION

Heat and irradiation tests, getter tests and thermoelectric generator tests were conducted during this investigation. Each is discussed in detail.

A. HEAT AND IRRADIATION TESTS

A total of 10 samples of thermal insulation were tested in the course of the irradiation effects tests.

The Series A tests included the following five samples:

(1) Min-K preconditioned	Heat and radiation
(2) Min-K raw	Heat and radiation
(3) Min-K preconditioned	Heat only
(4) Min-K raw	Heat only
(5) Min-K preconditioned	Radiation only

The remaining samples composed the Series B tests:

(6) AAA	Heat and radiation
(7) Min-K raw	Radiation
(8) Min-K preconditioned	Heat (stored in air for one week after burning)
(9) AAA	Heat only
(10) AAA	Radiation only
(11) Same as Test No. 7 with heat applied after 48 hours.	

In most of the tests where the internal pressure changed, usually an increase, equilibrium was reached within about 24 hours. In all tests where heat was applied, the surface temperature of the heater was maintained at 540° C. The wall temperature at the outer surface of the insulations was 16° C in the irradiation tests under water and 65° C in the tests in air. Since each canister was initially pressurized with argon to approximately 1.4 psig, the net pressure increase must

be taken as the difference between the observed pressure (corrected for atmospheric pressure) and 1.4 psig. In Table 2, the maximum net pressure buildup for each test is tabulated.

TABLE 2
Pressure Increase in Irradiation Tests

		(psi)
1. Min-K 1301 raw	Heat and radiation	2.17
2. Min-K 1301 raw	Heat	2.30
3. Min-K 1301 preconditioned	Heat and radiation	0.85
4. Min-K 1301 preconditioned	Heat	1.05
5. Min-K 1301 preconditioned	Heat (stored in air one week)	1.05
6. Min-K 1301 preconditioned	Radiation	~0.05
7. Min-K 1301 raw	Radiation	0.05
8. Corning Glass AA	Heat and radiation	0.45
9. Corning Glass AA	Heat	0.05
10. Corning Glass AA	Radiation	0.05
11. Repeat of No. 1 (Test 7 with heat applied)		1.95

Inspection of the data indicated that gamma radiation has little or no effect on pressure buildup. Conversely, it is shown that a heat-induced reaction is responsible for the pressure buildup. Presumably, outgassing is responsible for the pressure increase noted in Tests 3, 4, and 5, and outgassing plus binder decomposition are responsible for the pressure increase in Tests 1, 2, and 11. Test 5 was intended to show that exposure of the preconditioned Min-K 1301 to moisture-laden air with subsequent release of hydrogen and absorption of oxygen, nitrogen and moisture would present no different outgassing characteristics than hydrogen saturated preconditioned Min-K 1301 as in Test 4. A further comparison of Tests 4 and 5 with 9 leads one to the conclusion that the Corning Glass AA material must have been almost completely outgassed during the test setup, whereas Min-K 1301 was not. The pressure buildup in Test 8 indicates that temperature-pressure equilibrium may not have been reached at test initiation. Test 11 is an extension of

Test 7. Test 7 was initiated as usual. After 48 hours, there was no significant pressure buildup; therefore, heat was applied while the canister remained in the radiation field, thereby providing a rerun and check of the Test 1 results. Figures 6 and 7 are graphic presentations of Test Series A and B, respectively, except Test 11 replaces Test 7 in Test Series B. Exposures ranged from 150 to 190 hours.

At 170 hours exposure, the accumulated radiation dose was $6 \times 10^6 \text{R}$, while at 190 hours exposure, the accumulated dose was $6.7 \times 10^6 \text{R}$.

The environment of each canister was sampled following test completion. The analytical results of these samples are tabulated in Table 3. Inspection of the data pertaining to the argon sample shows that the sample was contaminated with air after sampling; otherwise, all of the other samples would show at least as much nitrogen. These data agree roughly with the data obtained earlier in that hydrogen is the major constituent evolved by raw Min-K 1301 upon heating. One obvious conclusion is that the assumption that nearly all of the hydrogen is removed from the preconditioned Min-K during evacuation is a fallacy as is seen by comparing Tests 1 and 3. A comparison of Tests 4 and 5 shows that storing the preconditioned, hydrogen-saturated Min-K in air allows an exchange of oxygen and nitrogen for hydrogen. Generally, the analytical results confirm the pressure rise results shown in Table 2.

For the first time analyses were available that were truly representative of what could be expected in a generator where raw Min-K had undergone binder decomposition and outgassing. None of the samples from the generators are considered representative because of the number of times each has been evacuated and backfilled with a variety of gases, including hydrogen, argon and helium. The amount of hydrogen and other gases were not necessarily representative of the environment resulting from the decomposition of binder and outgassing of insulation.

B. GETTER TESTS

Twenty-one individual tests were run in the Pyrex devices, not counting three that were lost because of furnace failure. When the tests with raw Min-K were run, a tar-like condensate was noted on the inner wall of the Pyrex tube immediately outside the furnace. The material condensed during the first and second hours of exposure to the heat. Undoubtedly, some of this material had already been distilled from the system during the test setup procedure. The condensate consists of an amber colored tar-like substance, presumably binder residue or reaction products, with some white crystalline material dispersed throughout the tar-like layer. Perhaps the crystalline material is hexamethylenetetramine.

Fig. 6. Gas Pressure Buildup Test, Series A--Corrected for Atmospheric Pressure

Fig. 7. Gas Pressure Buildup Tests, Series B--Corrected for Atmospheric Pressure

TABLE 3
Analytical Results from Gas Samples (mol %)

	<u>CO₂</u>	<u>CO</u>	<u>N₂</u>	<u>H₂</u>	<u>Methane CH₄</u>	<u>Ethane C₂H₆</u>	<u>Ethylene C₂H₄</u>	<u>Propane C₃H₈</u>	<u>Propylene C₃H₆</u>	<u>A</u>	<u>O₂</u>
Argon	0.0	0.0	22.2	0.0	0.0	0.0	--	0.0	--	72.0	5.8
Raw Min-K Heat and Radiation	1.2	1.0	1.3	6.5	2.0	0.2	--	0.0	--	87.8	0.0
Raw Min-K Heat Only	1.2	1.0	2.5	31.0	3.5	2.1	--	0.1	--	58.4	0.2
Preconditioned Min-K Heat and Radiation	0.1	0.0	2.0	7.3	0.2	0.0	--	0.0	--	90.2	0.0
Preconditioned Min-K Heat Only	0.0	0.0	2.2	13.6	0.0	0.0	--	0.0	--	84.2	0.0
Preconditioned Min-K Heat Only (stored in air)	0.1	0.0	14.7	0.3	0.1	0.0	0.0	0.0	0.0	82.3	2.5
Preconditioned Min-K Radiation Only	0.0	0.0	1.1	0.3	0.2	0.0	--	0.0	--	98.4	0.0
Raw Min-K Heat and Radiation	1.2	0.0	3.2	3.7	0.3	0.1	0.1	--	0.0	90.7	0.7
Corning Glass AA Heat and Radiation	0.0	0.0	1.1	0.3	0.1	0.0	0.0	--	0.0	98.0	0.5
Corning Glass AA Heat Only	0.5	0.0	1.6	0.8	0.7	0.0	0.1	--	0.1	95.6	0.6
Corning Glass AA Radiation Only	0.0	0.0	0.9	0.1	0.0	0.0	0.0	--	0.0	98.6	0.4

Weight loss determinations were run on 13 samples of raw Min-K 1301. Seven of these determinations were run in the getter test devices in an atmosphere of argon and the remainder were run in air. The former tests, then, were determinations of the percent volatiles which simulated the volatilization of constituents from raw Min-K in a generator. The weight loss data are shown in Table 4.

TABLE 4
Weight Loss of Min-K 1301 After 24 Hours at 350° C

<u>Sample Weight (gm)</u>	<u>Weight Loss (%)</u>
2.6638	3.1
1.4138	5.0
1.5331	3.8
2.0038	0.97
2.0539	0.84
2.0525	5.5
2.0501	12.7
2.3636	6.4
2.0908	6.5
2.7507	6.5
3.2567	6.5
3.5302	6.5
3.6696	6.7

The values range from 0.84 to 12.7% which indicates that the binder is quite unevenly distributed. The first seven samples in Table 3 were chosen randomly from miscellaneous scrap pieces of Min-K while the last six were all taken from a single small piece. The first seven values average about 4% while the last six average about 6.5% with an overall average of 5.5%. Six samples of preconditioned Min-K lost an average of 3.2% in weight. The difference between these averages, 2.3%, is a rough estimate of the initial binder loading, which according to Johns Manville, is 2 to 3%. The contribution of the decomposed binder to the total volume of gases produced is greater than the volume resulting from outgassing because of the formation of gaseous reaction products from the solids in the binder. A calculation of the total volume of gas evolved from the raw Min-K averaged over all tests versus the

preconditioned Min-K averaged over all the tests indicated about a 30% greater volume of gases was evolved from the raw Min-K. This figure is not quantitative but does establish a trend. The last six tests given in Table 4 were returned to test temperature for an additional 86 hours. There was virtually no weight change, proving that the preconditioning cycle is complete within 24 hours.

Experimentally, four getter tests were run with zirconium, four with columbium, three with titanium, three with tantalum and two with uranium. The weight gains of the getters are shown in Table 5. The test duration was a minimum of 96 hours.

TABLE 5
Weight Gain of Getter Materials (%)

<u>Getter Metal</u>	<u>Raw</u>	<u>Min-K 1301</u>
		<u>Preconditioned</u>
Zirconium	0.2	0.7
	0.7	0.8
Columbium	0.35	0.4
	0.5	0.5
Titanium	0.04	0.06
	--	0.2
Tantalum	*	*
Uranium	*	*

*Surface reaction product flaked off, making it impossible to get a weight.

Except for titanium, the percent weight increases reflect what was expected from the information on occlusive capacity shown in Table 1. However, as was stated earlier, titanium forms a protection oxide film if oxygen is present in the gaseous mixture being absorbed, so this, too, was as expected. If all of the absorbed material is considered to be hydrogen, admittedly unlikely, the data in Table 5 can be presented in a more meaningful way, i.e., volume of gas absorbed per gram of metal so that a direct comparison can be made with the data in Table 1.

TABLE 6
Occluded Hydrogen in Getter Metals

<u>Getter Metal</u>	<u>Occluded Gas (cc H₂(STP)/gm metal)</u>
Zirconium	23
	80
	80
	93
Columbium	40
	58
	45
	58
Titanium	4
	7
	25

The quite low volumes of occluded gases may be explained in two ways. First, the solubilities shown in Table 1 were determined under ideal laboratory conditions with high purity hydrogen at one atmosphere contrasted with the tests run with a highly contaminated gaseous mixture and getter metals that were not outgassed (to simulate actual requirement in a generator). Second, it may be that all of the hydrogen present was absorbed to equilibrium pressure. This cannot be determined because these tests were not sampled for gas analysis.

The pressure increases in these tests generally follow the same pattern. Generally, the pressures rose rapidly initially then gradually tapered off, reaching a maximum in about 24 hours. The two exceptions to this were the tests with tantalum and uranium present. Both of these metals outgassed initially, causing the maximum pressure to occur within about eight hours. The pressures in all tests decreased gradually to near the initial pressure after reaching a maximum--in the order of 40 to 60 minutes. There was no real significance to the pressure buildup in either the irradiation or getter tests because the final pressure was a function of the void volume versus the volume of insulation.

A set of two tests was run with a conglomeration of materials used in the SNAP generators to demonstrate that they make no significant contributions to the pressure buildup problem. These parts included lead-telluride elements, graphite, bushings, springs, stainless screws, washers and aluminum module plates. These tests were initiated exactly the same as the getter tests and operated at 530° C as before. Only insignificant pressure changes occurred.

1. Preconditioning Treatment for Min-K

A single test was run to test the efficacy of a preconditioning treatment for Min-K 1301 for subsequent use in SNAP generators. The procedure is simply to burn off the Min-K in air, evacuate, remove all gases and backfill with any one of several inert gases. The test apparatus consisted of a Pyrex tube with an attached stopcock, manometer, vacuum pump, helium supply and reference barometer. Raw Min-K was placed in a Pyrex test tube and a stopcock was fused to the open end. The test procedure was as follows:

- (1) The tube was evacuated overnight with a Hy Vac-14 pump and backfilled to one atmosphere with helium and weighed.
- (2) The stopcock barrel was removed and the tube containing the raw Min-K was inserted into the split tube furnace at 490° C for 24 hours to decompose the binder.
- (3) The stopcock barrel was replaced and the tube was re-evacuated (pumped for 30 minutes) and cooled to room temperature to test the system for leaks. The pressure remained at < 1 mm during cooling and reheating to 490° C.
- (4) Helium was admitted to the Min-K and the test tube was cooled to room temperature. Helium pressure was maintained at one atmosphere during cooling.
- (5) The tube and its contents were weighed. The initial weight of the raw Min-K saturated with helium was 2.8154 grams, the second weight after burnoff and saturation with helium was 2.6847 grams--a loss of 4.64%.
- (6) The apparatus was reassembled and the tube was reheated to 490° C, during which helium was released to maintain a pressure slightly above one atmosphere.
- (7) The pressure was adjusted to atmospheric pressure, 759 mm, at temperature equilibrium.
- (8) The tube was cooled to room temperature. The pressure decreased to 614 mm during cooling.
- (9) The tube was reheated to 490° C. The pressure stabilized at 759 mm.

The most significant result of this test is the last step where the pressure returned to but did not exceed one atmosphere when the tube was reheated. The temperature was maintained for 20 hours to be

certain that temperature and pressure equilibrium was reached, establishing that the Min-K did not continue to desorb or generate gas and cause a pressure buildup.

It is concluded that proper preconditioning of the Min-K can possibly eliminate the need for getters. After final shaping, the Min-K should be burned off in air at about 490° C in a vessel or a furnace that can then be evacuated to a low pressure while at temperature to desorb the gases from the Min-K. It is then backfilled with argon or other inert gas, preferably the gas that will ultimately be used to charge the generator, furnace cooled and, finally, packaged in a plastic bag.

Recognizing that the materials in the generator's outgas, also that handling of preconditioned Min-K in moisture-laden air will permit exchange of moisture, oxygen, nitrogen and carbon dioxide for adsorbed inert gas, it may be desirable to incorporate getters in the generators to absorb these gases as they are released.

C. THERMOELECTRIC GENERATOR TEST

Tests conducted on the 60-watt, electrically heated SNAP generator were of three types. First, the generator was thoroughly evacuated and outgassed at several elevated temperatures. A performance parametric test was then conducted. When the parametric test was completed the generator was placed on a two-month steady-state stability test.

1. Generator Outgassing and Evacuation

The thermoelectric generator was delivered to the Engineering Test Laboratory with 2143 grams of zirconium sponge installed in the center fuel capsule hole of the fuel block. (The zirconium serves as a gas getter for hydrogen and oxygen.) At the time of delivery, the generator had been evacuated to a pressure of ~4 microns of Hg, presumably a stability point for room temperature conditions.

The generator electrical heater power was slowly increased to 500 watts at which time the average hot junction temperature was 525° F. During this time and the period while the generator was being held at this temperature (8 days) the generator was under continuous evacuation. The products of evacuation were passed through a cold trap during discrete periods of the evacuation cycle to determine when the water vapor had been removed. Measured quantities and pumping times are shown in Table 7.

TABLE 7
Water Vapor Removal

<u>Evacuation Time (min)</u>	<u>Quantity of Liquid (ml)</u>	<u>Rate (ml/min)</u>
900*	5	0.00556
110	2.5	0.0227
2820	0.5	0.000177

* The 900-minute evacuation time should be ignored since the cold trap froze during the overnight period. The following day, however, 2.5 milliliters of liquid were collected in 110 minutes.

The main conclusion drawn from this test phase was the fact that rather large quantities of water vapor are released from the thermal insulation as the temperature is increased. This water vapor would be detrimental to the generator performance if it were allowed to remain.

It is not truly known how much water vapor was removed from the Min-K insulation during the elaborate outgassing procedure. If the water vapor removed during the long evacuation at room temperature (~ 4 weeks) and vapor that may have reacted with the zirconium sponge is neglected it can be estimated that approximately 120 milliliters of water were removed during an eight-day evacuation period. This estimate is made by using the rate data in Table 7 and integrating graphically.

After eight days continuous evacuation, the generator power input was increased from 500 to 1480 watts in approximately 100-watt steps (14-day period). During this period, the generator argon gas fill was changed 42 times (approximately 4 times/day), with each evacuation cycle lasting about 10 minutes. The trapped water vapor was measured at the end of each day. Generally, one to three drops of water had collected. After the generator had operated at a 960°F hot junction temperature for two days, there was no further accumulation.

2. Generator Parametric Test

A five-point performance parametric test was conducted on the generator with the generator immersed in a 60° to 65°F water bath. The results of this parametric test are shown in Fig. 8. The generator gas fill was 100% helium. The electrical power input was maintained at 1485 watts. Peak power was measured at 68 watts.

Fig. 8. Sixty-Watt SNAP Generator

3. Generator Stability Test

After the parametric performance test was completed, the generator was subjected to a two-month steady-state stability test. During this period, the power input to the generator, the generator external load and the generator gas fill were maintained constant. The results of the stability test are shown in Table 8.

It can be seen from the results that the power output decreased slightly with time. There was an accompanying decrease in temperature difference between the thermoelectric hot and cold junctions which appears to explain the small loss in generator output power since the generator internal resistance remained relatively constant. The reduction in temperature difference across the thermoelements appeared to be due to increased parasitic heat losses and/or increase in the thermal conductivity of the thermoelements.

The generator gas fill was changed at the end of the stability test and one additional set of performance readings was recorded. In comparing the final set of data with readings obtained just prior to the gas change, it can be seen that replacing the prior helium gas fill with fresh, dry helium did not have a noticeable effect on the generator performance.

There was a very slight decrease in temperature difference between the hot and cold junctions throughout the two-month stability test with a corresponding small reduction of less than one percent in output power. Since the gas change did not produce an increase in the temperature difference, it indicated that the prior helium gas fill did not become contaminated with other higher conducting gases. This, therefore, suggests that the thermoelements or the Min-K-1301 insulation have become slightly more thermally conductive.

The internal resistance of the generator displayed a small increase during the last three weeks of operation. Likewise, the Seebeck voltage displayed a correspondingly small increase during the same period, as indicated by the open circuit voltage divided by the hot-to-cold junction temperature difference. Since the Seebeck voltage did increase, it would be normal to expect that the generator internal resistance would also increase.

Generator power output displayed a downward trend during the stability test. However, the calculated decrease in power was only about 0.8% which is within normal instrumentation accuracy. Considering the overall data evaluation, it was concluded that the 60-watt electrically heated generator displayed very good performance stability. The elaborate outgassing procedure employed during the initial heatup of this generator was of contributory value in obtaining a stability in generator performance.

TABLE 8
Stability Test Results

Date	Power (watts)	T _h (°F)	ΔT _{h-c} (°F)	T _c (°F)	Cooling Water (°F)	Internal Pressure (psia)*	Load Voltage (volts)	Load Current (amp)	Open Circuit Voltage (volts)	$\frac{E_{oc}}{\Delta T}$ x 10 ⁻³	Output Power (watts)	Resistance Load Internal (ohms) (ohms)	
11-4-63	1480	945	830	115	63.5	16.86	12.60	5.268	21.40	25.8	66.38	2.39	1.67
11-5-63	1478	942	827	115	63.2	16.86	12.57	5.266	21.38	25.8	66.19	2.39	1.67
11-6-63	1478	943	829	114	62.8	16.87	12.54	5.256	21.32	25.7	66.0	2.39	1.67
11-13-63	1480	942	829	113	61.0	16.85	12.57	5.244	21.29	25.7	66.0	2.40	1.66
11-20-63	1480	944	830	114	60.0	Not Measured	12.55	5.232	21.32	25.65	65.66	2.40	1.68
11-26-63	1480	942	830	112	59.0	16.77	12.53	5.234	21.32	25.65	65.58	2.39	1.68
12-4-63	1480	945	830	115	58.0	16.76	12.54	5.222	21.32	25.65	65.48	2.40	1.68
12-11-63	1480	932	821	111	55.0	16.67	12.33	5.206	21.09	25.7	64.19	2.37	1.68
12-16	1480	922	812	110	52.8	16.54	12.34	5.198	21.03	25.9	64.14	2.37	1.67
12-18	1480	938	813	125	66.0	17.05	12.5	5.276	21.54	26.55	65.95	2.37	1.71
12-24-63	1480	940	816	124	65	17.07	12.61	5.308	21.82	26.8	66.93	2.38	1.74
1-2-64	1490	935	814	121	61	16.96	12.49	5.262	21.50	26.4	65.72	2.37	1.71
1-3-64	← Helium gas fill replaced with 100% helium →												
1-6-64	1490	939	817	122	58	16.43	12.50	5.268	21.60	26.4	65.85	2.37	1.73

4. Gas Sample Analysis

Two different gas samples were removed from the generator for gas analysis. The first sample was removed from the gas that was used during the parametric performance test (7-day test period). The generator was then evacuated and refilled with 100% helium. This gas fill was kept in the generator throughout a two-month stability test. A second gas sample was then removed for analysis. The results of the first gas analysis are shown in Table 9. Results from the second analysis will be incorporated by addendum to this report if significantly different from the first, after the analysis data are available.

Table 9 shows that there were only trace quantities of contaminants in the gas, indicating that the outgassing procedure used on this generator was successful.

TABLE 9
Gas Sample Analysis

<u>Component</u>	<u>mol %</u>
Carbon dioxide	0.003
Oxygen	0.007
Ethylene	0.006
Nitrogen	0.024
Methane	0.003
Argon	0.005
Hydrogen	0.023
Helium	<u>Balance</u>
	100.000

V. DISCUSSION OF RESULTS

After careful consideration of the data resulting from this work, the applicability of getters without appropriate outgassing procedures to the gas pressure problem in those generators which contain raw Min-K is doubtful, if not physically impossible. This conclusion was arrived at by determining the percentage weight loss during decomposition of the Min-K and estimating the volume and types of gaseous products that evolve from the process. The percent weight loss was rounded off at 6% and two representative compositional analyses of gaseous decomposition products (not including argon carrier) have been selected for the illustrations. The first is Min-K decomposed under heat and irradiation which resulted in an accumulation of gaseous products containing 53 mol % hydrogen, 16% methane, about 11% nitrogen, 10% carbon dioxide, 9% carbon monoxide and about 1% ethane. The second is the Min-K that was decomposed by heat only which resulted in a gaseous accumulation containing 75 mol % hydrogen, 8% methane, 6% nitrogen, 5% ethane, 3% carbon dioxide, 2.5% carbon monoxide, 0.5% oxygen and 0.2% propane. The decomposition of each 100 grams (286 cc) of Min-K produces volumes of gases shown in Table 10.

TABLE 10

Volumes of Gaseous Products from 100 Grams of Min-K 1301
(liters)

<u>Gas Sample</u>	<u>H₂</u>	<u>CH₄</u>	<u>N₂</u>	<u>C₂H₆</u>	<u>C₃H₈</u>	<u>CO₂</u>	<u>CO</u>	<u>O₂</u>	<u>Total</u>
Heat and ir- radiation	5.1	1.5	1.1	0.1	--	1.0	0.9	--	9.7
Heat only	12.2	1.3	1.0	0.8	<0.1	0.5	0.5	0.1	16.5

Using the data in Tables 1 and 10, it is apparent that 22 to 53 grams of zirconium are required to occlude the hydrogen from 100 grams of Min-K. These weights appear optimistic because the partial pressure of hydrogen is less than one atmosphere in almost all practical situations and because the presence of other gases, particularly oxygen, is known to interfere with the occlusion process. On the other hand, hydrogen is almost impossible to contain quantitatively, especially under elevated temperature conditions, because of its reactivity with the containment metal and its subsequent diffusion through the metal. It might be anticipated, then, that hydrogen evolved from Min-K in a thermoelectric generator might ultimately diffuse or leak from the generator,

even though the generator were leaktight to helium and other gases. Also, the presence of uranium metal in the SNAP 7 series of generators will ensure that some hydrogen is removed by the chemical action of that metal.

Experimentally the four samples of zirconium heated in the presence of gases evolved from decomposition of Min-K binder exhibited an average weight increase of 0.6% over a period of 90 hours. If the entire weight increase is assumed to be hydrogen, as in Table 6, the average volumetric occlusion capacity is found to be 69 cc (STP)/gm, or about 30% of the literature value, in the time period noted. It, therefore, appears that a practical range of zirconium weight is 50 to 100 grams of zirconium per 100 grams Min-K.

Zirconium chips offer the most efficient shape for gas gettering purposes. The SNAP 7A and C generators contain an estimated 900 grams (about 2 pounds) of Min-K which would require about 650 grams of zirconium chips. The SNAP 7B and D generators contain an estimated 4500 grams (10 pounds) of Min-K which would require about 3400 grams of zirconium chips.

In the 60-watt electrically heated SNAP thermoelectric generator, consideration has been given to filling the central fuel channel with getter. The volume of the channel is about 660 cubic centimeters. Zirconium chips have a very low bulk density, perhaps 0.4 to 0.5 gm/cc, therefore, only about 300 or 400 grams would be required to fill the channel or about enough getter to adsorb the hydrogen from 600 to 800 grams of raw Min-K. On the basis of the preceding calculations, it does not appear attractive to adsorb the off-gases with metallic getters, at least with chips. If zirconium sponge is used, perhaps 2000 grams could be placed into the central channel but the lower surface area would slow the adsorption process. However, the slower adsorption rate may be of no consequence.

Further evidence of the ability of Min-K to adsorb vapors and gases was received recently from Johns-Manville. Min-K 1301 was shown to adsorb substantial quantities of water and to retain the water after long periods of evacuation. The residual pressure after a 24-hour pump-down period, as a function of initial water content, is shown in Table 11.

TABLE 11
Effect of Water Content on Evacuation of Min-K 1301

Water (%)	Pressure (mm Hg in 24-hr pumpdown)
6	18
4	15.5
3	11
2	5.4
1.5	3
1.0	1.3
0.75	0.75
0.6	0.45
0.5	0.3
0.4	0.01

Johns-Manville personnel also have observed that samples of Min-K 1301 which have been exposed to air with 25 to 30% relative humidity for several months, contain 2.5% water. This information indicates that it is important to prevent adsorption of water vapor from the air after oxidizing the binder. Minimizing the adsorption of water vapor could measurably decrease the subsequent pressure buildup in the generators.

Even though the testing of the 60-watt thermoelectric generator was directed primarily toward protecting the generator and preparing it for future use rather than using it as a proof-of-principle test, significant results toward the gas pressure buildup problem have been achieved.

The tests have demonstrated that even with raw Min-K 1301 insulation, the gas pressure buildup can be greatly alleviated if proper generator heatup and outgasing procedures are used. This is confirmed by the relatively constant pressure exhibited in the generator throughout the stability test.

The measured water vapor removed from the generator shows that large quantities of water vapor adsorb on the insulation fibers when exposed to atmospheric air.

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VI. CONCLUSIONS

As a result of the investigation to determine the cause of the gas pressure buildup, the following conclusions have been reached:

- (1) Gamma radiation has no significant effect on the pressure buildup of raw Min-K, preconditioned Min-K or Corning Glass AA insulations.
- (2) Thermal decomposition of the binder in Min-K is the major source of gaseous products.
- (3) Outgassing and desorption are a second source of gaseous products.
- (4) Raw Min-K should not be used in generators.
- (5) Preconditioned Min-K should be used exclusively in generators.
- (6) The usefulness of getters is questionable, particularly with raw Min-K, if appropriate outgassing procedures are not used during generator heatup. Getters are useful with preconditioned Min-K to adsorb incidental contaminating gases that are retained after preconditioning.
- (7) Zirconium is the most effective getter of the metals tested.
- (8) The stability of the 60-watt electrically heated SNAP generator has been demonstrated after using technical knowledge developed during this test program.

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VII. RECOMMENDATIONS

To avoid the recurrence of this problem in future generators, the following recommendations should be considered:

- (1) Precondition Min-K 1301 for all generators as follows:
 - (a) Burn off Min-K in air at 490° to 500° C for 24 hours.
 - (b) Evacuate insulation at temperature with a HyVac-14 pump (or equivalent) until the pressure stabilizes. This will require about three hours.
 - (c) Backfill with argon or other inert gas while holding the temperature at 490° to 500° C.
 - (d) Cool to room temperature in the presence of inert gas.
 - (e) Seal Min-K in gastight containers until ready for use.
 - (f) Minimize subsequent exposure of conditioned Min-K to humid air. Store generator assembly (if Min-K is present) in evacuated vessel or inert gas purged vessel overnight and on weekends during assembly. Preconditioning results in a very slight shrinkage so no major allowance is required during fabrication.
- (2) If a getter is used with preconditioned Min-K, it should be zirconium metal that is canned in a stainless steel cloth cylinder (about 200 mesh) to prevent dusting of the zirconium-gas reaction product.