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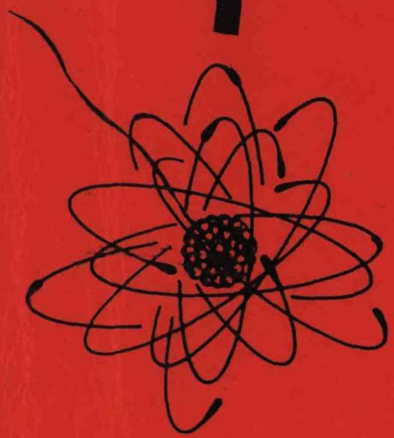

THERMOELECTRIC NUCLEAR FUEL ELEMENT
FINAL REPORT

Contract No. AT-(30-3)-500

FEBRUARY 10, 1962

Prepared for the

U. S. ATOMIC ENERGY COMMISSION

WESTINGHOUSE ELECTRIC CORPORATION
ATOMIC POWER DEPARTMENT
PITTSBURGH,30 P. O. BOX 355 PENNSYLVANIA

DISCLAIMER

WCAP-1900

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The results of a research and development program to determine the feasibility of an in-pile thermoelectric direct conversion reactor are summarized. The development of a suitable fuel element containing thermoelectric materials "wrapped" around the fuel is emphasized. Studies of irradiation damage, electrical measurements, preparation of uranium thermoelectric materials, and basic fabrication problems are also summarized.

I. INTRODUCTION

The research and development program on the thermoelectric nuclear fuel element commenced on February 27, 1958. The objective of this program was to determine the feasibility of a thermoelectric nuclear fuel element.

In order to achieve the program objectives, work was initiated in the following areas:

A. Thermoelectric Materials Studies

Under this task, new thermoelectric materials were explored. These materials included:

1. $Li_xNi_{1-x}O$
2. $M_xU_{1-x}O_2$ where $M = Na^{+1}, Ca^{+2}, Y^{+3}, Ta^{+5}, W^{+6}, Tl^{+3}$
3. $La_xBa_{1-x}TiO_3$
4. $Y_xCa_{1-x}TiO_3$
5. $Na_xMn_{1-x}Te$ and $Li_xMn_{1-x}Te$
6. CeS_x $(1.5 \geq x \geq 1.3)$

B. Fabrication of Thermoelectric Materials

Methods of fabricating the materials into useful geometries were investigated. Initial studies were limited to cold pressing and sintering, flame spraying, cold swaging and sintering, and hot pressing. Initial studies were concentrated on $Li_xNi_{1-x}O$ compositions.

C. Physical and Chemical Characteristics of Thermoelectric Materials

Studies were made on the corrosion characteristics, mechanical properties and thermal stability of the thermoelectric materials. Emphasis of these studies was placed on $Li_xNi_{1-x}O$ and $Li_xCu_{1-x}O$.

D. Bonding Studies

Techniques of bonding thermoelectric materials to suitable electric conductors were investigated. Requirements of the bonds were low electrical contact resistance, good strength, long life, and compatibility with the thermoelectric materials. Preliminary investigations were made on $Li_xNi_{1-x}O$ and $Li_xCu_{1-x}O$ compounds.

E. Irradiation Studies

The irradiation program was divided into two parts:

1. Reactor Irradiation, which consisted of pre- post- measurements of thermoelectric properties and in-situ measurements, and
2. Van de Graaff Irradiation; hot cell apparatus for measurement of electrical resistivity, Seebeck coefficient, and thermal conductivity was designed and constructed.

In-situ experiments were designed to measure the electrical resistivity and Seebeck coefficient, and the necessary instrumentation was provided. The apparatus for the Van de Graaff experiment was designed and constructed. This equipment permitted the measurement of electrical properties and thermal conductivity during electron bombardment.

After the first year of the development program, it was decided to concentrate upon the reactor irradiation experiments (pre- post- and in-situ measurements) in order to screen as many thermoelectric materials as possible. Preparation work on new materials and the Van de Graaff experiments were discontinued. Fabrication studies were limited to the preparation of irradiation samples.

By September of 1959, the results of the irradiation experiments on a number of thermoelectric materials revealed that the materials could be used in a reactor environment with no significant change in the figure of merit, provided the material was operated above some critical temperature. These data established the feasibility of a thermoelectric nuclear fuel element concept.

The development program entered a second phase in October, 1959, when several new work tasks were added. Since that time, the program has remained essentially unchanged, its work tasks set up as follows:

A. Preparation of the uranium thermoelectric compounds: uranium-sulfur, uranium-tellurium, and uranium-selenium.

B. Thermoelectric measurements on the new materials. These measurements consisted of electrical resistivity, Seebeck coefficient, and thermal conductivity over a wide range of temperatures.

C. Irradiation studies of pre- post- and in-situ type on a variety of thermoelectric materials such as lead telluride (N and P types), germanium telluride, etc.

D. Design and fabrication of thermoelectric nuclear fuel elements utilizing lead telluride thermoelectric materials. Fabrication of thermoelectric nuclear fuel elements by swaging was explored. Compatability studies between lead telluride and various structural and insulating materials were performed. Prototype elements were laboratory tested using electrical heat.

E. Preliminary reactor arrangement studies were performed to determine the nuclear, thermal, mechanical and electrical problems of a thermoelectric nuclear reactor core.

The results of the work on these tasks are briefly discussed herein.

II. MEASUREMENT OF THERMOELECTRIC PROPERTIES

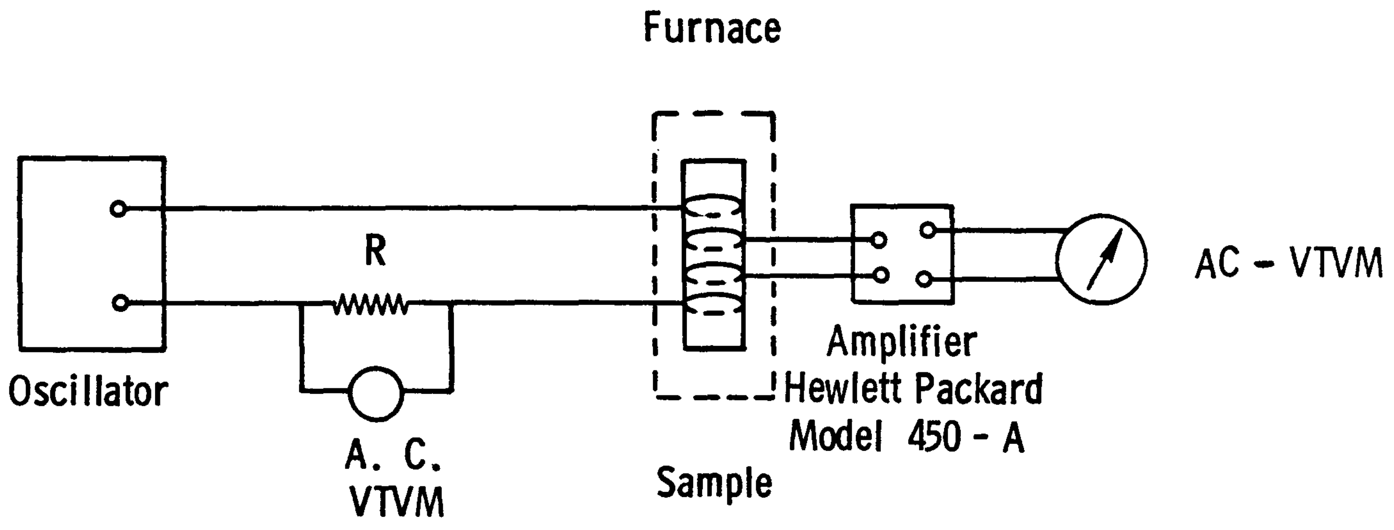
The most significant parameter in the screening of thermoelectric materials is the figure of merit, Z, which is itself made up of the parameters α, ρ and K (Seebeck coefficient, electrical resistivity and thermal conductivity). The determination of the individual parameters as well as Z has constituted a large part of the activity in the measurements program. Other quantities routinely measured have been power, voltage and current.

A. Resistivity

An alternating current technique was adopted for the determination of the resistivity of thermoelectric materials. The advantage of this method over DC methods is the elimination of temperature-gradient-induced errors. In the DC technique, it is necessary to reverse the polarity during measurement in order to average out these errors. The AC method, on the other hand, is more difficult to instument and may be subject to stray pick-up. The former difficulty in the AC method was overcome by the use of a stable amplifier and AC voltmeter combination; the latter was avoided by careful shielding of the leads to the sample. The four-probe contact scheme is desirable for both AC and DC methods since the voltage drop across contact surfaces does not affect the measurement. Figure 1 shown the circuit for making the measurement. The probes consist of loops of Number 30 wire wrapped around grooves in the sample and twisted. This arrangement proved quite suitable for both resistivity and figure-of-merit measurements.

The resistivity is calculated from the relation

$$\rho = \frac{V_S}{V_R} \cdot \frac{A}{L} R$$



A. C. CONDUCTIVITY MEASUREMENT
Figure I

where ρ = resistivity

V_S = voltage drop across sample

V_R = voltage drop across resistor R

A = cross sectional area of sample

L = distance between voltage probes

R = value of series resistor

Figure 2 shows the 100 cps oscillator developed for the measurement. This self-contained, transistorized unit was found to be as accurate as the 1000 cps one originally tried, and was more readily designed.

B. Figure of Merit

The advantages of a direct figure of merit measurement are the speed with which routine samples can be run and the avoidance of the cumulative error effect of measuring the component parts of Z.

The figure of merit of a thermoelectric substance can be measured directly by application of Peltier heating to the sample.[1] A temperature gradient is established across the sample by the Peltier pumping produced by the passage of a small current through the sample. The voltage across the sample is now measured as a function of time. This voltage consists of an ohmic and a thermoelectric component. The ratio of the thermoelectric to the ohmic voltage divided by the absolute temperature of the sample is numerically equal to the figure of merit. This relation can readily be derived by means of the following relations. The heat transferred from the higher to the lower temperature region is

$$Q = KA \frac{\Delta T}{\Delta X} \tag{1}$$

where K = thermal conductivity

A = cross-sectional area of sample

$\frac{\Delta T}{\Delta X}$ = temperature gradient along sample (produced by Peltier pumping)

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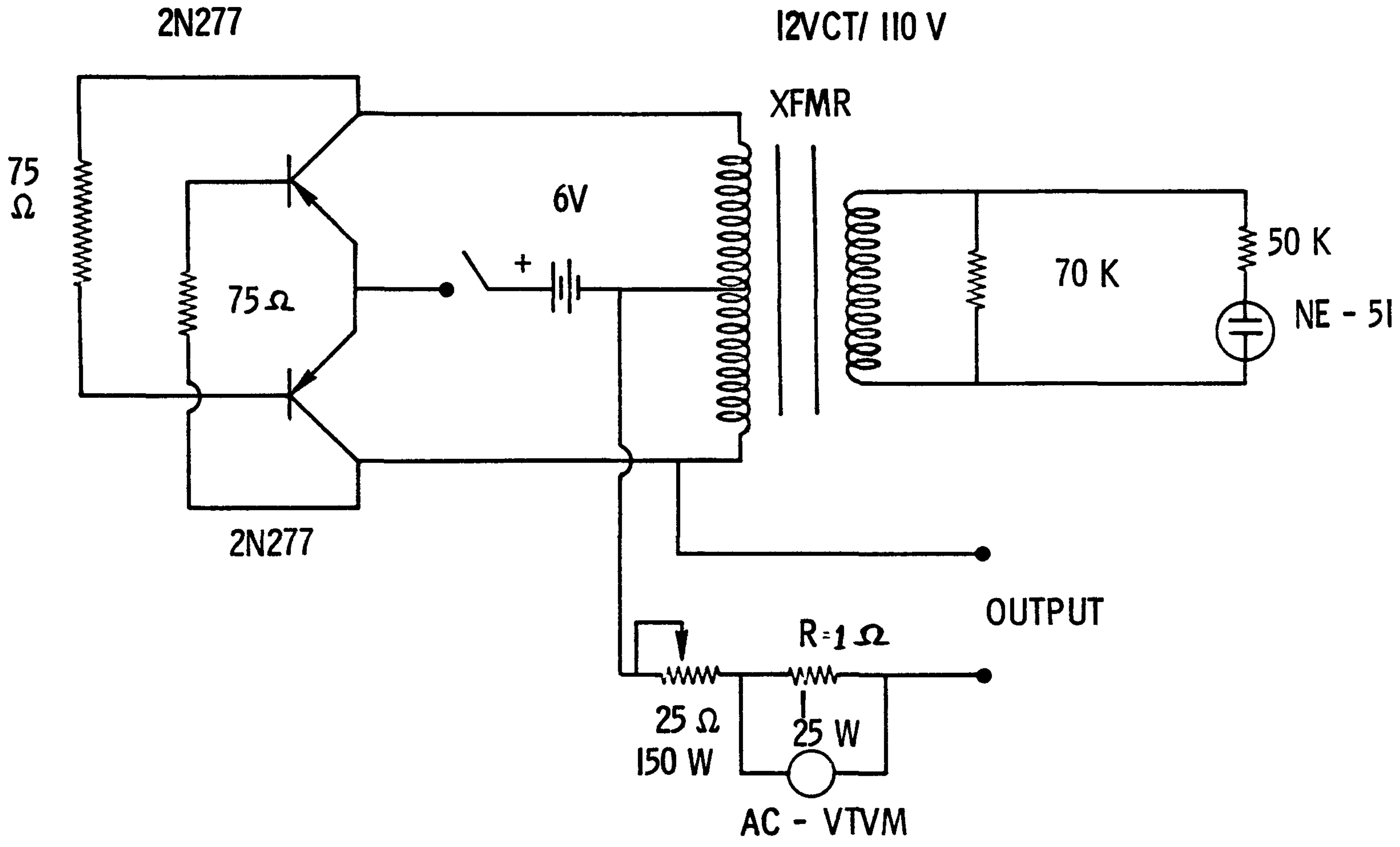
[1] "Thermoelectricity," P. H. Egli, J. Wiley & Sons (1958), p. 235.



100 CPS OSCILLATOR FOR CONDUCTIVITY MEASUREMENT
Figure 2

The heat transferred can also be expressed in terms of the Peltier effect

$$Q = \alpha i T \qquad (2)$$

where α = Seebeck coefficient
i = current passed through sample
T = absolute temperature of sample

Solving (1) and (2) for ΔT gives

$$\Delta T = \frac{\alpha i T \Delta X}{KA} . \qquad (3)$$

The Seebeck voltage is

$$V_\alpha = \alpha \Delta T = \alpha \left(\frac{\alpha i T \Delta X}{KA} \right) . \qquad (4)$$

The ohmic voltage across the sample is

$$V_\rho = iR = i \frac{\rho \Delta X}{A} \qquad (5)$$

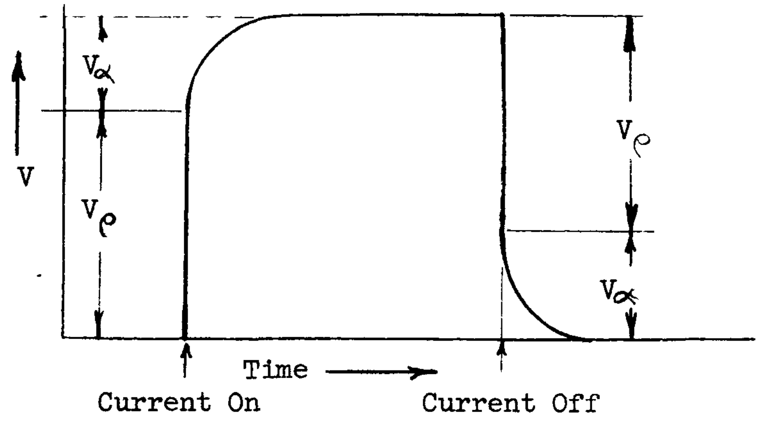
where R = resistance
ρ = resistivity

Dividing (4) by (5) gives

$$\frac{V_\alpha}{V_\rho} = \frac{\alpha^2 i T \, \Delta X/KA}{i \rho \, \Delta X/A} = \frac{\alpha^2 T}{K \rho} = ZT$$

where Z is the figure of merit.

The voltage-time relationship for both a current-on and a current-off situation is shown below:



In practice, it is not essential to record the entire voltage-time curve. The limits of V_α and V_ρ are readily observed on a meter. The ratio is then calculated and divided by the absolute temperature.

The circuit of the instrument is shown in Figure 3. Current to be used for Peltier heating is adjusted by a rheostat. A reversing switch permits the determination of anisotropic effects. The amplifier is a Leeds and Northrup Model 9835-B with self-contained output meter. The small, twisted leads were found sufficiently flexible to permit insertion of the sample into a tube furnace for the measurement of Z as a function of temperature.

Typical values obtained in the apparatus are shown below.

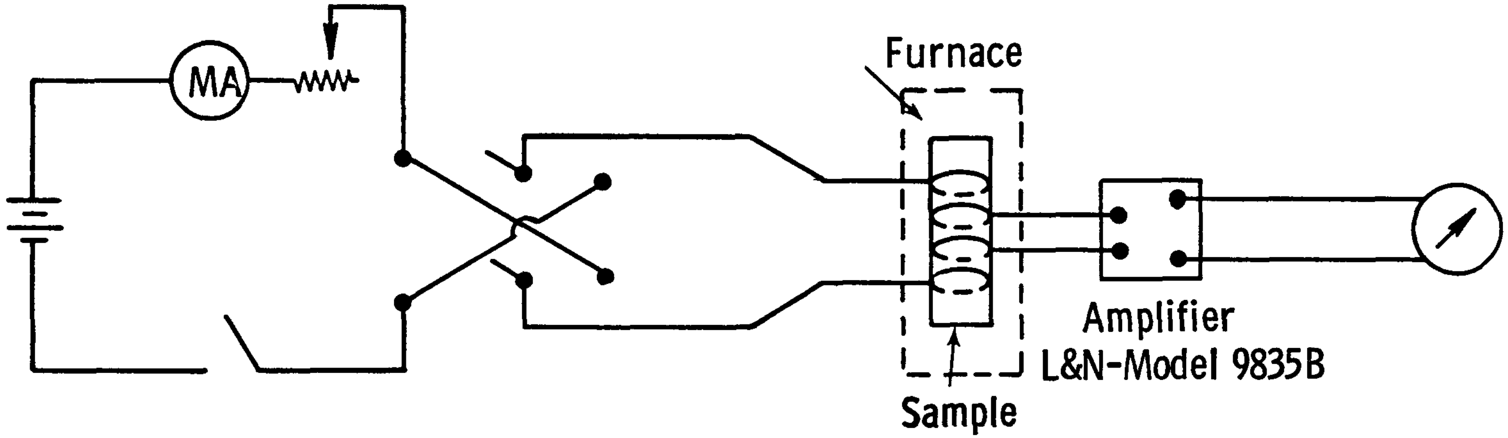
TABLE I

Z-METER READINGS OF FIGURE OF MERIT
(Room Temperature)

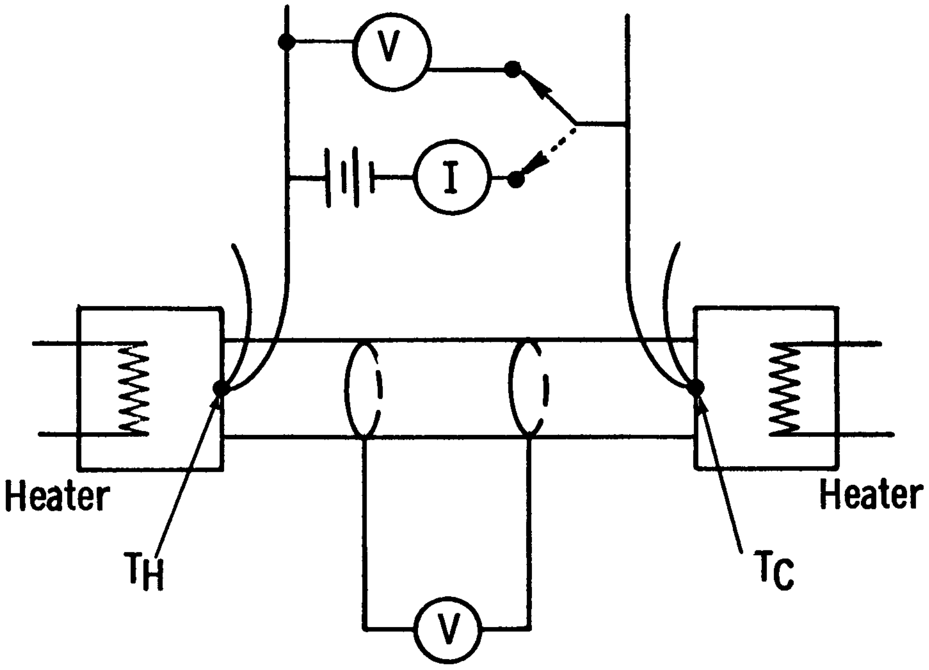
Sample	Z (1/K°)	Z (Literature Value)
PbTe	1.1×10^{-3}	1.2×10^{-3}
	4.2×10^{-4}	6.0×10^{-4}
USeTe	1.3×10^{-5}	---

C. Seebeck, Resistivity

The approach used for determining Seebeck coefficients and resistivity (by the DC method) is diagrammed in Figure 4. The desired average temperature and temperature differential is established in the sample by alternately adjusting the upper and lower heaters. End thermocouples permit the measurement of the temperature differential, the average temperature and the Seebeck voltage. A pair of twisted probes applied to the sample allow a resistivity measurement to be made (the end thermocouples being used as application electrodes in this case). The inside of the instrument casing is evacuated to reduce radial heat losses. The apparatus may also be used for determining thermal conductivity if guard heaters are carefully adjusted.



Z METER CIRCUIT
Figure 3



CIRCUIT FOR SEEBECK COEFFICIENT & RESISTIVITY
Figure 4

The unit described gives accurate results; it was used for samples which required lengthy study. For the rapid screening of thermoelectric materials, however, the time required for this measurement was too great to justify its use.

For the preliminary checking of Seebeck coefficient or for the determination of polarity, a quite simple apparatus was employed. This consisted of a pencil-type soldering iron with a lead wire brazed to its point. This lead wire and a wire from the sample were connected to a center-scale millivoltmeter. When the iron was heated and then momentarily pressed against the sample, the response of the meter indicated the polarity and approximate Seebeck voltage of the sample.

III. THERMOELECTRIC MATERIALS DEVELOPMENT - Uranium Chalcogenides

A. Purpose

The purpose of this program was to investigate the possibility of introducing high-temperature fissile-bearing thermoelectric materials into the design of a direct-conversion reactor system. Work was performed to ascertain the physical and electrical properties of compounds occurring in certain uranium-alloy systems.

The materials chosen were alloys of uranium with sulfur, selenium, and tellurium.

B. Preparation of Materials

1. Introduction

Table II lists the compounds that were prepared for this program. The general approach was to prepare each of the compounds listed, fabricate into samples suitable for measurement of α, ρ, and K, and then measure these parameters as a function of temperature to the highest temperature possible.

TABLE II

URANIUM COMPOUNDS

US, U_3S_5, U_2S_3, US_2
USe, U_3Se_4, U_3Se_5, U_2Se_3, USe_2
UTe, U_3Te_4, UTe_2
$US_{2-x}Te_x$

Table III illustrates the purity of starting materials used in the preparation of the above compounds.

TABLE III

TYPICAL SPECTROGRAPHIC ANALYSES FOR RAW MATERIALS

Results in PPM ± 30 per cent Relative

Element	Uranium[1]	Sulfur[2]	Selenium[3]	Tellurium[4]
Ag		< 1	< 1	< 0.3
Al	25	< 15	< 30	4
B	0.3	< 1	< 3	< 1
Ba		< 1		3
Be		< 0.1	< 0.3	< 0.3
Bi	< 0.5	< 15	< 10	2
Ca	13	5	50	2
Cd	< 0.5	< 50	< 30	< 30
Co	< 1	< 15	< 10	< 3
Cr	< 10	< 15	< 10	< 3
Cu	45	< 15	10	< 1
Fe	125	25	< 10	< 3
Ge		< 50	< 30	< 3
In	< 1	< 50	< 300	
K			< 100	
Li			< 1	
Mg	45	10	2	< 0.3
Mn	13	< 5	< 3	< 0.3
Mo	< 1	< 5	< 30	< 1
Na		< 150	10	
Nb		< 5	< 100	< 10
Ni	72	< 15	< 10	< 3
Pb	< 1	< 50	30	< 3
Sb	60	< 50	< 30	< 10
Si	< 1	15	40	22
Sn		< 50	< 10	< 3
Sr		< 5	< 10	< 6
Ti	12	< 5	< 30	< 3
V	< 1	< 5	< 30	< 10
W	< 20			
Zn	< 20	< 50	100	< 100
Zr		< 5	30	6

1 - Supplied by Davison Chemical Co., Erwin, Tenn.

2 - Supplied by Fisher Scientific Co., Fair Lawn, N. J.

3 - Supplied by American Smelting & Refining Co., South Plainfield, N. J.

4 - Supplied by American S & R, etc.

2. Methods of Preparation

The following methods were used for preparation of the compounds.

a) Solid Gas Reactions

Often,metal sulfides can be prepared by reacting a hot metal or metal oxide with hydrogen sulfide gas. Preparation of uranium-sulfur compounds was attempted in this manner. There was no apparent method to control the stoichiometry of the reaction products, and the H_2S gas was very hard to control in a flowing gas system. Any further hope of success was dashed because of the strong oxide-forming tendency of sulfur and the thermodynamic stability of UO_2.

b) Direct Synthesis of the Elements

It was then decided that the best way to control stoichiometry and purity of the materials would be by direct synthesis of the elements involved. Experiments were therefore begun in which cleaned uranium shavings and the anion of interest were reacted in sealed argon-filled Vycor tubes. The two elements were mixed as thoroughly as possible by shaking the tubes. They were then heated to temperatures as high as $850^{\circ}C$ for periods up to eight hours. It soon became evident that sulfur reacted with the uranium shavings much more readily than did selenium or tellurium. Because all of the reactions were diffusion controlled, homogeneous samples were very difficult to obtain. The end product usually contained free uranium in the center of the chip, the compound in question, and free anion. Changing from Vycor to quartz reaction tubes allowed temperatures as high as $1100^{\circ}C$ and reaction times up to 200 hours. The samples still lacked homogeneity. These high temperatures and long reaction times were responsible for as much as 400 ppm of silicon pick-up from the quartz reaction tube.

c) The Hydride Process

In order to obtain a more homogeneous product, the uranium starting material should be more finely divided than shavings. Preferably, it should be a powder. Uranium shavings were reduced to powder by the hydride process as described by Chiotti and Rogers.* Briefly, uranium reacts with hydrogen to form UH_3 at about 250°C. This can be reduced to uranium powder by heating to 450°C under a vacuum. This powder is then used as a starting material for making compounds. Weighed portions of uranium powder and appropriate anion were placed in a quartz tube and sealed off under one atmosphere of argon. The reactants were mixed by shaking the tube. Several experiments ended violently due to the high heat of reaction of the components.

d) Dual-Chamber Solid-Vapor Process

It soon became evident that the uranium powder was so highly reactive that interaction with the chalcogens at elevated temperatures would invariably result in an explosion. It was necessary to control the speed of reaction.

Since sulfur, selenium, and tellurium boil below the operating temperature limit for quartz, a quartz reaction tube was designed with separate but interconnected chambers for the uranium powder and sulfur. The quartz was sealed under a high vacuum and placed in a two-zone furnace assembly which permitted independent control of each zone. The temperature was raised slowly in both sides of the reaction chamber, but more slowly on the sulfur side. The final temperature reached was 925°C on the sulfur side and 975°C on the uranium side. The reaction product appeared homogeneous;

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* AECD-2974 "The Production of Uranium and Thorium in the Powder Form," P. Chiotti and B. A. Rogers

no free sulfur or uranium was observed. The compound (US_2) was sintered into loose lumps which were reduced to powder by slight agitation of the tube.

After several more encouraging results under various experimental conditions, it appeared that independent temperature control of each zone was unnecessary. The reactions proceeded rapidly with no explosions. This process became the exclusive method for preparation of the uranium chalcogen compounds. It can best be summarized as follows:

(1) Prepare uranium powder by "Hydride Method."

(2) In argon-filled glove box, load two-chamber quartz tube with weighed uranium and anion.

(3) Seal tube under high vacuum.

(4) Heat to above anion melting point; hold for about four hours. Raise to 1000°C over a 24 hour period; hold for 24 hours and furnace cool.

The only problem not completely solved by this process was the tendency of the compound and/or the uranium powder to react with the quartz. This was prevented by stopping the process at some intermediate temperature (500 to 700°C), cooling the furnace and agitating the reaction chamber so that any free uranium which remained on the quartz could be mixed in with the already-reacted portion. The tube was then returned to the furnace and heated to 1000°C. Since no reaction with the quartz was subsequently observed, it is believed that the silicon pick-up was greatly reduced.

e) Melting

Frequently, the best way to prepare a homogeneous compound is to heat the constituents above the melting point of the compound and then cool at such a rate that segregation and decomposition do not occur.

The first melting experiements with USe_2 utilized a molybdenum crucible sealed via a platinum O-ring and about 500 psi applied to the crucible cover. The sample was induction heated to 1650°C in argon so that complete melting was observed. However, selenium vapor leaked out of the crucible. Other samples were melted this same way, but in each case, anion vapor could not be contained even with pressures as high as 6000 psi on the cover.

It was decided that a tantalum or molybdenum crucible welded shut in an argon atmosphere held the most promise. Because of the extreme difficulty encountered with obtaining crack-free welds in molybdenum, all of the melting experiments were performed in tantalum crucibles welded shut in an argon-filled chamber.

The uranium-sulfur compounds could not be melted in the thin tantalum crucibles (20 ml wall) as they were constructed. A severe embrittlement of the tantalum occurred with resultant failure of the crucible and loss of the material being prepared. None of the uranium-sulfides were successfully melted because heavy-walled tantalum was not available when needed. Molybdenum was not utilized because a welding technique had not been perfected for its use.

No difficulties have been encountered with melting of uranium selenides or tellurides. The tantalum pick-up in the cast material was less than 400 ppm in all cases. Table IV is a summary of the data from melting experiments.

3. Fabrication of Samples

Since most convenient methods of measuring electrical resistivity and thermal conductivity require a sample of regular and preferably simple geometry, it was necessary to develop methods of fabricating the uranium-chalcogen compounds into dense,

TABLE IV

SUMMARY OF MELTING EXPERIMENTS ON URANIUM COMPOUNDS

Sample No.	Composition (Nominal)	Bomb Material	Heat Source	Ultimate Temp. (°C)	Results
4-19-60	USe_2	Mo	RF Coil	1650	Melting achieved; some Se leakage
U-Se-1	USe_2	Graphite	RF Coil	>1450	Melting achieved; some Se leakage
U-Se-2	U_2Se_3	Mo	RF Coil	>1400	Melting achieved; some Se leakage
U-Te-1	U_3Te_4	Graphite	RF Coil	>1400	Melting achieved; some Te leakage
US-B-1	US	Ta	RF Coil	?	Bomb exploded; sample lost
B-U-S-H-8	U_3S_5	Ta	Vacuum Resistance Furnace	1885	Bomb failed; sample lost
USe-B-1	USe	Ta	RF Coil	1800	Melting achieved
B-U-Se-H-2	USe_2	Ta	RF Coil	1400	Melting achieved
B-U-Se-H-4	U_3Se_4	Ta	Vacuum Resistance Furnace	1800	Melting achieved
UTe-B-1	UTe	Ta	RF Coil	1770	Bomb failed; sample lost
B-U-Te-H-2	UTe_2	Ta	RF Coil	1390	Melting achieved
B-U-Te-H-3	U_3Te_4	Ta	RF Coil		Melting achieved
B-U-Te-H-4	UTe	Ta	RF Coil	1500	Melting achieved
B-U-Te-H-6	U_3Te_4	Ta	RF Coil	1430	Bomb failed slightly; sample saved
B-U-Te-H-7	UTe_2	Ta	RF Coil	1480	Melting achieved
U-Se-Te-1	$USe_{1.29}Te_{0.71}$	Ta	RF Coil	1500	Bomb exploded; sample lost
U-Se-Te-2	USeTe	Ta	RF Coil	1700	Melting achieved
U-S-Te-2	USTe	Ta	RF Coil	1800	Melting achieved

structurally sound samples, suitable for making these measurements. Since the compounds were being prepared essentially as powders, the logical method for such fabrication was by powder metallurgy techniques. The various fabrication methods are discussed in the following paragraphs.

a) Cold Pressing and Sintering

The most common method of making thermoelectric samples from powders is cold-pressing of cylindrical pellets followed by sintering at temperatures and times sufficient to achieve diffusion bonding between the close-packed powder particles. Unfortunately, the uranium-chalcogen compounds are so ceramic that the use of pressures sufficient to make pellets which would not crumble on handling resulted in jamming of the pellets in the die. The use of a die lubricant was not in keeping with the desire to maintain high purity samples. Several dies were ruined before this method was abandoned.

b) Hot-Pressing

Hot-pressing, which combines the cold-press-and-sinter technique into a single operation, was the next approach. Graphite was the only material available which was readily machinable and could accommodate die pressures of 5000 psi or more at temperatures in excess of 1000°C. The dies were loaded in argon and placed in an argon-filled apparatus capable of simultaneous hydraulic pressing and induction heating.

The major difficulty encountered in hot-pressing uranium-chalcogen pellets was the loss of volatile sulfur, selenium, and tellurium during the process, because the dies could not be made pressure tight. Thus, the nominal compositions of the compounds incurred shifts of unknown magnitude, so that the electrical measurements subsequently obtained from the materials represented compositions somewhat different than those originally specified. Aside from this problem, the samples made by hot-pressing were generally quite satisfactory, which indicates that a procedure which simulates hot-pressing and also prevents volatilization should produce excellent samples of known composition. Table V presents hot-pressing data on a number of representative samples.

c) Swaging

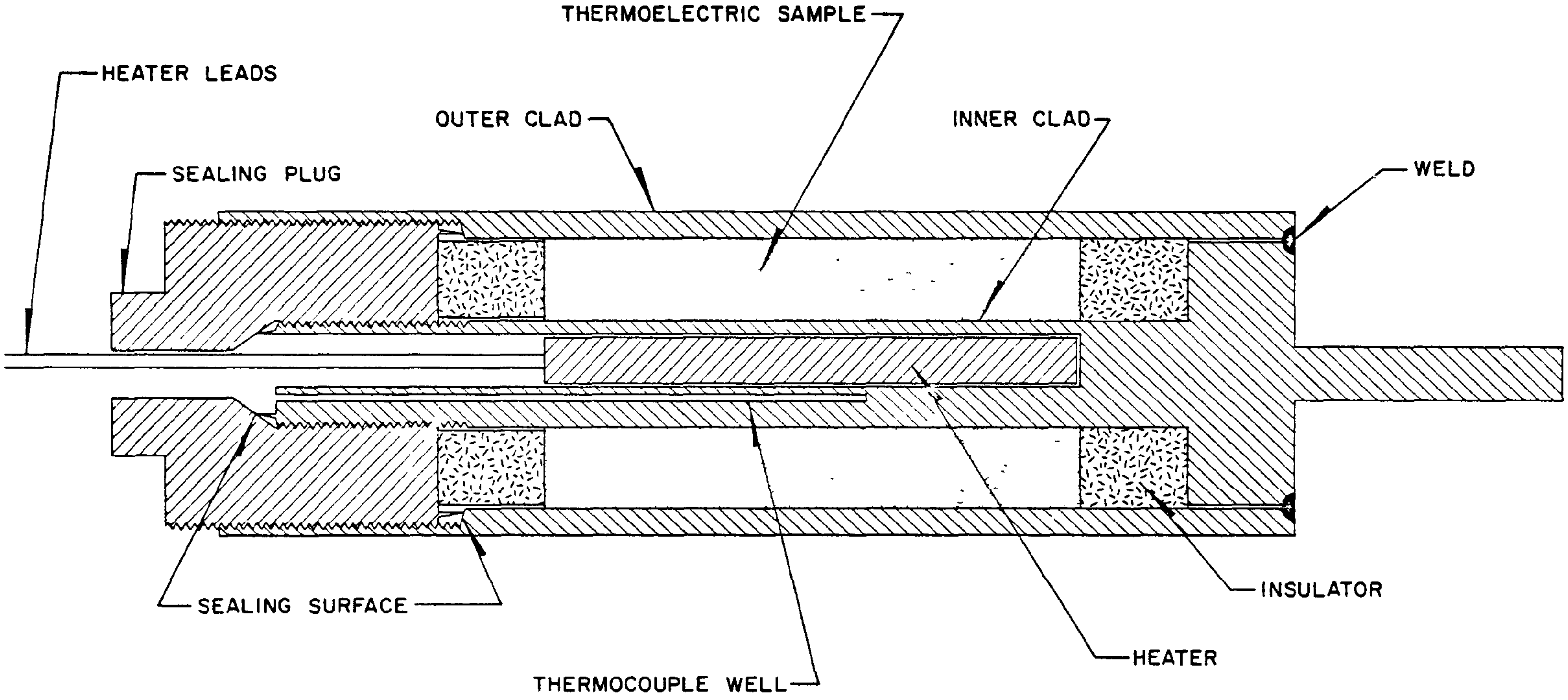
It has been demonstrated that powdered thermoelectric materials may be swaged to compact them in a manner similar to cold-pressing. Heat treating swaged material yields samples with properties similar to those of cold-pressed and sintered specimens. In the case of the uranium-base materials, two approaches to fabricating swaged samples were employed. To avoid the volitilization encountered in hot-pressing, the technology of swaged cylindrical-geometry thermoelectric generators developed in other work performed under this contract was applied in designing several sealed cylindrical-geometry test samples containing electrical heaters, test leads, and thermocouples to permit measurement of α, ρ, and K.

A typical sample resulting from this first approach is shown in Figure 5. These samples were assembled in the argon-filled glove box, sealed via threaded plugs as shown in Figure 5, swaged to compact the powder, sealed in quartz, heat-treated to sinter the powder particles, and machined to yield a fully-instrumented test device. The swaging reductions were 30 to 75 per cent by volume and the heat treatments 1000 to 1100°C for up to eight hours. In the few samples that were made, however, severe distortion of the device could be avoided only by limiting the densification of the uranium-chalcogen powders to 79 per cent of theoretical.

TABLE V

HOT-PRESSING DATA FOR URANIUM-CHALCOGEN SAMPLES

Sample	Nominal Composition	Pressure (psi)	Temperature (°C)	Time (min)	Weight (gms)	Density (gm/cc)	Per Cent of Theoretical Density of Nominal Composition (gm/cc)
11-11-59	US_2	3000	1000	25	7.95	7.06	86.5
1-6-60	US_2	3000	1200	20	12.72	7.66	93.9
1-29-60	US_2	3000	1350	15	18.60	7.76	95.1
3-4-60	US_2	1000	1200	30	13.87	7.49	91.6
3-18-60	US_2	2000	1200	30	11.01	7.86	96.3
U-S-2	US_2	2500	1200	30	16.80	7.85	96.2
U-S-H-2	US_2	6070	1330	30	14.19	7.93	97.1
11-20-59	USe_2	4000	965	30	20.74	8.77	95.8
12-16-59	USe_2	4000	1025	30	24.31	8.66	94.6
2-11-60	USe_2	3000	1100	20	11.68	8.72	95.2
3-9-60	USe_2	2000	1125	30	15.78	8.91	97.4
U-Se-2	U_2Se_3	2000	1200	30	15.75	8.34	88.6
U-Se-3	USe	7600	1430	60	17.46	9.73	87.9
B-U-Se-H-4	U_3Se_4	7600	1300	30	18.54	9.21	91.9
11-23-59	UTe_2	4000	975	30	22.32	8.90	?
1-18-60	UTe_2	3000	1050	30	15.77	8.85	?
2-23-60	UTe_2	2500	1000	30	24.07	9.16	?



CYLINDRICAL GEOMETRY TEST SAMPLE
READY FOR SWAGING

FIGURE 5

The second approach was the fabrication of pellets by swaging. In protective environments, powder was loaded into metal tubes and sealed in by welded end plugs. The sealed tubes were given a swaging reduction of about 30 per cent by volume, and heat-treated at 1000°C or higher for eight hours or more. Problems encountered in removing the cladding without breaking up the pellets delayed the evaluation of this method.

d) Pressure Sintering

One drawback to the swaging process as applied to the hard uranium-chalcogen compounds was the tendency for the material to extrude before full compaction was effected by the swaging pressures. A process which tends to overcome this effect is pressure sintering, carried out in an inert-gas-filled autoclave at elevated temperature and pressure. Since the applied pressure is isostatic, the tendency to axial elongation should be reduced if not eliminated. The proper combination of pressure, temperature, and time should yield results similar to those obtained by hot pressing, and losses by volatilization could be eliminated by proper encapsulation.

One experiment of this type was performed. An Armco iron tube was filled with USe powder and sealed at both ends with welded caps. The tube was swaged to a reduction of about 23 volume per cent, and then heat-treated in a helium autoclave at 750°C and 10,000 psi for six hours. The pressure sintering increased the total volume reduction to about 34 per cent and, more significantly, shortened the sample by 5 per cent. The use of higher temperature and the same or higher pressure could well make pressure sintering the best fabrication technique of all.

4. Physical and Chemical Evaluation

The criteria of density, compatibility, thermal shock resistance, chemical composition, microstructure, and crystal structure were used for evaluation of the uranium-chalcogen samples.

a) Density

It was desirable to attain the highest possible densities in fabricated samples, both to achieve mechanical strength and to ensure that the results of electrical measurements were truly representative of a particular composition. Table V shows that the majority of hot-pressed samples had densities over 90 per cent of theoretical, although some account must be taken of the increase in density which probably resulted from the loss of volatile anion material. Of the other fabrication methods, only pressure sintering yielded a sample of encouraging density.

b) Compatibility

Very little work was done on formal compatibility studies, but considerable information was gathered indirectly during various preparation and fabrication procedures. This information is presented below:

(1) Armco Iron: Little attack by Se and Te compounds to 1000°C.

(2) Low Carbon Steel: Somewhat less resistant than Armco iron to Se and Te compounds.

(3) Stainless Steels: High Cr - low Ni grades suffer little attack by S and Te compounds to 800°C.

(4) Nickel and Inconel: Violently attacked by all chalcogens at moderate temperatures.

(5) Platinum and Palladium: React with sulfur compounds above 700-900°C.

(6) Chromel: Resistant to chalcogens to about 900°C.

(7) Alumel: Attacked by chalcogens above 400-600°C

(8) Molybdenum: Resistant to solid and liquid Se and Te compounds to 1650°C.

(9) Tantalum: Resistant to solid and liquid Se and Te compounds to 1800°C; attacked by sulfur compounds above 600-1000°C.

(10) Graphite: No apparent attack by chalcogens to 1600°C.

c) Thermal Shock Resistance

Although no quantitative data were obtained in this area, observations indicate that the most-metallic compounds of the chalcogen systems (e.g., US, USe) have fairly good thermal shock resistance, while the more-ceramic-like compounds (e.g., US_2) definitely crack upon rapid thermal cycling.

d) Chemical Composition

The quantitative analysis of uranium-chalcogen compounds proved difficult. Early results were not precise, but recently techniques have been developed which seem reliable.

Uranium was determined to ±0.05 weight per cent absolute as U_3O_8, using a standard ignition to constant weight procedure. Sulfur contents were determined reproducibly to ±0.10 weight per cent absolute by a titrametric process involving formation of hydrogen sulfide gas and subsequent precipitation of cadmium sulfide. A new titrametric procedure for selenium yielded results reproducible to ±0.05 per cent absolute. Tellurium was determined gravimetrically, but an adaptation of the selenium process was being evolved to improve the reliability.

Impurity analyses were performed using spectrographic methods on the ignited U_3O_8 samples.

e) Microstructure

Very few fabricated or cast samples survived electrical measurements and other processing sufficiently to permit worthwhile metallographic examination. Most of those actually examined were two phase; some had a third phase.

f) Crystal Structure

A number of x-ray powder photographs were taken, mostly prior to sample fabrication. Due to the complexity of most of the structures and the lack of precise reference data, analysis of the patterns was a difficult procedure.

Most of the patterns indicated the presence of a phase different from that which should be present according to the sample stoichiometry. Two patterns indicated that the samples were strictly single phase. One encouraging fact was the complete absence of reflections corresponding to oxychalcogenide compounds, which speaks well for the preparation procedures employed.

C. Thermoelectric Properties

The technique used to measure the electrical properties of the uranium compounds will be discussed in a later section of this report entitled Electrical Measurements.

In general, the uranium sulfur compounds have a high Seebeck coefficient (up to 375 $\mu v/^{o}C$) and high resistivity (up to 0.8 ohm-cm).

The uranium-selenium compounds also seem promising as thermoelectric compounds. They have low resistivities (10^{-2} to 10^{-4} ohm-cm) and Seebeck coefficients up to 130 $\mu v/^{o}C$.

The uranium-tellurium compounds are quite metallic in nature, with low resistivities (10^{-3} to 10^{-5} ohm-cm) and low Seebeck coefficients (25 μv/°C).

Since no doping experiments were carried out, the effects of doping on electrical properties were not determined.

A detailed account of the results obtained from the work on uranium chalcogenides may be obtained by referring to WCAP-1866, Preparation and Preliminary Evaluation of Some Uranium Chalcogenides.

IV. IRRADIATION STUDIES

The resistance of thermoelectric materials to irradiation damage was naturally of primary interest when the Thermoelectric Nuclear Fuel Element Project was proposed. The dearth of information on irradiation effects necessitated the institution of an extensive program on irradiation testing into the overall Thermoelectric Nuclear Fuel Element Program. As originally conceived, the irradiation studies were to quickly establish the feasibility of using thermoelectric materials in a nuclear reactor, and to qualitatively compare representative thermoelectric materials. The choice of thermoelectric materials to be extensively investigated was deferred until high efficiency thermoelectric materials suitable for reactor application (low neutron capture and high operational temperature) were developed.

The initial irradiation program was divided into three areas as follows:

A. Van de Graaff Studies (electron irradiation)

B. In-Pile Studies (reactor irradiation concurrent with measurements)

C. Post-Irradiation Studies (reactor irradiation followed by out-of-pile measurements).

A. Van de Graaff Irradiation Studies

Since the Van de Graaff studies were discontinued relatively early in the contract period, they contributed very little information to the irradiation damage studies. A brief investigation of $Li_{.037}Ni_{.963}O$ was carried out using 1.8 and 2.0 mev electrons with dosages up to 4.35×10^{19} electrons/cm^2. The results of these experiments suggested a decline in resistivity and Seebeck coefficient with dosage. For a detailed explanation of the experimental apparatus, methods, and results, refer to WCAP-1162, Thermoelectric Nuclear Fuel Element Annual Progress report dated April 10, 1959.

B. In-Pile Irradiation Studies

The initial in-pile irradiation studies were carried out at the test reactor at Brookhaven National Laboratory, which is basically a thermal neutron source; the ratio of thermal-to-fast neutrons is about 10:1. Flux levels encountered were about 10^{12} nv of energies less than 0.3 ev and 10^{11} nv of energies greater than 0.3 ev.

Samples were instrumented with thermocouples, DC current leads, and electrical heaters in such a manner that Seebeck coefficient and the electrical resistivity could be obtained as a function of time (neutron flux). Initially, attempts were made to insert a thermal conductivity standard in thermal series with the thermoelectric sample, to obtain a relative measurement of thermal conductivity, K, in addition to α and ρ. Since difficulties arose in the series bonding of the low-thermal-conductivity standards, measurements of thermal conductivity were delayed until satisfactory sample arrangements could be achieved. It was presumed that changes in K would almost assuredly be in the direction of low electron volt values which would improve rather than degrade the net thermoelectric efficiency.

A summary of in-pile experiments performed in the Brookhaven reactor is presented in Table VI, which shown that the thermal neutron exposure was in the range 8×10^{18} to 5×10^{19} nvt. The corresponding fast flux was of course about an order of magnitude lower for these samples.

The data obtained from these samples is typified by the results displayed in Figures 6 and 7 for $Li_{.06}Ni_{.94}O$ and P-type PbTe, respectively. Although there is considerable scatter in these data, it can be seen that the Seebeck coefficients for both materials remained relatively unchanged and that of PbTe showed a steady increase. The resistivity increase was later attributed to a chemical

TABLE VI

BROOKHAVEN REACTOR IN-PILE IRRADIATION EXPERIMENTS

Experiment No.	Material	Total nvt (t)	Remarks
1	$Li_{.013}Ni_{.987}O$ $Li_{.013}Ni_{.987}O$ $Li_{.035}Ni_{.965}O$	1.7×10^{19}	
2	$Li_{.05}Ni_{.95}O$ GeTe Bi_2Te_3	1.3×10^{19}	
3	$Li_{.05}Ni_{.95}O$ $Li_{.05}Ni_{.95}O$		lead failed
4	$Li_{.05}Ni_{.95}O$ $Li_{.05}Ni_{.95}O$	8×10^{18}	
5	N-type PbTe P-type $Bi_{.1}Ge_{.9}Te$	5×10^{19}	

FIGURE 6

TE PROPERTIES OF $Li_{.06}Ni_{.94}O$ VS. THERMAL FLUX

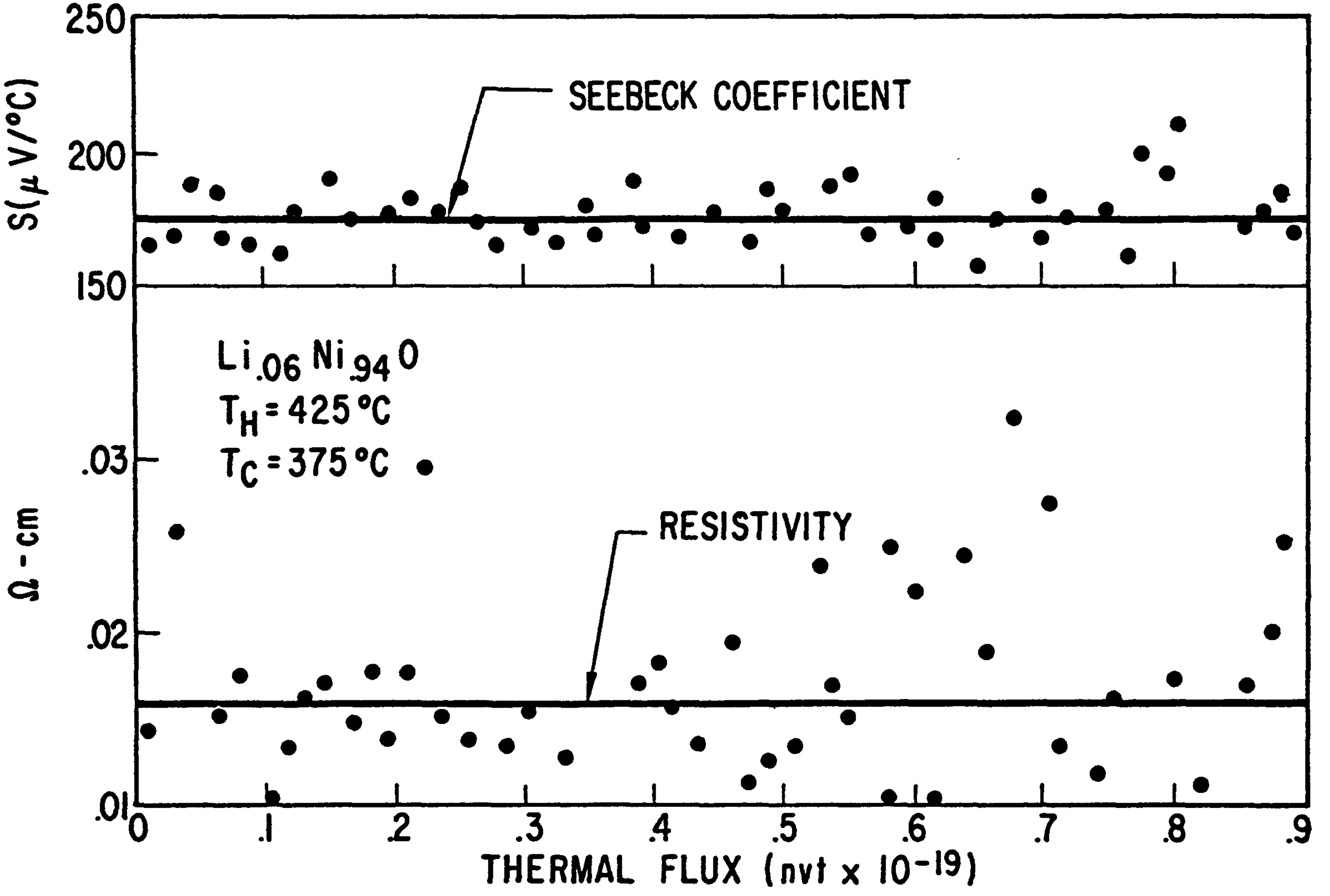
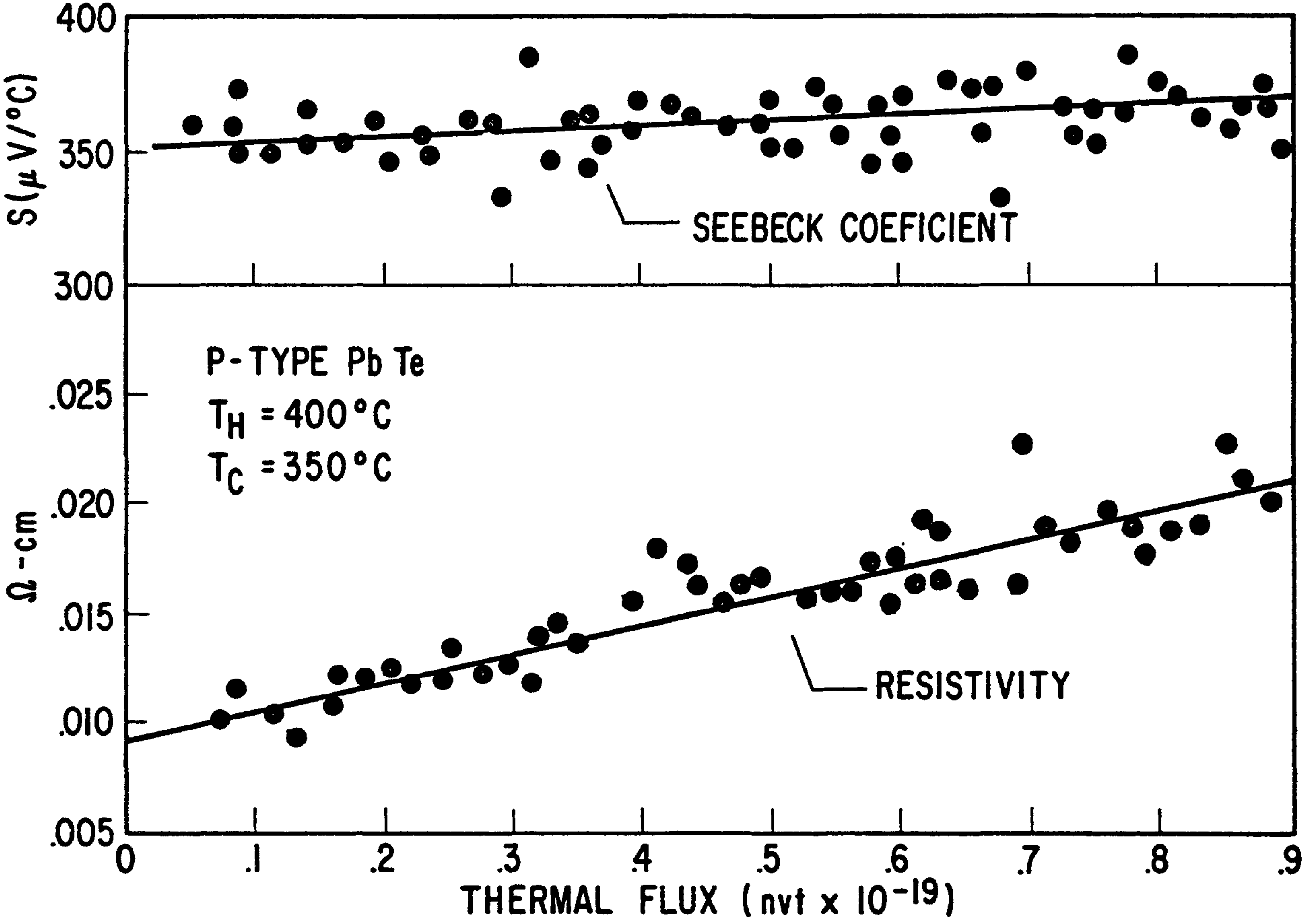


FIGURE 7

TE PROPERTIES OF P-TYPE PbTe VS THERMAL FLUX



problem rather than to irradiation damage effect when it was discovered that P-type PbTe behaved similarly out-of-pile as well. Later data on P-type PbTe based on pre- post-irradiation measurements also suggested that the resistivity increase was too large at the ambient temperature utilized (350-400°C) to be attributable to irradiation damage.

The samples which were subjected to in-pile measurements of resistivity and Seebeck coefficient in the Brookhaven reactor other than those shown in Figures 6 and 7 generally indicated that no gross irradiation effects were incurred at the dosage levels indicated. It was noted that several bonded samples suffered an overall resistance effect due to an increase in bond resistance, but this was not interpreted as a fundamental irradiation problem since the state-of-the-art of bonding was then quite unsatisfactory even for out-of-pile applications.

In-pile experiments were then shifted to the Westinghouse Testing Reactor in order to obtain higher flux capabilities, particularly fast flux (energies $>$ 0.3 ev). The reactor was rated depending on core position at nv levels up to 10^{14} fast and about the same thermal. At these levels an integrated fast flux of greater than 1×10^{20} was obtainable in only one reactor cycle (21 days).

Since at this time PbTe was considered to be the best all-around thermoelectric material for in-pile use, subsequent irradiation studies were limited to PbTe only. The mechanical problems associated with bonding pellets of PbTe indicated that the "swaged" tubular geometry of this type of sample also permitted securing thermal conductivity measurements in-pile, an accomplishment which with other geometries was extremely difficult.

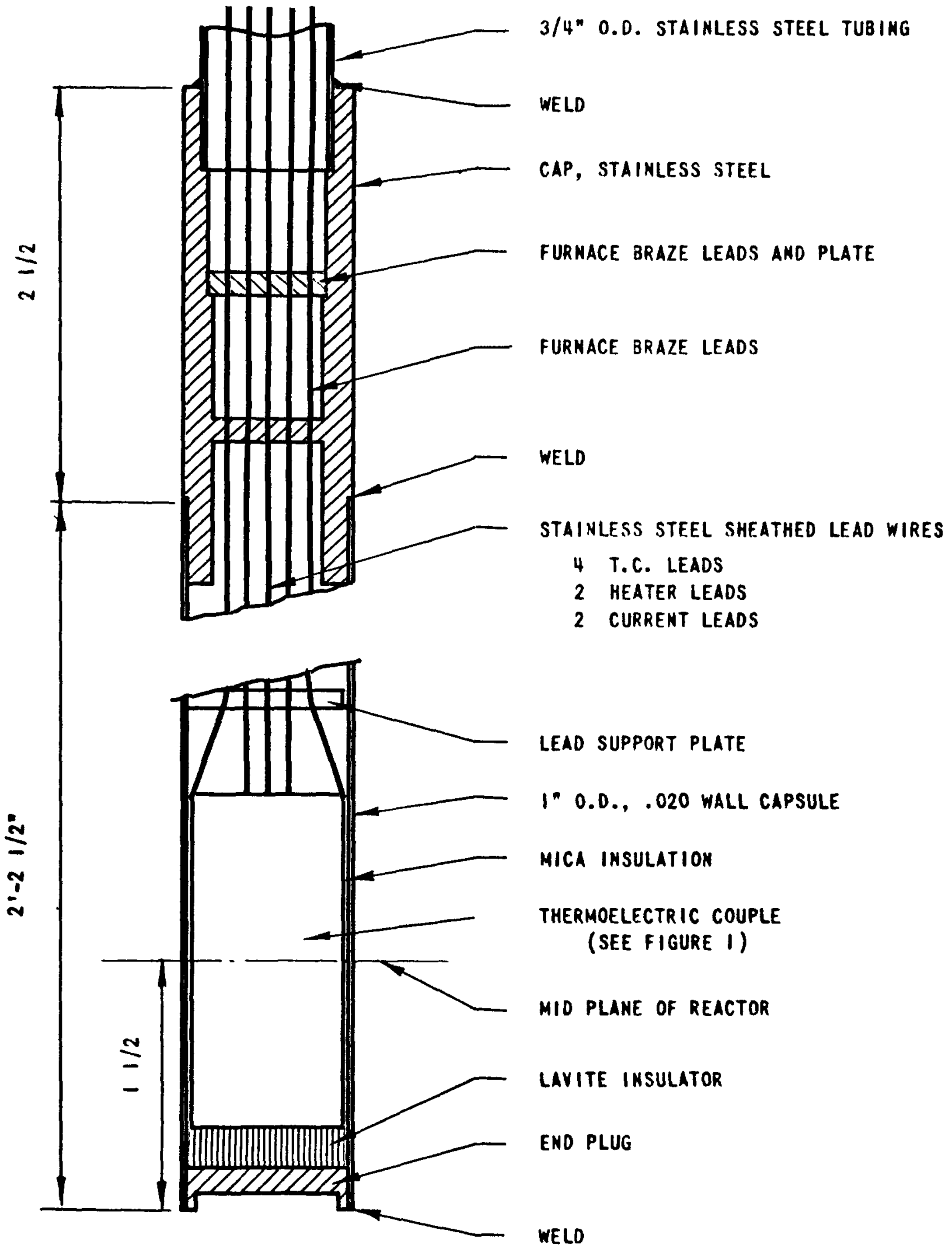
Two in-pile experiments performed in WTR on the cylindrical geometry sampler were disappointing due to a series of instrumentation difficulties. The necessity to completely insulate the sample electrically from the capsule in order not to set up circulating currents, plus the large number of leads required to obtain the necessary data, impaired the reliability of the samples. A typical sample and capsule arrangement are illustrated in Figures 8 and 9. Qualitatively, the results of these in-pile experiments indicated no gross changes had occurred in the Seebeck coefficient and electrical resistivity of N- and P-PbTe, but unfortunately no useful thermal conductivity data were obtained.

For a more detailed discussion of in-pile measurements, refer to report WCAP-1680, Radiation Effects on Thermoelectric Materials.

C. Post-Irradiation Measurements

Samples of thermoelectric material were prepared in the form of right cylinders approximately 1/2 inch in diameter and 1/2 to 1 inch long. All specimens were carefully graded by visual observation and density measurements in an attempt to reject those with detectable imperfections. Room temperature resistivity measurements were then made on the better samples with a K-3 potentiometer to determine if the material had normal thermoelectric properties for its particular composition. Representative samples could then be selected for pre-irradiation measurements over the appropriate temperature range. The samples were then heated to elevated temperatures appropriate to their temperature range, and measurements were taken to establish these properties as a function of temperature.

After the preliminary measurements were made, the samples were encapsulated and irradiated as shown in Table VII. It is noted in Items 12 and 13 that use was made of the Experimental Testing Reactor (ETR) at the National Reactor Test Station for the last irradiation study. This reactor subjected the samples to a flux of 4.9×10^{14} thermal and 4.5×10^{13} fast.



CAPSULE ARRANGEMENT

FIGURE 8

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FIGURE 9 - Capsule Arrangement

TABLE VII

PRE- POST-IRRADIATION STUDIES

	Type of Sample	Reactor	Integrated Flux (nvt) t=thermal, f=fast
1.	$Li_{.013}$	Brookhaven	1.5×10^{19} (t)
2.	$Bi_{.05}Ge_{.95}Te$	Brookhaven	9.4×10^{18} (t)
3.	GeTe	Brookhaven	4.5×10^{18} (t)
4.	MnTe	Brookhaven	4.5×10^{18} (t)
5.	$CeS_{1.43}$	Brookhaven	5.6×10^{18} (t)
6.	ZnSb	Brookhaven	5.6×10^{18} (t)
7.	PbTe (N)	Brookhaven	1.4×10^{19} (t)
8.	$Bi_{.05}Ge_{.95}Te$	WTR	1.5×10^{20} (f)
9.	GeTe	WTR	1.5×10^{20} (f)
10.	PbTe (N)	WTR	1.5×10^{20} (f)
11.	PbTe (P)	WTR	1.5×10^{20} (f)
12.	PbTe (N)	ETR	12.1×10^{20} (t), 10.3×10^{19} (f)
13.	PbTe (P)	ETR	12.1×10^{20} (t), 10.3×10^{19} (f)

Of the samples listed in Table VII, only $Li_{.013}Ni_{.987}O$, $Bi_{.05}Ge_{.95}Te$, GeTe, and PbTe were extensively investigated. The MnTe, CeS and ZrSb samples were not considered attractive for in-pile use but were included to furnish a broad picture of the irradiation damage characteristics of thermoelectric materials. Subsequent pre- post-irradiation studies were eventually limited to PbTe only, since it represented the most attractive material based on nuclear characteristics and efficiency potential.

In general, the results of pre- post-irradiation studies showed that up to the irradiation dosages utilized there exists a damage potential which is influenced by the ambient temperature of the sample during irradiation. This damage is in most cases characterized by an increased resistivity and a slightly elevated Seebeck coefficient. There also exists a manifestation of "damage" associated with transmutation of atoms, which is of course irreversible, i.e., cannot be annealed. These transmutation effects are dependent on the particular thermoelectric material, its nuclear cross-sections, and the nature and intensity of the neutron flux. The other forms of irradiation damage, i.e., interstitials, etc. apparently can be annealed by post-irradiation heating of the sample to temperatures greater than the ambient irradiation temperature.

Fortunately, these annealing temperatures need not be high compared to the useful temperature range of most of the thermoelectric materials, so that their use in-pile is not prohibited. This can be illustrated by PbTe, which has a useful temperature range from room temperature to $600^{\circ}C$ with an annealing temperature of 150 to $200^{\circ}C$. The resultant temperature difference (400-$450^{\circ}C$) is adequate to give an overall efficiency of the order of 5 to 7 per cent.

A more detailed account of pre- post-irradiation studies is presented in WCAP-1680.

V. DESIGN AND FABRICATION OF THERMOELECTRIC NUCLEAR FUEL ELEMENTS

This task covers the design, fabrication and evaluation of thermoelectric nuclear fuel elements, in which the heat of nuclear fission is converted directly to electrical energy by thermoelectricity as shown in Figure 10. A hot junction is established at the nuclear fuel-thermoelectric material interface, while a cold junction is established at the thermoelectric material-reactor coolant side of the element.

Initial fabrication techniques evaluated for forming suitable thermoelectric element geometries included flame-spraying, hot and cold pressing, powder rolling and swaging. Initial swaged elements, both bench tests and in-pile tests, gave such encouraging results that swaging was chosen as the fabrication technique to be explored in detail.

Figure 11 shows four element designs chosen as likely to provide the most useful data:

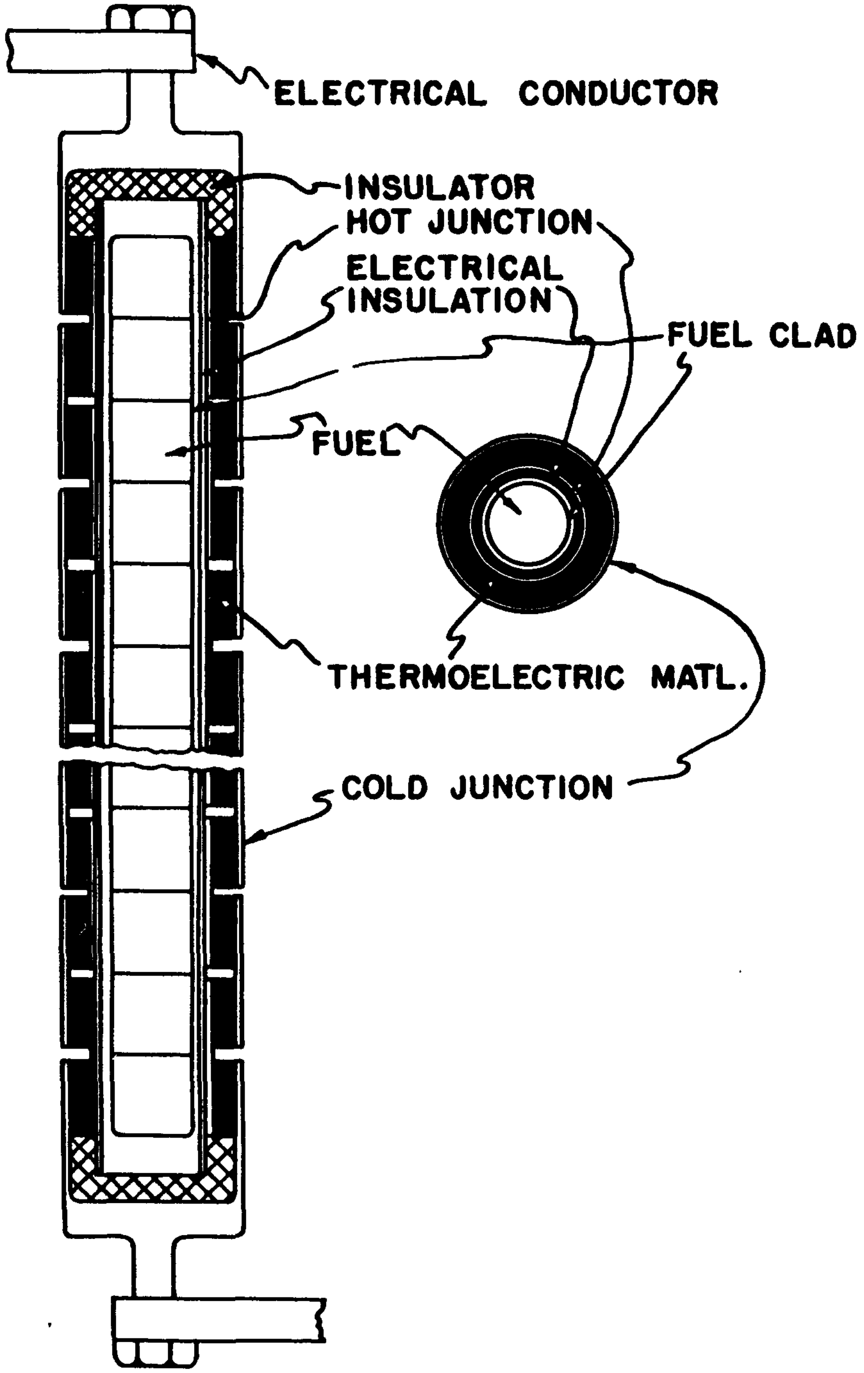
1) Single leg (Fig. 11A) for providing scientific data (viz., Seebeck EMF, electrical resistivity, and thermal conductivity of a specific material).

2) Double leg or single couple (Fig. 11B) for providing engineering data (viz., total Seebeck EMF and resistivity, and average thermal conductivity of two specific materials).

3) & 4) Multi-junction elements (Figs. 11C and 11D) for providing useful power.

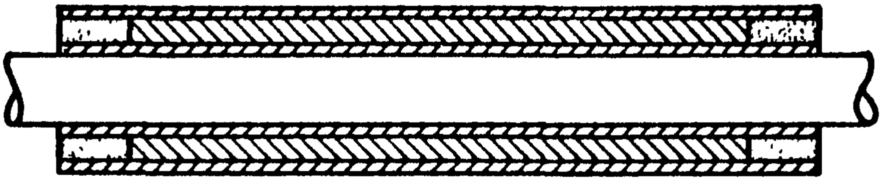
All additional work has been expended on improving these designs and finding new and better materials and processes from which to fabricate prototype elements of these designs.

Prototypes of all four designs were made using Type 304 stainless steel or low carbon steel conductors, Lavite insulating members, and PbTe. The initial prototypes of Designs (1) and (2) were generally fabricated using powdered PbTe while those of Designs (3) and (4) were

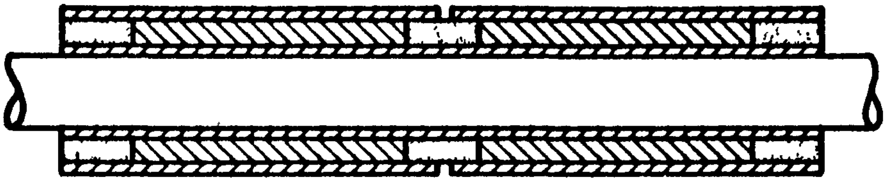


SERIES THERMOELECTRIC ELEMENT

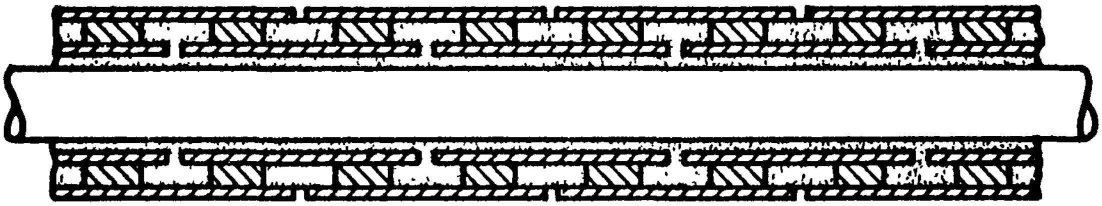
FIGURE 10



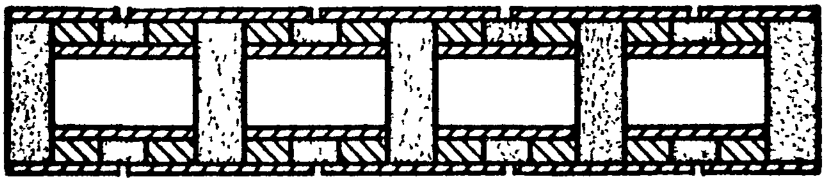
A - SINGLE LEG



B - DOUBLE LEG



C - MULTI-JUNCTION (NOTCHED BAR)



D - MULTI-JUNCTION (PELLETIZED)

▨ CLAD-MILD STEEL

□ HEAT SOURCE: HEATER OR FISSION HEAT

▩ INSULATION

▧ TE MATERIAL

FIGURE 11
SECTION VIEW OF PROTOTYPE ELEMENT DESIGNS

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fabricated using crudely-pressed PbTe washers. Lavite insulators were quite thick, and shaped rubber stoppers were used to contain components during swaging.

Simultaneously, several supporting studies were initiated. Subjects included in the first of several materials properties studies were the cold pressing of thermoelectric and insulating materials, the effect of powder preparation procedures on the thermoelectric properties of PbTe, and the effects of heat treating on pressed insulating materials.

Pressing data for N-PbTe, P-PbTe, Lavite powder, and mica powder were obtained; the per cent theoretical densities were plotted versus pressing pressure. Also, mechanical integrity was noted as a function of density. For both N- and P- PbTe, a pressed density of 90 per cent theoretical seemed optimum, and elements have since been assembled with 90 per cent dense PbTe pellets.

Results of the study of powder preparation procedure and its effect on the thermoelectric properties of PbTe indicated a need for change in the handling of fine PbTe powder. Chemisorbed impurities, probably mostly oxygen, adversely affected the α^2/ρ values of both N- and P- PbTe. Also, heat treatments of six hours at 600°C resulted in only partial recovery of the α^2/ρ values towards those calculated from published 3 M Company data (WCAP-1596-Quarterly Progress Report for April-June, 1960 and WCAP-1647-Quarterly Progress Report for for July-September, 1960). Thus, the simple expedient of crushing PbTe just before pressing and swaging was adopted.

Expansion data (per cent volume change versus time at 600°C) were obtained for cut Lavite, uncontained and contained pressed Lavite, cut Mycalex, and uncontained and contained pressed mica (WCAP-1647).

A swaging study was conducted to determine the differences between cold and hot swaging (WCAP-1596). It was concluded that the swaging temperature below 300°C has little apparent effect on the as-swaged density of either N- or P- PbTe. That is, single-couple elements, alike before heat treating and swaging, each displayed essentially the same dimensional changes as a result of swaging them one at room temperature and one at 300°C. However, the swaging temperature did have an effect on the uniformity of thickness of the clad wall. Furthermore, a very distinct difference existed in the test results of the two elements. The cold-swaged element failed after approximately 250 hours at $T_H \sim 600^\circ C$ and $T_C \sim 100^\circ C$ (WCAP-1647). The hot swaged element exceeded 7000 hours of satisfactory operation (at $T_H \sim 500^\circ C$-$565^\circ C$ and $T_C \sim 50^\circ C$-$65^\circ C$) before the heater burned out (WCAP-1820 - Quarterly Progress Report for April-June, 1961).

Compatibility studies of PbTe and/or BiGeTe with a number of potential cladding materials were conducted for the temperature range 500°C to 700°C. PbTe was compatible, for the durations tested, with Armco iron, beryllium, molybdenum, AISI 430 and 304 stainless steels, and low carbon steel at 650°C and 700°C. BiGeTe was compatible, for the durations tested, with tungsten, aluminum, molybdenum and vanadium at 600°C, and with tungsten and aluminum at 650°C.

Compatibility studies of PbTe with potential insulating materials were similarly conducted for the temperature range 550°C to 750°C. PbTe was compatible with AlSiMag 222, Supramica 620, Synthamica 202, and alumina.

A topical report (WCAP-1868) entitled, "Compatibility Studies of PbTe and BiGeTe with Potential Cladding and Insulating Materials" records all of these studies in detail.

Next, a number of design and fabrication improvements were introduced, and a number of prototype elements were made to test the results.

In an attempt to increase reliability, the elements were designed for pre-instrumentation with a heat source, thermocouple leads, and potential leads. Initial results were encouraging. However, consistently successful fabrication of elements was prevented by (1) axial movement of the heaters during swaging, (2) too-severe swaging reductions resulting in shorting of heater elements, and (3) unexpected densification of

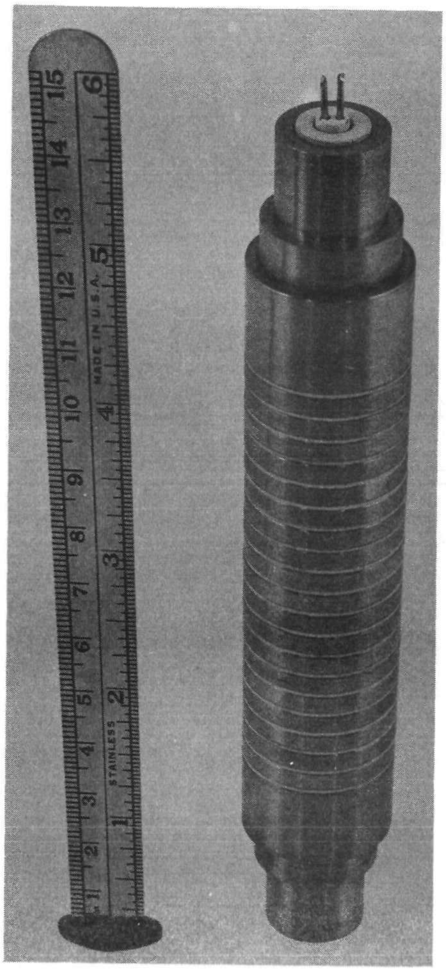

FIGURE 12 - Three-Inch-Long, Twenty-Couple PbTe Element

heaters, resulting in incomplete densification of thermoelectric materials during swaging. These items led to short element life and poor resistance to thermal cycling (WCAP-1647).

A more inclusive pre-instrumentation technique was also designed. An element was built up of pre-cut external and internal cladding sections (as well as the usual components), surrounded with insulation, sheathed in a stainless steel jacket, and swaged. This technique, precluding the need for circumferential grooving, allowed the use of thinner insulating members and provided a water tight jacket around the element. Although this technique showed a great potential for fabrication of power-producing elements, it suffered from the same problems of the lesser pre-instrumentation technique (WCAP-1647). One such element of note fabricated by this technique was a three inch long 20-couple element, which indicates the feasibility of fabricating elements with a number of couples per inch. This element is shown in Figure 12.

In an attempt to optimize efficiency, all of these pre-instrumented elements and all subsequent elements were fabricated with the ratio of length of P-PbTe leg to length of N-PbTe leg equal to

$$\sqrt{\frac{\rho_P}{K_P}\,\frac{K_N}{\rho_N}} \qquad \text{where}$$

$_P$ and $_N$ are the mean resistivities of the P- and N- legs, respectively, and K_P and K_N are the mean thermal conductivities of the P- and N- PbTe legs, respectively (over the design operating temperature range) as obtained from published 3 M Company data.

In a further attempt to increase element efficiency, PbTe segmentation was accomplished by placing one pressed PbTe pellet within another larger pellet containing a different proportion of the same doping agent (WCAP-1647). Doping levels chosen for a given element depended on the design operating temperatures. A number of subsequent elements have been segmented.

A second set of supporting studies was initiated.

Such non-thermoelectric properties of cold-swaged heat treated PbTe as particle fracturing, porosity, density, recrystallization, grain growth, and hardness were studied as functions of swaging reduction and heat treatment. This microstructural study indicated that a heat treatment of six hours at 750°C and a swaging reduction equal to a calculated 100 per cent of theoretical density should result in optimum thermoelectric properties (WCAP-1695 - Quarterly Progress Report for October-December, 1960). To verify these findings and to further explore the differences between cold and hot swaging, samples of both cold and hot swaged single leg elements of PbTe were tested for resistivity as a function of time at several constant temperatures. Simultaneously, microstructures of hot swaged PbTe were studied (WCAP-1820 and WCAP-1745 - Quarterly Progress Report for January-March, 1961).

A new insulating material was sought when it was discovered that unfired Lavite contained a large amount of chemically combined water, which when released during processing or testing of an element reacted with the PbTe and cladding material. AlSiMag 222, an anhydrous magnesium silicate compound, was found suitable because of its good machinability and swagability and its compatibility with PbTe (WCAP-1745).

A bonding study was initiated in an attempt to solve both the PbTe-to-PbTe bonding problem in segmented elements, and the PbTe-to-clad bonding problem in all elements. For segmented PbTe-to-PbTe bonding, the variables were (1) sign of PbTe, (2) reduction of area, (3) temperature of swaging, and (4) post swaging heat treatment. Test samples, examined for degree of metallurgical bonding and resistance drops across PbTe-to-PbTe interfaces, indicated good bonding for elements containing both N- and P-type PbTe, when they were swaged to $\sim$15 per cent area reduction, sintered 12 to 24 hours at 750°C, and furnace cooled (WCAP-1820 and WCAP-1865 - Quarterly Progress Report for July-September, 1961). For the PbTe-to-clad bonding, clads were pre-wet with PbTe at a temperature just slightly above the PbTe-Fe eutectic temperature, followed by an attempt at

PbTe-to-PbTe bonding. This study was not quite completed (WCAP-1820). However, more recent data indicates that low element resistance will result if stringent measures are taken to assure clean pressure contacts at all of the interfaces.

The last fundamental supporting study, subcontracted to Nuclear Materials and Equipment Corporation of Appollo, Pennsylvania, was an investigation of the feasibility of coating iron conductors with high density alumina in thicknesses in the range 0.001 inch to 0.020 inch. Several coating processes appeared promising and several sample coatings exhibited excellent stability to thermal cycling (WCAP-1820).

Another series of fabrication improvements was installed in attempts to improve efficiency, reliability, and life expectancy. Components were cleaned by new and improved operations and stored in vacuum. PbTe was pressed into pellets immediately after the crushing operation, and the pellets were stored at once under vacuum. Insulators were reduced in thickness to 0.010 in., with marked improvement in thermal efficiency. BN was occasionally used for sleeve-type insulators because of its good thermal conductivity. Phlogopite mica replaced AlSiMag 222 for washer-type insulators (except in in-pile elements). In several elements, iron-covered copper clads replaced the old iron clads to reduce electrical resistance. Elements were weld closed, vacuum outgassed (first at room temperature and later at 300°C to 500°C), sealed and swaged.

The most recent improvements concerned hydrogen firing of components and assembled elements. Hydrogen-fired components included iron clads (after a sand blasting operation) and PbTe (crushed powder and pressed pellets). Elements were purged for two hours at 300°C to 500°C, cooled to room temperature, vacuum outgassed to less than 5 microns, and sealed prior to (a) swaging and sintering, or (b) pressure sintering.

Two specific elements are worthy of mention. A twenty-couple element, designed to have 10 per cent efficiency, was assembled and fabricated, using all of the latest material preparation and fabrication procedures developed under this contract. The design resistance of 0.031 ohms was actually obtained during testing, but the Seebeck voltage was low (WCAP-1865).

The second element, a twenty-couple fission-fired element just completed by the latest material preparation and fabrication procedures, is ready for in-pile testing. This element is confidently expected to surpass the previous similar element (WCAP-1865). An addendum will follow.

A summary of the notable achievements of swaged elements includes:

Single couple elements:

1. Current output of 560 amps at matched load (2-1/2 inch long element).
2. Power output of 70 watts (2-1/2 inch long element).
3. Measured efficiency (electrical power out/heat in) of 5-6 per cent.
4. Life test of 7000 hours ($T_H \sim 550^\circ C$) with no appreciable change in electrical output since first 48 hours of test.
5. Power output of 1 watt/gram of PbTe.
6. Power densities of 8-10 watts/cm^2 and 80-100 amps/cm^2 of hot junction area.

Multiple couple elements:

1. Voltage output of 2 volts/inch of element (8 couples/inch for 2-1/2 inch long elements).
2. Power output of 125 watts for 6 inch long element.
3. Measured efficiency of 6-7.5 per cent (T_H $500^\circ C$, ΔT $450^\circ C$).
4. In-pile power output of 27.8 kilowatt hours.

VI. PRELIMINARY REACTOR ARRANGEMENT STUDIES

These studies were initiated to examine the capabilities and problems of a power generation system consisting of a fission heat source and a thermoelectric conversion device. The objectives of the study were (1) to identify the nuclear, thermal, mechanical and electrical problems, (2) to prepare fuel element and core designs, and (3) to evaluate the performance of the thermoelectric reactor core.

For this study, a light-water cooled and moderated reactor of 500 KW(e) was selected. Lead telluride of appropriate doping for P and N material was selected for the thermoelectric material. Four fuel element designs were studied; these were:

1. Fe- or Nb-UO_2 highly enriched fuel.
2. BeO-UO_2 highly enriched fuel.
3. Low enrichment UO_2.
4. Variation of the thickness of thermoelectric material with power density.

This study showed that the efficiency is dependent upon the hot channel factor, being in the range 4% to 5.3% efficiency for hot channels of 2.75 to 2.0, respectively. Two year lifetime loadings were in the range 43 to 99 kg of U-235 for various combinations of fuels with either separated or natural tellurium in the lead telluride.

BIBLIOGRAPHY

WCAP-1162 - Thermoelectric Nuclear Fuel Element Annual Progress Report - April 10, 1959

WCAP-1245 - Thermoelectric Nuclear Fuel Element First Quarterly Report - July 10, 1959

WCAP-1317 - Thermoelectric Nuclear Fuel Element Second Quarterly Progress Report - October 10, 1959

WCAP-1376 - Thermoelectric Nuclear Fuel Element Third Quarterly Progress Report - January 10, 1960

WCAP-1545 - Thermoelectric Nuclear Fuel Element Quarterly Progress Report - January-March, 1960 - April 10, 1960

WCAP-1596 - Thermoelectric Nuclear Fuel Element Quarterly Progress Report - April-June, 1960 - July 10, 1960

WCAP-1647 - Thermoelectric Nuclear Fuel Element Quarterly Progress Report - July-September, 1960 - October 10, 1960

WCAP-1655 - An Investigation of Mixed Valence Thermoelectric Materials - J. C. Danko, G. R. Kilp, & H. M. Ferrari, October, 1960

WCAP-1680 - Radiation Effects On Thermoelectric Materials - G. R. Kilp & P. V. Mitchell, May, 1961

WCAP-1695 - Thermoelectric Nuclear Fuel Element Quarterly Progress Report - October-December, 1960 - January 10, 1961

WCAP-1703 - Fabrication of Thermoelectric Materials by Rotary Swaging - J. C. Danko, R. C. Goodspeed, G. R. Kilp, & P. V. Mitchell, December, 1961

WCAP-1737 - Preliminary Core Design of A 500 KWe Thermoelectric Reactor - R. A. Markley & E. G. Schwartz, March, 1961

WCAP-1745 - Thermoelectric Nuclear Fuel Element Quarterly Progress Report - January-March, 1961 - April 10, 1961

WCAP-1820 - Thermoelectric Nuclear Fuel Element Quarterly Progress Report - April-June, 1961 - July 10, 1961

WCAP-1865 - Thermoelectric Nuclear Fuel Element Quarterly Progress Report - July-September, 1961 - October 10, 1961

BIBLIOGRAPHY (cont'd)

WCAP-1866 - Preparation and Preliminary Evaluation of Some Uranium-Chalcogenides - W. P. Blankenship, October 10, 1961

WCAP-1868 - Compatibility of PbTe and BiGeTe with Potential Cladding and Insulating Materials - R. C. Goodspeed, October 10, 1961