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September 1970

THE EVAPORATIVE EROSION OF
THERMOELECTRIC ELEMENTS IN
SOME THERMOELECTRIC GENERATORS

R. D. Kinney
Space Power Advanced Development Division

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Item 11 of the previously issued errata sheet for the referenced report was incorrect. It should read:

11. Page 19 - tenth line from top - insert "probably" between "model" and "will"

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SUBJECT: Errata sheet for SC-RR-70-534, The Evaporative Erosion of Thermo-electric Elements in Some Thermoelectric Generators, R. D. Kinney, Sandia Laboratories, Albuquerque, New Mexico, September 1970 (U), distributed 9/22/70.

Please make the following changes to the referenced report.

1. Page 9 - Equation (6) change coefficient 0.2235×10^{-10} to 0.2264×10^{-4}
2. Page 17 - bottom of page - change $M_2 = 40$ to $M_2 = 40$ (argon); change $\delta_2 = 3.67 \times 10^{-8}$ cm to $\delta_2 = 3.67 \times 10^{-8}$ cm (argon)
3. Page 18 - first line - add "cm" after 10^{-8}
4. Page 18 - in the definition of p_s , change atmospheres to dynes/cm³
5. Page 18 - in the definition of R, change cm³ atm g-mole⁻¹ °K⁻¹ to ergs · g-mole⁻¹ °K⁻¹
6. Page 18 - Equation 16 - change 0.2235×10^{-10} to 0.2264×10^{-4}
7. Page 18 - Equation 17 - change 0.507×10^{-9} to 0.5174
8. Page 19 - change $p_s = 1.36 \times 10^{-6}$ atmospheres to $p_s = 1.4$ dyne/cm³
9. Page 19 - change $\partial p_1 / \partial r = -6.3 \times 10^{-6}$ atmospheres/cm to $\partial p_1 / \partial r = -2.0 \times 10^{-6}$ atmospheres/cm
10. Page 19 - change $p \geq 3.22 \times 10^{-7}$ atmospheres = 0.2×10^{-3} torr to $p \geq 1.0 \times 10^{-4}$ atmospheres = 0.076 torr
11. Page 19 - seventh line from bottom - insert "probably" between "model" and "will"

SC-RR-70-534

THE EVAPORATIVE EROSION OF THERMOELECTRIC
ELEMENTS IN SOME THERMOELECTRIC GENERATORS

R. D. Kinney
Space Power Advanced Development Division
Sandia Laboratories
Albuquerque, New Mexico

September 1970

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ABSTRACT

A model is presented, and a parametric analysis is performed on the evaporative erosion of material from thermoelectric elements during operation of some thermoelectric generators. The relative influence of parameters is noted and limitations of the model are discussed.

Key words: Degradation, diffusion

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THE EVAPORATIVE EROSION OF THERMOELECTRIC ELEMENTS IN SOME THERMOELECTRIC GENERATORS

Introduction

A likely mode of performance degradation in thermoelectric generators is the evaporative erosion of material from the thermoelectric elements that comprise the generator. This erosion occurs primarily at the hot end of the elements, and it can significantly lower the area of contact between an element and its electrical connection. The mechanism by which erosion occurs depends partially on the design of the generator. This report presents an analysis of a mechanism present in generators which are pressurized with an inert gas to retard sublimation of the thermoelectric elements. The mechanism of erosion under this condition is different from that occurring in generators with no cover gas or in generators with low cover gas pressure. Specifically, this erosion is a result of diffusive transport of material from the elements due to concentration gradients in the surrounding cover gas.

The purpose of the following analysis is to determine to what extent the various design parameters, i.e., gas pressure, gas species, hot junction temperature, temperature gradient, and proximity of thermal insulation to the elements, contribute to or inhibit the erosion of the elements. The insight gained by such analyses could aid in the selection of future designs.

Model

Figure 1 depicts a longitudinal section of the configuration chosen for analysis, i.e., one element of a thermoelectric couple surrounded by thermal insulation. Referring to Figure 1, the annular region between the cylindrical PbTe thermoelectric element and the surrounding thermal

insulation is gas filled, and as a result of the element residing in the temperature gradient, $T_h - T_c/l$, concentration gradients of PbTe vapor exists in the annular region. These gradients promote the diffusion of material through the cover gas away from the hot end of the element, $z = 0$. Steady-state equilibrium is supported by material subliming from the element to replace that which diffuses away. Hence, the element erodes.

The configuration of Figure 1 is representative of only those generator designs, such as the SNAP-19, which use a molded insulation around the thermoelectric element and have a relatively uniform gas-filled annular region. However, the general trends revealed by the analysis can apply to more irregular geometries such as might occur on the SNAP-27, where the insulation has been powdered and lightly tamped around the thermoelectric elements, but where diffusion through the cover gas remains the dominant mode of mass transport.

Problem Description

The time rate of change in the radius of the thermoelectric element, due to the erosion described earlier, is given by the expression

$$dr/dt = - j_{r1}/\rho \quad (1)$$

where

j_{r1} = steady state radial component of mass flux at the
surface of the element as a function of axial position and
 ρ = density of thermoelectric material

Integration of Eq. (1) will provide an expression for the radius, r , as a function of time. Hence,

$$r = r_1 - j_{r1} t/\rho \quad (2)$$

where

r_1 = initial radius of element
 t = time

Equation (2) allows one to predict the contour of the thermoelectric element after time, t , and this information can then be used with existing thermoelectric design codes to determine the effect on generator performance of element erosion.

The radial component of mass flux, j_r , can be expressed by Fick's first law of diffusion in the following form:

$$j_r = - \frac{M_1 M_2}{M^2} \rho' D \frac{\partial x_1}{\partial r} \frac{g}{cm^2 \sec} \quad (3)$$

where

D = diffusivity of component 1 in mixture of 1 and 2,
 cm^2/sec

M_1 = molecular weight of 1

M_2 = molecular weight of 2

M = molecular weight of mixture of 1 and 2

ρ' = mixture density, g/cm^3

x_1 = molar fraction of component 1 in mixture of 1 and 2

It is important to note that Eq. (3) is an accurate description of j_r only if one assumes that the mass transport due to temperature gradients and bulk motion of the cover gas is negligible and the total gas pressure in the annular region is constant. These are appropriate assumptions for this analysis.

Recognizing that x_1 can be approximated, using the ideal gas law, as a ratio of the partial pressure of component 1 and the total pressure, j_r can be expressed as

$$j_r = - \frac{M_1 M_2}{P M^2} \rho' D \frac{\partial P_1}{\partial r} \frac{g}{\text{cm}^2 \text{sec}} \quad (4)$$

where

P = total pressure in system, and

P_1 = partial pressure of component 1

A first approximation to the mass diffusivity, D , based on kinetic theory, is given for a binary mixture¹ as

$$D = \frac{0.0018583 T^{3/2} \sqrt{\frac{M_1 + M_2}{M_1 M_2}}}{P \sigma^2 \Omega_{1,2}} \quad (5)$$

where

D = diffusivity of component 1 in mixture of 1 and 2,
 cm^2/sec

T = absolute temperature, $^{\circ}\text{K}$

M_1 = molecular weight of 1

M_2 = molecular weight of 2

P = total pressure, atmospheres

$\sigma = 1/2(\sigma_1 + \sigma_2)$ where σ_1 and σ_2 are the effective collision diameters of 1 and 2, respectively, angstroms

$\Omega_{1,2}$ = a dimensionless function of temperature and the inter-molecular potential field for one molecule of 1 and one of 2, based on the Lennard-Jones potential energy function; $\Omega_{1,2}$ is listed in tables as a function of the parameter kT/ϵ

ϵ = characteristic energy of interaction between the molecules 1 and 2 (the maximum energy of attraction)

k = Boltzmann's constant

Experimental data for the force constant, σ_1 , for PbTe vapor are not available. However, there are means of estimating σ_1 from other properties of the material.^{2,3} For this analysis, $\sigma_1 = 4.8$, which is a value based on an estimate by Romanychev.⁴ Likewise, the force constant necessary to calculate $\Omega_{1,2}$, ϵ/k , was estimated from special empirical laws.⁵ For this study, $\Omega_{1,2} = 1.156$ based on $T = 873^\circ\text{K}$ and $k/\epsilon = 0.00188$ for a mixture of argon and PbTe vapor.

Substitution of Eq. (5) into Eq. (4) will yield, after some tedious but straightforward algebraic manipulation, the following expression

$$j_r = - \frac{0.2235 \times 10^{-10} \sqrt{\frac{M_1(M_1 + M_2)}{M_2}} T^{1/2}}{1 + x_1 \frac{M_1 - M_2}{M^2} \sigma_{\Omega_{1,2}}^2} \frac{1}{P} \frac{\partial p_1}{\partial r} \frac{\text{g}}{\text{cm}^2 \text{ sec}} . \quad (6)$$

All that is required for completion is an expression for p_1 which satisfies Laplace's equation. It is important to note the substantial influence of the partial derivative of p_1 in Eq. (6). This property is used in the analysis of design parameters.

To acquire an expression for p_1 , one must find a solution to the following equation for appropriate boundary conditions:

$$\frac{\partial^2 p_1}{\partial r^2} + \frac{1}{r} \frac{\partial p_1}{\partial r} + \frac{\partial^2 p_1}{\partial z^2} = 0 \quad (7)$$

where

r = radial coordinate

z = axial coordinate

Application of Eq. (7) assumes that the coefficient for $\partial p_1 / \partial r$ in Eq. (6) is spatially independent. This is not entirely true since terms x_1 and T are functions of r and z . However, the influence of x_1 in the coefficient is not strong and can be disregarded. To further simplify the problem, T is assumed to be constant and equal to the hot junction temperature.

Boundary Conditions

The final success of this analysis depends on the selection of realistic boundary conditions for the solution of Eq. (7). In this respect, the following were assumed.

1. The mathematical boundary at r_2 in Figure 1 realistically represents the plane in the thermal insulation for which there is no net flux of PbTe vapor. Hence, $\partial p_1 / \partial r = 0$ at r_2 .
2. Steady-state conditions are attained in a relatively short period of time.
3. The mathematical boundary at $z = 0$ realistically represents the surface of electrical connection between thermoelectric elements, and at steady state there is no net flux of PbTe vapor across this boundary. Hence, $\partial p_1 / \partial z = 0$.
4. The mathematical boundary at $z = \ell$ realistically represents the cold end of the thermoelectric element and at steady state has zero partial pressure. Hence, $p_1 = 0$ at $z = \ell$.
5. The mathematical boundary at r_1 , the surface immediately adjacent to the thermoelectric element, has partial pressure equal to the equilibrium vapor pressure of PbTe. Hence, $p_1 = f(z)$ at r_1 where $f(z)$ describes the equilibrium vapor pressure as a function of z .

Discussion of Boundary Conditions

It is assumed that steady-state conditions are established in a short period of time compared to the total operating time of the generator. During the initial transient period, it is envisioned that vapor from the element will diffuse to and absorb on the surrounding thermal insulation and electrical connections. This absorption will continue

to remove vapor from the cover gas until a dynamic equilibrium is established between the molecules adhering to the surrounding material and those which are re-emitted. The net effect of this equilibrium is described by boundary conditions 1 and 3, i.e., no net flux of PbTe at surfaces $r = r_1$ and $z = 0$. It should be noted that the surfaces described by these boundary conditions are not necessarily coincident with the geometrical surfaces. The PbTe vapor will most probably permeate the thermal insulation to some depth depending on the porosity, and for this case, r_2 represents not the geometrical surface of the insulation but a mathematical boundary interior to the surface where $\partial p_1 / \partial r = 0$.

For materials with low equilibrium vapor pressures as compared to total system pressure, the partial pressure of vaporized material at a point immediately adjacent to the element surface is accurately approximated by the equilibrium vapor pressure of the material.⁶ For the materials and temperatures of interest in this analysis, i.e., PbTe-type thermoelectric materials at 400° to 600°C, these conditions are satisfied and boundary condition 5 is an appropriate choice. The boundary at r_1 is analogous to a time-constant temperature boundary in thermal problems, for here the partial pressure of the boundary remains constant as evaporation from the PbTe element replenishes material that is lost by diffusion.

Since the partial pressure at the boundary r_1 decreases very rapidly in the axial direction due to the exponential dependence of vapor pressure on temperature, it is assumed that there is no significant partial pressure of PbTe vapor in the lower portion of the annular region in Figure 1. This assumption is formally adopted in boundary condition 4.

Problem Solution

The formal solution for Eq. (7) for the selected boundary conditions is

$$p_1 = \frac{2}{\ell} \sum_{n=1}^{\infty} \frac{F(\lambda_n r_2; \lambda_n r)}{F(\lambda_n r_2; \lambda_n r_1)} \cos \lambda_n z \int_0^{\ell} f(z) \cos \lambda_n z \, dz \quad (8)$$

where

$$F(x;y) = I_1(x)K_0(y) + K_1(x)I_0(y)$$

I_ν = modified Bessel function of the first kind of order ν

K_ν = modified Bessel function of the second kind of order ν

ℓ = length of annular segment depicted in Figure 1

$f(z)$ = vapor partial pressure of component 1 at r_1

$$\lambda_n = (2n-1)\pi/2\ell$$

Derivations of equations similar to Eq. (8) are given by Carslaw and Jaeger.⁷

Under the assumptions of boundary condition 5, the function, $f(z)$, has the form:

$$f(z) = A \exp (-B/T) \quad (9)$$

where

T = surface temperature along axial coordinate of element

Assuming the temperature distribution along the lateral surface of the thermoelectric element is linear, T becomes

$$T = T_h - \frac{(T_h - T_c)}{\ell} z \quad (10)$$

where

T_h = hot junction temperature, °K

T_c = cold junction temperature, °K

Substitution of Eqs. (10) and (9) into Eq. (8) completes the solution. Constants A and B of Eq. (9) were determined experimentally for several PbTe thermoelectric materials.^{8,9} For this analysis,

$$A = \exp (16.23)$$

$$B = 25.97 \times 10^3$$

which are values based on work by D. Northrup.⁸

The factors of Eq. (8) were evaluated numerically and the partial sum of the first five hundred terms of the series was determined for several combinations of the ratios r/l , r_1/l , and r_2/l . Figures 2 through 6 are plots of the partial pressure of PbTe vapor, p_1 , for the dimensionless variable, z/l , at the surface of the thermoelectric element and a cylindrical surface in the annular region. Figures 7 through 12 are plots of partial pressure versus the variable r/l for a fixed value of z/l .

Examination of the distribution of p_1 for different conditions as shown by the above figures reveals some interesting characteristics. Figures 2 through 6 show that changes in the distribution of p_1 are quite large at the hot end of the element but becoming less notable as one proceeds along the axis of the element. This was to be expected since the equilibrium vapor pressure of the element decreases rapidly in this direction. For the examples plotted in Figures 2 through 6, only the distributions at the hot end of the element were retained since the determinative information, i.e., existence of erosion, is available within this portion, and, except for the case shown in Figure 6, the partial pressure and resultant gradients are relatively unimportant below the first 10 percent of the element. Further examination of Figures 2 through 6 reveals that the radial component of the partial pressure gradient is negative for only the first 3 to 7 percent of the element. Below this, the distribution is such that the radial component is positive, and vapor will be transported toward the boundary, r_1 . Physically, this is interpreted to mean the element will erode only in the extreme upper portion and will tend to build deposits of condensed material below this. For the examples of this analysis, the magnitude of the radial component is quite small for the lower portions of the element, and most all of the erosion and condensation should occur within the first 40 to 50 percent of the element.

Figures 7 through 12 show the behavior of the radial distribution of p_1 under different operating conditions for one value of z/l near the

hot end of the element. Figure 12 is of particular interest since it shows for comparison the effect of varying r_2 for three cases and the relative influence of varying the cold junction temperature, T_c , for one case.

Parametric Analysis

The distribution of p_1 as given by Eq. (8) and the mass flux given by Eq. (6) provide the tools necessary for analyzing the influence of various parameters on the system. The effects of changing the annular boundary, r_2 , hot junction temperature, and temperature gradient are available from a studied examination of the plots in Figures 2 through 12. Comparison of these figures, especially Figure 10 with Figure 12, will reveal the relative effectiveness of design parameters in retarding erosion.

The effect of increasing the boundary, r_2 , is twofold. One effect is to increase the slope of p_1 at the hot end of the element and thereby increase the transport of material from the element. The second effect is to lower the crossover position on the element at which erosion ceases and deposition begins. Hence, more of the element is subjected to erosion. It is therefore beneficial to surround the element with as much material (for example, thermal insulation) as possible within the constraints of generator design and assembly procedures. For example, Figures 7 and 8 illustrate that the material flux, j_r , at $z/\ell = 0.010$ can be decreased by 50 percent by decreasing the parameter, r_2/ℓ (this essentially moves the insulation closer to the element, assuming constant length) from 0.480 to 0.400.

The hot junction temperature is the most influential parameter in the system. As illustrated in Figure 10, a reduction of hot junction temperature to 500°C reduces the initial slope for the radial distribution of p_1 , and therefore the material flux by about 98 percent from the slope in Figure 8 for the same boundary parameters and temperature gradient. Also, as is evident from Figures 3 and 5, the portion of the element subjected to erosion is substantially less for the lower hot junction temperature. Hence, reducing the hot junction temperature is beneficial

in the same fashion, except more so, as narrowing the annular region with insulation, i.e., reduced material flux and total area effected.

The temperature gradient along the element is another parameter which can be manipulated by the designer. As shown in Figures 6, 11, and 12, a decrease in temperature gradient tends to reduce the flux of material from the element but substantially increases the portion of the element subjected to erosion, i.e., condensation of material occurs further down the element than in the example of Figure 3. Although not shown, the crossover point from the negative to the positive radial component of the gradient for p_1 in Figure 6 occurs at about $z/l = 0.44$. It is the author's conclusion that there is nothing of significance to be gained by decreasing the temperature gradient of the elements.

The total system pressure, P , has a very substantial effect on system behavior. This is most readily seen by inspection of Eq. (6). Ignoring any contribution from x_1 , the flux of material from the element is proportional to the inverse of P . Hence, erosion of the element can be reduced substantially by increasing the cover gas pressure. For example, increasing pressure in the system from one to four atmospheres would reduce j_r by 75 percent. As discussed later, this relationship of P to j_r holds equally for large system pressures. It is, therefore, possible to extend generator life by simply increasing the cover gas pressure. There are, of course, design limitations on the amount one can increase pressure in current generators.

The consequence of changing cover gas species can be examined by referring to Eq. (6). Such a change manifests itself primarily in the radical expression in the numerator of j_r where the molecular weight, M_2 , changes. Since for most cases

$$x_1 \frac{M_1 - M_2}{M_2} \ll 1 ,$$

the expression in the denominator involving molecular weights can be ignored. Hence, the change in mass flux due to a change in cover gas specie can be approximately expressed as

$$j_r(2)/j_r(1) \simeq \sqrt{\frac{M_2(1)}{M_2(2)} \frac{[M_1 + M_2(2)]}{[M_1 + M_2(1)]}} \quad (11)$$

where

$j_r(n)$ = radial component of mass flux with cover gas specie, n

$M_2(n)$ = molecular weight of cover gas specie, n

M_1 = molecular weight of thermoelectric material

Evaluation of Eq. (11) for

$$M_1 = 335 \text{ (PbTe)}$$

$$M_2(1) = 40 \text{ (Argon)}$$

$$M_2(2) = 131 \text{ (Xenon)}$$

gives

$$j_r(2)/j_r(1) \simeq 0.6 .$$

Therefore, a factor of 3 change in the molecular weight of the cover gas specie causes a 40-percent reduction in mass flux.

Model Limitations

Since incorrect and misleading interpretations can result if the model is wrongfully applied, it is important that the limitations of the model be recognized. The foundation of this analysis is based on the assumption that mass transport in the system is by a diffusive process; for most pressures of cover gas, this is a correct description. However, for low pressures where the mean free path of the gases is larger than the dimensions of the annular region, the gas molecules act independently of each other and the system can no longer be described by Eq. (4). For low pressures, the molecules collide, adhere, and re-emit from surrounding material without prior collision with neighboring molecules. This

is the molecular flow regime of mass transport and can best be described by Knudsen equations¹⁰ for gas migration in annular geometries. The mean free path of PbTe vapor molecules in a cover gas can be expressed as

$$1/L_1 = \pi N_2 \delta_{12}^2 \left(1 + \frac{M_1}{M_2}\right)^{1/2} \quad (\text{see Reference 10, p. 67}) \quad (12)$$

where

L_1 = mean free path of component 1, cm

N_2 = number of molecules of component 2/cm³

$\delta_{12} = 1/2(\delta_1 + \delta_2)$

δ_1 = diameter of molecule of component 1, cm

δ_2 = diameter of molecule of component 2, cm

M_1 = molecular weight of component 1

M_2 = molecular weight of component 2

Using the ideal gas law, N_2 can be expressed as

$$N_2 = 9.656 \times 10^{18} P_{\text{mm}}/T \text{ molecules/cm}^3 \quad (13)$$

where

P_{mm} = system pressure, millimeters of Hg

T = system temperature, °K

Substituting Eq. (13) into Eq. (12) and solving for P_{mm} gives

$$P_{\text{mm}} = T/9.656 \times 10^{18} \pi L_1 \delta_{12}^2 (1 + M_1/M_2)^{1/2} \quad (14)$$

Substituting,

$L_1 = 0.0254$ cm

$\delta_2 = 3.67 \times 10^{-8}$ cm

$M_1 = 335$

$T = 873^\circ\text{K}$

$M_2 = 40$

Using a value for δ_1 of 6.46×10^{-8} , as reported by Fritts,¹¹ gives

$$P_{\text{mm}} = 0.14 \text{ millimeters of Hg .}$$

Therefore, assuming that the difference between r_1 and r_2 is on the order of 20 to 10 mils, this analysis is valid only for system pressures greater than 0.1 to 0.2 torr.

There is another limitation on pressure, since at no time can the mass flux from the element be greater than that given by Langmuir for evaporation in a vacuum. Therefore,

$$j_r \leq \alpha p_s \sqrt{M_1/2\pi RT} \quad (15)$$

where

α = Langmuir's coefficient, assumed here to be 1

p_s = equilibrium vapor pressure of component 1, atmospheres

R = Universal gas constant, $\text{cm}^3 \text{ atm g-mole}^{-1} \text{ } ^\circ\text{K}^{-1}$

Substituting Eq. (6), Eq. (15) takes the form

$$- \frac{0.2235 \times 10^{-10} \sqrt{M_1(M_1 + M_2)/M_2} T^{1/2}}{\left[1 + x_1(M_1 - M_2)/M_2\right] \sigma^2 \Omega_{1,2} P} \partial p_1 / \partial r \leq p_s \sqrt{M_1/2\pi RT} . \quad (16)$$

Under most conditions, one can assume

$$x_1 (M_1 - M_2)/M_2 \ll 1$$

Hence,

$$P \geq - \frac{0.507 \times 10^{-9} \sqrt{(M_1 + M_2)/M_2} T}{\sigma^2 \Omega_{1,2} p_s} \partial p_1 / \partial r \text{ atmospheres .} \quad (17)$$

Choosing the following typical values for the components of Eq. (17)

$$\begin{aligned} T &= 873^{\circ}\text{K} \\ M_1 &= 335 \\ M_2 &= 40 \\ p_s &= 1.36 \times 10^{-6} \text{ atmospheres} \\ \sigma^2 \Omega_{1,2} &= 19.5 \\ \partial p_1 / \partial r &= -6.3 \times 10^{-6} \text{ atmospheres/cm} \end{aligned}$$

results in the limitation

$$p \geq 3.22 \times 10^{-7} \text{ atmospheres} = 0.2 \times 10^{-3} \text{ torr} .$$

Thus, the lower limitation on this model will be determined by the proximity of the material surrounding the element, i.e., whenever the mean free path of PbTe molecules are comparable to the width of the annular region.

Referring to the upper end of the pressure range, the use of Eq. (4) is limited by one's ability to approximate the diffusivity, D . Equation (5) is apparently an accurate expression for D up to about 30 to 35 atmospheres.² This is well within the range of interest.

Implicit in the derivation of Eq. (2) is the assumption that the boundary r_1 is constant with time. This is not true since the shape and size of this boundary will change with erosion of the element. However, the shape and size change significantly only at one end on the element, and, based on Figure 12, the results of the change should be to increase the transport of material, thus leaving this analysis conservative. Ignoring the time dependence of r_1 should not change the conclusions of this analysis.

The error in calculating j_r , Eq. (6), is introduced primarily by inaccuracies in the force constants σ_1 and ϵ/k , especially σ_1 . It is expected that the maximum relative error in choosing σ_1 will not exceed 25 to 30 percent, so the maximum relative error in calculating will not exceed 50 to 60 percent.⁴

As discussed earlier, some caution must be exercised in strictly applying the numerical results of this analysis for configurations other than that shown in Figure 1. For example, if the thermal insulation is packed tightly around the thermoelectric element, the transport of material may not be diffusive or the diffusivity, D , may be radically different from that given in Eq. (5). However, it is envisioned that even for designs with insulation in close proximity to the element, the mean free path of the vapor molecules, at least for most pressures, is smaller than the distance between individual fibers of the insulation; therefore, the results of this analysis are generally applicable.

Conclusions

General conclusions drawn from the analysis are:

1. Element erosion occurs for typical cases within the first 10 percent of the hot end of the thermoelectric element, with deposition of material occurring immediately below this portion.
2. Listed by order of influence, the design parameters which effect erosion are hot junction temperature, gas pressure, proximity of insulation gas specie, and temperature gradient.

The design of thermoelectric generators can promote longer element life by eliminating the void between the thermal insulation and the element, increasing the cover gas pressure, lowering the hot junction temperature, and using a cover gas of high molecular weight. However, complete freedom is not available with all these parameters. Lowering the hot junction temperature is contrary, in most cases, to good generator performance, and selection of cover gas specie often depends on other considerations such as the amount of thermal by-pass induced. Relying entirely on cover gas pressure to retard erosion is less than desirable, especially for long-term missions, since the probability of losing gas pressure during mission life from leaky seals or meteoroid punctures makes this a low reliability choice.

All things considered, a more basic approach to deterring erosion is recommended. By selecting compatible, low vapor pressure materials and thinly coating the hot end of the element, one can maintain the integrity of the element without depending on the above parameters. Some developmental effort will be needed to find compatible materials that will not alter the thermoelectric characteristics of the elements and to find efficient means of applying the coatings, but such effort is justified by the improvement in generator reliability.

Figure 1. Configuration of thermoelectric element and thermal insulation used for analysis

Figure 2. Plot of pressure versus z/l for $r_2/l = 0.400$

Figure 3. Plot of pressure versus z/l for $r_2/l = 0.480$

Figure 4. Plot of pressure versus z/l for $r_2/l = 0.580$

Figure 5. Plot of pressure versus z/l for $T_h = 773^\circ\text{K}$

Figure 6. Plot of pressure versus z/l for $T_c = 573^\circ\text{K}$

Figure 7. Plot of pressure versus r/l for $r_2/l = 0.400$

Figure 8. Plot of pressure versus r/l for $r_2/l = 0.480$

Figure 9. Plot of pressure versus r/l for $r_2/l = 0.580$

Figure 10. Plot of pressure versus r/l for $T_h = 773^\circ\text{K}$

Figure 11. Plot of pressure versus r/l for $T_c = 573^\circ\text{K}$

Figure 12. Comparison of Figures 7, 8, 9, and 11

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