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MODELING HELIUM AND OXYGEN BEHAVIOR OF A PLUTONIA PELLET IN AN MMRTG

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The PuO_2 pellets in the Multi-mission Radioisotope Thermoelectric Generator (MMRTG) were studied to understand the thermal, chemical and diffusion properties of the internally produced gases, to mitigate material interactions during the mission. Helium gas, produced from the alpha decay of the plutonium, and oxygen ions, produced by the reduction reaction of the PuO_2, were modeled in COMSOL to demonstrate the behavior as the gases escape from the pellet. Helium and oxygen ions were produced by internal reactions which diffused through the grains. The thermal model produced an approximately 92 K temperature gradient from the centerline of the pellet to the surface. The physical properties of both elements were temperature dependent, and models were made for each depending on the rate of diffusion and permeation. The helium model of the open porosity demonstrated a higher pressure in the center, with a pressure gradient of approximately 0.065 Pa to the surface. The oxygen model showed the difference between two sizes of grains in the pellet, taking approximately 0.07 s to diffuse to the grain boundary for a 10 μm grain and approximately 1.65 s for a 50 μm grain. However, inaccuracies of this model resulted from the use of the diffusion coefficient of oxygen gas, and not that of an oxygen ion. A more accurate model can be produced with the correct diffusion coefficient.

I. INTRODUCTION

The Multi-mission Radioisotope Thermoelectric Generator (MMRTG) is an important technology used for space exploration. Modeling processes within the MMRTG could help scientists improve this technology and make it more efficient, which would allow for more space missions to understand and explore the universe.

I.A. The MMRTG

The MMRTG creates electricity with thermoelectric couples utilizing the temperature difference between the environment and the heat given off from the decay reaction of the nuclear material. The thermoelectric couples can convert decay heat energy to electricity for many years. They are well-suited for spaceflight as they do not require specific external conditions to function and can be designed using suitable isotopes with a long half-life, in contrast to solar cells and other battery types which have certain limitations as the mission progresses. One MMRTG consists of 8 General Purpose Heat Sources (GPHSs), each housing 4 plutonium dioxide (PuO_2, plutonia) pellets.

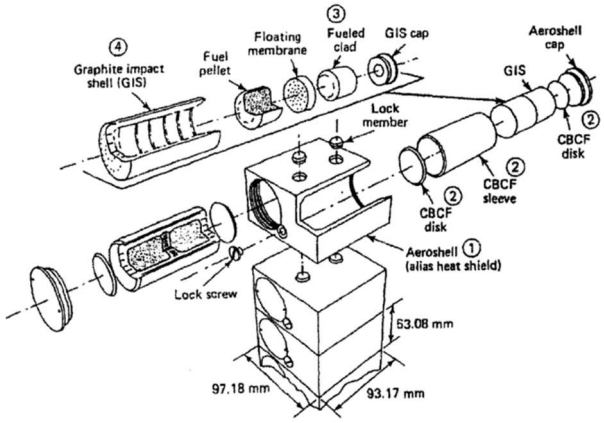

Fig. 1. The PuO_2 pellets are housed in the GPHS shown.[1]

I.B. Physical and Chemical Processes

Two elements were included in this study of the internal pellet behavior, oxygen and helium. The production of helium results from the alpha-decay reaction of ^{238}Pu.

$$^{238}Pu \rightarrow {}^{234}U + {}^{4}He + \sim 5.6\ MeV \qquad (1)$$

For every decay event of the ^{238}Pu, one helium atom is discharged. As time increases and decay events occur, helium builds up in the pellet and the internal pressure increases. It is produced in the grains of the PuO_2 and eventually diffuses out through the grain boundaries. As temperature increases, diffusion of helium gas out of the pellet will also increase. Helium bubble damage occurs when gas aggregates at the grain boundaries, however it does not contribute to the diffusion rate out of the pellet.

Production of oxygen in the pellet comes from a natural chemical reaction of the PuO_2. The PuO_2 pellets undergo decomposition reactions, which allows oxygen to

separate from the structure. The reduction reaction in Eq. (2), shows when the pellet is reduced, an O_2 molecule is released, resulting in substoichiometric (reduced) PuO_2. The oxygen ions produced gain electrons upon entering the grain boundary, and the oxygen gas is formed.

$$PuO_2 \rightleftharpoons PuO_{2-x} + \frac{x}{2}O_2 \quad (2)$$

Like the behavior of the helium, oxygen ions are produced by the PuO_2 and then diffuses in the grain. The oxygen ions self-diffuse, exchanging with vacancies in the lattice until it exits the grain. After becoming a gas, the oxygen flows through the grain boundaries to the surface of the pellet. The plutonia reduction reaction shown in Eq. (2) can also reverse at high partial pressures of oxygen to re-oxidize. However, this oxidation reaction is not as frequent as the reduction reaction due to the escaping of the oxygen.[2]

Once the oxygen is in the gap between the pellet and the cladding, it will react with existing CO to form CO_2. The CO_2 gas can leak out of the cladding through the frit vent to react with and oxidize other components, such as the carbon from the GIS and the thorium in the cladding. The rate at which these reactions occur is a concern to scientists, as the pressure will increase from the gas buildup in the GIS. Reducing these unwanted reactions may prolong the lifetime of an MMRTG.

I.C. Modeling the Pellet

To understand and quantify the CO_2 reactions, the amount of oxygen released by the pellet over time must first be calculated. In addition, the helium amount must also be calculated as it will affect the pressure in the GIS. A model of these reactions will allow scientists to consider the release of oxygen and helium, as well as the interactions with the surrounding elements in the RTG system.

II. MODELING METHODS

When the MMRTG was designed and configured in 2008, the software was limited and not as advanced as it is today. COMSOL Multiphysics can be used to build complex geometries which represent physical objects and subsequently simulate processes, named “modules”, to model various chemical and physical behaviors together. A model of the gas behavior in the pellet will generate the kinetic coefficients and production rates of both types of gases, as well as give an understanding of how the gas leaves the pellet and the damage done to the PuO_2 structure.

II.A. Geometry

Every COMSOL model begins by forming a geometry. Both cylindrical and spherical geometries were used for the models in this project. The density of the fuel pellet was calculated as 9.89 x 10^6 $\frac{g}{m^3}$. Summation of different grain sizes multiplied by their volume fractions was substituted in the equation to get a permeability of 2.24 x 10^{-14} m^2. The thermal and helium model was set as a cylindrical pellet.

The oxygen model depended on the diffusion rates through the grain to represent oxygen ion behavior. Therefore, the model was modified to encompass two grains and study their diffusion coefficients. Due to the different grain sizes in the microstructure, a model was created for each extreme: the smallest average grain size of 10 μm and the largest average grain size of 50 μm. The diffusion rate through these grains could be averaged based on their respective volume percentage to find an average diffusion rate for oxygen.

II.B. Thermal Model

A thermal model was needed as fuel temperatures play an essential role in the diffusion processes and gas release. COMSOL was used to create this model, with the geometry shown in Fig. 2, and linked it to the helium model since the processes interact with each other.

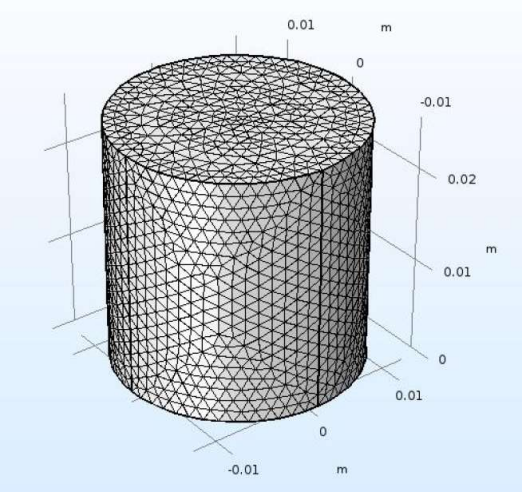

Fig. 2. Pellet geometry and mesh used in COMSOL.

II.B.1. Theory

The thermal model was made in conjunction with the helium model to allow for the interdependence between the gas movement and temperature to be shown. Similarly, the resulting temperatures were used to create the oxygen model. The thermal model was built to understand the specific element behaviors and the chemical processes inside the pellet. First, the generated heat rate, Q'', was calculated based on the alpha decay equation of ^{238}Pu.

Given the density of a PuO_2 pellet with 14% porosity, $\rho = 0.86\rho'$, where ρ' is the density of a 100% dense pellet. The number density, N, can be calculated and used in the constant decay rate equation of the ^{238}Pu, shown in Eq. (3), where $\frac{dN}{dt}$ is the rate of change of the number density, λ is the decay constant of ^{238}Pu and N_0 is the initial amount of ^{238}Pu atoms.

$$\frac{dN}{dt} = -\lambda N_0 \quad (3)$$

This equation was assumed as constant since the scope of the project was only for one year, while the MMRTG is in storage before launch. The decay rate was also considered to be the production rate of helium, since one atom of helium is released in each decay. The generated heat rate of PuO_2, Q'', was found using Eq. (4).

$$Q'' = -\lambda N_0 \cdot \frac{E}{decay} \quad (4)$$

The calculated value was 4.95 x $10^6 \frac{W}{m^3}$ and was used to find the energy per pellet as 54.8 W.

II.B.2. Methods

To build the thermal model, the dimensions of the pellet were first defined as parameters. Thermal conductivity and heat capacity at constant pressure depend on the thermal profile, so they were defined as a function of temperature. Values were found in the material library of COMSOL or from other publications. Heat capacity at constant pressure for helium was approximately constant with the ΔT for the thermal model, and the value used was calculated with a temperature of 1400 K.

II.C. Helium Model

Once the thermal model was completed, the helium model was built using the same geometry. This allowed both models to be coupled, creating a single helium model which also generated a thermal profile.

II.C.1. Theory

Only the year-long time span before launch of the MMRTG was considered for this project. The first step of this model was to determine the helium flow through the open porosity of the PuO_2. For simplicity, the flow rate of helium from the grain was considered constant. The majority of the helium does not flow through the open porosity. Therefore, to make a more accurate model, diffusion through the closed porosity and grain boundaries would also need to be considered. However, this was out of the scope of the project and only flow through the open porosity was considered for the oxygen model.

According to Ref. 3, 4, and 5, hot pressed plutonia microstructures with 14% porosity have pores located at the triple point of the grain structure, creating an open porosity through the grain boundaries.[6] Since Knudsen diffusion applies to smaller pores than those found in this model of plutonia[5], Darcy's Law of fluid flow though porous media was used, shown in Eq. (5).

$$Q = -\frac{\kappa_{eff} A \nabla p}{\mu L} \quad (5)$$

Where Q is the total discharge, κ_{eff} is the effective permeability of the medium, A is the cross-sectional area of flow, μ is the viscosity of the fluid, ∇p is the total pressure gradient, and L is the length of the gradient. Darcy's law was further modified in terms of cylindrical coordinates in Eq. (6).[7]

$$Q = -\frac{\kappa_{eff} A}{\mu L}\left(\frac{1}{r}\left(\frac{\partial p}{\partial r} r\right) + \frac{1}{r}\left(\frac{\partial p}{\partial \theta}\right) + \left(\frac{\partial p}{\partial z}\right)\right) \quad (6)$$

The second term, $\frac{\partial p}{\partial \theta}$, goes to zero since the helium gas is assumed to have a radially-symmetric flow in the pellet. The Knudsen diffusion term in κ_{eff}, shown in Eq. (7), was neglected since the mean free path of the gas was smaller than the pore size. This results with κ_{eff} being equal to the permeability, κ.

$$\kappa_{eff} = \kappa\left(1 + \frac{b}{p}\right) = \kappa\left(1 + \frac{D_\kappa \mu}{\kappa}\frac{1}{p}\right) \quad (7)$$

Where κ is the permeability and D_κ is the Knudsen diffusion term.

II.C.2. Methods

Simulating a helium model in COMSOL was a Multiphysics problem, requiring different models to be coupled with the proper interdependence. First, the thermal profile of the pellet was coupled with the heat transfer by defining all the fluid and porous material properties as functions of temperature.

Once the heat transfer module was built, a flow module was needed to simulate helium flow through the open porosity to the pellet surface. Production of the helium was calculated using the decay rate and mass of helium, producing a source of 3.67 x 10^{-8} $\frac{kg}{m^3 \cdot s}$. After all the conditions were defined, a fine mesh was used to compute the solution. A stationary study generated a thermal and pressure profile after a set length of time has passed.

II.D. Oxygen Model

An oxygen ion diffusion model for an individual grain was constructed for investigating the oxygen gas release rate from the PuO_2 fuel.

II.D.1. Theory

The oxygen ion diffusion within the grain was governed by Fick's second law, shown in Eq. (8). By solving, the oxygen concentration distribution over time can be calculated with given boundary conditions.

$$\frac{\partial C}{\partial t} = D\nabla^2 C \quad (8)$$

Where D is the diffusion coefficient and C is the concentration of oxygen. The diffusion coefficient was found using the given partial pressure of oxygen, which is described in Refs. 8 and 9. It was determined the diffusion coefficient obtained was compatible for values of the substochiometry, x, ranging from 0.003 and 0.12. However, the diffusion coefficient used was for oxygen gas and not an oxygen ion, resulting in an inaccurate model.

II.D.2. Methods

In the model, it was assumed the permeation of oxygen gas through the pellet was faster than the diffusion of the oxygen ions inside the grain. Therefore, the permeation rate was neglected and only diffusion of the ions was considered in the model. The temperature of the grain was assumed to be isotropic. The substoichiometry of PuO_2 can be related to the partial pressure of oxygen by the formula created by Bessman-Lindemer.[9] The diffusion coefficient formula provided by Kato[8] was compatible with the pressure-substoichiometry relation. It was later discovered this diffusion coefficient was not for oxygen ions diffusing through the grain. The following models were created with the Kato coefficient and were inaccurate.

The oxygen concentration at the surface of the grain was calculated by setting the substoichiometry value to $x = 0.12$. This was related to the concentration using Eq. (9).

$$C = \frac{1}{2} C_0 (2 - x) \tag{9}$$

Where C_0 was the concentration of oxygen when $x = 0$. The concentration was set to 8088 $\frac{mol}{m^3}$ at the surface of the grain. The temperature depends on the location of the grain of interest. For example, a grain at the center of the pellet was 1500 K, and a grain at the surface was 1400 K. The diffusion coefficient in COMSOL was defined as a function of concentration and time. The initial value was set to be $0.999C_0$ and the concentration of oxygen at the boundary was set to be $\frac{2-0.12}{2} C_0$.

III. RESULTS AND ANALYSIS

Thermal, helium and oxygen models were all created in COMSOL to show temperature and concentration variations. The thermal model showed the temperature gradient for the cross section of a PuO_2 pellet. The helium model generated a pressure profile of a slice of an entire pellet, giving the amount of helium gas pressure at every point. The oxygen model showed the concentration of oxygen ions throughout spherical grains.

III.A. Thermal Model

A temperature gradient of approximately 120 K was simulated from the surface of the pellet to the centerline of the pellet. The change in temperature of the thermal model alone was around 92 K, but the helium thermal model had a larger gradient due to the two modes of heat transfer: conductive heat transfer through the grains and convection at the grain boundaries.

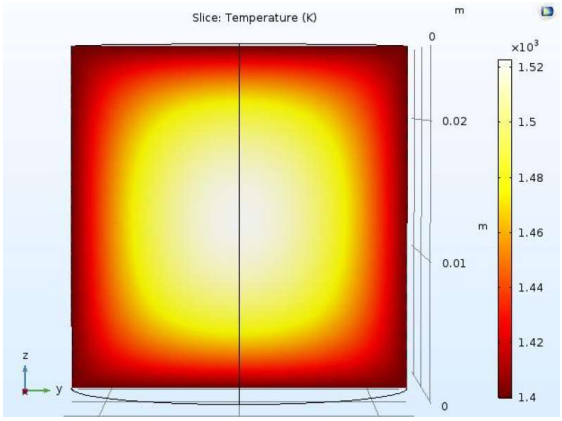

Fig. 3. Thermal profile of the PuO_2 pellet.

Figure 3 shows the cross-sectional view of the temperature in a pellet with an initial surface boundary condition of 1400 K. The temperature increases near the center, with the overall gradient as approximately 120 K.

III.B. Helium Model

The helium model showed a centerline pressure of approximately 0.065 Pa, which was relatively large compared to the surface boundary condition of 10^{-24} Pa.

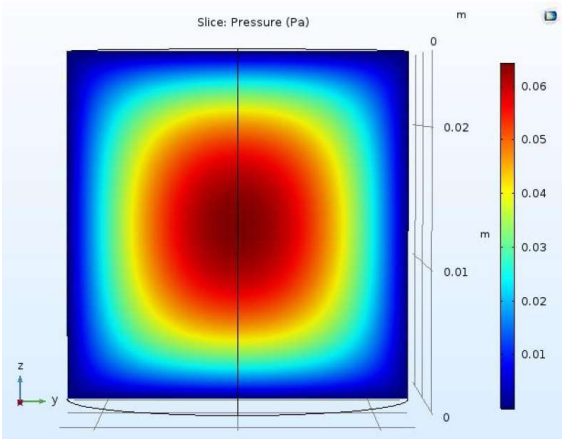

Fig. 4. Pressure profile for helium gas inside the fuel pellet.

Figure 4 shows the pressure profile for the helium flow module generated using Darcy's law. The pressure profile provides the concentration variation in the pellet. The higher the pressure, the more helium atoms were present.

III.C. Oxygen Model

An oxygen model was created to show the given oxygen ion concentration throughout a spherical grain of PuO_2 with respect to time at a temperature of 1400 K. The model was run for both 10 μm and 50 μm grain diameters. This created two different oxygen models showing how quickly oxygen diffuses out of these sizes.

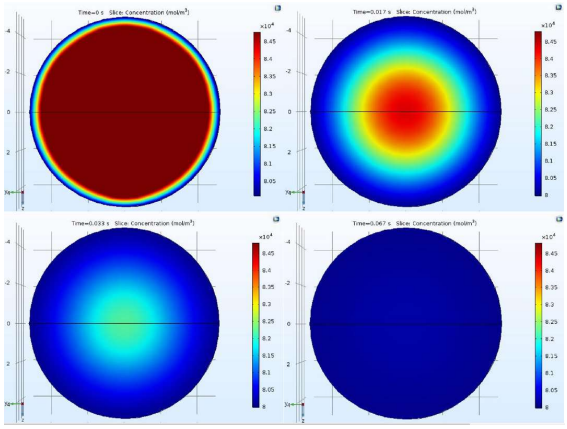

Fig. 5. Oxygen ion concentration through a 10 µm grain of PuO_2 fuel at various points in time. Steady state was reached at 0.07 s when 6% of the oxygen was released.

As shown in Figure 5, it took approximately 0.07 s to release 6% of the oxygen from a grain of diameter 10 µm. However, it required approximately 1.6 s to release 6% of the oxygen in a grain of diameter 50 µm, shown in Figure 6.

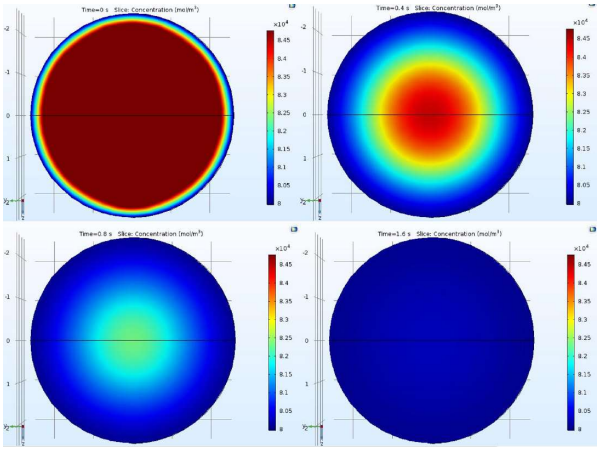

Fig. 6. Oxygen ion concentration through a 50 µm grain of PuO_2 fuel at various points in time. Steady state was reached at 1.6 s when 6% of the oxygen was released.

In both cases, the diffusion occurred more quickly than expected due to the diffusion constants chosen. The substoichiometry value decreased and the concentration of oxygen on the grain surface was higher than the concentration corresponding to $x = 0.12$. To obtain a more realistic result, the oxygen model must consider the permeation of oxygen gas through the pellet at the grain boundaries, which was neglected for simplification. The permeation can be coupled with the diffusion of oxygen ions for one cohesive model.

IV. CONCLUSION

Understanding the chemical and physical processes in the MMRTG helps scientists extend the lifetime of this space exploration technology. By using the modern Multiphysics software COMSOL to model the behavior of helium and oxygen in a PuO_2 pellet, the reactions inside the MMRTG can be studied and mitigated. The thermal model of the pellet was coupled with the helium model, which showed an approximately 120 K gradient from the centerline of the pellet to the surface. The helium model, created to demonstrate flow through the open porosity of the PuO_2, produced a pressure gradient of approximately 0.065 Pa, showing the higher concentration of helium in the center of the pellet. Both models were designed for a representative cylindrical pellet geometry.

The oxygen model was created to represent the diffusion through a single grain and was repeated for grain sizes of 10 µm and 50 µm which diffused within 0.07 s and 1.6 s, respectively. However, the diffusion coefficient used for the models was for oxygen gas instead of oxygen ions. The resulting models were inaccurate and can be simulated again with the correct coefficient.

The next step of this project is to include other mechanisms of diffusion in the helium model, as well as couple diffusion of oxygen ions and the permeation of oxygen gas into one singular oxygen model, encompassing all grain sizes. Once completed, the two models can be combined to simulate a more accurate description of their interdependence, as the partial pressure of one gas will affect the diffusion and flow rate of the other. Finally, the amount of oxygen and helium escaping into the GIS can be calculated to study the chemical reactions of carbon and thorium and mitigate negative effects from these elements during the lifetime of an MMRTG.

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