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Title: **Mechanisms of Thermal Induced
Gallium Removal (TIGR) from
Plutonium dioxide**

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ABSTRACT

This study was initiated in order to determine the advantages of using a mixed-bed rather than a fixed-bed reactor (i.e. furnace) for separation of gallium from PuO_2 by the Thermal Induced Gallium Removal (TIGR) process. The TIGR process is based upon vaporization of gallium suboxide (Ga_2O) from essentially nonvolatile PuO_2 . The gallium suboxide is formed by passing a reducing gas (i.e. hydrogen) over the PuO_2 particles. Several mechanisms are involved in the reduction and convective vaporization of the gallium suboxide. If the mass transfer of the gallium suboxide across the solid to gas interface significantly affects the processing time, it may be advantageous to use a mixed-bed reactor rather than a fixed-bed reactor. However, due to the difficulty of handling PuO_2 powder, a mixed-bed reactor should be used only if significant advantages can be demonstrated.

Based on available data, the results of this study provide strong evidence that a mixed-bed reactor (i.e. furnace) would provide little advantage over a fixed-bed reactor. This is due to the conclusion that the mechanism of internal gallium diffusion within the particle has the predominant affect on the processing time. This is an important conclusion since the use of a mixed-bed would require development of more complex hardware than for a fixed-bed.

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NOMENCLATURE

A	mass transfer area
C_i	molar concentration of component "i"
$C_{i,R}$	molar concentration of "i" at surface of particle
$C_{i,max}$	maximum possible concentration of "i" in solid phase
C_t	total molar concentration of all components
d_p	particle diameter
D	diffusion coefficient
DO	direct oxidation
DOE	Department of Energy
Ga_2O	gallium suboxide
HYDOX	hydride/oxidation
$k_{g,i}$	gas-phase mass transfer coefficient for species "i"
K_f	forward chemical reaction rate
K_b	backward chemical reaction rate
$m_{i,s}$	mass of species "i" in solid phase
M	bulk gas mole weight
MOX	mixed oxide
N_i	moles of component "i"
N_{sh}	Sherwood number
N_{sc}	Schmidt number
N_{re}	Reynolds number
P_i^v	vapor pressure of component "i"
$P_{i,R}$	pressure of component "i" at surface of sphere "R"
$P_{i,\infty}$	pressure of component "i" in bulk gas stream
P_t	total gas pressure of all components
PuO_2	plutonium dioxide
R	universal gas constant
t	time
T	temperature
TIGR	thermal induced gallium removal
$v_{g,\infty}$	bulk gas velocity with respect to particle
V	volume
y	distance over which diffusion occurs
$\rho_{g,\infty}$	bulk gas mass density
$\mu_{g,\infty}$	bulk gas viscosity
σ	hard-sphere diameter
∇	laplacian

INTRODUCTION

The United States Department of Energy (DOE) Fissile Material Disposition Program is based in part, on the disposition of plutonium by mixed oxide (MOX) fuel irradiation in commercial light water reactors (see Figure 1). The weapons-based plutonium is converted to PuO_2 and combined with UO_2 to form the MOX fuel. Prior to fabricating the MOX fuel, it is necessary to remove excess gallium from the weapons-based plutonium. Thermally Induced Gallium Removal (TIGR) has been selected as a potential process for separation of gallium from the PuO_2 . The plutonium is first converted from a metallic weapons form to PuO_2 by either direct oxidation (DO), or a 3-step hydride/nitride/oxidation (HYDOX) process, at which time the gallium is also converted to predominantly Ga_2O_3 . The gallium is then removed through chemical reduction of the Ga_2O_3 by hydrogen to Ga_2O followed by convective vaporization of the volatile Ga_2O . The TIGR process is being considered due to its dependency on only dry processing rather than aqueous, which has potential for reducing waste and criticality risks.

Figure 1. DOE fissile materials disposition program for plutonium

The complete set of mechanisms defining the TIGR process is shown in Figure 2. The sequence and description of these mechanisms are as follows.

- (1) Adsorption of the hydrogen from the gas phase to the solid phase (PuO_2). Langmuir's isotherm can be used to model this process. The hydrogen gas is mixed with a carrier gas such as argon to reduce explosion risks.
- (2) Diffusion of hydrogen into the solid phase.
- (3) Chemical reaction of hydrogen with Ga_2O_3 to form Ga_2O .
- (4) Diffusion of Ga_2O from the solid phase interior to the surface.
- (5) Vaporization of the Ga_2O followed by convective mass transfer from the solid phase to the gas phase.

Figure 2. Gallium separation mechanisms

Certain initial arguments can be made for eliminating several of the mechanisms as insignificant with respect to their affect on the processing time.

- (I) Since hydrogen is constantly replenished at the particle surface by a flowing gas stream, it is likely the adsorption of hydrogen is much more rapid than its internal diffusion within the particle. Therefore, hydrogen adsorption from the gas phase to the solid phase can be ignored.
- (II) It has been demonstrated often that diffusion of hydrogen is far more rapid than more complex molecules such as the gallium suboxide. Therefore, the hydrogen diffusion within the solid phase can be ignored.
- (III) The rate of a chemical reaction is essentially determined by the concentration of hydrogen, gallium oxide, and gallium suboxide within the particle. Since the gallium oxide is present in the beginning, and the hydrogen diffuses much faster than the gallium suboxide, the reaction rate is likely limited by the gallium suboxide reverse reaction. This suggests that the chemical reaction rate is probably dictated by the gallium suboxide diffusion rate.

Following the previous arguments, two dominant mechanisms remain which may dictate the processing time required for separating the gallium and PuO_2 . These mechanisms are (1) diffusion of gallium suboxide from the particle interior to its surface, and (2) gallium suboxide vaporization by convective mass transfer from the solid phase to the gas phase. It can be further rationalized that initially, convective vaporization is the predominant rate controlling mechanism as the outer layer of gallium in the solid phase becomes depleted, and then following the gallium surface loss internal diffusion of gallium suboxide is probably rate controlling. This is shown by Figure 3.

Figure 3. Rate controlling mechanisms

SUMMARY

The principal purpose of this study was to determine if possible, whether or not a significant advantage exists for the use of a mixed-bed rather than fixed-bed reactor (or furnace) for gallium separation from PuO_2 by the TIGR process. Because of the incomplete physical property data for gallium suboxide, it was necessary to make significant assumptions at several points throughout this study. However, conclusions drawn from this study which are dependent upon these assumptions have all been made in light of their respective margins of error.

The primary conclusion of this study is that there is no significant advantage for using a mixed-bed reactor rather than a fixed-bed reactor for the TIGR process. This conclusion is not intended to replace that which will be derived from the current testing, only shed some light early-on, regarding the complexity of the potential processing operations required. Considering the tight schedule required for TIGR demonstrations, and the potential long lead time required for a complex reactor if a mixed-bed with refractory materials is required, early indication of a simplified design should provide confidence that the TIGR process can be implemented within the time frame required.

ANALYSES

As discussed in the Introduction section, the predominant mechanisms controlling gallium separation are assumed to be (1) gallium suboxide diffusion within the solid particle, and (2) gallium suboxide convective vaporization from the surface of the solid particle. The gallium suboxide is assumed to vaporize rather than sublime since its melting point is below the anticipated processing temperature; however, the PuO_2 will remain a solid at the anticipated processing temperature. If the processing temperature does not exceed 1200 C, then there will not be a need for refractory reactor/furnace materials and excess sintering of the PuO_2 will be limited.

Gallium Suboxide Convective Vaporization

The gallium suboxide convective vaporization can be viewed as convective diffusion through the gas boundary layer (1) surrounding a particle for the case of a mixed-bed, or (2) flowing over a surface for the case of a fixed-bed. This type of behavior can be modeled by Fick's law, as shown by Equation 1.

$$-\frac{1}{A} \frac{dN_i}{dt} = D \frac{dC_i}{dy} \quad \text{Equation 1}$$

If the concentration gradient is approximated as a difference, then Equation 1 can be rearranged as follows.

$$-\frac{1}{A} \frac{dN_i}{dt} = \left(\frac{D}{\Delta y} \right) \Delta C_i \quad \text{Equation 2}$$

The $\left(\frac{D}{\Delta y} \right)$ term in Equation 2 is referred to as the gas-phase mass transfer coefficient " k_g ", where Δy can be estimated from boundary layer theory. Often the mass transfer coefficient is modified to be defined in units of mass flux as described in Chapter 3 of Treybal and shown by Equation 3.

$$-\frac{1}{A} \frac{dN_i}{dt} = k_g \left(\frac{P_{i,R} - P_{i,\infty}}{P_{t,\infty}} \right) \quad \text{Equation 3}$$

By comparing Equations 2 and 3, the gas-phase mass transfer coefficient can be further defined as shown by Equation 4.

$$PV = nRT$$

$$C = \frac{n}{V}$$

$$\left(\frac{D}{\Delta y}\right)\Delta C_i = \left(\frac{D}{\Delta y}\right)\left(\frac{1}{RT}\right)(P_{i,R} - P_{i,\infty})$$

$$\left(\frac{D}{\Delta y}\right)\left(\frac{1}{RT}\right)(P_{i,R} - P_{i,\infty}) = k_g \left(\frac{P_{i,R} - P_{i,\infty}}{P_{t,\infty}}\right)$$

$$k_g = \frac{P_{t,\infty}}{RT} \left(\frac{D}{\Delta y}\right) \quad \text{Equation 4}$$

The boundary layer thickness “ Δy ” can be defined by boundary layer theory, and is often expressed in terms of the Sherwood, Schmidt, and Reynolds dimensionless numbers. Defining the mass transfer coefficient in units of mass flux has the advantage of being consistent with a classical form of the mass transfer coefficient typically used in the Sherwood number.

Consequently, given specific solid-phase geometry and gas-phase flow velocity, it is often possible to find a theoretical expression which defines the gas-phase mass transfer coefficient in terms of a Sherwood, Schmidt, and Reynolds numbers.

For the example of gallium suboxide convective vaporization from solid PuO_2 , the following simplifying assumptions can be made.

- (1) Due to the relatively low gallium concentration ($\leq 1\text{wt\%}$ in PuO_2), and the significant carrier-gas velocity, the gallium suboxide concentration in the bulk gas stream is zero.

$$P_{i,\infty} = 0$$

- (2) The gallium suboxide partial pressure at the particle surface is defined by the vapor pressure and Raoult's law. While Henry's law is more applicable for low concentrations typical of the gallium suboxide for this study, the only relevant data available is the vapor pressure. Additionally, this study will focus on comparative analyses rather than absolute.

$$P_{i,R} = \left(\frac{C_{i,R}}{C_{t,R}} \right) P_i^v$$

Equation 3 can be solved for differing solid geometries as follows.

$$-\frac{1}{A} \frac{dN_i}{dt} = k_g \left(\frac{C_{i,R}}{C_{t,R}} \right) \left(\frac{P_i^v}{P_{t,\infty}} \right)$$

At early times in the separation process, the gallium suboxide concentration throughout the solid phase can be estimated as homogeneous.

$$C(t \sim 0) = C_R = \frac{N}{V}$$

$$-\frac{1}{A} \frac{d(VC_i)}{dt} = k_g \left(\frac{C_i}{C_t} \right) \left(\frac{P_i^v}{P_{t,\infty}} \right)$$

$$\int_{C_i(t=0)}^{C_i(t)} \frac{dC_i}{C_i} = -k_g \left(\frac{A}{V} \right) \left[\frac{M_{PuO_2}}{\rho_{PuO_2}} \left(\frac{P_i^v}{P_{t,\infty}} \right) \right] \int_0^t dt$$

where

$$C_t = C_{Ga_2O} + C_{PuO_2}$$

$$C_{Ga_2O} \ll C_{PuO_2}$$

$$C_t \sim C_{PuO_2} = \frac{M_{PuO_2}}{\rho_{PuO_2}}$$

And finally, integration yields Equation 5,

$$C_{Ga_2O} = C_{Ga_2O}^{(t=0)} e^{-k_g \left(\frac{A}{V} \left(\frac{M_{PuO_2}}{\rho_{PuO_2}} \right) \left(\frac{P_{Ga_2O,1}^v e^{\left[\frac{\Delta H_{Ga_2O}^v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]} \right)}{P_{t,\infty}} \right) t} \quad \text{Equation 5}$$

based upon the Clausius-Clapeyron equation for vapor pressure,

$$P_2^v = P_1^v e^{\left[\frac{\Delta H^v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]}$$

Mass Transfer from a Sphere (Mixed-bed)

Mass transfer from a sphere can be used to represent conditions of maximum mass transport from a mixed-bed. Equation 6 was developed by Ranz & Marshall (1952) to describe evaporation from a drop by convection.

$$N_{Sh} = 2.0 + 0.6 N_{Sc}^{1/3} N_{Re}^{1/2} \quad \text{Equation 6}$$

where
$$N_{Sh} = \frac{k_g M_{g,\infty} d_p}{\rho_{g,\infty} D}$$

$$N_{Sc} = \frac{\mu_{g,\infty}}{\rho_{g,\infty} D_{AB}}$$

$$N_{Re} = \frac{d_p v_{g,\infty} \rho_{g,\infty}}{\mu_{g,\infty}}$$

Equation 6 can be solved in terms of the mass transfer coefficient by rearranging as shown by Equation 7.

$$k_g = \frac{\rho_{g,\infty} D_{AB}}{M_{g,\infty} d_p} \left[2.0 + 0.6 \left(\frac{d_p v_{g,\infty} \rho_{g,\infty}}{\mu_{g,\infty}} \right)^{1/3} \left(\frac{\mu_{g,\infty}}{\rho_{g,\infty} D} \right)^{1/2} \right] \quad \text{Equation 7}$$

The maximum gallium evolution by convective vaporization from a mixed-bed of PuO_2 particles can be then defined by combining Equations 5 and 7 to yield Equation 8.

$$C_{\text{Ga}_2\text{O}} = C_{\text{Ga}_2\text{O}}^{(t=0)} e^{-\left[\frac{\rho_{g,\infty} D}{M_{g,\infty} d_p} \left[2.0 + 0.6 \left(\frac{d_p v_{g,\infty} \rho_{g,\infty}}{\mu_{g,\infty}} \right)^{\frac{1}{3}} \left(\frac{\mu_{g,\infty}}{\rho_{g,\infty} D} \right)^{\frac{1}{2}} \right] \left[\frac{A}{V} \left(\frac{M_{\text{PuO}_2}}{\rho_{\text{PuO}_2}} \right) \left(\frac{P_{\text{Ga}_2\text{O},t}^v}{P_{L,\infty}} e^{\left[\frac{\Delta H_{\text{Ga}_2\text{O}}^v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]} \right) \right] \right] t} \quad \text{Equation 8}$$

Mass Transfer from a Semi-Infinite Plate (Fixed-Bed)

Mass transfer from a semi-infinite plate should represent conditions of minimum (i.e. assumes a smooth surface) mass transfer from a fixed-bed. Boundary layer theory for convective heat transfer from a semi-infinite plate has been described by Kays & Crawford (1980), and can be modified for mass transfer as shown by Equation 9. Equation 9 is applicable for fully developed laminar flow and moderate Schmidt numbers.

$$N_{\text{Sh}} = 0.332 N_{\text{Sc}}^{1/3} N_{\text{Re}}^{1/2} \quad \text{Equation 9}$$

Equation 9 can be rearranged to solve for the mass transfer coefficient as done with Equation 7, and combined with Equation 5 to describe the gallium evolution by convective vaporization from a fixed-bed of PuO_2 particles, as shown by Equation 10.

$$C_{\text{Ga}_2\text{O}} = C_{\text{Ga}_2\text{O}}^{(t=0)} e^{-\left[\frac{\rho_{g,\infty} D}{M_{g,\infty} d_p} \left[0.332 \left(\frac{d_p v_{g,\infty} \rho_{g,\infty}}{\mu_{g,\infty}} \right)^{\frac{1}{3}} \left(\frac{\mu_{g,\infty}}{\rho_{g,\infty} D} \right)^{\frac{1}{2}} \right] \left[\frac{A}{V} \left(\frac{M_{\text{PuO}_2}}{\rho_{\text{PuO}_2}} \right) \left(\frac{P_{\text{Ga}_2\text{O},t}^v}{P_{L,\infty}} e^{\left[\frac{\Delta H_{\text{Ga}_2\text{O}}^v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]} \right) \right] \right] t} \quad \text{Equation 10}$$

Physical Properties

In order to utilize Equations 8 and 10, a number of physical properties for gallium suboxide must be estimated. This presents a problem since gallium suboxide is poorly characterized. The following properties for gallium suboxide were listed in the oxide handbook of Samsonov (1973).

Ga_2O melting point:
925 K

Ga_2O boiling point:
1000 K

Ga₂O heat of vaporization:

$$\Delta H_{\text{Ga}_2\text{O}}^v(T = 1000 \text{ K}) = 83,736 \text{ J/gmole}$$

Ga₂O vapor pressure:

The vapor pressure above the melting point can be estimated with the heat of vaporization. The gallium suboxide vapor pressure at 1000 K is one atmosphere (i.e. boiling point).

$$P_{\text{Ga}_2\text{O}}^v (\text{atm}) = e^{\left\{10,071 \left[\frac{1}{1000} - \frac{1}{T(\text{K})} \right] \right\}}$$

Ga₂O Density:

$$\rho = \frac{NM}{V} = \frac{PM}{RT} \quad \text{assuming an ideal gas}$$

$$\rho_{\text{Ga}_2\text{O}} = \frac{P(156 \text{ g/mole})}{(0.082056 \text{ l-atm/K-mole})(1000 \text{ cm}^3/\text{l})T} = \frac{1.90[P(\text{atm})]}{T(\text{K})} \left(\frac{\text{g}}{\text{cm}^3} \right)$$

Gas Viscosity:

Equation 11 was used to estimate the gas viscosity of Ga₂O; however, in order to do so the an estimate of the hard-sphere diameter was necessary.

$$\mu \left(\frac{\text{g}}{\text{cm-s}} \right) = 0.0000267 \frac{\sqrt{MT(\text{K})}}{\left[\sigma \left(\text{\AA} \right) \right]^2} \quad \text{Equation 11}$$

The only significant thermodynamic data for Ga₂O was found to be the (1) heat of fusion, (2) heat of convective vaporization, (3) melting temperature and (4) boiling temperature. Consequently, the author found a rough correlation between boiling temperature and the hard-sphere diameter as shown by Figure 3. Since time proven correlations for estimating the hard sphere diameter are more complex than assumed here, a sensitivity analysis about the 95% confidence interval indicated the uncertainty was insignificant. A weighted sum-of-the-squares linear regression analysis was used for determining the correlation of Figure 3.

Figure 3. Estimation of the hard sphere diameter for Ga_2O
(Data from Reid et al., Appendix C, 1977)

$$\mu_{\text{Ga}_2\text{O}} = 0.0000267 \frac{\sqrt{156T(\text{K})}}{(9.4)^2} = 3.77 \times 10^{-6} \sqrt{T(\text{K})} \left(\frac{\text{g}}{\text{cm} \cdot \text{s}} \right)$$

Ga₂O Diffusion coefficient:

The only property which remains to be estimated in order to solve Equations 8 & 10, is the diffusion coefficient. The diffusion of interest is Ga₂O into Ar/H₂ where $P_{Ar} \gg P_{H_2}$ and $P_{Ar} \gg P_{Ga_2O}$. Therefore, as an approximation the diffusion coefficient for Ga₂O diffusing into pure Ar was estimated. The following correlation for the diffusion coefficient was used (Equation 11-3.1 of Reid et. al., 1977).

$$D_{AB} = 0.001858 T^2 \left(\frac{\sqrt{\frac{M_A + M_B}{M_A M_B}}}{P_t \sigma_{AB}^2 \Omega} \right)$$

$$\Omega = \frac{1.06036}{(kT/\epsilon_{AB})^{0.1561}} + \frac{0.19300}{e^{0.47635(kT/\epsilon_{AB})}} + \frac{1.03587}{e^{1.52996(kT/\epsilon_{AB})}} + \frac{1.76474}{e^{3.89411(kT/\epsilon_{AB})}}$$

(k/ϵ) for Ga₂O can be estimated with the use of Equation 11-5.1 of Reid

$$(k/\epsilon)_{Ga_2O} = 1.15 T_b = 1150 \text{ (K)}$$

$$(k/\epsilon)_{AB} = \sqrt{(k/\epsilon)_{Ga_2O} (k/\epsilon)_{Ar}} = \sqrt{(1150)(93.3)} \text{ (K)} = 327 \text{ (K)}$$

$$\sigma_{AB} = 0.5(3.542 + 9.4) = 6.47 \text{ \AA}$$

Gallium Suboxide Diffusion within Solid PuO₂

Diffusion within a sphere is described by Fick's law in much the same way as shown by Equation 1 for the gas phase; however, because the sphere is bounded mass continuity must be accommodated by a three dimensional analysis. Equation 12 describes such diffusion within a sphere.

$$\frac{\partial C_i}{\partial t} = D \nabla^2 C_i \quad \text{Equation 12}$$

In order to solve Equation 12, two substitutions will be made.

$$C^* = C_i^{t=0} - C_i$$

such that $C^*(t=0) = 0$, which will permit solution by way of Laplace transforms, and

$$\eta = C^* r$$

which will eliminate non-constant coefficients in the partial differential. The following substitutions are then made in Equation 12 to yield Equation 13.

$$\frac{\partial C_1}{\partial t} = -\frac{\partial C^*}{\partial t}$$

$$\frac{\partial^2 C_1}{\partial t^2} = -\frac{\partial^2 C^*}{\partial t^2}$$

and then

$$\frac{\partial C^*}{\partial t} = D \nabla C^*$$

upon expanding

$$\frac{\partial C^*}{\partial t} = D \left(\frac{2}{r} \frac{\partial C^*}{\partial r} + \frac{\partial^2 C^*}{\partial r^2} \right)$$

Additionally

$$\frac{\partial C^*}{\partial t} = \frac{1}{r} \frac{\partial \eta}{\partial t}$$

and

$$\frac{\partial C^*}{\partial r} = \frac{\partial (\eta/r)}{\partial r} = \frac{1}{r} \frac{\partial \eta}{\partial r} - \frac{\eta}{r^2}$$

following substitution

$$\frac{\partial \eta}{\partial t} = D \frac{\partial^2 \eta}{\partial r^2}$$

Equation 13

Equation 13 can be solved by way of Laplace transforms.

$$\mathcal{L}\left\{\frac{\partial \eta(r,t)}{\partial t}\right\} = s\mathcal{L}\{\eta(r,s)\} - \eta(r,t=0)$$

where

$$\eta(r,t=0) = [C^{*,t=0}_1] = [(C^{t=0}_1 - C^{t=0}_1)r] = 0$$

and then

$$\mathcal{L}\left\{\frac{\partial \eta(r,t)}{\partial t}\right\} = s\mathcal{L}\{\eta(r,s)\}$$

Additionally

$$\mathcal{L}\left\{D\frac{\partial^2 \eta(r,t)}{\partial r^2}\right\} = D\frac{d^2 \mathcal{L}\{\eta(r,s)\}}{dr^2}$$

And finally, the partial differential is converted to a total differential by virtue of the Laplace transform as shown by Equation 14.

$$\frac{d^2 \mathcal{L}\{\eta(r,s)\}}{dr^2} - \frac{s}{D} \mathcal{L}\{\eta(r,s)\} = 0 \quad \text{Equation 14}$$

The solution to the total differential is now shown by Equation 15, where a_2 must equal zero for the solution to be bounded.

$$\mathcal{L}\{\eta(r,t)\} = a_1 e^{-\sqrt{\frac{s}{D}}r} + a_2 e^{+\sqrt{\frac{s}{D}}r}$$

or

$$\mathcal{L}\{\eta(r,t)\} = a_1 e^{-\sqrt{\frac{s}{D}}r} \quad \text{Equation 15}$$

In order to determine a_1 we will apply the boundary condition at $r=R$, prior to inverse transforming.

$$\eta(R,t) = C^*R$$

At $r=R$ and $t=0^+$:

$$\eta(R,t) = (C^{t=0}_1 - C_1)R = C^{t=0}_1 R$$

Therefore, a unit step function of $C_1^{t=0}$ will be applied at $t=0^+$.

$$\mathcal{L}\{\eta(r=R, t)\} = RC_1^{t=0} \mathcal{L}\{u(t)\} = \frac{RC_1^{t=0}}{s}$$

and then

$$\frac{RC_1^{t=0}}{s} = a_1 e^{-\sqrt{\frac{s}{D}}R}$$

or

$$a_1 = \frac{RC_1^{t=0}}{s} e^{+\sqrt{\frac{s}{D}}R}$$

The Laplace transform can then be expressed as

$$\mathcal{L}\{\eta(r, t)\} = \frac{RC_1^{t=0}}{s} e^{-\sqrt{\frac{s}{D}}(r-R)}$$

And finally the inverse Laplace transform can be represented as the complimentary error function.

$$\eta(r, t) = \mathcal{L}^{-1}\left\{\frac{RC_1^{t=0}}{s} e^{-\sqrt{\frac{s}{D}}(r-R)}\right\} = RC_1^{t=0} \operatorname{erfc}\left(\frac{1}{2}\sqrt{\frac{(r-R)^2}{Dt}}\right)$$

With the final reconstitution of original substitutions Equation 16 is produced.

$$C_1 = C_1^{t=0} \operatorname{erf}\left(\frac{1}{2}\sqrt{\frac{(r-R)^2}{Dt}}\right) \quad \text{Equation 16}$$

RESULTS & CONCLUSIONS

Diffusion Coefficient from Experimental Data

The gallium suboxide diffusion coefficient in PuO_2 can be determined from experimental data with the use of Equation 16. Since experimental data is based upon an entire particle, rather than the gallium concentration at a single radius, Equation 16 must be integrated over the entire radius to determine the average gallium concentration as shown below.

$$\bar{C} = \frac{1}{R} \int_0^R C dr$$

$$\bar{C} \approx \frac{1}{n} \sum_{i=1}^{i=n} C_{i-1/2}$$

$$n = \frac{R}{\Delta r}$$

$$\frac{\bar{C}}{C^{t=0}} = \left(\frac{\Delta r}{R} \right) \sum_{i=0}^{i=R/\Delta r} \text{erf} \left(\frac{1}{2} \sqrt{\frac{(r_{i-1/2} - R)^2}{D t}} \right)$$

$$r_{i-1/2} = i(\Delta r) + \frac{\Delta r}{2} = \left(i + \frac{1}{2} \right) \Delta r$$

The error function can be approximated as follows.

$$\text{erf}(x) = 1 - \left[\frac{0.34802}{1 + 0.47047x} - \frac{0.09587}{(1 + 0.47047x)^2} + \frac{0.74785}{(1 + 0.47047x)^3} \right] e^{-x^2}$$

or

$$\text{erf} \left[\frac{1}{2} \sqrt{\frac{(r - R)^2}{D t}} \right] = 1 -$$

$$\left\{ \frac{0.34802}{1 + 0.47047 \left[\frac{1}{2} \sqrt{\frac{(r - R)^2}{D t}} \right]} - \frac{0.09587}{\left(1 + 0.47047 \left[\frac{1}{2} \sqrt{\frac{(r - R)^2}{D t}} \right] \right)^2} + \frac{0.74785}{\left(1 + 0.47047 \left[\frac{1}{2} \sqrt{\frac{(r - R)^2}{D t}} \right] \right)^3} \right\} e^{-\left[\frac{1}{2} \sqrt{\frac{(r - R)^2}{D t}} \right]^2}$$

Given actual test data for gallium concentration change with time, the diffusion coefficient can then be determined by iteration. The test data for

gallium evolution from PuO₂ shown in Table 1, was collected by D. Kolman at Los Alamos National Laboratory.

Table 1. Gallium loss from PuO₂ versus time and temperature (Kolman, June 1998)

	Temp	Sample	Time	Ga Loss	Diffusion Coefficient
Test No.	(C)	(g)	(hr)	(%)	(cm ² /s)
24	900	0.9	0.5	-10.8	1.3x10 ⁻¹²
30	1100	0.9	0.5	-74.6	1.5x10 ⁻¹⁰
18	1200	0.9	0.5	-97.2	1.5x10 ⁻⁸
9	1200	0.9	4.0	-99.1	1.7x10 ⁻⁸
estimate	1400	n/a	n/a	n/a	4.6x10 ⁻⁶

The diffusion coefficient data of Table 1 at temperatures up to 1200 C, were used to estimate the diffusion coefficient at 1400 C, as shown in Figure 4.

Figure 4. Diffusion coefficient for Ga_2O in PuO_2

The gallium suboxide diffusion coefficients as shown in Table 1 were then used to estimate time dependent gallium loss due to internal diffusion.

The following Figures 5 through 9 show the predicted time dependent gallium loss for the three mechanisms of interest, (1) gallium mass transfer across the solid/gas phase boundary for a particle (i.e. mixed-bed), (2) gallium mass transfer across the solid/gas phase boundary for a slab (i.e. fixed-bed), and (3) gallium diffusion within the solid particle.

Figure 5 shows the time dependent gallium loss from a PuO_2 particle based on mass transfer across the solid/gas phase boundary. It can be seen that this is a rapid process with essentially all of the gallium separated in less than one second. This is due to the small particle size and high Ga_2O vapor pressure.

The processing conditions evaluated for a mixed-bed represent the following cases.

- 5 micron particle size considered the minimum for adequate gas de-entrainment.
- 40 micron particle size considered the maximum based upon the MOX fuel specification.
- 1200 C based upon the maximum temperature for conventional oven materials.
- 1400 C based upon the maximum temperature for which a reliable diffusion coefficient could be estimated from the experimental data of Table 1.
- 1.5 cm/s as the minimum gas flow which can be controlled.
- 6.0 cm/s as the maximum gas flow without excessive entrainment.

It can be seen from Figure 6 that gallium separation with a fixed-bed occurs over a period of hours; whereas, it occurs over a period a seconds with a mixed-bed. The processing conditions evaluated for a fixed-bed represent the following cases.

- 4.4 Kg PuO_2 which is the maximum based on criticality.
- 0.0009 Kg PuO_2 which is the sample size used for test data of Table 1.
- L/D of ten which yields a square bed of approximately 15cm x 15cm for 4.4 Kg PuO_2 , as nominal for a typical oven tray.
- L/D of five which would reduce the tray size to 12cm x 12cm for 4.4 Kg PuO_2 .

Figure 7 shows the predicted behavior of gallium suboxide diffusion within PuO_2 . It should be noted that based on the logarithmic scale, and assuming that the initial gallium concentration is 1 wt% (10,000 ppm), the gallium concentration exceeds 1 ppm for all conditions shown up to 10^5 seconds (~28 hours) of processing time. It can be projected that processing at 1600 C would achieve ≤ 1 ppm Ga in PuO_2 in 24 hours. This conclusion is dependent on the data of Table 1 being accurate, and the phase structure of the Ga_2O_3 in PuO_2 being consistent throughout the range of gallium concentrations.

Figure 8 shows the relative affect of the fixed-bed solid/gas mass transfer resistance as compared with the internal particle resistance for gallium diffusion. If two 15cm x 15cm trays with 2.2 Kg PuO_2 each are used as fixed-beds (to achieve a L/D of 20), it can be seen that after ~1000 seconds (15-20 minutes), internal diffusion controls the processing time. Additionally, based upon internal diffusion alone, the gallium concentration in PuO_2 would be 10 to 20 ppm at 1000 seconds (initial Ga at 10,000 ppm). This corresponds to ~ 1 ppm Ga in the MOX fuel after UO_2 blending. If much less ($\ll$) than 1 ppm Ga in the MOX fuel is desired, internal Ga diffusion will dictate the majority of the processing time regardless of the bed type, i.e. mixed or fixed.

Because of the uncertainties related to estimates of the physical properties used in this analysis, a limited sensitivity study was performed and the results are shown as Figure 9. The internal diffusion coefficient and the gallium vapor pressure were varied appropriately to see if a mixed-bed could be advantageous. If ~ 1 ppm Ga in the MOX is acceptable, rather than say $\ll 1$ ppm, then Figure 9 indicates a fixed-bed may dictate the processing time rather than internal diffusion, if the physical properties used in this analysis were incorrect, i.e. a diffusion coefficient of 3.4×10^{-4} rather than 4.6×10^{-6} as shown in Figure 4, and a gallium suboxide vapor pressure two to three times lower than predicted. However, it should be noted that even if a mixed-bed could reduce the processing time, Figure 9 indicates a fixed-bed would still yield gallium adequate separation with several hours of processing time. If it is desired to achieve $\ll 1$ ppm Ga in the MOX fuel, then it is likely internal diffusion will dictate the processing time regardless of the physical property uncertainty, in which case the fixed-bed would provide no advantage.

Figure 5. Ga_2O loss from particle by convective mass transfer

Figure 6. Ga_2O loss from fixed-bed by convective mass transfer

Figure 7. Ga_2O loss from particle or fixed-bed by diffusion in PuO_2

Figure 8. Ga_2O loss from particle by diffusion in PuO_2 and loss from fixed-bed

Figure 9. Ga_2O vapor pressure sensitivity

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