

Thermodynamic and Kinetic Studies on the Pyrophoricity of Uranium Flakes

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Abstract: The objective of this work was to arrive at quantitative estimates of pyrophoricity of uranium in different geometries. The major source of heat generation was identified to be exothermic chemical reactions of uranium with moist air. Time evolution of temperature was studied for uranium considering 3D conduction and convection heat loss routes using Finite Element Analysis. Auto ignition temperature for uranium flakes was quantified using heat balance equation and was found to be around 500 K. Excess heat generation rates needed to cause auto ignition of uranium flakes at room temperature were also estimated. The major sources of excess heat leading to its ambient ignition could be attributed to friction and other exothermic chemical reactions of process impurities in uranium.

Keywords: Pyrophoricity, Uranium flakes, Finite element method, Geometry dependence

1. Introduction: Fossil fuels take several thousand years to get formed. However, its rate of consumption is very rapid. Considering the current energy crisis, it has been felt that the nuclear fuel can be considered to be an appropriate alternative. The conventional fuel used for the nuclear reactors is uranium (U) in several forms viz. metallic, oxide etc. Different nuclear reactors use uranium in different forms as a fuel for an optimized power profile. U is mined and is processed before it can be used as nuclear fuel for use in reactor. Spent fuel removed from a reactor, after it has reached the end of its useful life, can be reprocessed to recover valuable fissile materials.

An ‘open nuclear fuel cycle’ means direct disposal of the spent fuel from the reactor and a ‘closed nuclear fuel cycle’ includes reprocessing of the spent fuel for recovery and reuse of valuable fissile materials. India has a poorer reserve of U than many other countries; so, closed nuclear fuel cycle is adopted here for proper utilization of the resources.

The ‘front end’ of the nuclear fuel cycle includes, U mining, milling, conversion and fuel fabrication.

Handling/processing of spent nuclear fuel is carried out in ‘back end’ of the nuclear fuel cycle which includes, spent fuel storage, reprocessing, U and Pu recycling, spent fuel disposal and waste management.

Both the front end and the back end processes involve storage and handling of U in various forms. U is subjected to mechanical operations like machining, cutting and metallurgical operations like melting and casting into different shapes and sizes. Also storage and handling of U in finely divided powder forms is a common requirement during processing. It is observed that U in finely divided forms is highly pyrophoric even at ambient conditions. ‘Pyrophoricity’ is a property of a material used to describe how easily it ignites at ambient conditions. Thus there exists a potential for fire accidents in the nuclear facilities which deal with U in various forms especially in form of fine powders and turnings. Moreover, U could attain high temperature due to internal self-heating and hence demands proper ventilation in storage areas. From a radiological perspective it may be noted that the fine air suspended particles formed during burning can cause inhalation hazards due to the toxicity.

USDOE Report, ANS, 1994 suggested a description of cause, effect and preventive measures of metallic fires [1]. It states that spontaneous combustion is the ignition of a combustible material caused by the accumulation of heat from oxidation reactions. The extent of pyrophoricity mainly depends on the following factors viz. the specific surface area of the reacting metal, concentration of moisture and other vapors in air, temperature, oxygen concentration and presence of protective oxide layer.

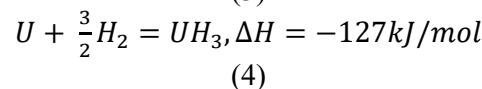
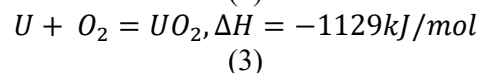
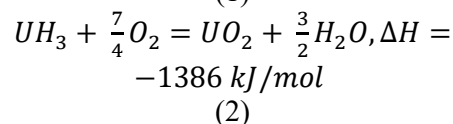
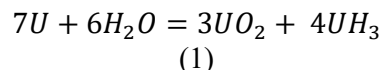
In case the rate at which the heat is generated, via oxidation, is larger than that of heat being removed through thermal radiation, convection and conduction the material could ignite spontaneously. Ignition temperature and the specific area of the pyrophoric substance are two important factors of concern. As a best practice, inflammable materials are not stored in contact with radioactive substances.

Special techniques are to be adopted towards extinguishing the fire in case of any emergency associated with fire in radioactive material. Eutectic mixture of Ba, K and Na (commercial name: ANSUL powder) is the commonly used fire extinguisher in case of fire involving U in metallic form.

The first source of heat generation for pyrophoricity that can be thought of is radioactive decay heat due to U (considering Nat. U) and its progeny. The progeny concentration of the decay products can be calculated using the Bateman Equation [2]. The second source of heat leading to pyrophoricity of U is the exothermic chemical reactions when exposed to the ambient environment. The rate and exothermicity of the reactions are to be studied for a better understanding of the pyrophoricity phenomena and the design of engineering controls for U-storage systems. Studies show that the heat generation due to radioactive decay is insignificant in comparison to the heat generation due to chemical reactions [3]. Hence, for this study we have focused on heat generation by chemical reactions only.

Guyadec et al in 2009, proposed a mechanism for spontaneous ignition of U powders [3].

This includes a set of exothermic reactions which take place when the same is exposed to the ambient conditions.



Totemeier in 2000 suggested that the kinetics of oxidation and corrosion of U are characterized in terms of the specific reaction rate (k) [4]. This constant is related either to the weight gain of the specimen per unit area or the amount of metal reacted per unit area related by an equation,

$$\frac{\Delta W}{A} = kt^n \quad (5)$$

Where, ΔW is weight gain of the specimen after reaction or mass of the metal reacted, A is the reacting surface area of the material, 't' is the time, 'n' is the empirical exponential factor.

The two principal methods for the estimation of the specific reaction rate are as follows,

- (i) Continuous measurement of the specific mass of the specimen which is exposed to the oxidizing environment, gravimetrically.
- (ii) Amount of gas reacted for closed systems can be estimated using pressure sensing devices like manometer.

The modes of gaseous oxidation reactions of U in environment are segregated into three main groups viz. i) reaction with oxygen and dry air, ii) reaction with water vapor and iii) reaction with moist air (i.e. moisture and oxygen). U on reaction with oxygen forms a superstoichiometric UO_2 . For temperatures below 400°C , the initial kinetics was found to be linear quadratic rather than linear. A subsequent transition to higher linear rate is generally observed. This final linear rate of oxidation is pertinent with respect to long term storage. The initial parabolic rate law

commonly observed for U oxidation in air suggests that the rate limiting step of the initial U oxidation process is the diffusion of oxygen ions through the growing oxide lattice. The transition to linear oxidation rate is related to the onset of oxide cracking, with the linear rate controlled by diffusion of oxygen ions through the oxide layer whose thickness remains constant throughout the further oxidation process. The mechanism of U oxidation by water vapour is similar to the dry air oxidation mechanism. The first step is the adsorption of water molecule on the oxide surface. Winer et al (1987) postulated that the oxidation occurs via dissociation of water molecule via hydrolysis reaction [5]. In case of oxidation of U in moist air, oxygen has an inhibitory effect. Addition of oxygen considerably lowers the rate of the U-water vapour reaction. Ritchie et al in 1986 showed that the reaction rate increases as water vapour is added to U-oxygen system up to relative humidity of 1-2% [6]. In the range of 2%-90% relative humidity, the reaction rate is constant. Above 90% relative humidity, the reaction rate again increases.

McGillivray et al in 1994 performed a detailed investigation on the oxidation of U-oxygen-water vapour system [7]. They developed a model based on Langmuir monolayer adsorption isotherm in the temperature range of 115°C to 350°C and a water vapour pressure range of 0-47 kPa. Their experimental results concluded that the reaction of U with water vapour predominates over all the other possible reaction routes. On increasing the water vapour pressure, the specific reaction rate increases. Moreover, from the heat of the reaction consideration we see that the uranium hydride oxidation has the highest exothermicity. Thus, for a conservative estimate of pyrophoricity due to chemical reaction, we choose this pathway for an in depth analysis.

The most common method to characterize the pyrophoric nature of uranium is the burning curve method [8]. In this method the specimen and furnace temperatures are recorded as a function of time. When the specimen ignites i.e. the oxidation reaction becomes self-

sustaining the specimen temperature increases drastically. The ignition temperature is determined as the specimen temperature curve deviates from the furnace temperature curve. Ignition temperature can also be estimated from the shielded ignition test. In this test, the specimen is heated in an inert atmosphere till the furnace reaches a specified temperature. Then an oxidizing atmosphere is admitted and the specimen temperature is noted as a function of time. If the test temperature is higher than the specimen ignition temperature, the specimen will ignite with a corresponding dramatic change in temperature. Else the self-heating to oxidation will be very feeble. The most important parameter for estimating pyrophoricity of a material is the ignition temperature of that specimen. It is the temperature at which the heat generation rate is more than that of the heat loss, thus leading to drastic rise in temperature. Thus, estimation of ignition temperature of U in different forms and geometries was an important exercise to do.

Plys et al in 2000 suggested a basic model for the estimation of pyrophoricity of U fines in spent fuel [9]. The model considers heat generation due to chemical reactions and dissipation due to conduction and convection. They coined a term called the ignition parameter (B), whose value gives an idea of pyrophoricity. B is basically defined as the ratio of heat generation to that of the heat dissipation. If $B > 1$, the system is pyrophoric and for $B < 1$, the system is not pyrophoric. However, the model by Plys et al doesn't consider the effect of the extent of diffusion in the oxide layer formed at initial phase of oxidation. Kanouff et al in 2013 proposed an 'ionic diffusion oxidation' model of U for the low temperature oxidation of U exposed to air [10]. The model is based on the diffusion of oxygen ions through oxide film driven by the electrostatic potential generated between the metal and the adsorbed oxygen ions. The value of the diffusion coefficient (D) is defined as,

$$D = 4 \cdot a^2 \cdot v \cdot \exp\left(-\frac{W}{k_b \cdot T}\right) \quad (6)$$

where, a = Lattice parameter i.e. distance between two U atoms in the crystal, v = Vibrational frequency of O atoms in UO_2 , W = Activation energy for chemical diffusion of O_2 in U, T = Ambient temperature, k_b = Boltzmann constant

This formula was adapted to estimate the diffusion coefficient for oxygen in U matrix.

Then the depth till which the moisture penetrates into the U-matrix was determined using the solution of Fick's Second Law of Diffusion for the case where the surface is in contact with an infinite long reservoir of fixed concentration of solute.

$$\frac{C_s - C_x}{C_s - C_0} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (7)$$

where, C_s = surface concentration of solute, C_0 = initial concentration of solute in the solid, x = distance from the surface, D = diffusivity of solute and t = time

The most prominent heat loss mechanism for a large body is conduction. It is a method of heat loss due to internal molecular collisions [11]. Fundamental equation for non-steady state conduction is,

$$\nabla^2 T + \frac{1}{k} Q_v - \frac{1}{\kappa} \frac{\partial T}{\partial t} = 0 \quad (8)$$

where, $\kappa = \frac{k}{\rho \cdot c_p}$, k = conductivity of U, ρ = density of U, c_p = specific heat capacity, Q_v = volumetric heat generation rate

First term takes care of the heat diffusion (the Fickian term), second term caters for the heat generation in the body and third term takes care of the temporal behavior of heat loss.

2. Computational Details: Initially, a benchmarking exercise was carried out to verify the agreement of the FEM based software with traditional methods to study heat transfer. The results are presented in the supplementary section [13].

Convection is a more prominent method of heat loss for flakes and turnings, where air can flow through the cavities and remove the heat.

$$q = h \cdot A \cdot (T_s - T_a) \quad (9)$$

where, q = heat generation rate, h = coefficient of convection, A = Area of the body, T_a = Air temperature, T_s = surface temperature

Radiation is less prominent. But for a condition when the metal is about to burn, it will play a significant role. Again this method of heat loss will be encountered in metallic fines and chips.

The governing equation is,

$$q = \sigma \cdot \epsilon \cdot A \cdot (T_s^4 - T_a^4) \quad (10)$$

where, σ = Stefan-Boltzmann Constant, ϵ = Emissivity of the surface

The time evolution of temperature in different geometries of U was studied using a Finite Element Method (FEM) based software. The FEM analysis generally converts a partial differential equation to a set of algebraic (or at most ordinary differential) equations which are solved through a variational technique that makes the method robust. Moreover, it can be applied to systems with irregular shapes [12].

Herein we have presented the conservative estimates of the rise in temperature and ignition temperature of U in different geometries (especially flakes) and in different conditions, using basic thermodynamics and kinetic equations considering relevant chemical reactions. The results of this study provide upper bound estimates of pyrophoricity of uranium in different forms, which could be utilized for safe storage and handling.

The thermal analysis module of the software was used to study the 3D chemical heat generation, conduction and convection losses in the most vulnerable geometries of U. Three cuboids of different dimensions as shown in *Figure 1* were considered for the study [14].

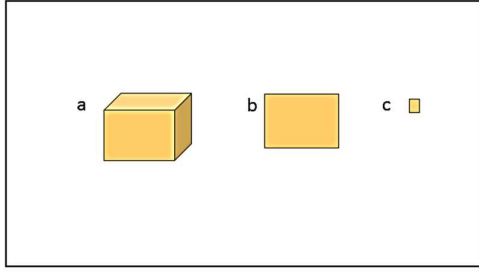


Figure 1. Representative models of a (a)cuboidal block, (b)sheet and a (c)flake of U.

It is assumed that the heat generation rate on the outer surface area is nearly equal to the volumetric heat generation rate in the outermost reacting layer. This assumption is supported by the fact that the reacting depth obtained from ionic diffusion oxidation model is nearly four orders lesser than that of the thinnest dimensions considered for different geometries. The volumetric heat generated rate is defined as,

$$Qv = (A_s/V).k_0.\Delta H.\exp(-T_E/T) \tag{11}$$

where, ‘A_s’ is the surface area, ‘V’ is the volume, ‘k₀’ is the specific reaction rate, ‘ΔH’ is the heat of UH₃ oxidation reaction, ‘T_E’ is the normalized activation energy of the same reaction and ‘T’ is the ambient temperature.

The values of the relevant parameters are obtained from Pearce correlation (Pearce, 1989) as it matches with the storage condition. Pearce correlation in the given condition are as follows [15],

For relative humidity < 100%, UH₃ oxidation reaction route and T < 192°C, k₀ = 1.023 x 10⁵ kg/m²/s, T_E = 11490 K and n = 0.3.

The reacting depth (d) was used as obtained from Eqns. 6 & 7. Volume under consideration can be defined as the product of the surface area (A_s) and the reacting depth.

At 313K the volumetric heat generation rate comes out to be,

$$Qv = \left(\frac{1}{d}\right).k_0.\Delta H.\exp\left(-\frac{T_E}{T_m}\right) = 3970 \text{ Jm}^{-3}\text{s}^{-1} \tag{12}$$

Thus the areal heat generation rates on all surfaces is assumed to sufficiently account for the heat generation due to chemical reactions. Heat losses are simulated by providing

convective boundary conditions on all the surfaces. For a restrictive study, for heat loss by air convection the convective heat transfer coefficient was taken as 10 Wm⁻²K⁻¹.

In FEM, the material model is created by specifying the conductivity, specific heat capacity and density of U. Conductivity (k) = 27.5 Wm⁻¹K⁻¹, Specific Heat (C_p) = 117.23 Jkg⁻¹K⁻¹, Density (ρ) = 19,000 kgm⁻³. Hexagonal meshing is chosen for the FEM calculations as it gives the best approximation to solid block geometries.

A transient thermal analysis is carried out to see the temperature evolution in a time range of 10⁵ s (~ a day). 100 numbers of stepwise iterations were carried out for optimum computation efficiency.

Employing a simplistic approach, the auto-ignition temperature of U flakes was estimated using heat balance equation.

Heat generation due to chemical reactions = Heat loss due to convection + Heat loss due to radiation

$$Ak_0 \exp\left(-\frac{T_E}{T}\right)\Delta H = hA(T_s - T) + \sigma \epsilon A(T_s^4 - T^4) \tag{13}$$

where ‘T_s’ is the surface temperature and rest of the symbols have their usual meanings.

When we plot the heat generation rate due to reactions, heat loss rate due to convection and radiation, heat loss due to pure convection and heat loss due to pure radiation vs. temperature in the same plot, we arrive at the steady state temperatures from the intersection points.

Further, the excess heat generation rates ($\frac{Q}{A}$) needed to cause ignition at room temperature were estimated using the following equation,

$$k_0.\Delta H.\exp\left(-\frac{T_E}{T_m}\right) + \frac{Q}{A} = h.(T_m - T_s) + \sigma.\epsilon.(T_m^4 - T_s^4) \tag{14}$$

and their probable sources are discussed in subsequent sections.

3. Results & Discussions: Using the Ionic Diffusion Oxidation Model and substituting the values of the parameters in Eq. 7, we get a plot of how deep the moisture penetrates into

the U-matrix when exposed to the ambient moisture for different time ranges.

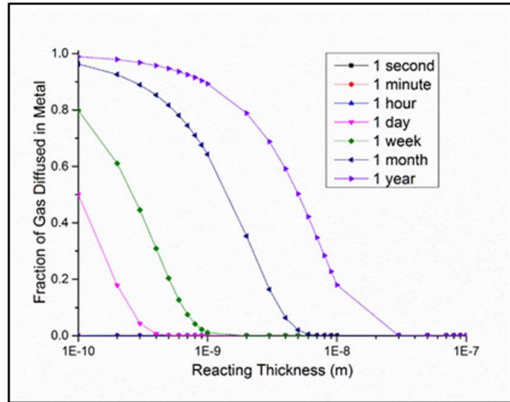


Figure 2. Plot of fraction of solute gas diffused into the metal with varying reacting thickness

Figure 2 shows that for a long term storage of about one year, moisture diffuses up to a thickness of 0.1 μm . This conservative estimate of reacting thickness was used for further studies to simulate extended storage periods. Extent of diffusion for time ranges viz. seconds, minutes and hours are negligible. The output from the FEM analysis i.e. the rise in temperature of U considering the three different geometries as a function of time is presented in a consolidated graphical form in Figure 3.

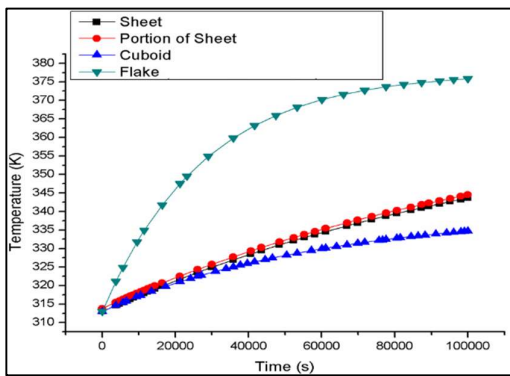


Figure 3. Plot of temperature evolution of U in different geometries

It is observed from Figure 3 that in the given model, the rise in temperature is steepest for the thinnest geometry i.e. the flake, followed by sheet and then a cuboid. This is because the only mode of predominant heat loss is convection for a flake. Thus, the heat generated

by chemical reactions is not quickly dissipated leading to the steep rise in temperature.

When we plot the heat generation rate due to reactions, heat loss rate due to convection and radiation, heat loss due to pure convection and heat loss due to pure radiation vs. temperature in the same plot (using Eqn. 13), we arrive at the steady state temperatures from the intersection points. Any temperature higher than the steady state temperature will have heat generation larger than heat loss, indicating the onset of auto-ignition phenomenon.

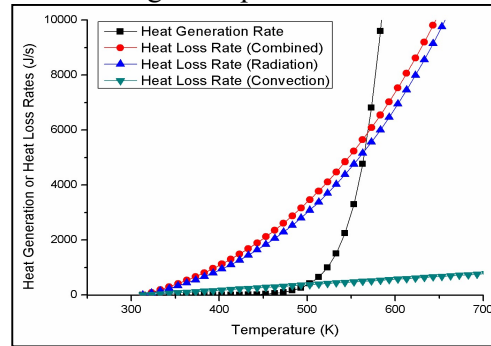


Figure 4. Plot of heat generation or heat loss rates vs. temperature

For the most conservative estimate, the heat loss only by convection was considered. The above equation was further solved numerically to obtain the steady state temperatures for the U-flakes.

Table 1: Table for Steady State Temperature achieved for Different Heat Loss Modes

Heat Loss Type	Steady State Temperature (K)
Combined Loss	569
Radiation	566
Convection	501

From Table 1 it is seen that the ignition temperature for flakes is much higher than ambient temperature (~ 300 K). Thus a significant amount of other heat source is required for U to auto-ignite at room temperature. Also, larger exposed surface area to volume ratio, will render larger heat generation.

The excess heat generation rates needed for auto-ignition at different ambient temperatures are given in Table 2.

Table 2: Table for Excess Heat Generation Rates Needed for Auto-Ignition at Different Ambient Temperatures

Ambient Temperature (K)	Steady State Temperature (K)	Excess heat generation rate per unit area ($\text{Jm}^{-2}\text{s}^{-1}$)
298	502	3169
303	502	3121
308	501	3071
313	501	3018

The results in Table 2 depict, significant amount of additional heat source is required for uranium to auto-ignite at room temperature. Also, larger the exposed surface area to volume ratio, higher will be the heat generation. The major sources of heat leading to pyrophoricity may be in physical or chemical form. Friction during processing might be one of physical forms of heat generation. Contamination in U with other process related chemical species can lead to exothermic reactions, which can add up to the heat input.

Presence of chemical impurities and other physical phenomena could supply enough energy to cross the activation barrier for uranium oxidation reaction which might lead to a rise in temperature, finally causing ignition. These explanations will be useful to corroborate with the observed pyrophoricity behaviour of uranium compounds in various storage-handling conditions and to design the appropriate engineered control measures. Further specific studies using known concentration of chemical impurities in uranium will help in arriving at impurity-specific heat generation rates to suit various processing conditions in facilities.

4. Conclusions: Pyrophoric behaviour of U flakes is studied using a finite element based technique. It has been observed that the thin geometries are associated with the steep rise in

temperature. Quantitative estimates of the steady state temperatures for ignition of flakes are obtained. Important insights into the mechanism of pyrophoricity is also attained i.e. the pyrophoric behaviour of uranium flakes is mainly due to the exothermic reactions it undergoes with moist air; which can be further aggravated in the presence of other heat sources like friction, chemical contamination etc. [16]

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Conflict of Interest: Authors declare No conflicts of interest.

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