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# Empirical and physics-based mathematical models of uranium hydride decomposition kinetics with quantified uncertainty



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## HIGHLIGHTS

- The measured UH<sub>3</sub> decomposition kinetics data found in the literature is scattered and limited.
- The predicted decomposition kinetics uncertainty and mean are comparable with measured values.
- The pressure buildup in the porous bed during the decomposition delays the H<sub>2</sub> extraction.
- The particle shrinkage in the bed during decomposition results in a 10 × increase in the permeability.
- The uncertainty in the decomposition time predicted by a continuum bed model is amplified.

## ARTICLE INFO

### Article history:

Received 30 January 2014

Received in revised form

21 April 2014

Accepted 19 May 2014

Available online 28 May 2014

### Keywords:

Uranium hydride

Decomposition kinetics

Empirical model

Physics-based model

Parametric uncertainty

## ABSTRACT

Metal hydride particle beds have recently become a major technique for hydrogen storage. In order to extract hydrogen from such beds, it is crucial to understand the decomposition kinetics of the metal hydride. We are interested in obtaining a better knowledge of the uranium hydride decomposition kinetics. We first developed an empirical model fit to measurements compiled from different experimental studies in the literature and quantified the uncertainty resulting from the scattered data. We found that the decomposition time range predicted by the obtained kinetics is in a good agreement with published experimental results. Secondly, we developed a physics-based mathematical model to simulate the rate of hydrogen diffusion in a spherical hydride particle during the decomposition. We used this model to evaluate the kinetics for temperatures ranging from 300 K to 1000 K while propagating parametric uncertainty. We have compared the kinetics parameters derived from the empirical and physics-based models and found that the uncertainty in the kinetics predicted by the physics-based model covers the scattered experimental data. Finally, we used the predicted kinetics parameters to simulate the effects of boundary resistances and powder morphological changes during decomposition in a continuum level model. We found that the phase change within the bed occurring during the decomposition accelerates the hydrogen flow by increasing the bed permeability, while the pressure buildup and the gap forming at the wall significantly impede the hydrogen extraction. We also found that there is significant uncertainty in the bed decomposition time at the lower range of the kinetics.

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## 1. Introduction

Hydrogen (H<sub>2</sub>) storage in metal hydrides has the potential to store hydrogen in a safe and stable manner for long periods of time and to release the hydrogen quickly when it is needed (Wiswall, 1978). Uranium (U) stores hydrogen at a density of  $8.3 \times 10^{22}$  atoms per cm<sup>3</sup> of material, higher than most metal hydrides,

and at a low equilibrium pressure (less than 0.1 Pa) (Kolasinski et al., 2010). Uranium hydride (UH<sub>3</sub>) powder beds have been used extensively for hydrogen isotope storage (Bowman and Vis, 1990; Heung, 1995; Hayashi, 2008). Stored hydrogen isotopes can be recovered by heating the hydride up to temperatures of 400–450 °C. Understanding the decomposition kinetics of UH<sub>3</sub> is important for hydrogen storage applications. However, a large amount of variation exists between the few empirical models developed to date (Condon and Larson, 1973; Stakebake, 1979; Lindner, 1990) and no published physics-based models are available.

Condon and Larson (1973) studied the reaction kinetics of the U–H system in a high vacuum environment at lower temperatures

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(60–250 °C). The dehydriding reaction was found to be nearly a zero-order reaction with an activation energy of 72.82 kJ/mol. Significant scattering in the measured dehydriding kinetics data was observed due to the existence of oxide contaminants. Stakebake (1979) performed dehydriding experiments at moderate temperatures (200–300 °C) and found an activation energy of 39.76 kJ/mol. The discrepancy between this value and the one measured by Condon and Larson was attributed to the presence of oxidizing contaminants during Stakebake's experiments. Finally, the recent study of Lindner (1990) resulted in a better understanding of the decomposition mechanism. Through a more thorough experimental study at high temperatures (400–500 °C), it was proved that the reaction is controlled by the advance of the U–UH<sub>3</sub> phase such that the reaction fraction can be expressed as

$$\alpha = 1 - [1 - k(T, P)t]^3 \quad (1)$$

where  $k(T, P)$  is the temperature and pressure dependent kinetic coefficient and  $t$  is time. Lindner derived a more accurate dependence of  $k$  on the temperature and pressure given by

$$k = k_0 e^{-E_a/RT} \log(P_0(T)/P) \quad (2)$$

where  $P_0$  is the hydrogen plateau pressure as a function of temperature. In a recent multiphysics finite element study (Kanouff et al., 2013), oxidation of UH<sub>3</sub> was used to generate a high temperature sufficient to decompose a UH<sub>3</sub> bed. The study relied on the decomposition kinetics of Condon and Larson (1973) while the UH<sub>3</sub> oxidation kinetics were fit to the measured experimental data (Salloum et al., 2012, 2013). No attempt was made to improve upon the decomposition kinetics found by Condon and Larson. On the other hand, plateau pressure, below which decomposition of the UH<sub>3</sub> occurs, was evaluated as a function of temperature.

Other empirical models of the U–H reaction have been published (Condon, 1980; Kirkpatrick, 1981; Powell et al., 1990; Chernov et al., 2008), but did not study the decomposition. A mathematical model of the kinetics of isothermal UH<sub>3</sub> formation under constant near equilibrium pressure was developed by Chernov et al. (2008). They considered four stages of hydriding: nucleation, skin development, skin growth, and final saturation. The model was then used to fit a series of experimental curves and evaluate the output for the kinetic parameters.

In this work, we derive UH<sub>3</sub> decomposition kinetics in two ways. First, we gather the data obtained from previous experimental studies (Condon and Larson, 1973; Stakebake, 1979; Lindner, 1990) and fit an empirical model of the decomposition kinetics as an Arrhenius dependence on the temperature. Such empirical model is more accurate than the previous individual models since it involves more data and covers a larger temperature range. Second, we develop a physics-based model of the UH<sub>3</sub> decomposition that accounts for the hydrogen diffusion and solubility in U. This model enables the computation of the kinetics as a function of temperature. In both models, we quantify the uncertainty in the obtained kinetics using polynomial chaos expansions (PCE). This uncertainty is due to experimental error and limited data. Finally, we apply the computed kinetics to a continuum level model to study the effect of boundary thermal resistance and powder morphological changes in a UH<sub>3</sub> particle bed during decomposition.

## 2. Polynomial chaos expansions

In this section we briefly outline the concept of a PCE. We consider random entities parametrized by a finite collection of real-valued independent and identically distributed (*i.i.d.*) random variables  $\xi_1, \dots, \xi_d$  that share a common distribution function. If,

for example,  $\xi$  is a standard normal random variable, we write  $\xi \sim \mathcal{N}(0, 1)$  such that any random variable with finite variance admits an expansion of the form

$$u(\xi) \approx \sum_{i=0}^Q u_i \Psi_i(\xi), \quad (3)$$

where the  $\{\Psi_i\}_{i=0}^Q$  is an orthogonal basis with respect to the density of  $\xi = (\xi_1, \dots, \xi_d)$ . The expansion (3) is known as the truncated polynomial chaos expansion (PCE) (Wiener, 2007; Cameron and Martin, 1947; Janson, 1997; Ghanem and Spanos, 1991; Le Maître and Knio, 2010) of  $u$ . Particularly, in the case where  $\xi_{1\dots d} \stackrel{iid}{\sim} \mathcal{N}(0, 1)$ , the  $\{\Psi_i\}_{i=0}^Q$  are  $d$ -variate Hermite polynomials (Abramowitz and Stegun, 1970). The number of terms  $Q$  in the summation of Eq. (3) is finite and depends on the number of stochastic dimension  $d$  and the expansion order  $p$  according to the following equation:

$$Q + 1 = \frac{(d+p)!}{d!p!}. \quad (4)$$

Here  $p$  refers to the largest polynomial degree in the expansion. One way to derive the PC coefficients of  $u$  is by projection on the PC basis following

$$u_i = \frac{\langle u \Psi_i \rangle}{\langle \Psi_i^2 \rangle}, \quad k = 0, \dots, Q \quad (5)$$

This requires numerical evaluation of the projection integrals  $\langle u \Psi_i \rangle$  using quadrature rules. This method is referred to as non-intrusive spectral projection (NISP) (Le Maître and Knio, 2010) and will be used in this study. More details about PCEs and their numerical implementations are found in Le Maître and Knio (2010).

## 3. Chemical kinetics experimental data

### 3.1. Experimental data

The measurement of UH<sub>3</sub> decomposition kinetics was the subject of few experimental studies (Condon and Larson, 1973; Stakebake, 1979; Lindner, 1990). In our work, we consider that the UH<sub>3</sub> decomposition kinetics are equivalent to the dehydriding kinetics measured by these studies. The kinetics data is reported as the kinetics Arrhenius pre-exponent as a function of temperature and exhibit significant scattering. In all studies, the kinetics were measured after several hydride–dehydride cycles of the UH<sub>3</sub>. Fig. 1 shows the data gathered from different studies where the units of  $k$  were suitably converted to s<sup>-1</sup>. The empirical fits to the individual datasets exhibit significant discrepancies which induces uncertainty in the overall kinetics coefficient and activation energy. We combine different measured kinetics data in order to cover a bigger temperature range and increase the amount data. Inferring the Arrhenius relationship from such enriched dataset incurs significant decrease in the uncertainty of the fitting parameters (Salloum et al., 2011).

We use Bayesian inference to build a parametric Arrhenius dependence of the kinetics coefficient as a function of the temperature according to the method described in Salloum et al. (2011). Namely, we infer a parametric linear dependence between  $\log(k)$  and  $1/T$ . The noise due to scattering in this data is not uniform as a function of temperature. A Gaussian noise model is the most reasonable assumption for such cases regardless of how noisy and scattered the data are (Rasmussen and Williams, 2006; Salloum et al., 2011). Thus, the Bayesian inference results in two normally distributed uncertain variables  $k_0$  and  $E_a$ . The resulting

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