Mathematical analysis of the hydrogen–uranium reaction using the shrinking core model for hydrogen storage application

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ABSTRACT

The reaction of metallic uranium particles with hydrogen at ambient or above ambient temperature has been used as the basis for the solid state storage of hydrogen in the form of uranium hydride for various applications in the nuclear industry. This work models the reduction of a single particle of metallic uranium to uranium hydride using available kinetic data, the well known shrinking core model and the pseudo-steady state hypothesis. No single rate controlling regime was assumed apriori and the various interfacial gas concentrations were calculated by an iterative procedure as function of the core radius at any time and for given operating conditions. The volumetric expansion or increase in the outer radius of the uranium particle as it is progressively hydrided was also considered in this work. The time required for complete conversion of the pellet to the hydride was then calculated by numerical integration and the rate controlling regime was identified. A spherical geometry was considered in this work for illustrating the technique, but the method is applicable to any kinetic model and any geometry of the pellets after simple modifications to the governing equations.

Introduction

The use of hydrogen as a clean energy carrier and a fuel of the future have been extensively documented [1]. The widespread use of hydrogen needs the development of efficient storage technology for it. Reversible metal hydride based solid state hydrogen storage systems have been given particular importance in this context. Uranium is one of the most extensively studied metallic species for this purpose, especially for storage of heavier hydrogen isotopes [2].

The reaction of metallic uranium takes place quite readily depending on the gas pressure, temperature and the uranium particle size. The hydride that forms starts decomposing at temperatures of about 250 deg C to yield very pure hydrogen gas. Owing to the reversibility of the reaction, the maximum hydriding reaction rates have been observed to occur in a temperature range of 225–250 deg C after which the dehydriding reaction assumes greater importance [3]. Thus the importance of this reaction system with respect to hydrogen storage technology cannot be undermined.

Serial number [Reference]	Area of focus	Main results
1 [4]	The kinetics for reaction of hydrogen with uranium powder over the temperature range of 50–250 deg C and at two hydrogen pressures (13.3 kPa and 26.6 kPa) were investigated using a gravimetric technique involving an electro-microbalance.	Surface adsorption phenomenon of hydrogen on uranium on reaction kinetics was offered as the explanation of the observed decrease in reaction rate with increase of temperature, even when adsorption was not the rate controlling step. Hydriding of uranium was found to follow 2/3rd order kinetics for 13.3 kPa hydrogen pressure which rose to 1st order kinetics at the higher pressure. Decomposition or dehydriding was found to follow zero order kinetics.
2 [5]	The effect of the shape of uranium particles on the hydriding kinetics under isothermal and isobaric was studied.	A diffusion based hydriding mechanism was considered and using basic symmetrical particle shapes like cylinders, slabs and spheres for mathematical and experimental analysis, it was shown that the particle shape had negligible influence on overall hydriding kinetics.
3 [6]	Development of a mathematical model considering four steps in series (nucleation, skin development, skin growth, and final saturation) for hydriding of uranium was carried out.	Experimental data and the mathematical model developed were used to evaluate the kinetic parameters for the various steps in hydriding.
4 [7]	A survey of the existing literature for various properties of the uranium–hydrogen system was carried out to identify areas which require further study for making extensive use of uranium for solid state storage of hydrogen isotopes in the nuclear industry.	Emphasis was given on identifying the gap areas from the materials science perspective before uranium can be effectively used as a long term, reliable storage medium for hydrogen isotopes. The work presents a fair amount of thermodynamic and kinetic information about this system as also highlights issues like accidental air ingress into a storage system and the release of helium gas from the solid matrix when it is used for tritium storage.
5 [8]	The various rate models for hydriding and dehydriding of uranium based spent nuclear fuel sent for final disposal in geological repositories were reviewed critically for various conditions of temperature and pressure, with a focus on ensuring the safety and reliability of the multi-canister overpacks for spent fuel storage.	Comparisons of the predicted rates of hydriding and dehydriding were made between the most well known models and rate equations viz. the Bloch-Mintz and Condon-Kirkpatrick models. It was seen that the second model provides higher rates of hydriding as also dehydriding at any given temperature and hydrogen overpressure.
6 [9]	The hydriding kinetics of activated metallic uranium was studied at near equilibrium pressure over a temperature range of 290–370 deg C to arrive at the reaction mechanism.	Kinetic data were obtained and explanations were provided as to the origin of the parabolic pressure dependence of the linear hydriding rate constant by assuming a nucleation and growth model for the reaction for the low pressure ranges. At higher pressures there is a shift in the pressure dependence, as noted by various other researchers as well.
7 [10]	An investigation of the fundamental mechanisms of reaction of hydrogen and moisture with clean and contaminated uranium surfaces was carried out using sophisticated experimental techniques.	Sticking probabilities and binding energy of the gases to the metal surface have been calculated. Desorption rates of hydrogen from the surface have also been evaluated.
8 [11]	Temperature programmed desorption and supersonic molecular beams have been used to study the dynamics of hydrogen–uranium reaction on very clean metallic surfaces.	Two modes of hydrogen adsorption on uranium were observed-a non activated mode and an activated mode. Sticking probabilities were also calculated.
9 [12]	Reaction kinetics of high purity uranium rods with hydrogen was studied over the temperature range of 96–400 deg C and hydrogen overpressure of 70–430 mm Hg.	Linear rate laws as function of temperature and pressure were obtained and reported. The reaction mechanisms corresponding to the different conditions of reaction were not explicitly studied or discussed but it was mentioned that there could be at least two different rate controlling regimes in the range of conditions examined in this work.
10 [13]	Reaction kinetics of uranium and hydrogen over a significantly large range of pressure and temperature was determined and two different reaction models were used to explain the results.	Owing to the large pressure range examined, different pressure dependencies of the rate law were obtained. An extensive mathematical analysis was also performed to arrive at a rate law that takes into account both the hydriding and dehydriding processes in a single equation.
11 [14]	Reaction kinetics of fine uranium powder and hydrogen was studied and a new reaction mechanism was proposed to explain the observations.	The hydriding rate was found to have a first order dependence on the mass of uranium remaining unreacted and a hydrogen pressure dependence of 0.5. Dehydriding appeared to follow zero order kinetics.
12 [15]	Reaction kinetics of massive uranium with hydrogen was studied over a wide range of pressure and temperature. The effect of conditions on the formation of the alpha or the beta hydride of uranium was also studied. Isotope effects have also been considered.	Linear hydriding rates were shown to follow 0.5 order pressure dependence. Isotope effects were determined to be less significant for this reaction. The importance of previously reported studies in explaining the rate data over different ranges of conditions was also highlighted.

Table 1 – Summary of kinetic studies of the hydrogen–uranium reaction.