

DEVELOPMENT OF A PROCESS TO NEUTRALIZE WATER-REACTIVE WASTES

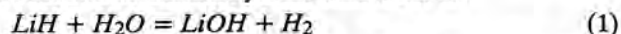
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ABSTRACT

The mixed waste storage area at Los Alamos National Laboratory contains a considerable amount of lithium hydride and other water-reactive wastes. A process to neutralize these wastes by controlled hydration in an atmosphere of humid nitrogen is being developed. The kinetics of reaction of lithium hydride with water vapor has been studied at bench scale. The reaction progress can be predicted using the Unreacted Shrinking Core Model for noncatalytic solid-fluid reactions. This model will be utilized in designing a skid-mounted treatment unit to neutralize water-reactive wastes.

INTRODUCTION

Water-reactive compounds react with water and generate hydrogen. The reaction is exothermic and sometimes extremely rapid. Hydrogen may ignite or even form an explosive mixture. To comply with the regulations of the Resource Recovery Conservation and Recovery Act (RCRA), the reactivity must be neutralized before these wastes can be land-disposed. LANL and other DOE facilities have various radioactively contaminated water-reactive wastes. The most abundant at LANL is lithium hydride; other wastes include magnesium, sodium, calcium, and some finely divided metals. The reaction of lithium hydride with water is:



A treatment is being developed to neutralize lithium hydride by controlled hydration, according to equation (1), by humid nitrogen. Nitrogen prevents a flammable or explosive mixture from forming in the reactor. A bench-scale testing program has been performed to determine the kinetics of reaction (1) and to obtain the engineering data necessary to design a skid-mounted plant to neutralize lithium hydride and other water-reactive wastes. The first experimental data from this program have been presented at the International Symposium on Mixed Waste in Baltimore in August 1993 (1). As could be anticipated, the reaction rate increases when both humidity and temperature are increased. This work continues the study of kinetics of hydration of LiH. It demonstrates that the reaction is well represented by Unreacted Shrinking Core Model (USCM) for heterogeneous fluid-solid reactions.

EXPERIMENTAL APPARATUS

The experimental set-up is presented in Fig. 1. The measured amount of nitrogen flows through the humidifier, whose temperature is controlled. The gas becomes saturated with water vapor by bubbling through the metal cylinder filled with glass beads. The humidity of the gas can be calculated from the weight loss of the cylinder over test duration. Humid nitrogen may be diluted with dry nitrogen to adjust the humidity to the desired level. The mixture of nitrogen and water vapor then enters the reactor, where a small sample of lithium hydride, in the powder form, is placed in a ceramic crucible. The temperature of the reactor is controlled. A thermocouple immersed in the powder measures temperature changes due to reaction exothermicity. The gas exiting the reactor flows through the condenser to remove excess moisture, then through Drierite column to remove the residual moisture before the hydrogen concentration is measured. The reaction progress is monitored by changes in hydrogen concentration. The delay time between the reactor and the point of concentration measurement is incorporated in the flow model, so the concentration used in the results represents the concentration in the reactor.

REACTION MODEL

The reaction of lithium hydride with water vapor falls under a category of heterogeneous noncatalytic solid-fluid reactions (fluid being either gas or liquid). Several models for such reactions have been introduced in the past 30 years. An overview of the most practical reaction models is given in the

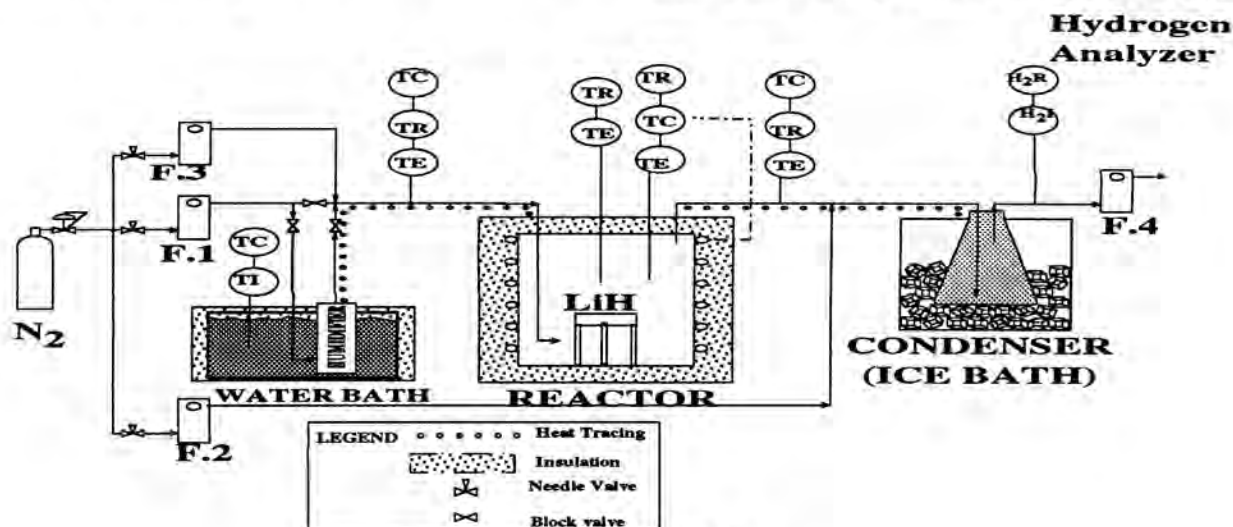


Fig. 1. Experimental set up.

work by Dziejewski (2). The most commonly known and quoted model, the USCM, was first introduced by Yagi and Kuni in 1955, and it is well described in Octave Levenspiel's *Chemical Reaction Engineering* (3). The USCM is popular for its ease of application, clear physico-chemical interpretation of the phenomena it describes, and good predictability of many reacting systems. The model assumes that the reaction between fluid and solid takes place on a surface of the unreacted core of a solid particle (in a macroscopic sense) and that the fluid reagents must diffuse through the external layer of the gas film and through the porous structure of the solid reaction product, which forms around the core (Fig. 2).

Depending on reacting species and the process conditions, one of the reaction steps - film diffusion, internal diffusion, or surface reaction - may be much slower than the others and it controls the reaction rate. To be able to use appropriate equations for prediction of reaction course, it is practical to know which is the reaction-controlling step. Simple mathematical expressions describe time vs. reaction progress relationships once the controlling step is known. Some more

complexity must be introduced, if there is no distinct controlling step and the reaction rate is affected by two or even three steps. The equations describing these relationships for spherical particles are presented in Table I.

EXPERIMENTAL RESULTS

To check whether the studied reaction follows the USCM, we compared the theoretical lines according to the model, with the data points obtained in experiments. To avoid determining such unknown parameters as surface reaction rate constant, diffusion coefficient, and external mass transfer coefficient, we rearranged the equations in Table I. At 80% of reaction time (t_{80}), the hydrogen volume will be 80% of stoichiometric volume, and at 50% of reaction time (t_{50}), the hydrogen volume will be 50% of stoichiometric volume. Assuming that the reacting particles have a spherical shape, it is easy to calculate the core radius at 80% and 50% reaction time. Substituting 50% and 80% volumes and 50% and 80% radii into equations showed in Table I, it is possible to derive dimensionless expressions such as, those presented in Table

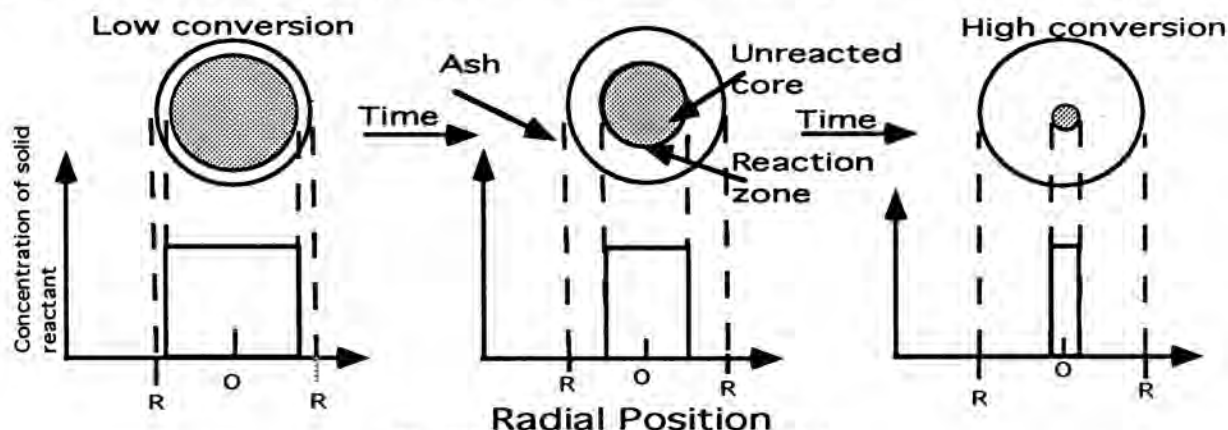


Fig. 2. Unreacted shrinking core model.

TABLE I
Time Expressions for Reacting Spheres According to USCM

Time Expression	Surface Reaction Controls	Internal Diffusion Controls	Gas Film Diffusion Controls
In Terms of Radius	$t = \frac{\rho}{k_s C} (R - r)$	$t = \frac{\rho R^2}{6DC} \left(1 - 3\left(\frac{r}{R}\right)^2 + 2\left(\frac{r}{R}\right)^3 \right)$	$t = \frac{\rho R}{3k_g C} \left[1 - \left(\frac{r}{R}\right)^3 \right]$
In Terms of Conversion	$t = \frac{\rho R}{k_s C} \left[1 - (1 - X)^{\frac{1}{3}} \right]$	$t = \frac{\rho R^2}{6DC} \left[1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X) \right]$	$t = \frac{\rho R}{3k_g C} X$

Where:

- t = reaction time
- ρ = density of solid reagent
- k_s = surface reaction rate constant
- C = concentration of fluid reagents
- R = initial radius of solid particle
- r = radius of the shrinking core
- D = diffusion coefficient
- k_g = mass transfer coefficient
- X = fraction of converted solid.

II. We used 80% and 50% reaction times, rather than total reaction times, because by the end of reaction, hydrogen concentration was very low and the accuracy of the measurement much lower than for higher concentration. During our tests, we measured the volume of hydrogen generated in the reaction in time intervals. From equation (1) and hydrogen evolution, we could calculate the volume of solid lithium hydride consumed during these time intervals, which volume corresponds to the volume of hydrogen. Next, assuming that the reaction follows the shrinking core geometry, we could calculate the new core radius at the end of each time interval. We continued such iterations until the calculated core radius became zero. In most cases, the zero radius corresponded to the end of the reaction, when the total hydrogen volume was equal to the stoichiometrical volume equivalent to the total weight of reacted lithium hydride used in the experiment (Fig. 3-4).

The experimental results, when plotted as dimensionless time expressions, such as specified in the first column of Table II, showed a good agreement between experimental points and the theoretical lines for the Unreacted Shrinking Core Model. Figures 5 through 12 show comparisons of experimental points with theoretical lines for the relationships given in Table II. Figures 5, 7, 9, 11, represent tests at lower concentration, while Figs. 6, 8, 10, 12 represent tests at higher concentration of water vapor. Three theoretical lines are on each of these figures. Each line represents a different rate controlling regime - film diffusion, internal diffusion, or surface reaction. The closer the points line-up with a given theoretical line, the more certainty we have that the reaction rate was controlled by the step this theoretical line describes. If one can distinguish a rate-controlling step, then simple equations presented in Table I can be used to predict the reaction course. We concluded that the USCM can be used to model the

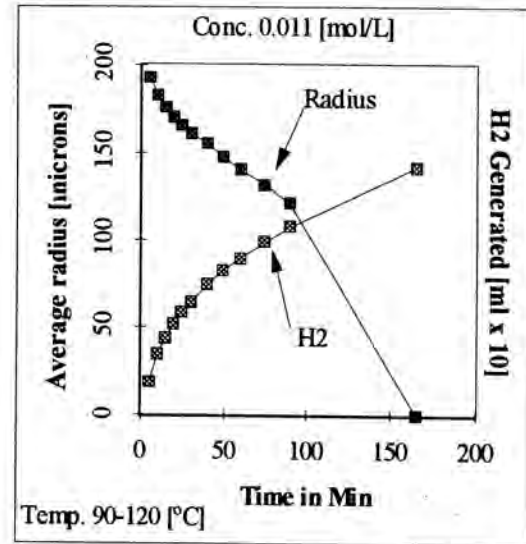
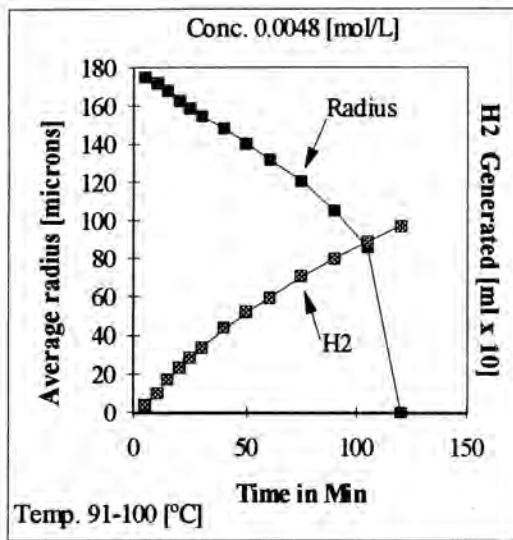


Fig. 3. Change of unreacted core with time for lower concentration test.

Fig. 4. Changes of the radius of unreacted core with reaction time for higher concentration test.

TABLE II
Dimensionless Time Expressions for USCM

Time Expression	Surface Reaction Controls	Internal Diffusion Controls	Film Diffusion Controls
$\frac{t}{t_{80}}$ vs. $\frac{r}{R}$	$\frac{t}{t_{80}} = 2.408 \left(1 - \frac{r}{R}\right)$	$\frac{t}{t_{80}} = 2.674 \left[1 - 3\left(\frac{r}{R}\right)^2 + 2\left(\frac{r}{R}\right)^3\right]$	$\frac{t}{t_{80}} = 1.25 \left[1 - \left(\frac{r}{R}\right)^3\right]$
$\frac{t}{t_{50}}$ vs. $\frac{r}{R}$	$\frac{t}{t_{50}} = 8 \left(1 - \frac{r}{R}\right)$	$\frac{t}{t_{50}} = 9.107 \left[1 - 3\left(\frac{r}{R}\right)^2 + 2\left(\frac{r}{R}\right)^3\right]$	$\frac{t}{t_{50}} = 2 \left[1 - R \left(\frac{r}{R}\right)^3\right]$
$\frac{t}{t_{80}}$ vs. $\frac{V}{V_T}$	$\frac{t}{t_{80}} = 2.408 \left[1 - \left(1 - \frac{V}{V_T}\right)\right]$	$\frac{t}{t_{80}} = 1.116 \left[1 - 3\left(1 - \frac{V}{V_T}\right)^2 + 2\left(1 - \frac{V}{V_T}\right)^3\right]$	$\frac{t}{t_{80}} = 1.008 \left[1 - \left(1 - \frac{V}{V_T}\right)^3\right]$
$\frac{t}{t_{50}}$ vs. $\frac{V}{V_T}$	$\frac{t}{t_{50}} = 4.845 \left[1 - \left(1 - \frac{V}{V_T}\right)^{\frac{1}{3}}\right]$	$\frac{t}{t_{50}} = 2 \left[1 - 3\left(1 - \frac{V}{V_T}\right)^2 + 2\left(1 - \frac{V}{V_T}\right)^3\right]$	$\frac{t}{t_{50}} = 1.143 \left[1 - \left(1 - \frac{V}{V_T}\right)^3\right]$

where:

- t = time from the beginning of the reaction
- t₈₀ = time when 80% of stoichiometric volume of H₂ was generated
- t₅₀ = time when 50% of stoichiometric volume of H₂ was generated
- V = volume of H₂ at time t
- V_T = total stoichiometric volume of hydrogen

reaction during equipment design. Verifying that our reaction follows a physico-chemical model gives an important tool in the designing process. After determining the parameters of the model, such as surface reaction rate constant, diffusion coefficient, and mass transfer coefficient, we can use the model in any conditions and extrapolate our experimental findings into the industrial-scale design. In contrast, if we derived mathematical equations, using our experimental points and giving the relationships between the parameters of our reaction but no physical interpretation, we would describe only our own experimental system, and any extrapolation to other conditions would be risky.

Comparing the experimental data with the theoretical lines represented by the equations shown in Table II, we noticed, that the tests performed at lower water vapor concentration and lower temperature tend to be in kinetic regime, which means that the surface reaction is the slowest step. The

tests performed at higher water vapor concentration and temperature tend to follow the internal diffusion regime, which means that the diffusion of water vapor through the pores of the product layer (LiOH) is the slowest step. Some tests are between the kinetic and diffusion regimes, which means that both, diffusion and surface reaction steps contribute to the reaction rate (Fig. 5 - 12).

EMPIRICAL MODEL

In addition to comparing the experimental data with the theoretical lines according to USCM, we developed a mathematical equation that correlates the investigated variables: water vapor concentration, temperature and reaction rate. We obtained this equation by best statistical fit of all data, without physical interpretation. The equation has the following form:

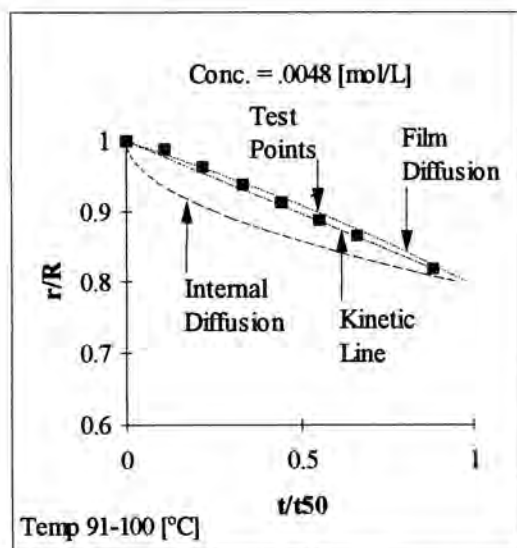


Fig. 5. Comparison of experimental points with theoretical lines for changes of ratio of core radius vs. ratio of time to time of 50% reaction for lower concentration test.

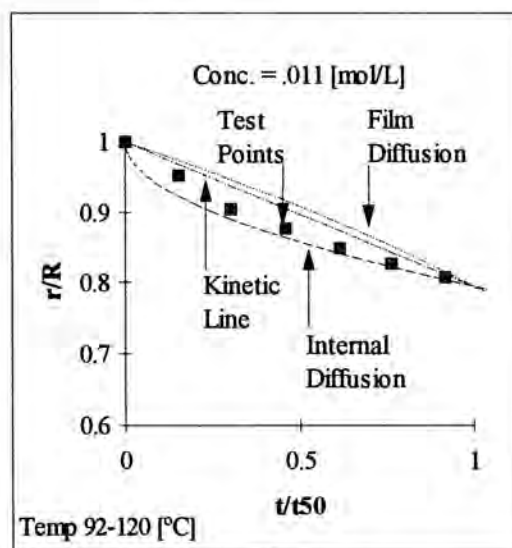


Fig. 6. Comparison of experimental points with theoretical lines for changes of ratio of core radius vs. ratio of time to time of 50% reaction for higher concentration test.

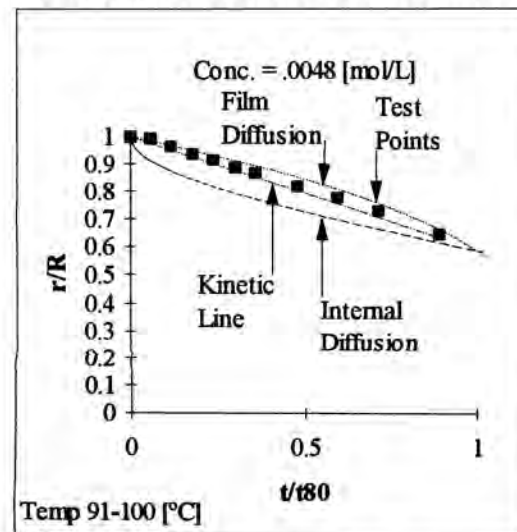


Fig. 7. Comparison of experimental points with theoretical lines for changes of a ratio of core radius vs. ratio of time of 80% reaction for lower concentration test.

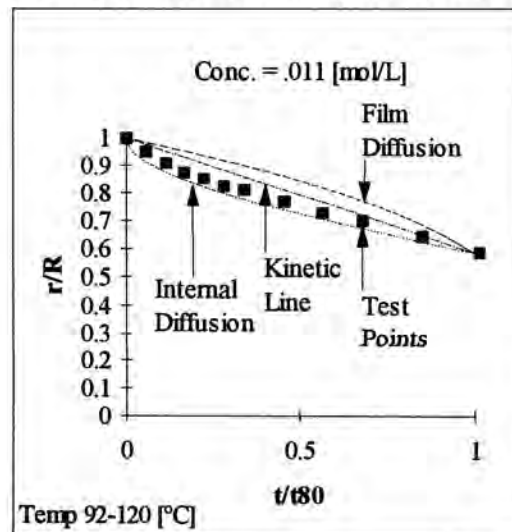


Fig. 8. Comparison of experimental points with theoretical lines for changes of a ratio of core radius vs. ratio of time of 80% reaction for higher concentration test.

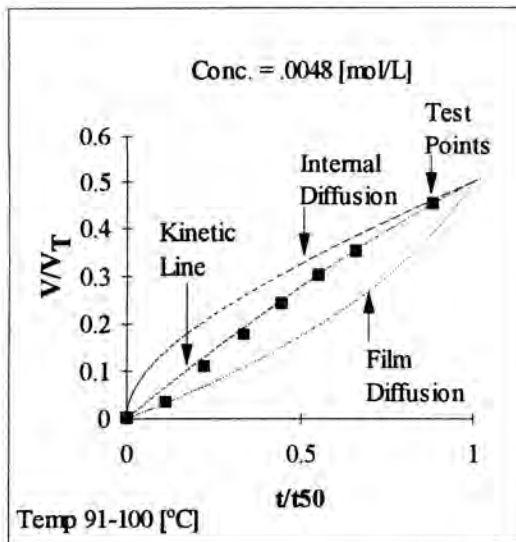


Fig. 9. Comparison of experimental points with theoretical lines for changes of ratio of hydrogen volume to stoichiometric hydrogen volume vs. ratio of time to time of 50% reaction for lower concentration test.

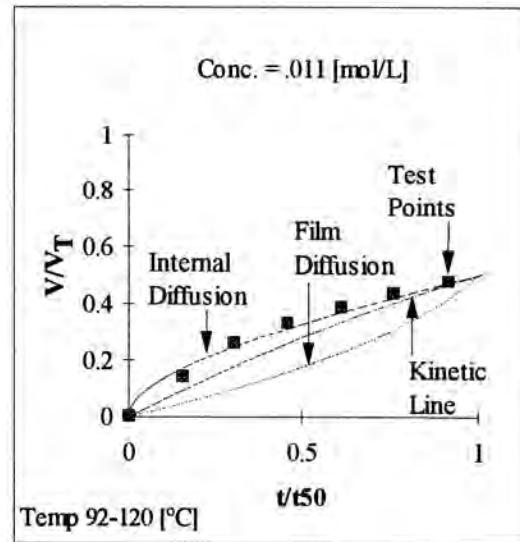


Fig. 10. Comparison of experimental points with theoretical lines for changes of ratio of hydrogen volume to stoichiometric hydrogen volume vs. ratio of time to time of 50% reaction for higher concentration test.

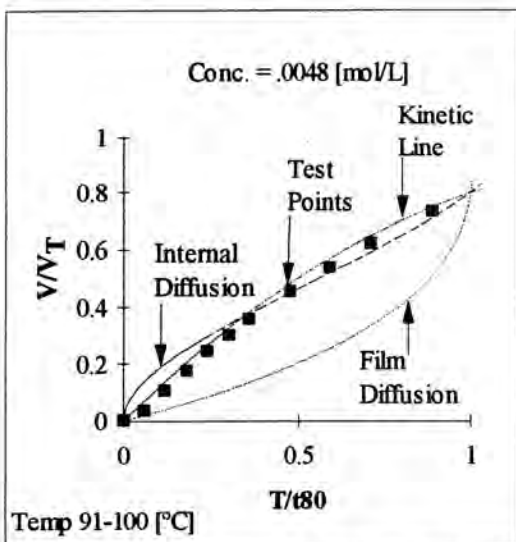


Fig. 11. Comparison of experimental points with theoretical lines for changes of ratio of hydrogen volume vs. ratio time to time of 80% reaction for lower concentration test.

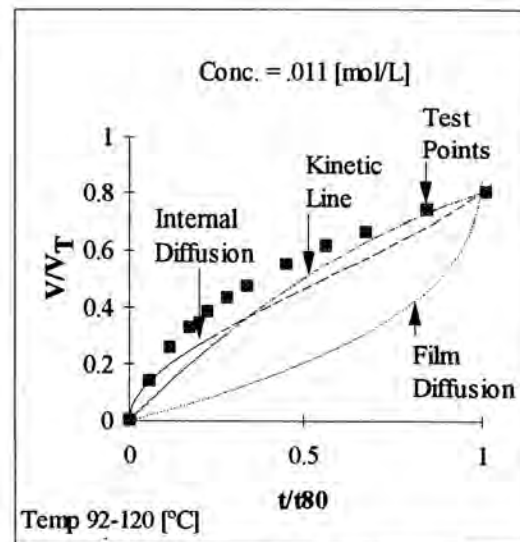


Fig. 12. Comparison of experimental points with theoretical lines for changes of ratio of hydrogen volume to stoichiometric hydrogen volume vs. ratio of time to time of 80% reaction for higher concentration test.

$$R_s = \left[0.019 + 2.18 \cdot 10^{-6} \exp \left(\frac{T}{12.6} \right) \right] \cdot \frac{18C}{1 - 24C} + 0.007 \quad (2)$$

where:

R_s = Reaction rate related to the surface area of the core [$l/dm^2/min$]

T = temperature [$^{\circ}C$]

C = water vapor concentration [mole/L].

The examples of equation predictions appear in Figs. 13 - 14.

The surface reaction rate increases exponentially with the temperature, however at a slower pace than according to

Arrhenius law, which roughly predicts that the reaction rate will double with every 10 degrees centigrade. That means that on average, the tests were not in kinetic control and that there was a share of internal diffusion resistance to the reaction rate. This agrees with the interpretation by the USCM discussed previously. Many tests were performed at conditions where the rate of internal diffusion dominates the overall reaction rate. These tests contributed to the data pool used to develop the equation (2). The dependence of the reaction rate on water vapor concentration is nonlinear. It bulges upward. This bulge may mean that either the surface reaction is not first order, or that the overall reaction rate is not controlled purely by the surface reaction rate. If all the reactions were controlled by the first-order rate of surface reaction, the rate-

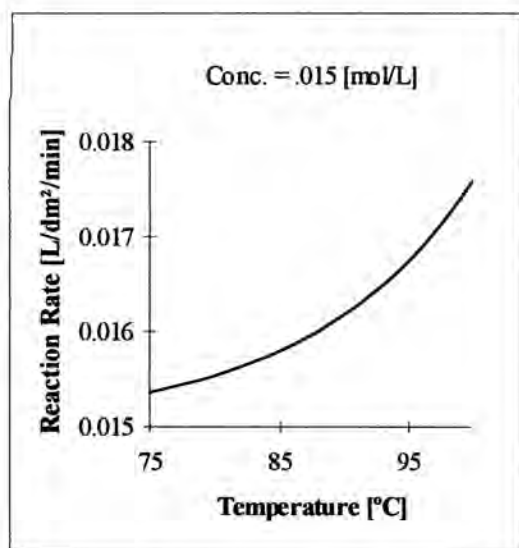


Fig. 13. Relationship between reaction rate and temperature at 0.015 mol/L water vapor concentration according to empirical Eq. 2.

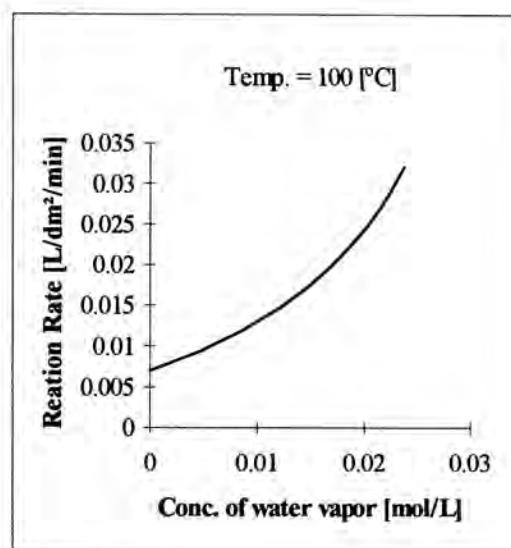


Fig. 14. Relationship between reaction rate and water vapor concentration at 100°C temperature according to empirical Eq. 2.

concentration relationship would be linear according to $R_s = k_s C$.

CONCLUSIONS

We have demonstrated that the reaction of lithium hydride with water vapor can be described by the Unreacted Shrinking Core Model. Verifying that the reaction of lithium hydride with water vapor follows the model gives a designer a useful tool. Thus, the predictability of reaction course in varying conditions becomes high. In our next experiments, we will focus on determination of the surface reaction rate constant and diffusion coefficient and on a more precise determining of the ranges, where given rate-controlling steps govern the reaction kinetics. We have recently installed a data acquisition system that will enable much more frequent and

precise measurements. Using the equipment we will also investigate the kinetics of hydration of other water reactive materials. We plan to complete the conceptual and then detailed engineering design of the treatment skid before the end of 1994.

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