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Review of Uranium Hydriding and Dehydriding Rate Models in GOTH_SNF for Spent Fuel MCO Calculations

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Review of Uranium Hydriding and Dehydriding Rate Models in GOTH_SNF for Spent Fuel MCO Calculations

September 2003

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SUMMARY

The present report is one of a series of three. The series provides an independent technical review of certain aspects of the GOTH_SNF code that is used for accident analysis of the multicanister overpack (MCO) that is proposed for permanent storage of spent nuclear fuel in the planned repository at Yucca Mountain, Nevada. The work documented in the present report and its two companions was done under the auspices of the National Spent Nuclear Fuel Program. The other reports in the series are DOE/SNF/REP-087 and DOE/SNF/REP-088.

This report analyzes the model for uranium hydriding and dissociation of the hydride that was documented in the SNF report titled *MCO Work Book GOTH_SNF Input Data*.[1] Reference 1 used a single expression from a model by Bloch and Mintz for both the uranium hydriding and dehydriding reactions. This report compares the results of the GOTH_SNF expression for both phenomena with those from the models proposed by J. B. Condon and further developed by Condon and J. R. Kirkpatrick.

The expression for the uranium hydriding rate used in GOTH_SNF (from the model of Bloch and Mintz) gives consistently lower values than those from the models of Condon and Kirkpatrick. This is true for all hydrogen pressures and for all temperatures. For a hydrogen pressure of 1 atm, the hydriding rates given by the models of Condon and Kirkpatrick are zero by the time the temperature reaches 400°C. That is, the term representing the dehydriding reaction has become large enough to overwhelm the term representing the hydriding reaction. The same is true for the expression used in GOTH_SNF. For lower hydrogen pressures, the hydriding rates reach zero at even lower temperatures for the Bloch and Mintz model and also for the Condon and Kirkpatrick models.

Uranium dehydriding rates can be calculated for temperatures as high as 2,000°C. The dehydriding rates from GOTH_SNF contain an assumption that there is a 0.22 psia hydrogen pressure in the atmosphere surrounding the hydride. For temperatures >~700°C, the expression from GOTH_SNF (the model of Bloch and Mintz) gives higher dehydriding rates than that from Condon. However, in calculations of MCOs using GOTH_SNF, the dehydriding is complete by ~400°C so that rates for temperatures higher than that are not relevant. In the temperature range 275–400°C, the dehydriding rate from the Condon model is much higher than that from GOTH_SNF.

The practical consequences of the differences in hydriding and dehydriding rates are not obvious. A way to evaluate the consequences is to repeat an important MCO calculation on GOTH_SNF using hydriding and dehydriding rates that have been artificially modified to be closer to those given by the expressions of Condon and Kirkpatrick and see if the conclusions about the safety of the MCO are changed.

FOREWORD

This report was prepared as the product of a technical review of chemical reactivity modeling and analysis activities performed by the National Spent Nuclear Fuel Program (NSNFP). The scope of the review is contained within the "Task Management Agreement for Chemical Reactivity Modeling Technical Review Activities," DOE/SNF/TMA-003. The administrative leadership for this review work was provided by staff from the NSNFP. The author of the present report, J. R. Kirkpatrick, is a staff member of the Computational Sciences and Engineering Division at the Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee.

The NSNFP chemical reactivity analysis provides information about the performance of the multicanister overpack (MCO) loaded with N-reactor spent fuel in the repository environment relative to the potential for intense chemical reactions on the corroded portions of the fuel elements. The review task was an independent review of the approach and reasonableness of results from the NSNFP chemical reactivity analysis. The chemical reactivity analysis performed by the NSNFP is not part of the primary licensing strategy for U.S. Department of Energy spent nuclear fuel in the repository. An additional technical review is not required to meet NSNFP Quality Program requirements. The review discussed in this report was performed as a good technical practice to provide an independent evaluation of the technical adequacy of the NSNFP chemical reactivity analysis. To ensure the technical independence of the review, ORNL personnel conducted the assessment and review to technical standards defined by ORNL without intervention from the NSNFP. NSNFP involvement in the definition of standards and requirements was limited to ensuring that work by ORNL personnel was performed under NSNFP procedures, using ORNL personnel as augmented staff. Preliminary review and discussion of results of the evaluation were conducted during the evaluation. This report presents the results of the investigation. NSNFP formal response to recommendations in this report will be documented in a future engineering design file, EDF-NSNF-031 "NSNFP Plan for Response Activities to Chemical Reactivity Technical Review Recommendations."

CONTENTS

FIGURES

ACRONYMS

B-M	Bloch-Mintz (the model of Bloch and Mintz for uranium hydriding and dehydriding)
C-K	Condon-Kirkpatrick (the models of these authors for uranium hydriding and dehydriding)
MCO	multicanister overpack
NSNFP	National Spent Nuclear Fuels Program

Review of Uranium Hydriding and Dehydriding Rate Models in GOTH_SNF for Spent Fuel MCO Calculations

1. INTRODUCTION

The manual for the GOTH_SNF code (see Reference 1) states that the calculations for uranium hydride formation and the destruction of hydride through decomposition are done using an expression developed by Bloch and Mintz and published in their 1981 *Journal of Less-Common Metals* paper.[2] In particular, Reference 1 repeats Equation 30 of Reference 2. For a small enough hydrogen overpressure and a large enough temperature, the Bloch and Mintz expression gives a negative hydride formation rate. This negative rate is used in GOTH_SNF for the model for dehydriding. The present author has been involved with modeling of uranium hydriding using the physics proposed by J. B. Condon,[3–5] Part of Condon's model includes a reverse reaction that simulates the decomposition of uranium hydride. In the present report, the author compares results from the model of Bloch and Mintz as used in GOTH_SNF with those of Condon to see how much difference one can see in the uranium hydride formation and decomposition rates.

2. HYDRIDING RATES

This section reviews the hydriding model in the GOTH_SNF Input Data (Reference 1). In GOTH_SNF, the model of Bloch and Mintz from their 1981 *Journal of Less-Common Metals* paper (Reference 2) is used. In particular, the rate equation is Equation 30 from Reference 2. While reviewing pp. 5-5 to 5-6 of Reference 1, it was discovered that there is an exponent of *n* missing in Equation 5-14 of Reference 1 compared to that in the Bloch and Mintz paper. The equation as published in Reference 2 reads

$$u_g(P_{H2},T) = K_{eq}(T) * \left(\left(\frac{P_{H2}}{P_d(T)} \right)^{\frac{n}{2}} * \left(\frac{1 + K_m(T) * P_d(T)^{0.5}}{1 + K_m(T) * P_{H2}^{\ 0.5}} \right)^{n} - \left(\frac{P_d(T)}{P_{H2}} \right)^{\frac{m}{2}} \right) \tag{1}$$

The term P_{H2} is the hydrogen pressure, and the term T is the absolute temperature. The remaining terms are functions of temperature specified in References 1 and 2. The exponent n for the middle of the three terms in brackets is the one that was missing in Reference 1. The author requested a sample reaction velocity from R. L. Bratton of the National Spent Nuclear Fuel Program (NSNFP) which Bratton returned by e-mail on March 25, 2003.[a] Once the missing exponent in the calculation was added, the numbers matched the numbers Bratton sent. Therefore, it seems clear that the missing exponent is a typographical error in Reference 1, not an omission in the GOTH_SNF code.

For a more detailed review, this report will compare the Bloch and Mintz model (from now on it will be called "B-M") to other available models—particularly that of Condon and Kirkpatrick, which will be called "C-K." There are two slightly different versions of the C-K model. The most recent publication is that of Powell et al. in *Z. Phys. Chem.* (1993) (see Reference 5). The fit using the constants from this

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[a] E-mail from R. L. Bratton (Idaho National Engineering and Environmental Laboratory) to J. R. Kirkpatrick (Oak Ridge National Laboratory) March 25, 2003.

paper will be called "C-K Powell." An older version was published by Kirkpatrick and Condon in the 1991 edition of *Journal of Less-Common Metals* that contained the proceedings of the 1990 metal hydrides meeting held at Banff (see Reference 4). The fit using these constants will be called "C-K Banff." The difference in the two C-K models is in constants that define two parameters. The first is the parameter N, which is defined as "the maximum concentration of free (i.e., not bound into hydride) hydrogen atoms in the metal lattice." The second is U_c, which is the fraction of uranium that is converted into hydride for which spall occurs. As will be shown, the C-K Banff parameters produce somewhat lower hydriding rates at 1 atm (as well as at other pressures) than the C-K Powell parameters.

First the results of Equation 1 must be verified against the graphs in the B-M paper (see Reference 2). Consider Figure 1, which shows the data from Figure 3 of Reference 2, together with lines from the results of Equation 1. If one compares the figure to the original in Reference 2, one may notice that Bloch and Mintz plotted Arrhenius lines to show that the data satisfied an Arrhenius form for a large portion of the temperatures. It appears from the text of Reference 2 that the Arrhenius lines did not come from their fit, but rather were drawn by hand. The lines shown in Figure 1 come from the B-M fit and, therefore, are not the same as the lines in the original version of this figure in Reference 2. For the most part, the fit undershoots the data. The undershoot is worse for the lower pressure (6.6×10^4 Pa).

Next, examine Figure 2. It would be best to compare the original Figure 6 from Reference 2 with Figure 2. Figure 2 does not show the data points that were present in the original. The author did some selected comparisons between the calculated curves and those on the original. The calculated curves are very similar to those in the original except for the 200°C curve. For that curve, the original shows the curve bending over and reaching the lower axis at ln[P(torr)]~1.6. By comparison, Figure 2 shows a steady increase in curvature until the line reaches the lower axis at ln[P(torr)]~0.4. In an effort to match the 200°C curve, the author experimented with the calculation for that temperature. One possibility that might have explained the difference was that there was an error in the value of P_d for that temperature. The value of P_d was increased to ~4 torr, a value that was sufficient to cause the curve to reach the lower axis at the correct value of ln(P). The change in P_d required forcing the term to have a different value from the one that was given from the expression documented in Reference 2. The results are not shown on any figure in the present report. The intercept for the right axis at ln[P(torr)] = 12 was about right. However, the rest of the curve was consistently lower than the values from the original. Another possible error was that the indicated temperature (200°C) was a misprint; so the author experimented with other temperatures. For 245°C, the resulting curve reached the lower axis at about the right place. However, the intercept for the right axis was too high, and the curve didn't match the shape from the original very well. In short, the author has not been able to explain the difference between the calculation using the B-M fit and the line shown on the original B-M figure for 200°C.

Next, examine Figure 3. In the original, Figure 6 of Reference 2, there are two lines that match the data quite well. The results in Figure 3 do not match nearly as well as in the original, particularly for 300°C. The text of Reference 2 does not explain the origin of the lines in the original figure. In particular, the text does not clearly state whether the lines in the original figure are from the B-M fit. The lines may have been created using a French curve just so that the reader could tell that the rate was not proportional to the square root of pressure.

Now that the B-M fit has been compared to the data and other plots in Reference 2, the B-M fit needs to be compared with the data Condon showed in his 1975 *Journal of Physical Chemistry* paper (Reference 3). The comparison is shown in Figure 4. The reader should note that the data and calculations are for a 1 atm H_2 pressure. The C-K Banff model fits the data best. However, that should not be a surprise as the constants for that model were adjusted to get a good match to these data. The C-K Powell model values are consistently higher than the C-K Banff values by a factor of ~1.5–2. The B-M fit values are consistently lower than the C-K Banff values by a factor of ~2–3. Also, the B-M values reach their

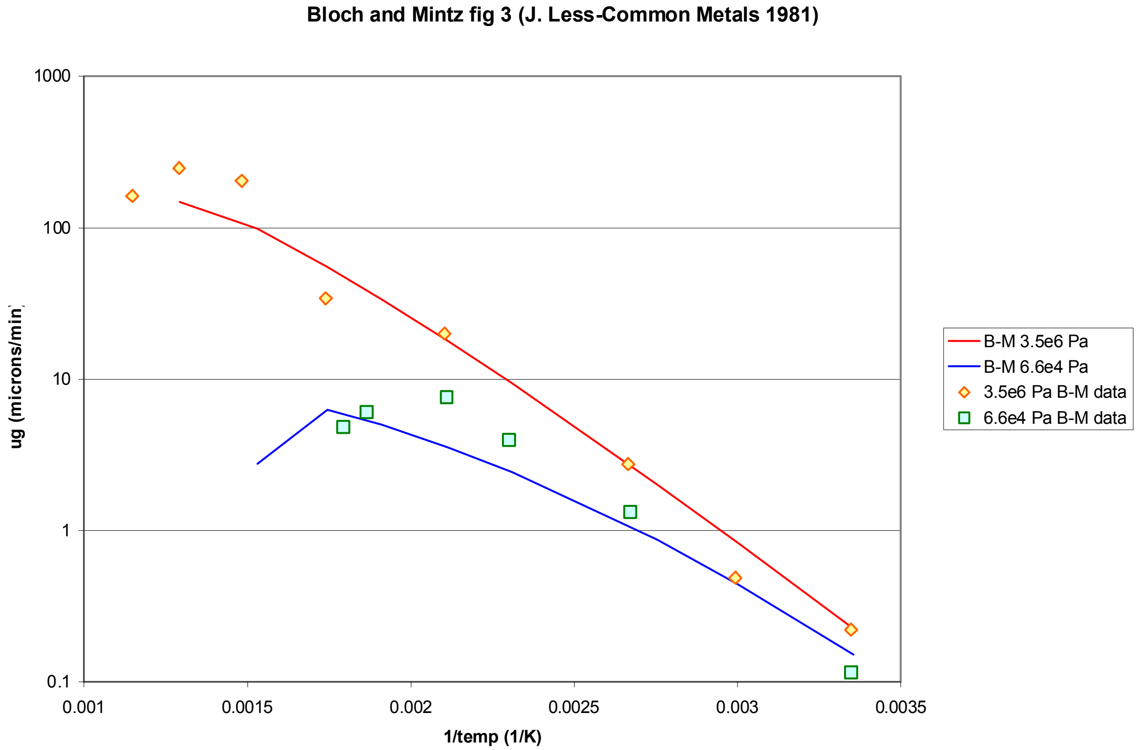

Figure 1. Comparison of data from Bloch and Mintz (Reference 2) Figure 3 with results from Bloch and Mintz fit.

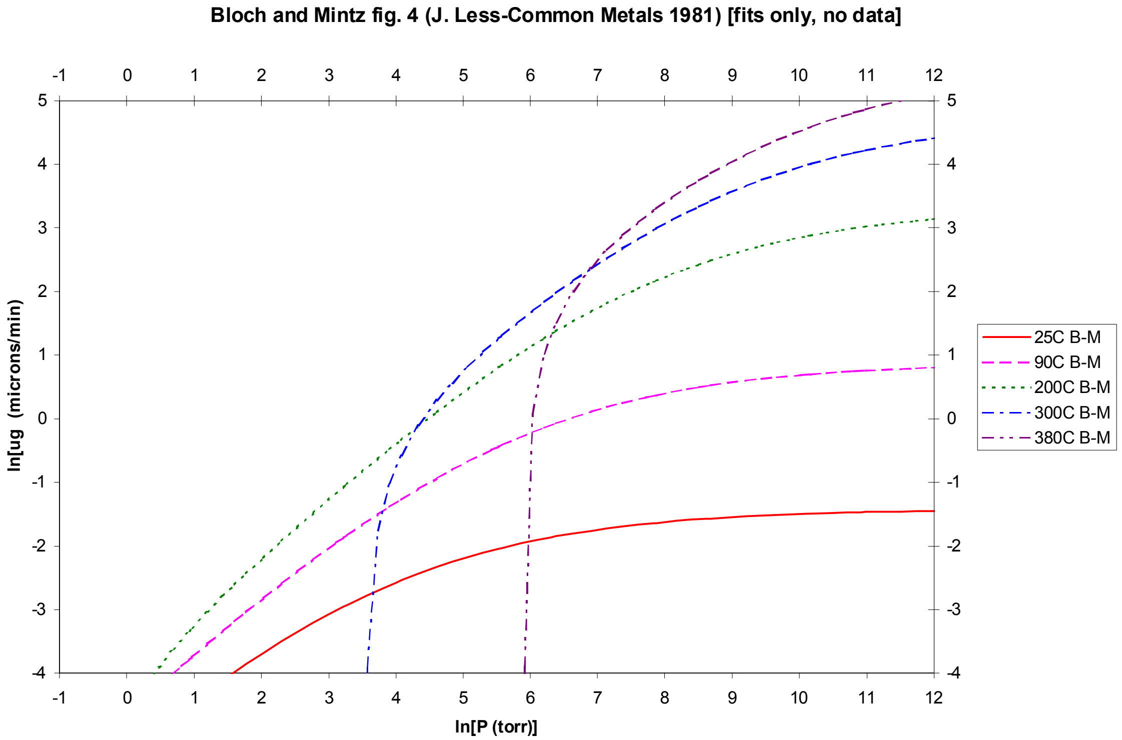

Figure 2. Calculation of linear rate vs pressure to compare with original version of Bloch and Mintz (Reference 2) Figure 4.

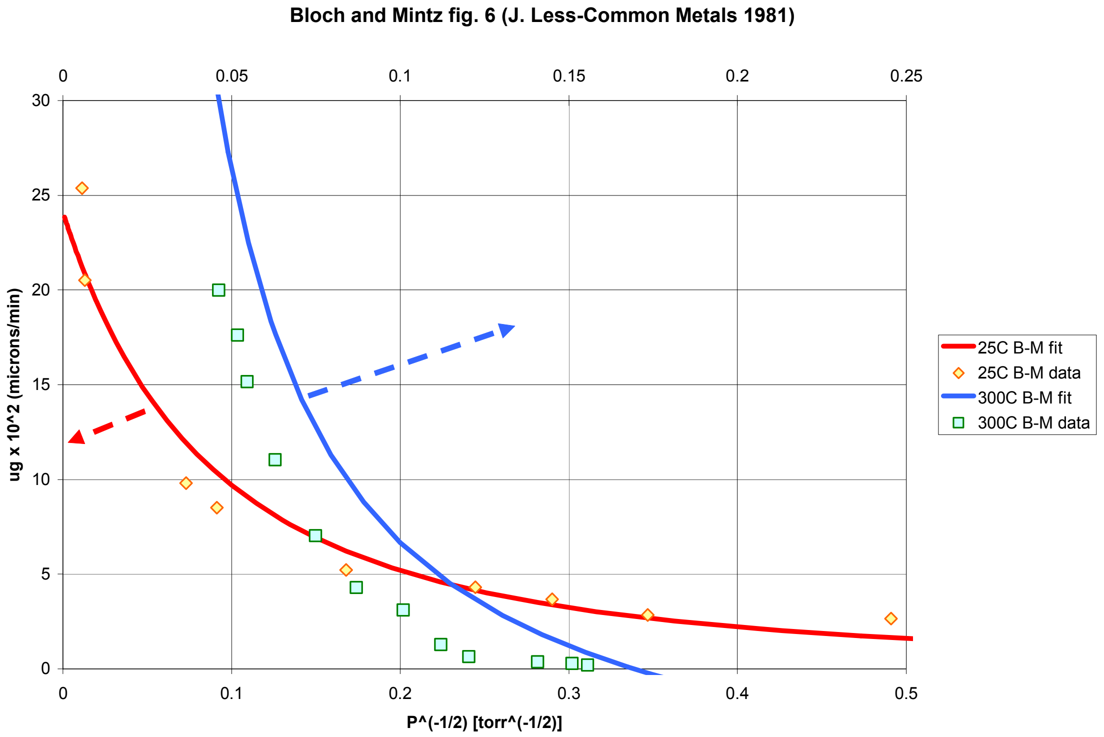

Figure 3. Calculation of linear rate vs pressure compared with data from Bloch and Mintz (Reference 2) Figure 6.

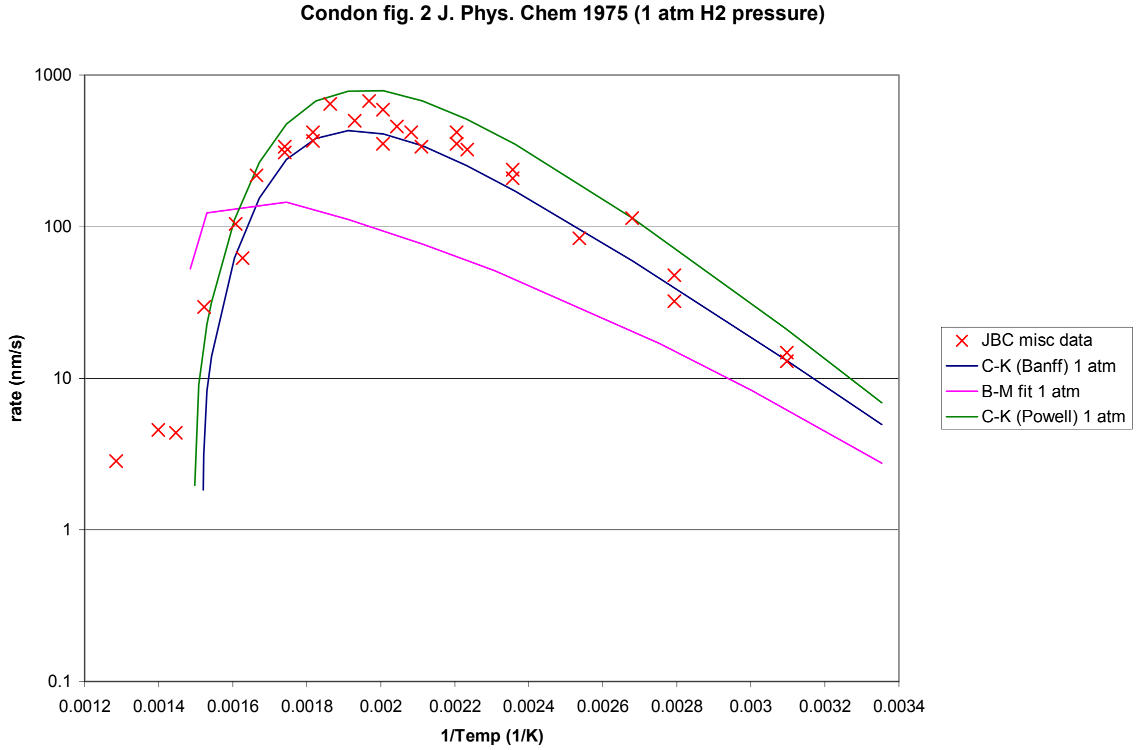

Figure 4. Calculations of linear rate vs temperature for 1 atm H_2 pressure using Bloch and Mintz fit and two different versions of Condon-Kirkpatrick model compared with data from Figure 2 of Condon's 1975 *J. Phys. Chem.* paper (Reference 3).

peak at a temperature ~50–70°C higher than is shown by either C-K model or the data. The author had hoped to find enough information on Figure 4 of Reference 2 to work out a plot of the B-M data versus temperature at 1 atm hydrogen pressure. Unfortunately, there are not enough data points in the right pressure range. However, most of the curves of rate versus pressure in Figure 4 of Reference 2 match the data rather well in the ~1 atm {ln[P(torr)] = 6.63} region. Therefore, the curve of rate versus temperature from the B-M fit on Figure 4 would be fairly close to the B-M data if there were any.

For the next comparisons, earlier figures in the present report are repeated with the addition of values from the C-K fits. First, Figure 5 is a repeat of Figure 1 with the addition of C-K Banff and C-K Powell model values for the two specified pressures. The plot is rather busy. As was true for the 1 atm results, the C-K models give consistently higher values than either the B-M fit or the B-M data.

Next, Figure 6 is a repeat of Figure 2 with the addition of C-K Banff model values for 25°C and 300°C. As was true for the 1 atm results, the C-K model gives consistently higher values than the B-M fit.

Last, Figure 7 is a repeat of Figure 3 with the addition of C-K Banff model values for 25°C and 300°C. As was true for the previous comparisons, the C-K model gives consistently higher values than the B-M fit or the B-M data.

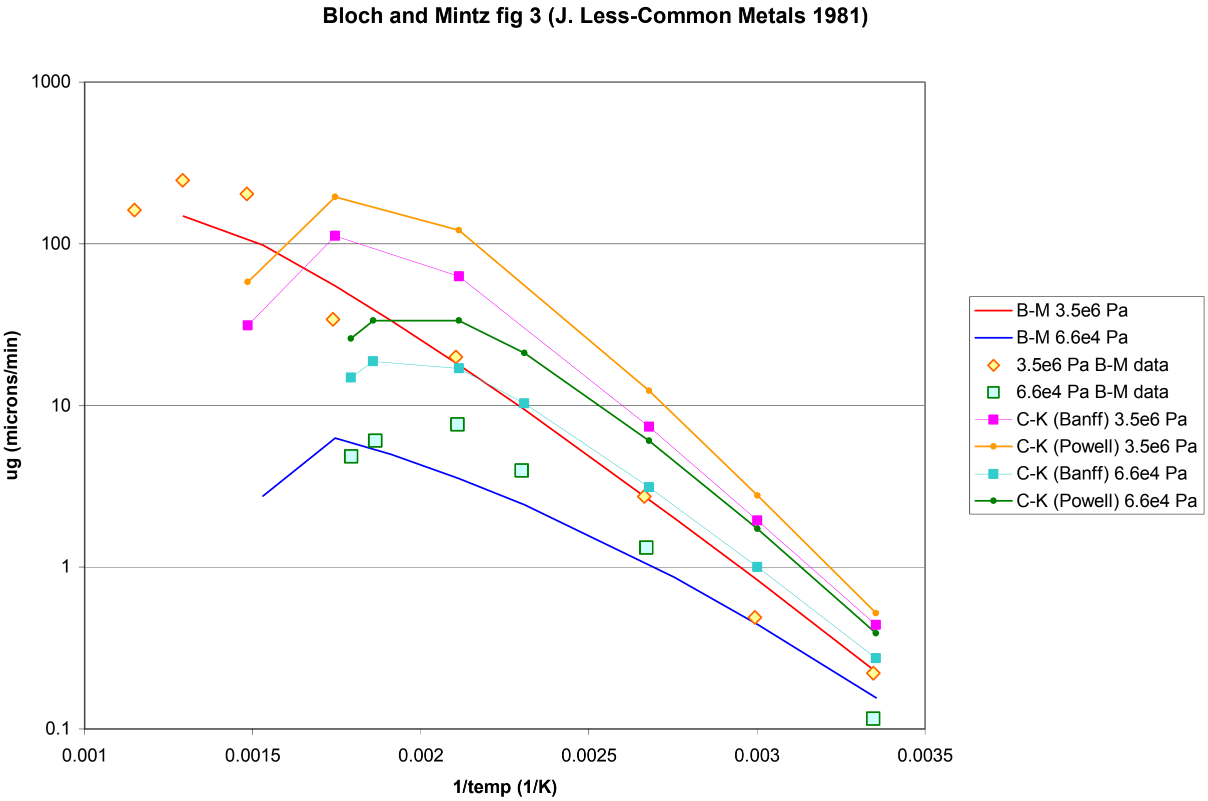

Figure 5. Comparison of data from Bloch and Mintz (Reference 2) Figure 3 to results from Bloch and Mintz fit with addition of values from Condon-Kirkpatrick “Banff” and Condon-Kirkpatrick “Powell” models.

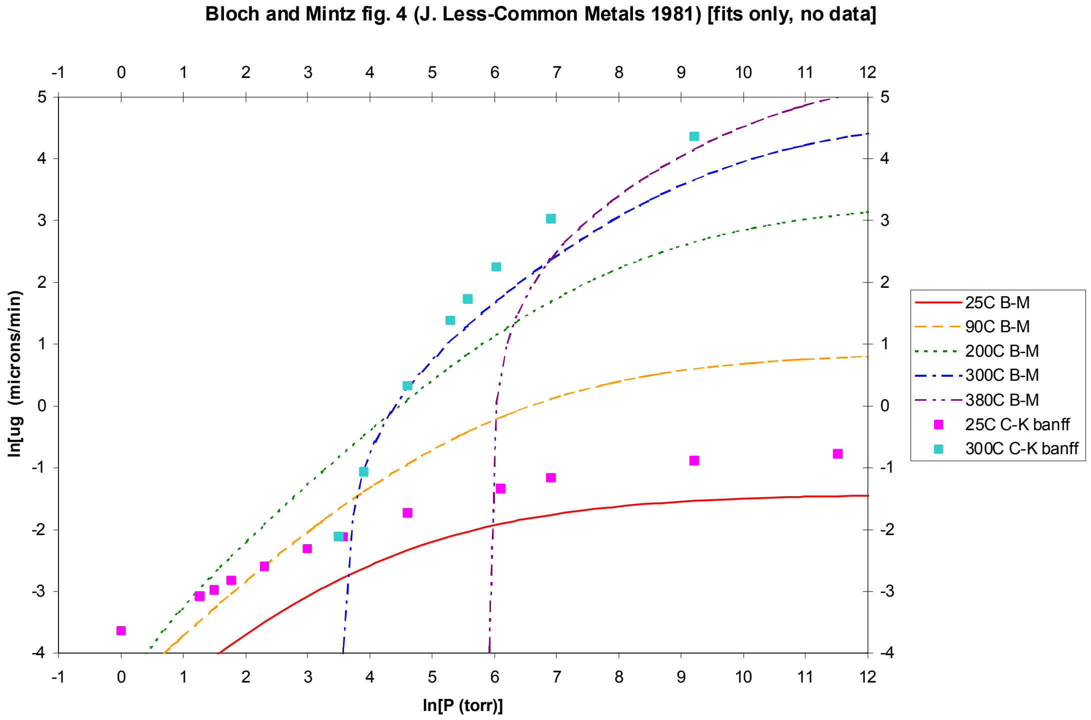

Figure 6. Calculation of linear rate vs pressure to compare with Bloch and Mintz (Reference 2) Figure 4 with addition of values from Condon-Kirkpatrick “Banff” model.

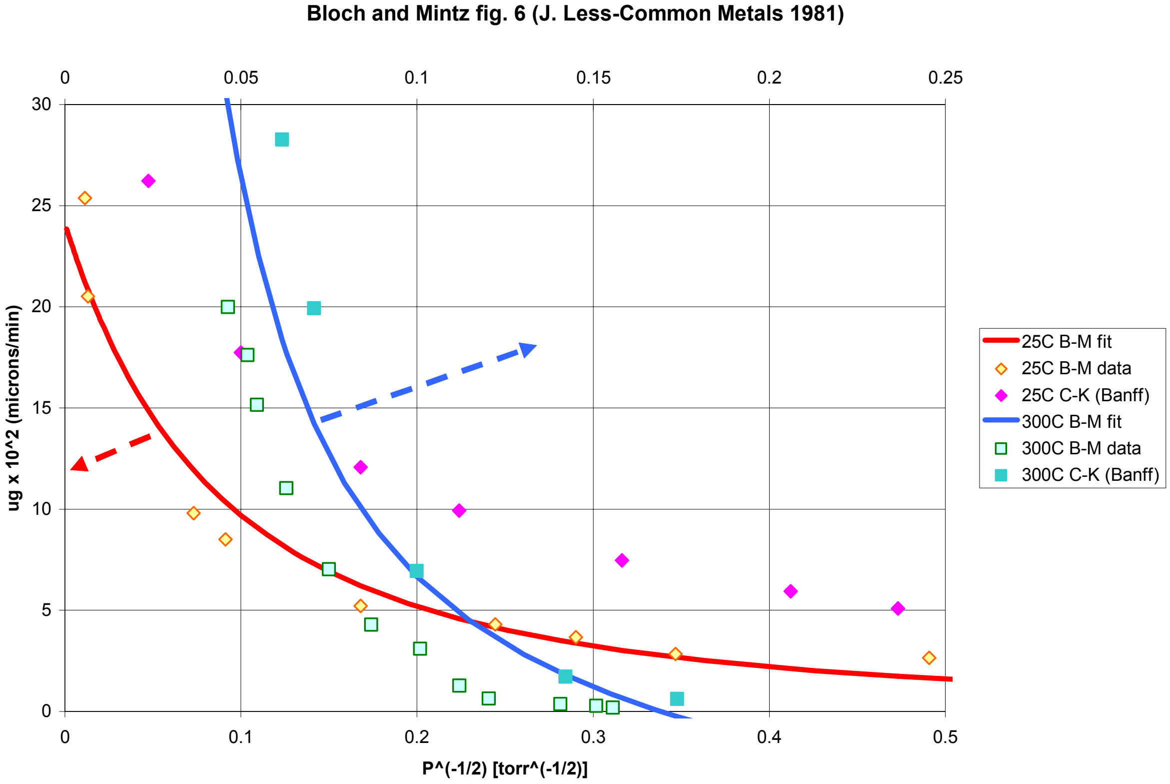

Figure 7. Calculation of linear rate vs pressure compared with Bloch and Mintz (Reference 2) Figure 6 with addition of values from Condon-Kirkpatrick “Banff” model.

3. DEHYDRIDING RATES

Another aspect of GOTH_SNF to examine is the dehydriding model. GOTH_SNF uses the Bloch and Mintz rate running in reverse. That is, for values of P_{H2} low enough, the reaction front velocity given by Equation 1 is negative. If one examines Equation 1 closely, one will see that for $P_{H2} = 0$ the value of u_g is infinite. Therefore, in order to calculate front velocities for comparison, one needs a value for P_{H2} that is greater than zero. According to Bratton,[b] the GOTH_SNF dehydriding calculations use a value of $P_{H2} = 0.22$ psia for all temperatures. When one plugs this value and the appropriate values of the temperature-dependent constants into Equation 1, one finds that the reaction front velocity is positive until T > 268°C. In other words, for temperatures at that level and lower for the specified hydrogen pressure, the dehydriding rate is negative.

Nominally, the result of Equation 1 is a reaction front velocity, which makes the reaction a surface effect. In the GOTH_SNF Technical Manual,[6] Thurgood describes the method used to convert the reaction front velocity to a bulk effect. The result is as follows:

$$\Delta m = u_g \rho_f r A_r \Delta t \tag{2}$$

where

Δm = change in UH_3 mass in a single time step

u_g = reaction front velocity from Equation 1

ρ_f = density of the uranium fuel (19 g/cm^3)

r = ratio of molecular weight of UH_3 to that of U (i.e., 241/238)

A_r = surface area of the reacting uranium or hydride

Δt = time step.

If one works out the units for Equation 2 (expressing all the terms in consistent units), one can demonstrate that both sides of the equation have the units of mass.

As already noted, Equation 2 was first thought to be a surface flux term. That is, it was thought that A_r was constant and that the ratio $\Delta m/(A_r \Delta t)$ was a mass flux in mass per unit area per unit time. However, after further communications with R. L. Bratton and further study of Thurgood's discussion of how the dehydriding term works in another piece of his documentation,[7] the author concluded that it was a bulk dehydriding mass rate. According to Bratton,[c] the MCO safety calculations use a value of 2 m^2/gU for A_r. Of course, that is actually an area per unit mass A/m. The author's reading of Reference 7 together with his telephone conversations with Thurgood on July 21, 2003,[d] suggest the following: First, the

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[b] Telephone discussion between R. L. Bratton (Idaho National Engineering and Environmental Laboratory) and J. R. Kirkpatrick (Oak Ridge National Laboratory) July 10, 2003.

[c] E-mail from R. L. Bratton (Idaho National Engineering and Environmental Laboratory) to J. R. Kirkpatrick (Oak Ridge National Laboratory) July 1, 2003.

[d] Telephone discussion between Marvin J. Thurgood (John Marvin, Inc.) and J. R. Kirkpatrick (Oak Ridge National Laboratory) July 21, 2003.

hydride is modeled as a large collection of individual hydride particles all the same size. Second, dehydriding is accomplished by converting these particles into uranium one particle at a time. That is, at a given instant, there are n_{UH3} particles of UH_3, n_U particles of uranium, and one particle that is partially converted. The sum total of particles is $n_{UH3} + n_U + 1$, which is a constant. The result is that the ratio A/m is a constant. This last is the key to making the B-M dehydriding rate into a bulk term rather than a surface term. Therefore, Equation 2 can be expressed as follows:

$$\Delta m = u_g \rho_f r \frac{A}{m} m \Delta t \tag{3}$$

Obviously, this reduces to an ordinary differential equation as follows:

$$\frac{1}{m}\frac{dm}{dt} = u_g \rho_f r \frac{A}{m} \tag{4}$$

Assuming an initial condition of

$$m(t = 0) = m_0 \tag{5}$$

the solution becomes

$$m = m_0 \, exp\left(u_g \rho_f r \frac{A}{m} t \right) \tag{6}$$

Note that, for dehydriding, $u_g < 0$ means that m declines to zero at a infinite time. If m_0 is the mass for which all the particles are 100% hydride, then the ratio m/m_0 has units of mass fraction, which for U and UH_3 are approximately equal to mole fractions. In other words,

$$\frac{m}{m_0} = exp\left(u_g \rho_f r \frac{A}{m} t \right) \text{ (mole fraction } UH_3\text{/s)} \tag{7}$$

If one has u_g in ft/s, t in s, and the other terms as have already been indicated, then the argument of Equation 6 and Equation 7 becomes

$$u_g \rho_f r \frac{A}{m} t = u_g \; t \times 10.97 \times 10^{-6} \tag{8}$$

From Equation 7, one can see that to reach a state of complete dehydriding for the B-M expression (i.e., $m/m_0 = 0$) requires infinite time.

Bratton and the author discussed[e] the justification for treating the hydride as a powder rather than a solid piece. Bratton said that the reactor fuel in the MCO has been hydrided and dehydrided through several cycles and thus the hydriding and dehydriding will be on powders.

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[e] Telephone discussion between R. L. Bratton (Idaho National Engineering and Environmental Laboratory) and J. R. Kirkpatrick (Oak Ridge National Laboratory) July 10, 2003.

Next, the above expressions for bulk dehydriding rate must be compared to that from Kirkpatrick and Condon (Reference 4). The term from Reference 4 that represents the reverse reaction (i.e., uranium creation by dehydriding) is as follows:

$$\frac{\partial U}{\partial t} = 137.5\, exp(-4900/T)(1-U)^{1/3} \quad \text{(mole fraction U/s)} \tag{9}$$

where

U = mole fraction of unreacted uranium and is equivalent to 1-mole fraction UH_3.

The units of mole fraction UH_3 are moleUH$_3$/moleU. The initial condition for a sample that is 100% hydrided is $U(t{=}0) = 0$. One might alternately write the dehydriding equation as

$$\frac{\partial UH_3}{\partial t} = -137.5\, exp(-4900/T)(UH_3)^{1/3} \quad \text{(moleUH}_3\text{/moleU/s)} \tag{10}$$

where

UH_3 = mole fraction of UH_3.

The integral of Equation 10 to produce an expression for hydride mole fraction versus time is as follows:

$$UH_3 = \left[1 - 1.5 * 137.5\, exp(-4900/T)t\right]^{3/2} \quad \text{(moleUH}_3\text{/moleU)} \tag{11}$$

As one can see, Equation 11 reaches a state of complete dehydriding (i.e., UH_3 mole fraction = 0) at a finite time.

In the Bloch and Mintz fit used in GOTH_SNF, both the hydriding and dehydriding rates are simulated. As was noted earlier, for the B-M equation to work, it is necessary that a pressure be defined for the hydrogen atmosphere. The value used is 0.22 psia. The Condon model also contains a hydriding rate. The combination of the hydriding and dehydriding rates yields a net hydriding rate that is as follows:

$$\frac{\partial U}{\partial t} = 137.5\, exp(-4900/T)(1-U)^{1/3} - 10.4\, exp(1592/T)c_0 U \quad \text{(mole fraction U/s)} \tag{12}$$

where the solubility c_0 is given by the following:

$$c_0 = 4.183\, x\, 10^{-6}\, exp(-894/T)\sqrt{P}N / [4.183\, x\, 10^{-6}\, exp(-894/T)\sqrt{P} + N] \quad \text{(mole fraction H)} \tag{13}$$

where P is the hydrogen pressure in Pa and the number of free sites for solution of hydrogen is given by

$$N = exp(-2.362 - 2305/T) \quad \text{(mole fraction H)} \tag{14}$$

The above expression for N is that used for the C-K Banff model and is slightly different from the expression used for the C-K Powell model. At the hydrogen pressure of 0.22 psia in the temperature range 250–2,000°C, the effect of including N in the expression for c_0 is minor (at most ~3%). If one examines Equation 12 closely, one will notice that it is constructed so that the dehydriding rate is zero at $U = 1$, and the hydriding rate is zero at $U = 0$. If one is calculating dehydriding, then for $c_0 > 0$, there is a value of U for which the rate is exactly zero. One can set the rate in Equation 12 to zero and solve the resulting cubic for the value of U at which the equilibrium is reached. In the temperature range 250–2,000°C with the hydrogen pressure at 0.22 psia, the constant multiplying the dehydriding rate (i.e., k_2) is orders of magnitude larger than those multiplying the hydriding rate (i.e., k_1c_0). Therefore, the hydriding rate will not rise to match the dehydriding rate until the dehydriding rate is very small, which requires that $1-U$ be very small. As a consequence, the effect of the hydriding rate on dehydriding is almost undetectable until the hydride is nearly consumed.

The only way the hydriding rate from Condon's model would significantly affect the dehydriding rate at a hydrogen pressure of 0.22 psia would be if there were particles of uranium hydride decomposing at the same time as other particles of uranium metal were hydriding. Of course, the difference between the hydriding and dehydriding rates would have to take into account the relative masses of the hydride and metal. Later figures (Figure 9 and Figure 10) will show what would happen to the net hydride rate if there were equal masses of hydride and metal.

Once the dehydriding rates for both the B-M and C-K models have been constructed in the same units, it is time to compare the results. After several conversations with Bratton, it was concluded that according to the GOTH_SNF runs, decomposition is rapid compared to the heatup rate. Figure 8 shows the comparison between the models over a wide range of temperatures. The dehydriding rates in Figure 8 for both the C-K and B-M models are the initial ones calculated for UH_3 mole fraction = 1 $molUH_3/molU$. The rates will fall as the UH_3 content falls. However, the C-K dehydriding rate is proportional to the UH_3 content to the 1/3 power so that the loss in rate will only be significant late in the excursion. For example, when 75% of the hydride has been lost (therefore only 25% left), the rate is still 63% of the initial (i.e., 100% hydride) value. Figure 9 shows the same information, but for a shorter range of temperatures. Figure 10 shows the same information as Figure 8 except that the axes are constructed as an Arrhenius scale. The C-K curve shows a straight line with slope of –4,900 (1/K) and, therefore, an activation energy of 9,736 cal/mol. The B-M results provide a curve rather than a straight line. The slope of the B-M curve

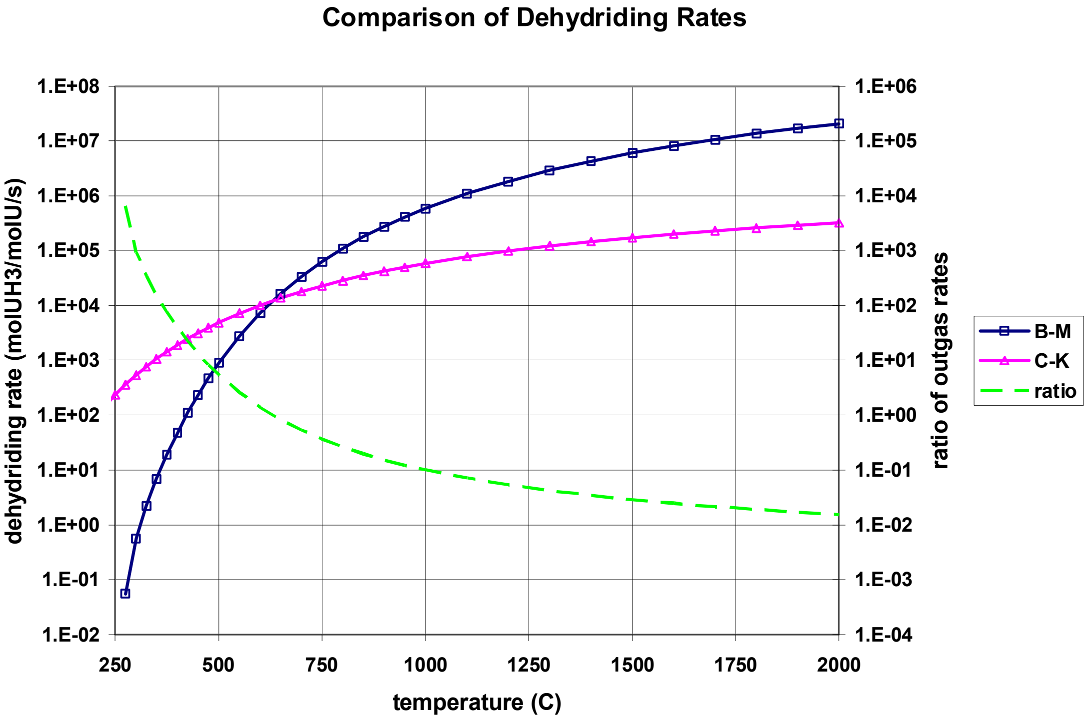

Figure 8. Comparison of dehydriding rates from model of Bloch and Mintz as used in GOTH_SNF to rates from the Condon-Kirkpatrick model over a wide range of temperatures.

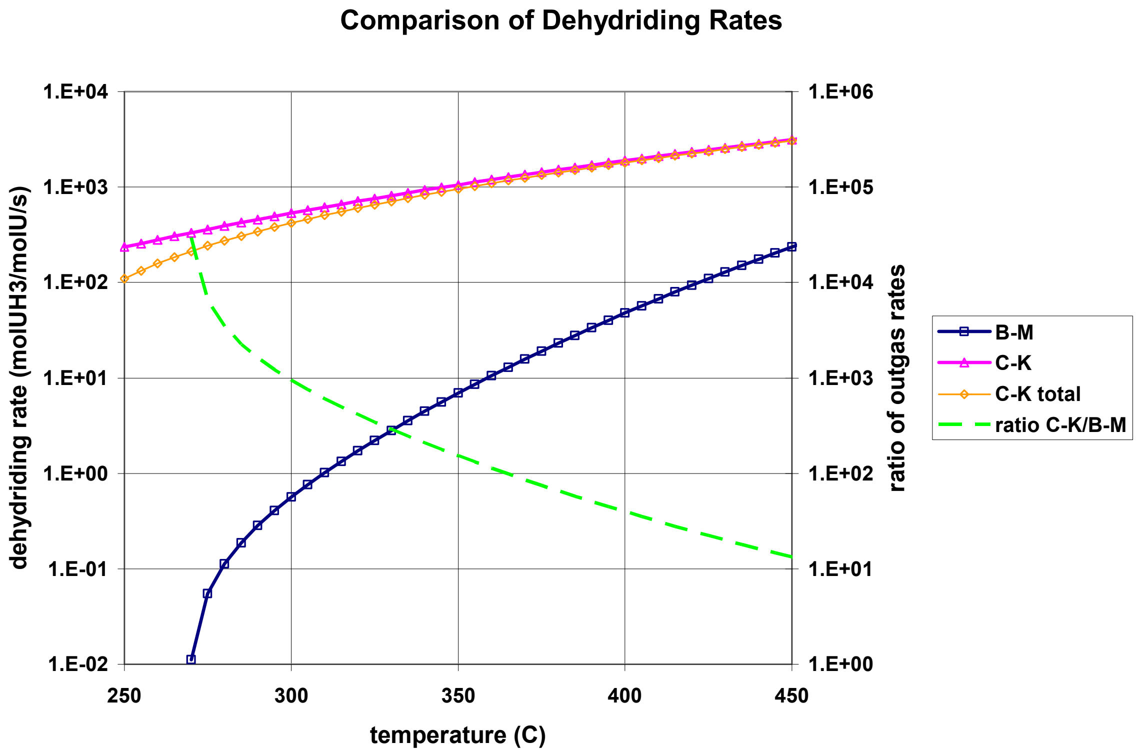

Figure 9. Comparison of dehydriding rates from model of Bloch and Mintz as used in GOTH_SNF to rates from the Condon-Kirkpatrick model over a range of temperatures (low temperature range).

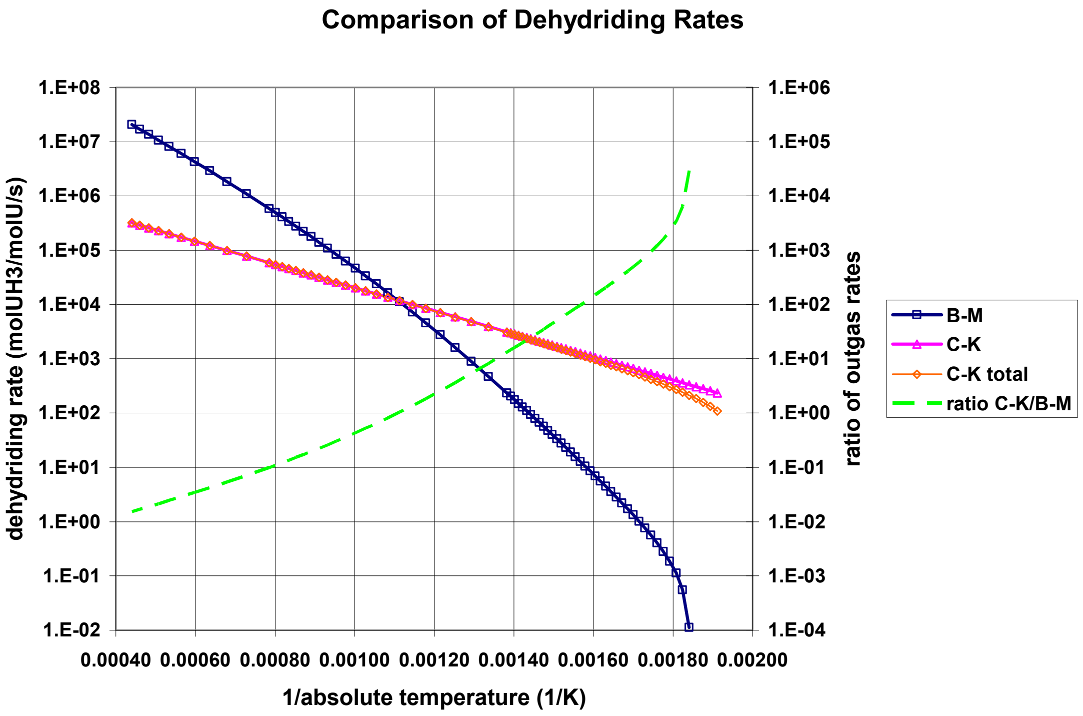

Figure 10. Comparison of dehydriding rates from model of Bloch and Mintz as Used in GOTH_SNF to rates from the Condon-Kirkpatrick model over a wide range of temperatures—Arrhenius scale (270–2,000°C).

is highest at the lowest temperature (275°C). The activation energy taken from the end points (275°C and 2,000°C) is ~28,000 cal/mol. However, if one used a higher value for the low-temperature end point, the activation energy would be lower than that. As was explained earlier, the effect of the hydriding term on the dehydriding rates for the Condon model is small until a very small amount of hydride is left. However, in a system in which hydride particles are decomposing at the same time that uranium particles are being converted to hydride, the effect of the hydriding might be noticeable. The lines with diamond symbols in Figure 9 and Figure 10 show the net dehydriding rate (using the Condon model) for a situation in which a collection of hydride particles have just begun to decompose at the same time that an equal number of moles of uranium metal particles have just begun to hydride at a hydrogen pressure of 0.22 psia. As one can see, there is a reduction factor of ~2 at 250°C. By 400°C, the effect of the hydriding term can not be seen on the plot. Even with the reduction due to the hydriding term, in the interval from 200–400°C, the C-K Banff version of the Condon dehydriding term is still far larger than that for B-M.

Figure 11 shows a comparison of dehydriding rates versus time for temperatures of 300°C and 400°C. The end points of each of the curves represent hydride mole fractions of 0.99 and 0.0001. The numbers in text along the B-M 300°C curve represent the hydride mole fractions for specific points. All four curves use the same sequence of hydride mole fractions. This plot reiterates the point that the dehydriding rates are much higher for the C-K model than for the B-M model. Also, it shows the difference in the shape of the curves of dehydriding rate vs time for the two models.

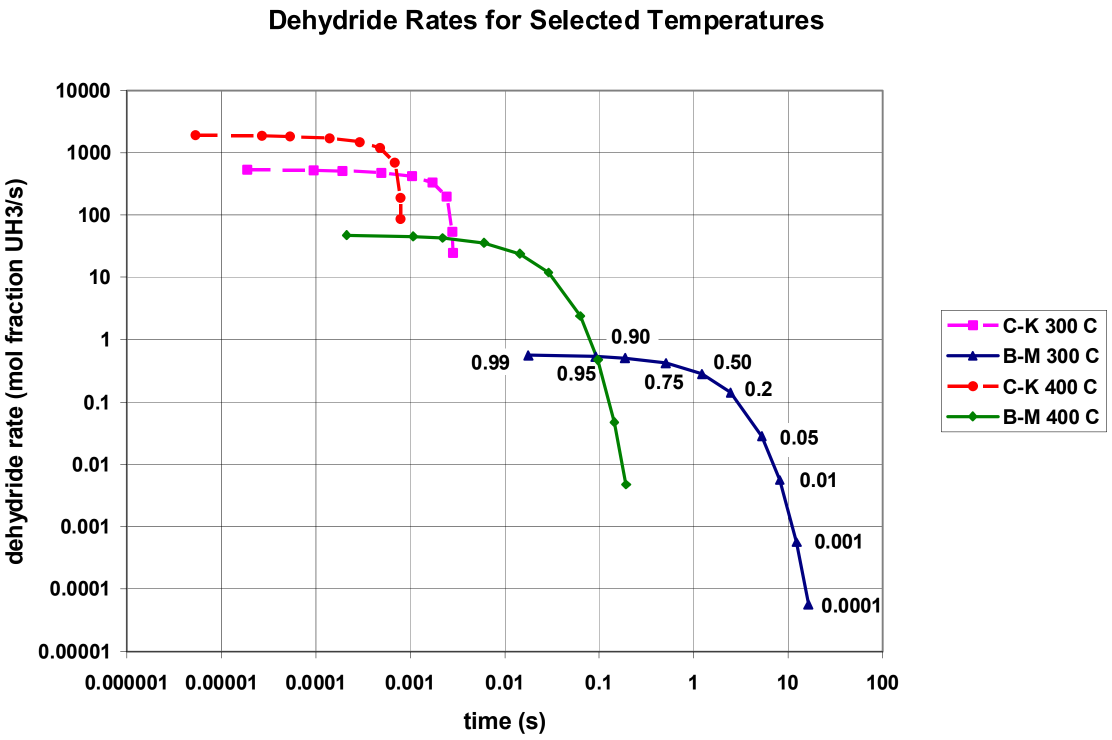

Figure 11. Comparison of dehydriding rate vs. time from model of Bloch and Mintz as used in GOTH_SNF to rates from the Condon-Kirkpatrick model for selected temperatures.

4. CONCLUSIONS AND RECOMMENDATIONS

So, what conclusions might be drawn from these comparisons? First, consider the differences in hydriding rate. Bratton[f] considers the C-K models better for mid to high ranges of pressure, but considers the B-M better for lower ranges. From Figure 4 through Figure 7, it is clear that the C-K models provide a consistently higher set of hydriding rates for a given pressure and temperature than the B-M fit. Also from Figure 6, the C-K models reach a zero rate at lower values of pressure than the B-M fit. The difference between C-K and B-M models is more pronounced at lower temperatures. The author is not sure how much difference in the results from the GOTH_SNF calculations the differences in models make. The only way to find out if the differences matter is to try calculations with altered rates.

Now, consider the differences in the dehydriding rates. As one can see, for T > ~700°C, the B-M dehydriding rate is higher than that from C-K. However, in the 275–400°C range, which is the relevant range for MCO calculations, the C-K dehydriding rate is much higher than the B-M rate. As always, the question is how much the differences matter. Again, the only way to find out if the differences matter is to try calculations with altered rates.

It is recommended that the effect of hydriding and dehydriding rates on the GOTH_SNF calculations be evaluated by modifying the values used. This recommendation assumes that alterations can be made that force the rates in the GOTH_SNF code to more closely match those from the C-K models in a temperature range that is important to the calculation, either by directly changing the number or by applying a scaling factor. A scale factor for the hydriding rate could be estimated from Figure 6, and a dehydriding scale factor could be estimated from Figure 8 or Figure 9. Once these rates are modified, a decision point case should be run. A decision point case would be one for which the results would determine whether the safety criteria are met and for which a modest change in the result in the "wrong direction" would indicate that the criteria are not met.

4.1 NSNFP Evaluation and Response to Review Recommendations

The author of this report consulted with the NSNFP during his evaluation of the computer modeling. Several items were resolved and clarified during these consultations. Preliminary review and discussion of results of the evaluation were also conducted during these consultations. This report contains recommendations for future action by the NSNFP. The NSNFP formal response to the recommendation in this report will be documented in a future engineering design file, EDF-NSNF-031, "NSNFP Plan for Response Activities to Chemical Reactivity Technical Review Recommendations."

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[f] Telephone discussion between R. L. Bratton (Idaho National Engineering and Environmental Laboratory) and J. R. Kirkpatrick (Oak Ridge National Laboratory) February or March 2003 (date uncertain).

5. REFERENCES

1. R. L. Bratton, *MCO Work Book GOTH_SNF Input Data*, DOE/SNF/REP-071 Rev. 1, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID, August 2002.

2. J. Bloch and M. H. Mintz, "Kinetics and Mechanism of the U-H Reaction," *Journal of the Less-Common Metals*, Vol. 81, 1981, pp. 301–320.

3. J. B. Condon, "Calculated vs. Experimental Hydrogen Reaction Rates with Uranium," *The Journal of Physical Chemistry*, Vol. 79, No. 392, 1975.

4. J. R. Kirkpatrick and J. B. Condon, "The Linear Solution for Hydriding of Uranium," *Journal of the Less-Common Metals*, Vol. 172-174, 1991, pp. 124–135.

5. G. L. Powell, R. N. Ceo, W. L. Harper, and J. R. Kirkpatrick, "The Kinetics of the Hydriding of Uranium Metal II," *Zeitschrift fur Physikalische Chemie*, Bd. 181, 1993, S. 275–282.

6. Marvin J. Thurgood, *Technical Manual for GOTH_SNF Version 5.3*, Report JMI-980306-3, Rev. 2, John Marvin, Inc., West Richland, WA, September 17, 2001.

7. Marvin J. Thurgood, *Software Development Report for Hydride Reaction Area*, Report JMI-0002-4, Rev. 0, John Marvin, Inc., West Richland, WA, May 21, 2001.