

Modeling the Pyrochemical Reduction of Spent UO_2 Fuel in a Pilot-Scale Reactor

International Pyroprocessing Research
Conference

Michael F. Simpson
Steven D. Herrmann

August 2006

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint should not be cited or reproduced without permission of the author. This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights. The views expressed in this paper are not necessarily those of the United States Government or the sponsoring agency.

MODELING THE PYROCHEMICAL REDUCTION OF SPENT UO_2
FUEL IN A PILOT-SCALE REACTOR

MICHAEL F. SIMPSON and STEVEN D. HERRMANN

Idaho National Laboratory

P.O. Box 1625

Idaho Falls, Idaho 83415

USA

e-mail: michael.simpson@inl.gov

Total number of pages: 19

Number of tables: 0

Number of figures: 5

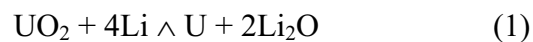
Abstract

A kinetic model has been derived for the reduction of oxide spent nuclear fuel in a radial flow reactor. In this reaction, lithium dissolved in molten LiCl reacts with UO_2 and fission product oxides to form a porous, metallic product. As the reaction proceeds, the depth of the porous layer around the exterior of each fuel particle increases. The observed rate of reaction has been found to be only dependent upon the rate of diffusion of lithium across this layer, consistent with a classic shrinking core kinetic model. This shrinking core model has been extended to predict the behavior of a hypothetical, pilot-scale reactor for oxide reduction. The design of the pilot-scale reactor includes forced flow through baskets that contain the fuel particles. The results of the modeling indicate that this is an essential feature in order to minimize the time needed to achieve full conversion of the fuel.

keywords: oxide reduction, kinetics, pyrochemical, pyroprocessing

I. Introduction

Pyroprocessing is a promising technology for treating and recycling metallic spent nuclear fuel [1-3]. Its benefits relative to aqueous reprocessing technology include inherent proliferation resistance, compactness of the process equipment, and superior waste management. Its application to the treatment of spent Experimental Breeder Reactor-II (EBR-II) fuel was successfully demonstrated in 1999. And the treatment of this fuel continues today using this technology at Idaho National Laboratory. In addition to treating metallic fuels, consideration has been given to pyroprocessing the much more ubiquitous spent oxide fuels. This requires a head-end reduction step generally referred to as *oxide reduction*. Various approaches to oxide reduction have been reported. One such method is referred to as Li-reduction and involves submerging the oxide feed into a bath of molten LiCl at 650°C. The LiCl is saturated with Li metal, and the reduction reaction proceeds as follows.



Development of the Li-reduction process at Argonne National Laboratory involved experimental work at both the lab-scale (50-150 g batch) and the engineering scale (3.7-5.2 kg batch) [4-5]. The objective of this experimental program was to provide a technical basis for designing a pilot-scale system (PSS). The PSS needed to accommodate 100 kg of spent oxide fuel in each batch. The specific design that was developed consisted of four baskets loaded with fuel. Each basket had a concentric design with fuel being packed in between two cylinders with mesh linings. The Li-LiCl

fluid would be forced through the center of each of these baskets simultaneously using an impeller and draft tubes. Flow would occur from the center of each basket to its outer edge via radial plug flow. In order to keep the lithium concentration at its saturation level, a molten lithium source would need to be kept in contact with the LiCl solvent. As lithium would be consumed by the reaction with UO_2 , Li_2O would be formed and more lithium would be dissolved into the solvent. An image of the proposed PSS is given in Figure 1 [4].

In the development of the PSS design, there was debate over the need for forced fluid flow. It was initially speculated that forced flow would minimize the residence time necessary for the spent fuel in the system and, thus, increase the effective processing rate. To verify this assumption, it was necessary to develop a reactor model that accounted for intrinsic reaction rates, material balances, and mass transfer resistances. Such a model would enable prediction of the effect of fuel particle size, liquid flow rate, lithium concentration, and basket geometry on the time required to achieve full conversion of the fuel. Such a model is presented in this paper and compared to experimental results.

II. Kinetic Model Development based on Laboratory-Scale Experiments

Karell et. al. published results of laboratory-scale Li-reduction experiments under varying conditions using both uranium oxide particulate and pellets. Details of their experimental set-up and procedure can be found elsewhere [5]. Visual inspection of partially reacted pellet cross-sections suggested that the reaction proceeds via a classical shrinking core mechanism [6]. In such a mechanism, an unreacted core shrinks as the

reaction proceeds. An “ash layer” of reacted material surrounds the core, since the particle itself does not shrink. Diffusion of the reactant across the ash layer becomes the rate limiting process. In the case of reaction of lithium metal with uranium oxide, a porous metallic uranium layer is formed and thickens as the unreacted oxide core shrinks. The effective reaction rate is then controlled by the diffusion of lithium through this layer of uranium metal to the oxide core surface.

To verify that this shrinking core kinetics model applied, kinetic data from Karell were reviewed and compared to model predictions. For both experiments with pellets and crushed material, there was always a good fit of the model to the data. One example fit is shown in Figure 2. For this experiment, cylindrical pellets of UO₂ with cladding still intact were reduced. The presence of the cladding meant that the Li could only diffuse axially. Based on the shrinking core model and this geometrical restriction, the following equation was derived for relating time to fraction of the UO₂ that had been reduced.

$$t = -\frac{\rho L^2}{DC_{Li}^{sat} \alpha_w} \left((1-f) - \frac{1}{2}(1-f)^2 - \frac{1}{2} \right) = -\frac{\rho L^2}{DC_{Li}^{sat} \alpha_w} g(f) \quad (2)$$

The variables in the above equation include intraparticle diffusivity (D), Li concentration in the liquid phase (C_{Li}^{sat}), density of UO₂ (ρ), pellet length (L), molecular weight of UO₂ (α_w), and fractional conversion of the oxide reduction reaction (f). For simplification, an original function ($g(f)$) has been introduced and is defined in Equation 2. The plot in Figure 2 shows the fit of this equation to data published by Karell. The quality of the fit

is supportive of the claim that a shrinking core mechanism dominates the kinetics. Granted, it would be desirable to have data available at various temperatures to further test the possibility that the reduction is chemical reaction controlled. Since estimates for all other parameters are available ($C_{sat} = 1.7 \times 10^{-4}$ moles/cm³, $L = 1.0$ cm, $\alpha_w = 270$ g/mole, $\rho = 10$ g/cm³), the slope of the line was used to estimate the diffusivity of lithium in the uranium metal layer ($D = 9.7 \times 10^{-4}$ cm²/sec). For other kinetic fits, the diffusivity was estimated to be 2.7×10^{-4} cm²/sec. Both of these estimates for the diffusivity appear to be high, since liquid phase diffusion coefficients are typically on the order of 10^{-5} cm²/sec. However, the high temperatures involved and small size of the lithium atom may explain the very high apparent diffusivity. Another consideration is that the estimate for the saturated concentration of lithium may be inaccurate, since it was based on a value cited from the literature rather than an actual measurement [7]. The cited value from the literature, it should be noted, was for Li in LiCl. The addition of a small amount of lithium oxide to the molten salt may appreciably change the Li solubility. If the actual lithium concentration was higher than the value assumed, the calculated lithium diffusivity would be lower as expected.

III. Pilot-Scale Reactor Model

With the shrinking core model verified for the oxide reduction reaction, the next step was to apply this model to a mathematical representation of the proposed PSS. This PSS consists of a packed bed of fuel particles filled in between two cylinders. Molten LiCl saturated with Li flows up through the center of the reactor and then radially outward through the fuel bed. A diagram of this geometry is given in Figure 3.

Using the shrinking core kinetic model, it can be shown that at any given position in the packed bed, the intrinsic rate of lithium consumption in a spherical UO_2 pellet is as follows.

$$\mathfrak{R} = \frac{3D(1-\varepsilon)C_{Li}}{R_p^2\left(1-\frac{R_p}{r_c}\right)} \quad (3)$$

In addition to the variables used in Equation (2), the above equation includes void fraction in the packed bed (ε), concentration of lithium in the fluid phase (C_{Li}), particle radius (R_p), and unreacted particle core radius (r_c). The equation must be combined with material balances over the packed bed and over the unreacted core in any given fuel pellet in order to facilitate prediction of lithium concentrations across the reactor and unreacted core size as a function of position and time. The material balance over the packed bed is accounted for in the following equation. The height of the packed bed is given by h , and the radial position within the basket is given by r . It is assumed that the salt flows evenly with parallel streamlines from the inner to the outer radius of the basket. It is also assumed that lithium saturation is being maintained in the bulk of the salt, via perpetual contact of the salt with a source of molten lithium.

$$\frac{1}{r} \frac{\partial C_{Li}}{\partial r} = \frac{6\pi h D (1-\varepsilon)}{F R_p^2} \frac{C_{Li}}{1-\frac{R_p}{r_c}}, \quad C_{Li} = C_{Li}^{sat} \text{ at } r=R_1 \quad (4)$$

In Equation (4), the new variable is volumetric salt flow rate (F). The material balance over any given fuel pellet is given below, assuming spherical pellets.

$$r_c^2 \frac{\partial r_c}{\partial t} = \frac{\alpha_w D}{\rho} \frac{C_{Li}}{\frac{1}{R_p} - \frac{1}{r_c}}, r_c = R_p \text{ at } t=0 \quad (5)$$

For ease of numerical simulation, the above equations were cast into dimensionless form. The resulting dimensionless equations are given below. The definition of the dimensionless variables is given in the *Nomenclature* section of this report. The equations were solved using finite differences.

$$\frac{1}{\bar{r}} \frac{\partial \bar{C}}{\partial \bar{t}} = \zeta \frac{\bar{C}}{1 - \frac{1}{\bar{r}_c}}, \zeta = \frac{6\pi h D (1 - \varepsilon) R_2^2}{R_p^2 F}, \bar{C} = 1 \text{ at } \bar{r} = \frac{R_1}{R_2} \quad (6)$$

$$\left(1 - \frac{1}{\bar{r}_c}\right) \bar{r}_c^2 \frac{\partial \bar{C}}{\partial \bar{t}} = \Omega \bar{C}, \Omega = \frac{D \alpha_w C_{Li}^{sat} V_{basket}}{4 \rho R_p^2 F}, \bar{r}_c = 1 \text{ at } \bar{t} = 0 \quad (7)$$

As needed, this model can be used to predict the time required to completely reduce the oxide fuel as a function of particle size, flow rate, reactor geometry, and lithium concentration in the LiCl. This allows for the operating parameters to be optimized prior to running actual tests. A convenient representation of the results generated from this model is to use an effectiveness factor, η —a ratio of the ideal time to completion of reaction to actual time to completion of reaction.

$$\eta = \frac{\tau_{ideal}}{\tau_{actual}} \quad (8)$$

The ideal time (τ_{ideal}) is based on a single particle suspended in perfectly stirred LiCl that is saturated with Li metal. It is the time required for completion of the reaction in the absence of external diffusion resistance (outside of the particle). For spherical particles, it can be calculated using the following equation.

$$\tau_{ideal} = \frac{2\rho R_p^2}{3\alpha_w DC_{Li}^{sat}} \quad (9)$$

In Figure 4, calculations for η are given at various particle sizes and flow rates. As expected, the effectiveness factors increase with increasing particle size and increasing flow rate. As the particle size is increased, the time scale for diffusion in the particle increases, and the reaction becomes more and more limited relative to mass transfer in the liquid phase. As the flow rate increases, the mass transfer in the liquid phase becomes faster and less of a limiting factor. It is important to note that in the case of a distribution of particle sizes that the largest particle will solely determine the endpoint of the reaction. However, the transient behavior is dependent on the whole distribution.

IV. Engineering-Scale Experiments

Engineering scale (ES) experiments were run with fuel batch sizes up to 20 kg in which there was no forced flow [5], with the results further supporting the need for forced

flow in the PSS. Analogous to the lab-scale experiments, the ES runs featured vigorous external fluid mixing around a basket packed with fuel particles. At one time it was anticipated that external mixing would be sufficient to deliver an adequate flux of lithium to the fuel particle surfaces. However, the graph in Figure 5 refutes this. The effectiveness factors for three different ES tests are compared to the computed effectiveness factor as a function of flow rate. In all cases, the particle diameter is assumed to be 4000 μm . Here it can be seen that even for flows as low as 500 cm^3/sec , the PSS greatly outperforms the ES system. Note that the horizontal lines for ES-5, ES-6, and ES-9 are not meant to imply any relationship between effectiveness factor and flow rate. As mentioned above, each experiment involved only external fluid agitation. Their vertical levels in Figure 5 were meant to be compared to the modeled PSS curve to show that performance could have been dramatically improved with the assistance of forced fluid flow through the baskets.

V. Summary

Analysis of lab-scale experiments indicates that a shrinking core model accurately represents the kinetics of uranium oxide reduction by lithium dissolved in molten LiCl. The diffusion coefficient for lithium in the fuel pellets has been estimated to be in the range of 2.7×10^{-4} to 9.7×10^{-4} cm^2/sec , extremely high for liquid state diffusion. Meanwhile, the kinetic model and value for the diffusion coefficient have been incorporated into an overall reactor model, encompassing the entire pilot scale oxide reduction reactor. That model has been solved numerically and can be used to predict the time at which complete conversion occurs for a number of different conditions. And

effectiveness factors have been used to demonstrate the advantage of implementing forced salt flow into the system. Compared to the results of 20 kg-batch oxide reduction experiments, a pilot scale system with forced flow is expected to yield superior results over a large range of flow rates. It is, thus, recommended that any large-scale implementation of the Li-reduction process include the ability to force salt flow through the fuel baskets.

VI. Nomenclature

\bar{C}	dimensionless concentration of reactant in liquid $\left(\frac{C}{C_{Li}^{sat}} \right)$
C_{Li}	concentration of Li in the molten salt at a particular basket position and time (moles/cm ³)
C_{Li}^{sat}	saturated concentration of Li in LiCl at 650°C (moles/cm ³)
D	effective intraparticle diffusion coefficient (cm ² /sec)
f	fractional conversion of uranium oxide to uranium metal
g(f)	original function of fractional conversion
h	height of packed bed in fuel basket (cm)
L	length of a fuel cladding-covered fuel pellet (cm)
R_p	average particle radius (cm)
r_c	radius of unreacted core (cm)
\bar{r}_c	dimensionless radius of unreacted core $\left(\frac{r_c}{R_p} \right)$
r	radial position in fuel basket (cm)

\bar{r}	dimensionless radial position in fuel basket $\left(\frac{r}{R_2}\right)$
\mathfrak{R}	rate of reaction (moles/cm ³ -sec)
t	time (sec)
\bar{t}	dimensionless time $\left(\frac{t}{\tau}\right)$
V_{basket}	internal volume of fuel basket (cm ³)
α_w	atomic weight (grams/mole)
ε	void fraction in fuel/zeolite basket
ξ	dimensionless parameter used in reactor model
Ω	dimensionless parameter used in reactor model
ρ	density (grams/cm ³)
τ_{ideal}	time required for complete conversion for a given particle size with no external diffusion resistance
τ_{actual}	actual time required for complete conversion for a given particle size

VII. References

1. J.J. Laidler, J.E. Battles, W.E. Miller, J.P. Ackerman, and E.L. Carls, "Development of Pyroprocessing Technology;" *Prog. Nucl. Energy*, **31**, 131 (1997).

2. R.W. Benedict and H.F. McFarlane; “Success Criteria for the Electrometallurgical Treatment Demonstration;” Proceedings of the American Nuclear Society Embedded Topical Meeting on DOE Spent Nuclear Fuel and Fissile Material Management, Charleston, SC, September 8-11, 1998.

3. K.M. Goff, R.W. Benedict, K.L. Howden, G.M. Teske, and T.A. Johnson; “Pyrochemical Treatment of Spent Nuclear Fuel;” *Proceedings of GLOBAL 2005*; Tsukuba, Japan, October 9-13, 2005.

4. S.D. Herrmann, K.R. Durstine, M.F. Simpson, and D.R. Wahlquist; “Pilot-Scale Equipment Development for Pyrochemical Treatment of Spent Oxide Fuel;” *Proceedings from Global '99*, Jackson, WY, August 29 – September 3, 1999.

5. E.J. Karell, K.V. Gourishankar, J.L. Smith, L.S. Chow, and L. Redey; “Separation of Actinides from LWR Fuel Using Molten-Salt-Based Electrochemical Processes;” *Nuclear Technology*, vol. 136, December 2001, 342-353.

6. O. Levenspiel, Reactor Engineering, Wiley and Sons: New York, pp. 361-366.

7. L.P. Cook and H.F. McMurdie; “Phase Diagrams for Ceramists;” VII:5, American Ceramics Society, Westerville, Ohio (1989).

LIST OF FIGURES

Figure 1. Proposed Design for Pilot Scale System (PSS) for Oxide Reduction.

Figure 2. Kinetics of Li-Reduction of Clad Cylinders of UO_2 . ($L=1.0$ cm, $C_{\text{Li}} = 1.7 \times 10^{-4}$ moles/cm³)

Figure 3. Geometry of the Pilot Scale System (PSS) for Oxide Reduction.

Figure 4. Computed Effectiveness Factors for the Pilot Scale Oxide Reduction System for Various Particle Diameters as a Function of Flow Rate.

Figure 5. Comparison of Effectiveness Factors Observed for Select Engineering Scale Experiments to Predicted Effectiveness Factors for the Pilot Scale System.