Progress on Plant-Level Modeling and Simulation of Used Nuclear Fuel Dissolution: Production of NO$_x$

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Letter Report ORNL/LTR-2014/107

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25 March 2014

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Abstract

This progress letter report is an account of the activities in the second quarter of FY14 which includes the improvement of the dissolution plant-level module, Nitron, to implement and add a gas phase model; here amounts of NOx are quantified. This report also has an appendix with two oral presentations made during the most recent project meeting. The first presentation (Appendix A) discusses an integration approach for coupling plant-level modules. The concepts have been explained in a previous report. The presentation covered details of the mathematical coupling of computational modules and the basic elements of what constitutes a module. A suggestion was made for the demonstration of these concepts in practice which is part of the FY14 tasks and deliverables of the project. The second presentation (Appendix B) explained the current status of the computation module for dissolution, Nitron, in light of the elements presented in the first talk.

An update to a previous report is presented here demonstrating the corresponding computed amounts of nitrogen dioxide and nitric oxide (respectively, NO2 and NO) that enter the vapor phase during the dissolution of used, oxide nuclear fuel.

This work is conducted in collaboration with Los Alamos National Laboratory, Savannah River National Laboratory, and University of South Carolina (Prof. Dan G. Cacuci) for integrating and coupling various reprocessing facility simulation modules with uncertainty quantification capability.

The aforementioned previous report on this dissolver module is a required reading for the understanding of this update.
## Contents

List of figures ii

1 Production of NO\textsubscript{x} 1

2 Results 1

\hspace{1em} 2.1 Breeder reactor fuel at 0.5 t d\textsuperscript{-1} dissolution capacity ............. 2
\hspace{1em} 2.2 Breeder reactor fuel at 1 t d\textsuperscript{-1} dissolution capacity ............. 4
\hspace{1em} 2.3 LWR reactor fuel at 1.7 t d\textsuperscript{-1} dissolution capacity ............. 6

3 Comments and future work 8

Acknowledgments 8

A Appendix: Integrating Architecture for Modeling and Simulation of Nuclear Fuel Reprocessing: A Commonality-Based Approach 9

B Appendix: Plant-Level Dissolution Model and Module 19

References 19

## List of Figures

2.1 Nitric acid molarity for each compartment of the dissolver. Capacity of 0.5 t d\textsuperscript{-1} \hspace{1em} 2

2.2 Accumulated production of NO for each compartment of the dissolver \( M^{(k)}_{NO_\text{x},g}(t), \text{ } k = 1 \ldots 10. \text{ Capacity of 0.5 t d}^{-1} \hspace{1em} 3

2.3 Nitric acid molarity for each compartment of the dissolver. Capacity of 1 t d\textsuperscript{-1} \hspace{1em} 4

2.4 Accumulated production of NO for each compartment of the dissolver \( M^{(k)}_{NO_\text{x},g}(t), \text{ } k = 1 \ldots 10. \text{ Capacity of 1 t d}^{-1} \hspace{1em} 5

2.5 Nitric acid molarity for each compartment of the dissolver. Capacity of 1.7 t d\textsuperscript{-1} \hspace{1em} 6

2.6 Accumulated production of NO for each compartment of the dissolver \( M^{(k)}_{NO_\text{x},g}(t), \text{ } k = 1 \ldots 10. \text{ Capacity of 1.7 t d}^{-1} \hspace{1em} 7
1 Production of NO$_x$

The production of NO$_x$ takes place at the third startup step (de Almeida, 2013) when sheared fuel enters the loading compartment (fig. 3.1, de Almeida, 2012). Only this third step is considered in this report. Denote the third step time interval as

$$I_3 := \{ t \in \mathbb{P} \mid T_2 \leq t \leq T_3 \}.$$

The governing equations for the dissolution startup process need to be integrated in $I_3$. These have been discussed before (de Almeida, 2012, sec. 4.3). Of particular attention here is the calculation of the produced NO$_x$ from the dissolution overall reaction mechanism (Lewis, 1984) when $c_{\text{HNO}_3} \leq 8$ M

$$\text{UO}_2(\text{s}) + 2.7 \text{HNO}_3 \xrightarrow{100^\circ C} \text{UO}_2(\text{NO}_3)_2 + 0.7 \text{NO} \_ (g) + 1.3 \text{H}_2\text{O} \_ (aq), \quad (1.1)$$

$$\text{PuO}_2(\text{s}) + 4 \text{HNO}_3 \xrightarrow{100^\circ C} \text{Pu}(\text{NO}_3)_4 + 2 \text{H}_2\text{O} \_ (aq), \quad \text{and} \quad (1.2)$$

$$\text{FPPO}_{1.18}(\text{s}) + 2.36 \text{HNO}_3 \xrightarrow{100^\circ C} \text{FP}(\text{NO}_3)_3_{2,36} + 1.18 \text{H}_2\text{O} \_ (aq), \quad (1.3)$$

or when using a higher acid strength $c_{\text{HNO}_3} > 8$ M (1.1) needs to be replaced by

$$\text{UO}_2(\text{s}) + 4 \text{HNO}_3 \rightarrow \text{UO}_2(\text{NO}_3)_2 + 2 \text{NO}_2(\text{g}) + 2 \text{H}_2\text{O} \_ (aq).$$

The foregoing allows for the computation of the following instantaneous NO$_x$ mass sources

$$\mathcal{M}^{(k)}_{\text{NO}_x,\text{g}}(t) := 0.7 \dot{n}^{(k)}_{\text{UO}_2} M_{\text{NO}} \text{ for } c_{\text{HNO}_3} \leq 8 \text{ M and} \quad (1.4)$$

$$\mathcal{M}^{(k)}_{\text{NO}_2,\text{g}}(t) := 2.0 \dot{n}^{(k)}_{\text{UO}_2} M_{\text{NO}_2} \text{ for } c_{\text{HNO}_3} > 8 \text{ M.} \quad (1.5)$$

For the presentation of the accumulated production of NO$_x$ per compartment of the rotary dissolver the following quantity is computed:

$$M^{(k)}_{\text{NO}_x,\text{g}}(t) := \int_{T_2}^{t} \mathcal{M}^{(k)}_{\text{NO}_x,\text{g}}(s) \, ds.$$

2 Results

The resulting mathematical problem and solution method has been discussed earlier (de Almeida, 2012). The next sections demonstrate tests for a startup of the rotary dissolver within a condition of quasi-developed flow and perturbed input acid concentration followed by the dissolution of solids.
2.1 Breeder reactor fuel at 0.5 t d\textsuperscript{-1} dissolution capacity

For this example the concentration of the nitric acid is never greater than 8 M (fig. 2.1). Therefore only NO is produced (fig. 2.2).

![Graph showing nitric acid molarity for each compartment of the dissolver. Capacity of 0.5 t d\textsuperscript{-1}. The zoom-in graph shows how the perturbation of the concentration in the feed compartment decays in the downstream direction.]

**Fig. 2.1:** Nitric acid molarity for each compartment of the dissolver. Capacity of 0.5 t d\textsuperscript{-1}. The zoom-in graph shows how the perturbation of the concentration in the feed compartment decays in the downstream direction.
Fig. 2.2: Accumulated production of NO for each compartment of the dissolver $M_{NO_{x,g}}^{(k)}(t)$, $k = 1 \ldots 10$. Capacity of 0.5 t d$^{-1}$. 
2.2 Breeder reactor fuel at 1 t d\(^{-1}\) dissolution capacity

For this example the concentration of the nitric acid is never greater than 8 M (fig. 2.3). Therefore only NO is produced (fig. 2.4).

Fig. 2.3: Nitric acid molarity for each compartment of the dissolver. Capacity of 1 t d\(^{-1}\). The zoom-in graph shows how the perturbation of the concentration in the feed compartment decays in the downstream direction.
Fig. 2.4: Accumulated production of NO for each compartment of the dissolver $M_{NO,g}^{(k)}(t), \; k = 1 \ldots 10$. Capacity of 1 t d$^{-1}$. 
2.3 LWR reactor fuel at 1.7 t d\(^{-1}\) dissolution capacity

For this example the concentration of the nitric acid is never greater than 8 M (fig. 2.5). Therefore only NO is produced (fig. 2.6).

\[\text{Fig. 2.5: Nitric acid molarity for each compartment of the dissolver. Capacity of 1.7 t d}^{-1}. \text{ The zoom-in graph shows how the perturbation of the concentration in the feed compartment decays in the downstream direction.}\]
Fig. 2.6: Accumulated production of NO for each compartment of the dissolver $M_{NO_{x,g}}^{(k)}(t), \ k = 1 \ldots 10$. Capacity of 1.7 t d$^{-1}$.
3 Comments and future work

This continued development implemented and tested the amounts of NO\textsubscript{x} calculated for different fuel dissolution conditions for the dissolver module described earlier (de Almeida, 2012, 2013).

Current and future work is focusing in adding various new components to the module including the vapor phase, heat balance, and batch processing mode. This effort is in collaboration with Los Alamos National Laboratory, Savannah River National Laboratory, and University of South Carolina (Prof. Dan G. Cacuci) for an integration (and coupling) of plant-level modules, and uncertainty quantification analysis of the modules.

Acknowledgments

This work was sponsored by the U.S. Department of Energy through the Office of Proliferation Detection of the National Nuclear Security Administration under contract DE-AC05-00OR22725 with UT-Battelle, LLC.
A Appendix: Integrating Architecture for Modeling and Simulation of Nuclear Fuel Reprocessing: A Commonality-Based Approach

Integrating Architecture for Modeling and Simulation of Nuclear Fuel Reprocessing:
A commonality-based approach

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Facility Modeling Project
Savannah River National Laboratory
04 February 2014

Oak Ridge National Laboratory
Managed by UT-Battelle for the Department of Energy
What are we really trying to do?

- Coupling of mathematical models arising from conservation or/and non-conservation principles
  - Initial, boundary-value problems (constrained)
  - Non-linear algebraic problems
  - Minimization and saddle point problems
  - Linear and non-linear eigenvalue problems
  - A mix of the above, etc...

- Models are realized in the form of scientific computer codes/software

- Integrating stand-alone software (in general) has its challenges:
  - E.g.: Getting a text editor to import spreadsheets
  - Getting a drawing application to embed and play movies, etc...

- Integrating stand-alone, “scientific” software IS a greater challenge:
  - Are variables compatible?
  - How are variables coupled?
  - What is the impact on the original stand-alone solution algorithm?
  - Is coupling two-ways? Etc...
  - Does the coupled code reflect the underlying coupled model?
  - How about sensitivity and uncertainty of the coupled codes?

Integrating Reprocessing Modeling and Simulation

- Best achieved if organized on a “level of theory” paradigm

- Multi-tiered approach
  - Plant-level: “time is the only independent variable”
    - Low-order, reduced models, time-dependent, tightly coupled, semi-empirical
  - Unit Operations: “continuum time and space are independent variables”
    - Higher order, time-dependent, loosely coupled, continuum
  - Sub-scale Domain: “time, space or hyperspace are independent variables”
    - Electronic, atomistic, particle-based, structured continuum, stand-alone

* Desktop computing
* Cluster computing
* High-end parallel computing
Plant-Level Process Modeling Commonality

➢ The plant-level tier has practical applications and opportunities

➢ There exists no systematic level of theory for plant-level models
  • Ad hoc basic balance equations
  • Equilibrium or quasi-equilibrium arguments
  • Semi-empirical (not a bad thing); but no systematic approach for fidelity improvement

➢ Chemical separation processes “modeling architecture”:
  • Re-usable mathematical architecture will help guide modeling of different processes
  • Paves the way for incorporating sub-scale calibrations
  • Reduces time of code development
  • Applies to many plant processes

➢ Commonality enables time-coupling

➢ Integration implements a particular time-coupling strategy

Integration approach

➢ Toolkit-based applications
  • End product is a software for composition of a system application (facility simulator)
  • Application developer builds application using the toolkit
  • Analyst uses the application as end user and interacts with developer

➢ Toolkit computational components

- A collection of plant-level modules (computational realizations of process models)
- An environment for coupling modules into an application and execute a simulation

➢ Coupling method provided by environment
  • Asynchronous evolution of time via message events
  • Message passing method for coupling data transfer

➢ Implications for modules
  • Have to implement an “external behavior”
  • Have to manage all internal aspects of the physicochemical model and solution algorithm involved (think: “stand-alone” mode)

  ➢ Environment provides “minimum” basic functionality for execution of an application: carry time-stamped messages to/from modules throughout the application

  ➢ Keep integration simple, focus is on modules: fidelity, accuracy and robustness
Architecture 1: External behavior of a module

1) $M_i$ advances its own time $t_i$
   - Time integration is very module dependent.

2) Needs a parameter vector $p_i(t_i)$
   - All parameters in a mathematical model. May couple to other parameter vectors of other modules via signals/alerts.

3) May require one or more coupling vectors $q_{j,i}(t_i)$ from one or more modules
   - Time-stamped data at $t_i$ required from other modules via the integration environment. Module will wait for data.

4) May need to provide one more coupling vectors $q_{i,n}(t_n)$ to one or more modules either in the past or in the future
   - Module needs to watch for message and provide time-stamped data at $t_n$ required from other modules via the integration environment. Environment may have to wait.

5) May be coupled to as many other modules $M_k$ as needed
   - Module cannot be self-coupled. High degree of connectivity will lead to cycles.

Architecture 2: An Application Network

- A facility application is a network composition of modules
- Integration environment provides the connectivity of modules

The network graph is a useful object for practical and theoretical uses
- Excellent graph libraries can be used for large composition of modules
- General applications will lead to a directed graph with possible cycles
- The computational realization of the integration environment is a network equipped with message event handling
Architecture 3: Application Time Evolution

- **All modules start at time 0**
  Initial conditions are provided

- **Modules advance time internally**
  Each module integrates the governing equations in time with its own time stepping algorithm; say, adaptive, etc.
  In the course of integration, needed data will be requested from coupled modules via the network.
  In the course of integration, each module listens for requests of data by the network. Modules need to store internal state history

- **Environment handles time-stamped message events**
  Environment does not keep time. Time evolution advances based on data on demand.
  Environment collects and delivers coupling data \( q(t) \) to all modules
  Grid lock will happen for realistic networks... Will cross that bridge when we come to it.

- **Comments:**
  - This integration approach requires small changes to an existing stand-alone module; minor intrusion
  - The network environment is simple to prototype: essentially a graph and a message passing capability
  - Quick progress can be made on coupling existing modules

What can we do now:

- **Rapid prototyping for integration of two modules**

  - **Shearing module**
    - Model?
    - Programing language?
    - Modifications for time coupling needed?

  - **Dissolution module (Nitron)**
    - Octave program (used with SANDIA SSPM)
    - Modifications for sheared fuel with hulls? etc.
    - Use rotary dissolver or other equipment?

  - **Integration**
    - Write a basic Python integration program

  - **Obtain results, verify correctness, consider uncertainty quantification of the application**

- **Identify the next module to be added**

  - **Off-gas**
    - Model?
    - Programing language?
    - Modifications for time coupling needed?

  - **Integration**
    - Extend integration program

- **Identify the next module to be added**
Plant-Level Process Modeling Commonality

➢ Chemical separation processes “modeling architecture”:
  • Re-usable mathematical architecture will help guide modeling of different processes
  • Paves the way for incorporating sub-scale calibrations
  • Reduces time of code development
  • Applies to many plant processes

Internal View of a Plant-Level Model

➢ Various plant-level processes admit this basic modeling framework

\[
F(x, \ldots, d_i^n, x, t; p(t), q(t)) = 0 \\
G(x, t; p(t), q(t)) = 0 \\
x(t_0) = x_0, \ldots, d_i^n, x = x_i^{(n)}; p(t_0) = p_0; q(t_0) = q_0
\]
Network Representation of Contactors

➢ What is (considered) a contactor?
  • Any device that facilitates a physicochemical process
    – Calciners, dissolvers, columns, tanks, furnaces, ...
  • Any device that is subjected to a physicochemical process
    – Pipes, pumps, valves, storage tanks, ...

➢ What is a contactor network?
  • Vertices
    – Significant spatial regions
  • Multi-directed edges
    – Material flow paths

➢ How is a network created?
  • Experience
    – Non-unique; evolutionary
  • Practice
    – Use a graph library

Network Transport Theory

➢ Plant-level models must be “reduced” models:
  • Derived from an underlying sub-scale theory
    – Typically a continuum mixture theory for multiphase, multicomponent systems
  • Upscaled by a volume averaged method
    – Integral or local balances over the network vertices

➢ Why does this matter?
  • Introduces a modeling standard
    – Provides a starting point for modeling uncommon processes
  • Solid theoretical coupling to sub-scale
    – This is the path for reducing empiricism and guide new experimental work
  • Allows for coupling of models
    – Enables rational development of computer code integration

➢ Approach taken here
  • Two extremes:
    Mixture regime
    – Vigorous agitation
    – Dispersion contact
    – Volume averaging
    Continuous regime
    – Mild agitation
    – Material body contact
    – Integral averaging
Network Transport Model

➢ An extension of the chemical engineering multistage modeling

➢ Basic vertex quantities (“10 quantities model”)

<table>
<thead>
<tr>
<th>Existing models</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^{(k)}_\alpha$</td>
</tr>
<tr>
<td>Volume</td>
</tr>
</tbody>
</table>

Some models

<table>
<thead>
<tr>
<th>New</th>
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</thead>
<tbody>
<tr>
<td>$g^{(k)}_{a,\alpha}$</td>
</tr>
<tr>
<td>Dispersion</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>New</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c^{(k)}_\alpha$</td>
</tr>
<tr>
<td>Internal energy</td>
</tr>
</tbody>
</table>

➢ Basic conservation and (im)balance equations (“4 major equations”)

Mass:

$$d_t \left( \rho^{(k)}_{a,\alpha} V^{(k)}_\alpha \right) = \sum_{j \neq k} \rho^{(k,j)}_{a,\alpha} \left( f^{(k,j)}_\alpha + g^{(k,j)}_{a,\alpha} \right) + M_{a,\alpha}^{(k)}$$

Power:

$$d_t \left( \frac{1}{2} v^{(2)}_\alpha V^{(k)}_\alpha \right) = \sum_{j \neq k} \rho^{(k,j)}_{a,\alpha} \frac{1}{2} v^{(2,j)}_\alpha + t^{(k,j)}_\alpha f^{(k,j)}_\alpha + P_{a,\alpha}^{(k)}$$

Energy:

$$d_t \left( \rho^{(k)}_{a,\alpha} s^{(k)}_\alpha V^{(k)}_\alpha \right) = \sum_{j \neq k} \rho^{(k,j)}_{a,\alpha} s^{(k,j)}_\alpha f^{(k,j)}_\alpha + \sum_{\ell} q^{(k,j)}_{a,\alpha} S^{(k)}_\alpha + E_{a,\alpha}^{(k)}$$

Entropy:

$$d_t \left( \rho^{(k)}_{a,\alpha} s^{(k)}_\alpha V^{(k)}_\alpha \right) = \sum_{j \neq k} \rho^{(k,j)}_{a,\alpha} s^{(k,j)}_\alpha f^{(k,j)}_\alpha + \sum_{\ell} q^{(k,j)}_{a,\alpha} S^{(k)}_\alpha + S_{a,\alpha}^{(k)}$$

Closure and Numerical Solution

➢ Closure: theory of constitutive restrictions
• Match number of variables and equations
  • All source terms require a functional form:
    $$M_{a,\alpha}^{(k)} P_{a,\alpha}^{(k)} E_{a,\alpha}^{(k)} S_{a,\alpha}^{(k)}$$
• Specialization of material behavior (constraints)
  • Incompressibility, non-ideality, dilute systems...

➢ Solution of Resulting Non-Linear Differential Algebraic Equations

$$\dot{x}(t) = F(x(t), p(t), q(t)) = 0$$
$$G(x(t), p(t)) = 0$$
$$H(x(t), p(t)) = 0$$

consistently

Consistent initial conditions

Robust Solvers

DASPK, DASSL
DASPKSO
(parallel versions)
Application Examples

➢ Dissolution
Fuel dissolution in hot nitric acid

Rotary dissolver

➢ Solvent Extraction
Metal ion separation by liquid/liquid extraction

Centrifugal contactors

➢ Voloxidation
Fuel oxidation and volatilization in hot gas

Rotary Calciner

0.5 ton/day processing capacity systems: DOE Fuel Reprocessing Program 70-80's

Voloxidation Model

➢ Oxidative (dry) dissolution of used fuel

Plant-level connectivity

Network modeling

Representative results: UO2 0.5 MT/d capacity

Oak Ridge National Laboratory Report ORNL/LTR-2014/107 pp. 1
Model Description Template

▶ A guide to plant-level model and simulation development

1) Plan-level Localization
   Plant-level tier system; connectivity

2) Physicochemical Phenomena
   Description of multi-scale phenomena

3) System Description
   Information on process operation

4) Mathematical Model
   A rigorous mathematical problem

5) Data Needed and Provided
   Parameters, initial conditions, deliverables

6) Solution Method and Results
   DAE solver used, setup, and representative results

7) Verification Method
   Plan and/or implementation of verification approach.

8) Uncertainty Quantification
   Plan and/or initial efforts in validation

9) Fidelity Improvement
   Needed sub-scale modeling/simulation, and/or experimental work

10) Model Transferability
    What other (sub)processes could be treated by the same model

Summary

▶ Development of a common modeling approach for plant-level processes
  • Provides a modeling “blue print” for all plant-level models
  • Provides “a” platform for the development of “predictive” models
  • Modules (codes) derived from this approach have well-defined internal mathematical structure and external computational behavior
  • Testing concepts in theory and practice for major recycle processes:
    • Dissolution, voloxidation, and solvent extraction

▶ References: ORNL reports (email dealmeidav@ornl.gov)
  • Plant Level Modeling and Simulation of Used Fuel Dissolution, ORNL/TM-2012/375, 2012
  • Plant Level Modeling and Simulation of Used Fuel Voloxidation, ORNL/TM-2012/508, 2012
B  Appendix: Plant-Level Dissolution Model and Module
Plant-Level Process Modeling Commonality

➢ Chemical separation processes “modeling architecture”:
  • Re-usable mathematical architecture will help guide modeling of different processes
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Model Description Template

➢ A guide to plant-level model and simulation development
  • Plant-Level Modeling and Simulation of Used Fuel Dissolution, ORNL/TM-2012/375, 2012

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    What other (sub)processes could be treated by the same model
1. Plant-Level Localization

➢ The dissolver is part of the dissolution sub-system in the head-end system. The dissolution sub-system includes the following stations:

- Dissolver/digester
- Receiver surge tanks
- Clarifier
- Off-gas sub-system
- Hull washing station
- Undissolved solids handling

1.1 Sub-System
2. Physico-Chemical Phenomena

➢ The model is trying to capture the process of dissolving the bulk of the used nuclear fuel in solid form into a liquid (this is a leaching separation process). The liquid is typically a boiling acid (nitric acid) which reacts at the surface of the fuel removing metal atoms in the form of cations.

➢ There is significant complexity in this process which involves the tumbling of pieces of sheared fuel with cladding and other fuel bundle internals in the dissolving liquid. A countercurrent, rotary contactor is one type of equipment used for industrial operations. Many prototypes have been investigated in the past. There is no standard contactor at the time of this writing; DOE reports have been reviewed in this subject.

➢ A typical contactor will flow the liquid by gravity and will propel the solid pieces or powder countercurrently. The liquid outflow contains the liquid product, and the solid outflow contains the hulls and other fuel bundle internals. The boiling temperature may be maintained by steam which participates in the recycling of acid within the contactor equipment. Whether a vapor stream is used or not, the flow in the contactor involves three-phases with vapor entrainment in the liquid/solid mixture.

➢ The dissolution of the fuel depends greatly on the type of fuel and burnup which affects the microstructure. Cracks in the fuel matrix (greater than ~10 μm) provide highways for fluid penetration in the fuel. Pretreatment of the fuel such as voloxidation will have a major effect on the operation of the dissolution process. It is also important to assess the release of volatile fission products into the vapor phase of the dissolver. This quantification depends on the local spatial distribution of fission products in the used fuel matrix. This information is also important in fuel performance analysis.

3. System Description

➢ Sheared fuel loading
  ● Fuel rods cut length: ~2.5 cm
  ● Fuel pellet diameter: ~0.5 cm
  ● Fines average diameter: ~100–200 μm
  ● Other fuel internals (incomplete)
  ● Load period: ~20 min
  ● Fuel load mass: ~7 kg/cycle

➢ Product stream
  ● Volumetric flow rate: ~1.6 l/min
  ● Solid particles average diameter: ~10–50 μm

➢ Steam inflow:
  • Flow rate: ?

➢ Acid aqueous feed:
  • HNO₃ concentration: ~7 M
  • Flow rate: ~1.8 l/min

➢ Rinse aqueous feed:
  • HNO₃ concentration: ~0 M
  • Flow rate: ~0.5 l/min

➢ Hulls outflow:
  • Fuel bundle internals ...

➢ Off-gas:
  • NOₓ flow rate: ?
  • Steam flow rate: ?

➢ Additional parameters:
  • Rotation rate: ~2 RPM
  • Compartment volume: ~110 L
  • Total length: 2.5 m
  • Total volume: ~1100 L
  • Liquid holdup: ~10 L/stage
3.1 System Operation

3.2 System Connectivity
4. Mathematical Model

➢ Contactor Network

 Governing Equations of Network Transport

\[ V^{(k)}_{\alpha} \quad \rho_{a,\alpha}^{(k)} \quad f^{(k)}_{\alpha} \]

\[ \rho_{v,\alpha}^{(k)} \quad \rho_{d,\alpha}^{(k)} \quad \rho_{s,\alpha}^{(k)} \]

\[ \frac{1}{2} \rho_{v,\alpha}^{2(k)} \quad \rho_{s,\alpha}^{2(k)} \quad \rho_{d,\alpha}^{2(k)} \]

Mass:

\[ \frac{d}{dt}(\rho_{a,\alpha}^{(k)} V^{(k)}_{\alpha}) = \sum_{j \neq k} \rho_{a,\alpha}^{(k,j)} \left( f_{\alpha}^{(k,j)} + g_{\alpha}^{(k,j)} \right) + \mathcal{M}_{a,\alpha}^{(k)} \]

Power:

\[ \frac{d}{dt}(\rho_{a,\alpha}^{(k)} \frac{1}{2} V^{(k)}_{\alpha}) = \sum_{j \neq k} \rho_{a,\alpha}^{(k,j)} \frac{1}{2} \left( f_{\alpha}^{(k,j)} + g_{\alpha}^{(k,j)} \right) \]

Energy:

\[ \frac{d}{dt}(\rho_{a,\alpha}^{(k)} (T^{(k)}_{\alpha} V^{(k)}_{\alpha})) = \sum_{j \neq k} \rho_{a,\alpha}^{(k,j)} (T_{\alpha}^{(k,j)} f_{\alpha}^{(k,j)} + g_{\alpha}^{(k,j)}) \]

Entropy:

\[ \frac{d}{dt}(\rho_{a,\alpha}^{(k)} S^{(k)}_{\alpha}) = \sum_{j \neq k} \rho_{a,\alpha}^{(k,j)} (S_{\alpha}^{(k,j)} f_{\alpha}^{(k,j)} + g_{\alpha}^{(k,j)}) \]

4.1 Closure

➢ Unknowns

\[ V^{(k)}_{\alpha} \quad \rho_{a,\alpha}^{(k)} \quad f^{(k)}_{\alpha} \quad \mathcal{M}_{a,\alpha}^{(k)} \]

➢ Material behavior

- Heterogeneous solid dissolution

\[ \mathcal{M}_{a,\alpha}^{(k)}(t) = -k_s^{(k)} \left( c_{\text{HNO}_3}^{(k)}(t) \right)^m f_{a}^{(k)}(t) \]

\[ k_s^{(k)} = \frac{0.48 \exp(-0.091 \rho_s^{(k)}) \pi_{\text{UO}_2} \left( 5 \exp(-0.27 \rho_s^{(k)}) \right)^{(1-\pi_{\text{UO}_2})}}{100 \rho_s} \]

\[ \rho_s := \frac{x_{\text{UO}_2} \rho_{\text{UO}_2} + x_{\text{N}_2} \rho_{\text{N}_2} + x_{\text{FP}} \rho_{\text{FP}} + x_{\text{FP}} \rho_{\text{FP}}}{m_2 = 2(2-x_{\text{UO}_2})} \]

- Overall reaction mechanism

\[
\begin{align*}
\text{UO}_2^{(s)} + 2.7 \text{HNO}_3^{(aq)} & \xrightarrow{100^\circ C} \text{UO}_2(\text{NO}_3)_2^{(aq)} + 0.7 \text{NO}_2^{(g)} + 1.3 \text{H}_2\text{O}^{(aq)} & (\text{CHNO}_3 \leq 8 \text{ M}) \\
\text{UO}_2^{(s)} + 4 \text{HNO}_3 & \xrightarrow{100^\circ C} \text{UO}_2(\text{NO}_3)_2^{(aq)} + 2 \text{NO}_2^{(g)} + 2 \text{H}_2\text{O}^{(aq)} & (\text{CHNO}_3 > 8 \text{ M}) \\
\text{PuO}_2^{(s)} + 4 \text{HNO}_3 & \xrightarrow{100^\circ C} \text{Pu}(\text{NO}_3)_4^{(aq)} + 2 \text{H}_2\text{O}^{(aq)} \\
\text{FP}^{18.1(\text{s})} + 2.36 \text{HNO}_3 & \xrightarrow{100^\circ C} \text{FP}(\text{NO}_3)_2^{2.36} + 1.2 \text{H}_2\text{O}^{(aq)}
\end{align*}
\]
Unknwonns

\[ V_{\ell}^{(k)} \quad V_{s}^{(k)} \quad f_{\ell}^{(k)} \quad \rho_{\text{H}_2\text{O},\ell}^{(k)} \quad \rho_{\text{HNO}_3,\ell}^{(k)} \quad \rho_{\text{UO}_2\text{(NO}_3)_2,\ell}^{(k)} \quad \rho_{\text{Pu(NO}_3)_4,\ell}^{(k)} \quad \rho_{\text{FP(NO}_3)_2\text{,36},\ell}^{(k)} \]

Constitutive equations

\[ \rho_{s}^{(k)} = \text{cte} \quad M_{\text{H}_2\text{O},\ell}^{(k)}(M_{s}^{(k)}) \quad M_{\text{HNO}_3,\ell}^{(k)}(M_{s}^{(k)}) \quad M_{\text{UO}_2\text{(NO}_3)_2,\ell}^{(k)}(M_{s}^{(k)}) \quad M_{\text{Pu(NO}_3)_4,\ell}^{(k)}(M_{s}^{(k)}) \quad M_{\text{FP(NO}_3)_2\text{,36},\ell}^{(k)}(M_{s}^{(k)}) \]

Volume constraints

- Non-ideal liquid mixture

\[ \rho_{s}^{(k)}(t) := \sum_{a=1}^{5} \rho_{a,\ell}^{(k)} = R(T, P, x_{a=1,\ldots,5}), \]

- Flow resistance

\[ d_{t}V_{\ell}^{(k)} = -C(V_{\ell}^{(k)}, V_{s}^{(k)}, \Omega) + f_{\ell}^{(k+1)} + \mathcal{F}_{\ell}^{(k)} \]

4.1 Mathematical Problem

Find, for all time segments \( I_{i} \), \( i \in \mathbb{N}_{\text{trf}} \), between solid transfers the time-dependent functions \((\cdot): t \in I_{i} \rightarrow \mathbb{R}\)

\[ \rho_{a,\ell}^{(k)}, \quad V_{\ell}^{(k)}, \quad f_{\ell}^{(k)}, \quad V_{s}^{(k)}, \quad \text{for } \forall \ a = 1, \ldots, 5, \ k = 1, \ldots, 10 \]

satisfying the network equations

\[ \rho_{s}^{(k)} d_{t}V_{s}^{(k)} = M_{s}^{(k)}, \]

\[ d_{t}(\rho_{a,\ell}^{(k)} V_{\ell}^{(k)}) = -\rho_{a,\ell}^{(k)} f_{\ell}^{(k)} + \rho_{a,\ell}^{(k+1)} f_{\ell}^{(k+1)} + M_{a,\ell}^{(k)}, \]

and constitutive equations

\[ d_{t}V_{\ell}^{(k)} = -C(V_{\ell}^{(k)}, V_{s}^{(k)}, \Omega) + f_{\ell}^{(k+1)} + \mathcal{F}_{\ell}^{(k)}, \]

\[ \sum_{a=1}^{5} \rho_{a,\ell}^{(k)} = R(T, P, x_{a=1,\ldots,5}). \]
4.2 Mathematical Model Summary

Separation Process \( F(\cdot), G(\cdot) \): behavior/model

- \( x(t) \): state
- \( p(t) \): parameter
- \( q(t) \): coupling

Mechanics of separation
- Multistage transport

Thermodynamics
- Extent of separation
- Phase equilibria

Transport Balances

Kinetics
- Speed of separation
- Rate mechanisms

Mathematical Model

\[
F(x, \ldots, d_i^n, x, t; p(t), q(t)) = 0
\]
\[
G(x, t; p(t), q(t)) = 0
\]
\[
x(t_0) = x_0, \ldots, d_i^n, x = x^{(n)}_0; p(t_0) = p_0; q(t_0) = q_0
\]

5. Data Needed and Provided

- Plant-Level Modeling and Simulation of Used Fuel Dissolution, ORNL/TM-2012/375, 2012

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_{UO_2} )</td>
<td>0.96</td>
<td>Mass fraction of UO₂ in the pellets</td>
</tr>
<tr>
<td>( x_{PuO_2} )</td>
<td>0.02</td>
<td>Mass fraction of PuO₂ in the pellets</td>
</tr>
<tr>
<td>( x_{FeO_{14}} )</td>
<td>0.02</td>
<td>Mass fraction of FPPO₄ in the pellets</td>
</tr>
<tr>
<td>( \tau )</td>
<td>20 min</td>
<td>Solid transfer period</td>
</tr>
<tr>
<td>( d_p )</td>
<td>1.1 cm</td>
<td>Initial diameter of the pellets</td>
</tr>
<tr>
<td>( N_p(0) )</td>
<td>378</td>
<td>Initial number of pellets</td>
</tr>
<tr>
<td>( f )</td>
<td>0.33</td>
<td>Solid surface roughness factor</td>
</tr>
<tr>
<td>( j_{L}^{(i)} )</td>
<td>2.0 L/min</td>
<td>Volumetric liquid flow rate of the rinse stream to the discharge (rinses) compartment</td>
</tr>
<tr>
<td>( V_o )</td>
<td>21 L</td>
<td>Yield volume parameter in the flow capacity function</td>
</tr>
<tr>
<td>( j_{F}^{(i)} )</td>
<td>3.1 L/min</td>
<td>Volumetric liquid flow rate of the feed stream in the penultimate compartment ( (i = 9) )</td>
</tr>
<tr>
<td>( \rho_{(i)}^{(k),r,Na_2SO_4} )</td>
<td>9.7 M</td>
<td>Initial nitric acid in the acid rinse stream in the penultimate compartment</td>
</tr>
<tr>
<td>( \rho_{(i)}^{(k),Na_2SO_4} )</td>
<td>35.6 M</td>
<td>Initial nitric acid in the acid rinse stream in the penultimate compartment</td>
</tr>
<tr>
<td>( \rho_{(i)}^{(k),Na_2SO_4} )</td>
<td>23 kg</td>
<td>Initial load of solids in the first compartment</td>
</tr>
</tbody>
</table>

\( \rho_{a,k}^{(k)}, V_{k}, f_{k}, V_{k}^{(k)}, V_{k}^{(k)} \)

Time depended unknowns
6. Solution Method and Results

➢ Programmed in Octave (2,000 lines w/ comments) and MATLAB

➢ Solution of Resulting Non-Linear Differential Algebraic Equations

\[
\frac{dx}{dt}, x, p(t), q(t) = 0 \\
G(x, p(t)) = 0 \\
H(x, p(t)) = 0
\]

Robust Solvers
DASPK, DASSL
DASPKSO (parallel versions)

➢ Programmed in Octave (2,000 lines w/ comments) and MATLAB

6.1 Results 1.7 t/d LWR Fuel

Oak Ridge National Laboratory Report ORNL/LTR-2014/107 pp. 33
6.2 Results 1.7 t/d LWR Fuel

![Graph showing liquid volume flow rate and liquid mass density over time.]

6.3 Results 1.7 t/d LWR Fuel

![Graph showing concentrations of UO₂(NO₃)₂ and HNO₃ over time.]

Oak Ridge National Laboratory Report ORNL/LTR-2014/107 pp. 1-33
6.4 Results 1.7 t/d LWR Fuel

6.5 Results 1.7 t/d LWR Fuel
6.6 Results 1.7 t/d LWR Fuel

6.7 Results 1.7 t/d LWR Fuel
6.8 Results 1.7 t/d LWR Fuel

7) Verification Method
No rigorous verification program done

8) Uncertainty Quantification
Collaboration with Dan Cacuci on Facility Modeling planned

9) Fidelity Improvement
There are different directions for improvement. Experimental data would be extremely helpful to guide what to do next.

10) Model Transferability
Other dissolution processes on different equipment can be treated by this method. Voloxidation has some commonality that can be explored.

- Plant Level Modeling and Simulation of Used Fuel Voloxidation, ORNL/TM-2012/508, 2012
Summary

➢ Common modeling approach for plant-level processes

• Provided rapid prototyping and testing of a dissolver module
• MATLAB version coupled with Sandia SSPM Simulink application

➢ References: ORNL reports (email dealmeidav@ornl.gov)

• Plant-Level Modeling and Simulation of Used Fuel Dissolution, ORNL/TM-2012/375, 2012
• Progress on Plant-Level Modeling and Simulation of Used Fuel Dissolution: Startup Condition with Quasi-Developed Flow and Varying Acid Concentration, ORNL/LTR-2013/437, 2013
References


Valmor F. de Almeida. Progress on plant-level modeling and simulation of used nuclear fuel dissolution: Startup condition with quasi-developed flow and varying acid concentration. Technical Manuscript ORNL/LTR-2013/437, Oak Ridge National Laboratory, Tennessee, TN 37831-6181, U.S.A., September 2013. Also available by request to dealmeidav@ornl.gov.