OAK RIDGE NATIONAL LABORATORY
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# FY 2007 LDRD Director's R&D Progress Summary

### Proposal Title: Developing a Science Base for Fuel Reprocessing Separations in the Global Nuclear Energy Program

### July 11, 2007

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ORNL/TM-2007/114

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# FY 2007 LDRD DIRECTOR’S R&D PROGRESS SUMMARY

## PROPOSAL TITLE: DEVELOPING A SCIENCE BASE FOR FUEL REPROCESSING SEPARATIONS IN THE GLOBAL NUCLEAR ENERGY PROGRAM

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## Project Description

This work is aimed at developing an experimentally validated computational capability for understanding the complex processes governing the performance of solvent extraction devices used for separations in nuclear fuel reprocessing. These applications pose a grand challenge due to the combination of complicating factors in a three-dimensional, turbulent, reactive, multicomponent, multiphase/interface fluid flow system. The currently limited process simulation and scale-up capabilities provides uncertainty in the ability to select and design the separations technology for the demonstration plan of the Global Nuclear Energy Partnership (GNEP) program. We anticipate the development of science-based models for technology development and design. This project will position ORNL to address the emerging opportunity by creating an expandable process model validated experimentally.

## Scientific/Technical Accomplishments

This project has three major thrusts, namely, a prototype experimental station, a continuum modeling and simulation effort, and molecular modeling and kinetics support. Excellent progress has been made in corresponding activities in this first year in: 1) defining, assembling, and operating a relevant prototype system for model validation; 2) establishing a mathematical model for fluid flow and transport; 3) deploying sub-scale molecular modeling.

*1. Prototype experimental station:* The purpose of this activity is to establish a realistic, well defined, and instrumented prototype to provide insights for modeling through observations and data acquisition, and experimental data for model validation.

The prototype system assembled is representative of the UREX solvent extraction process, of interest to GNEP, consisting of a centrifugal contactor with a transparent housing, an organic feed of tri-butyl phosphate (TBP) in dodecane, aqueous feed of plain water, metering pumps, and a high-speed video camera with attached microscope (fig. 1).

**Figure 1:** *Centrifugal contactor setups showing transparent case, feed lines, pumps, microscope (right), zoom lens (left) and attached high-speed camera.*

The centrifugal contactor is a commercially available, 5-cm rotor diameter model typical of systems used in solvent extraction operations for nuclear reprocessing (fig. 2).

**Figure 2:** *Main components of a typical centrifugal contactor commercially used in solvent extraction processes.*

A relevant operating window has been established with rotation rate of 3600 rpm, total volumetric flow rate of 1200 ml/min when curved vanes are used, and 500 ml/min with straight vanes. The volumetric flow ratio of organic to aqueous may vary from 5-to-1 to 1-to-5 covering the range for extraction, scrubbing and stripping operations. High-speed visualizations of important flow conditions have been obtained in the 254-µm resolution length-scale at rotations up to 3000 rpm (fig. 3). Current activities are aimed at improving visualizations for cases at higher rotation rate through improved lighting and imaging techniques and equipment.

We have identified from high-speed visualization that air entrainment is significant and bubbles are polydispersed with a wide range of diameters (fig. 3A and D). This is notable, since air entrainment is typically overlooked in models developed so far. It is also noticeable that larger bubbles are under enough shear to promote deformation from a reference spherical shape (fig. 3D). For rotation rates of 3600 rpm when using straight vanes, the bulk of the flow in the mixing zone is fairly featureless in the range of 10:1 and 1:10 flow rate ratios of organic to aqueous in the 254 µm spatial resolution (figs. 3B-C). These observations are the first of its kind for centrifugal contactors and are invaluable for supporting the modeling and simulation effort. Visualization of flow regimes when using curved vanes were also made (fig. 3D), for comparison, at a field of view of 10 mm with sharp results at low rotation rates.

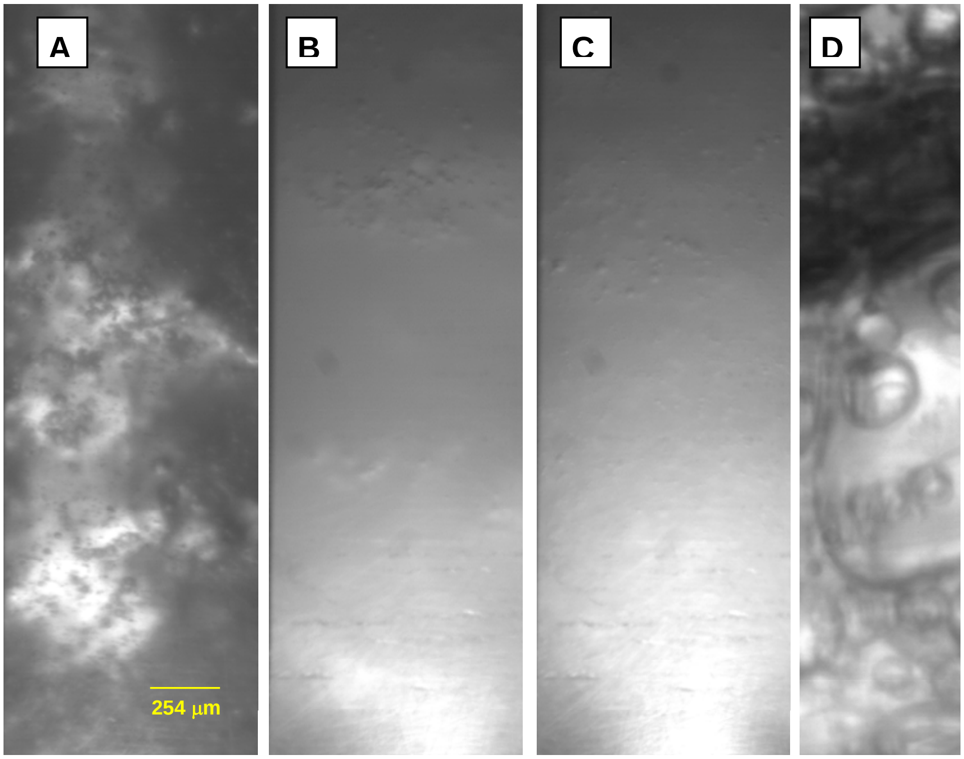

**Figure 3**: *Snapshots of flow in mixing zone of contactor. (A) Single-liquid water flow (700 mL/min, 3600 rpm; 1000 fps, exposure of 30 µs, and 29-mm vertical field of view), showing significant air entrainment in the flow. (B and C) 30% TBP in dodecane and water flow, 440 mL/min, B -10:1 organic to aqueous*

*flow ratio (O/A), C-1:10 O/A (3600 rpm, 1000 fps, exposure 30 $\mu$s, and 29-mm vertical field of view). The flow is relatively featureless, indicating drops of the dispersed phase are substantially smaller than the current resolution. (D) Dodecane-water mixture, 1200 ml/min, 5:1 O/A, 1800 rpm with curved vanes (2000 fps, exposure 30 $\mu$s, 10 mm vertical field of view).*

2. *Continuum modeling and simulation effort:* A critical aspect of a high-fidelity model is a realistic geometry. Based on our prototype system we have mapped the entire geometry of our centrifugal contactor with resolution up to 1 mm. All pieces of the centrifugal contactor were individually constructed via CAD (fig. 4). The rotor head is the most complex flow path followed by the flow at the top of the vanes under the foot of the rotor assembly.

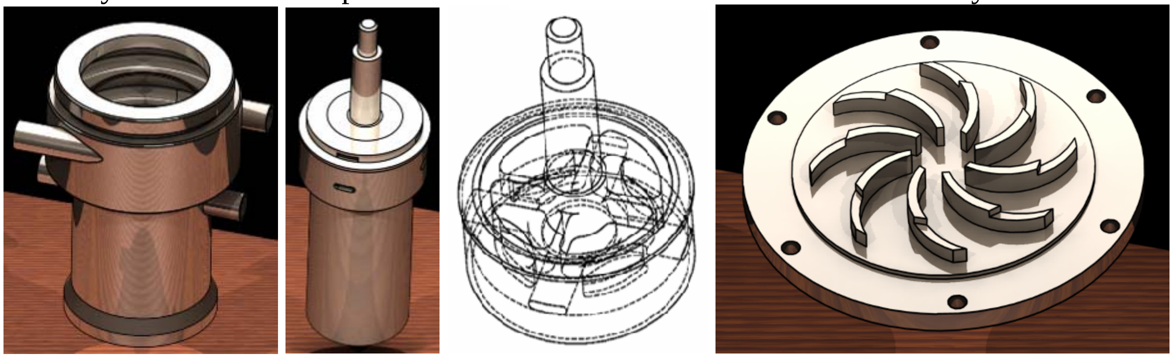

**Figure 4:** *Main components of the centrifugal contactor CAD model. From left to right: case, rotor assembly, rotor head, and vanes.*

After assembling all the parts into one solid model the complement volume was taken so the entire region of space available to the flow is obtained (fig. 5). This is the mathematical domain wherein the governing equations of fluid flow and species transport must be solved on. The boundary surfaces of the model all need to be marked so they become accessible for the application of mathematical boundary conditions, and the whole domain needs to be partitioned with a valid mesh for discretization of the mathematical problem (fig. 6). Current work in the continuum modeling and simulation effort is focused on solving the incompressible Navier-Stokes equations on the centrifugal contactor domain via a Galerkin method with mixed finite element basis functions. The single-phase flow solver will be in operation this year and work towards solving the three-phase flow model will start next year.

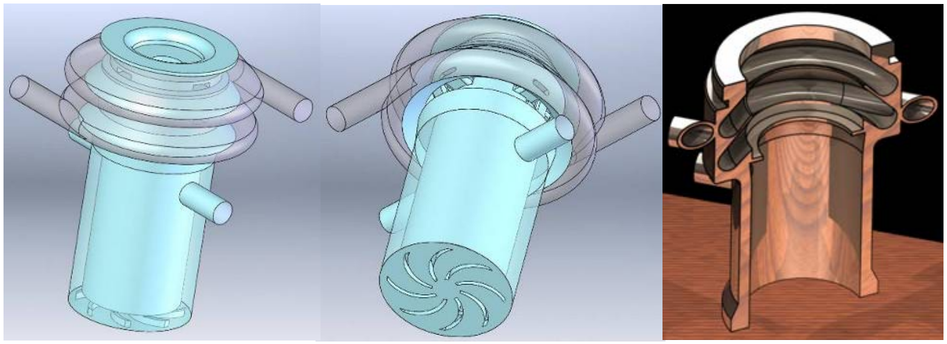

**Figure 5:** *Mathematical domain occupied by the fluid flow (left and center). Corresponding solid case that holds the fluids (right).*

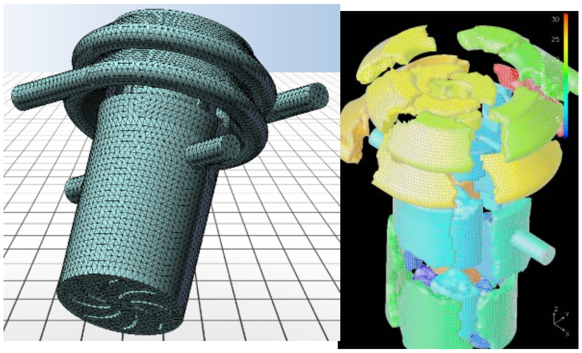

**Figure 6:** Boundary conditions on inflow, outflow and rotating surfaces, and meshing (left). Subdomain decomposition for parallel processing (right).

3. *Molecular modeling and kinetics support:* The prototype system described above is motivated by the UREX process for extraction of uranium via TBP complexation uranyl nitrate. There is much insight to be gained, and needed quantitative information to be obtained, by performing molecular dynamics simulation on such a system. We have started molecular simulation studies of TBP-dodecane-water (fig. 7), and uranyl nitrate (fig. 8) systems. Preliminary results have confirmed the surfactant behavior of TBP. These simulations involving tens of thousands of atoms until equilibrium is achieved are performed at ORNL on a dedicated cluster during this development phase. Work continues towards simulations with larger number of atoms, longer times, and additional chemical species.

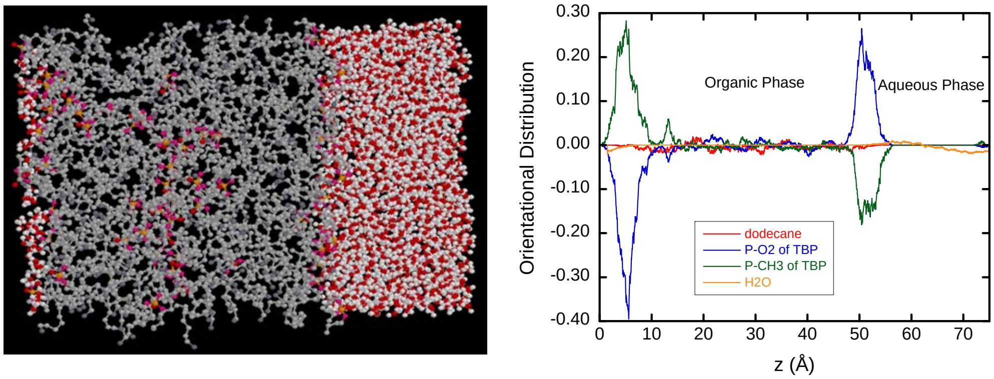

**Figure 7:** *30%-vol TBP-n-dodecane and water after 572 ps. Simulation with 216 dodecane molecues, 64 TBP, 1728 water. Colors: n-dodecane (gray), TBP phosphorous (orange), TBP oxygen (red), TBP butyl oxygen (pink), water H (white), and water O (red). The right plot predicts the orientation of the TBP molecules across the computational box; at the interface between aqueous and organic, the hydrocarbon legs point into the organic phase while the polar phosphoryl heads point into the water phase.*

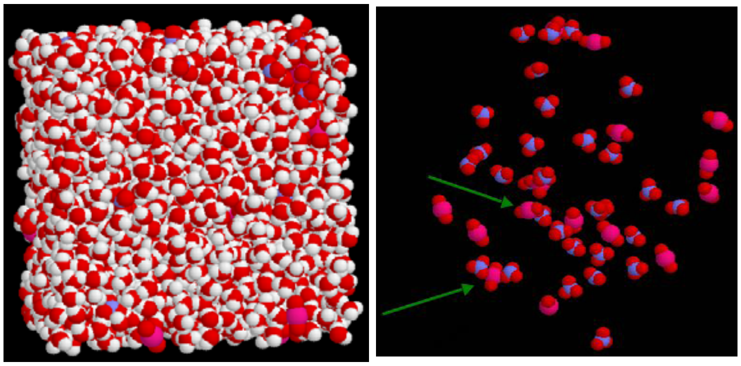

**Figure 8:** . Left: $UO_2$ (pink uranium, red: oxygen bonded to uranium), $NO_3$ (blue: nitrogen, red: oxygen bonded to nitrogen), and water as in Figure 7. Right: Arrows point to the formation of $UO_2(NO_3)_2$ and $(UO_2NO_3)^+$ .

Continued development of the

aforementioned three programs will provide a modern perspective for predicting the efficiency of solvent extraction of metals with applications to nuclear fuel reprocessing.

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