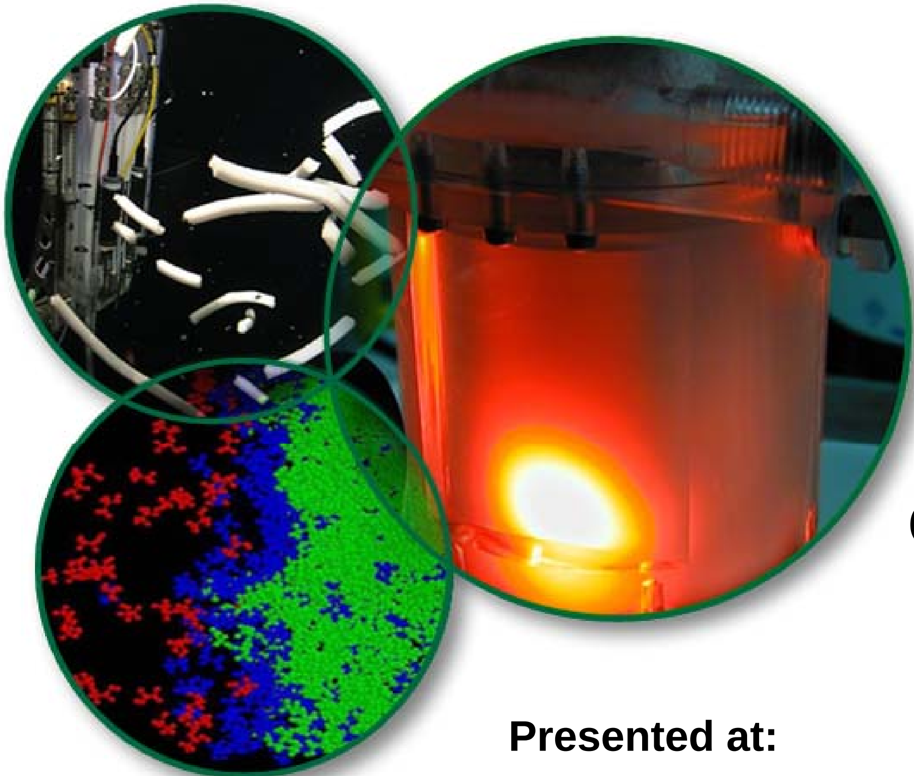
Role of Modeling and Simulation in Used Fuel Recycling



David DePaoli

Nuclear Science and Technology Division

Oak Ridge National Laboratory

Presented at:

Introduction to Nuclear Chemistry and Fuel Cycle Separations

Vanderbilt University

Aug 5, 2009

Oak Ridge National Laboratory

Outline

- **Introduction**
- **Some applications to date**
  - **Solvent extraction**
  - **Plant-level modeling**
  - **Agent design**
- **Key research needs**
- **Advancing to the future**
  - **NEAMS vision**
  - **Separations M&S development**

Used Nuclear Fuel Recycling Entails Many Interconnected Steps

Used fuel
varied composition
(burn-up, cooling time)

Products
meeting stringent specifications

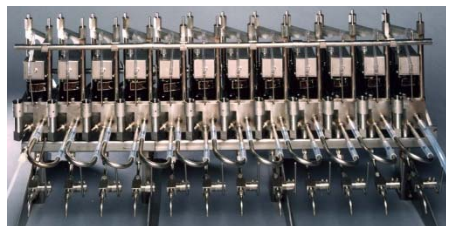
Environmental, safety, accountability constraints

shearing

dissolution

voloxidation

feed & accountability



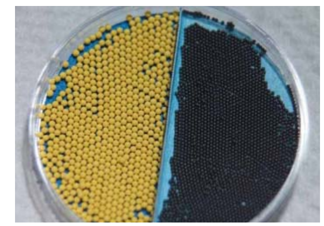
solvent extraction cycles

off-gas treatment

recovery systems

solidification

waste treatment



Fuel

Waste forms

- **Need new processes to meet future goals**
- **Emerging modeling and simulation capabilities can improve development and implementation** (better, cheaper, faster)

Benefits of modeling and simulation of nuclear reprocessing systems

- **Reduced cost of process development by guiding and minimizing the amount of experimental and piloting work required**
  - **Compare different separation and fuel cycle strategies**
  - **Develop new chemical processes with lower cost and waste generation**
- **Optimized system designs, with reduced design margins**
  - **Scale up with confidence**
  - **Reduce hot-cell footprint (surge capacity, throughput)**
  - **Process control**
- **Increase safety and acceptance of regulatory bodies**
- **Reduced risk of material diversion by providing accurate predictions of materials streams**

Modeling and simulation

- **Modeling is the development of an approximate mathematical description of physical and chemical processes at a given level of sophistication and understanding.**
- **Simulation utilizes computational m predictions of process performance**
- **"Together modeling and simulation**
  - **enhance understanding of know**
  - **provide qualitative/quantitative insights and guidance for experimental work, and**
  - **produce quantitative results that replace difficult, dangerous, or expensive experiments."**

Important Note:
Advanced modeling and simulation do not replace the need for theory or experiments!!!

(*Basic Research Needs for Advanced Nuclear Energy Systems,* http://www.sc.doe.gov/bes/reports/abstracts.html#ANES)

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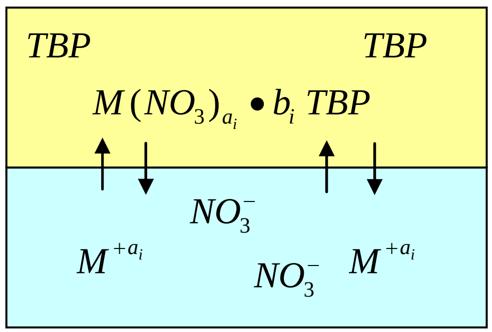
Modeling and simulation of nuclear separations has primarily focused on solvent extraction



$$M^{+a_i}_{(aq)} + a_i NO^-_{3(aq)} + b_i TBP_{(org)} \Leftrightarrow M(NO_3)_{a_i} \bullet b_i\, TBP_{(org)}$$

$$K_i = \frac{\left[M(NO_3)_{a_i} \bullet b_i\, TBP\right]_{org}}{\left[M^{+a_i}\right]_{aq} \left[NO_3^-\right]_{aq}^{a_i} \left[TBP\right]_{org}^{b_i}}$$

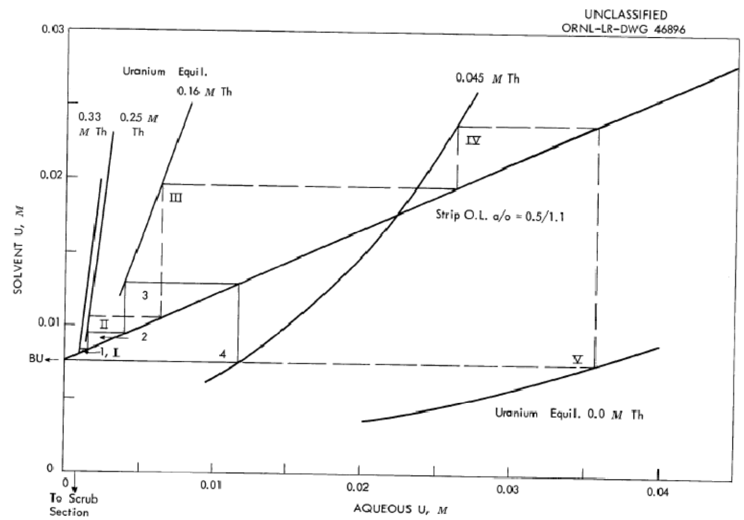


Fig. 3. Uranium diagram for strip section case for four stages shown by Arabic numerals; for five stages, by Roman numerals.

A. D. Ryon, ORNL-3045, 1961

- **Original predictions:**
  - **Graphical stage calculations using experimental equilibrium data and operating lines**

Existing models are based on empirical fits to experimental data

$$K_U^{'} = \frac{[UO_2(NO_3)_2 \bullet 2\ TBP]_{org}}{[UO_2{}^{2+}]_{aq}\ [NO_3^-]_{aq}^2\ [TBP]_{org}^2}$$

$$K_{Th}^{'} = \frac{[Th(NO_3)_4 \bullet 3\ TBP]_{org}}{[Th^{4+}]_{aq}\ [NO_3^-]_{aq}^4\ [TBP]_{org}^3}$$

$$K_H^{'} = \frac{[HNO_3 \bullet 3\ TBP]_{org}}{[H^+]_{aq}\ [NO_3^-]_{aq}\ [TBP]_{org}}$$

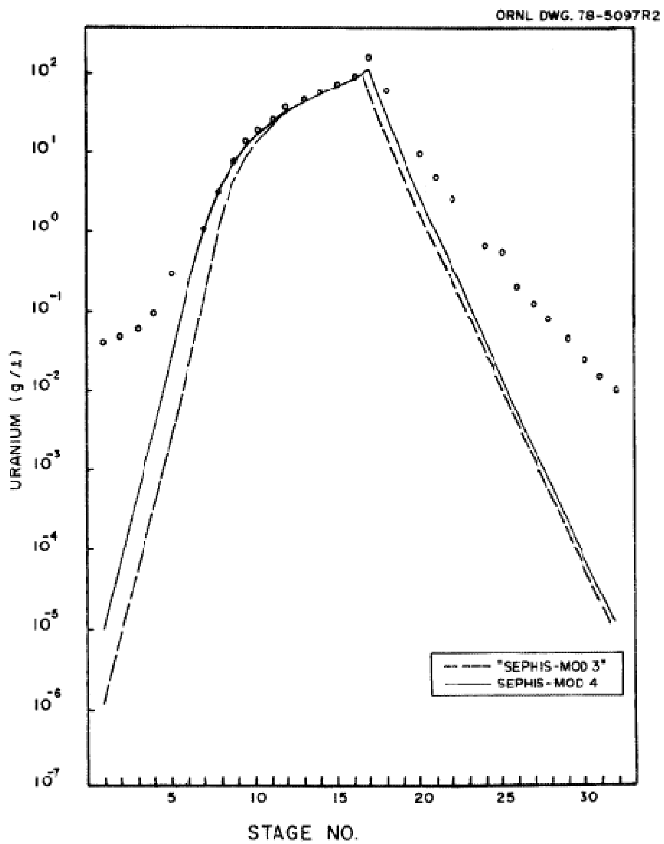
$$K_U^{'} = C_1 + C_2\ \mu + C_3\mu^2 + C_2\ \mu^3$$

$$K_{Th}^{'} = C_5 + C_6\ \mu + C_7\mu^2 + C_8\ \mu^3$$

$$K_H^{'} = C_9 + C_{10}\ \mu + C_{11}\mu^2 + C_{12}\ \mu^3$$

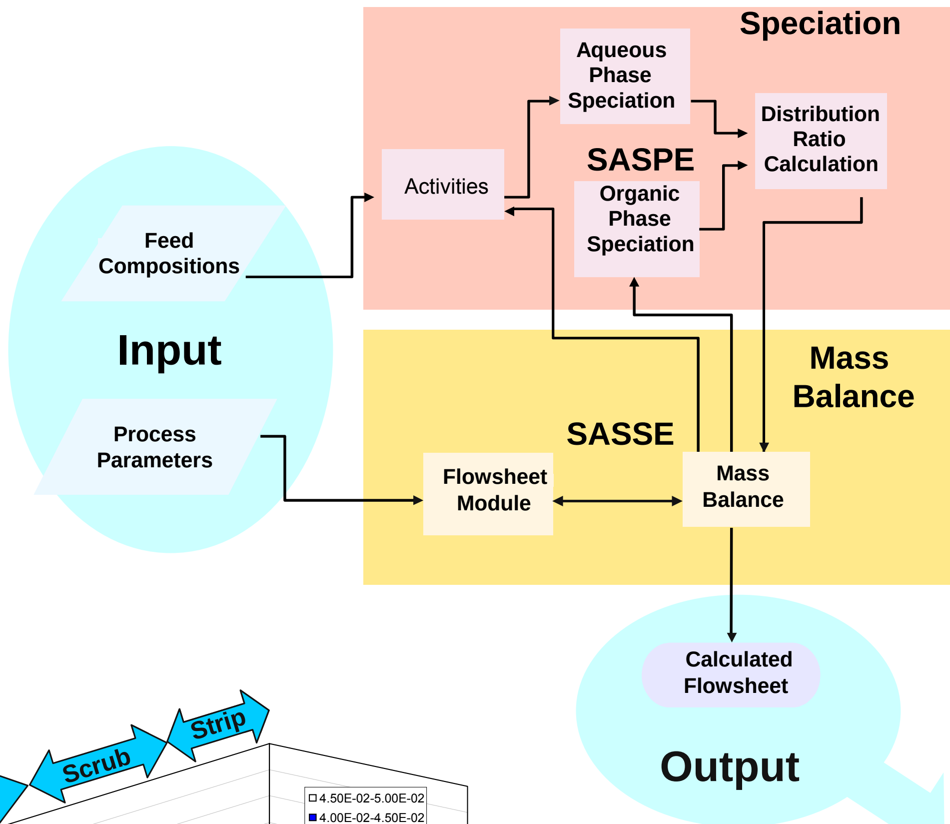
$$\mu \equiv [H^+] + 3[UO_2^{2+}] + 10[Th^{4+}]$$

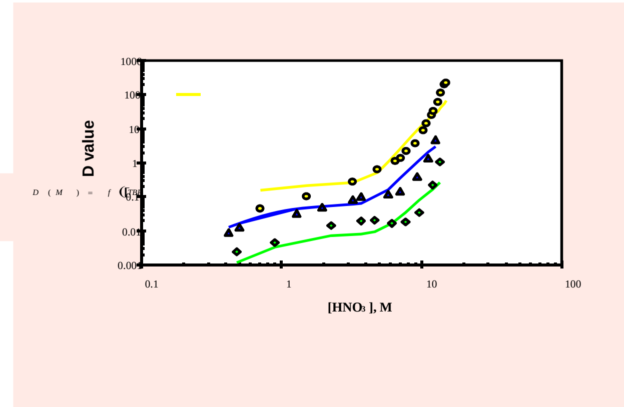
Rainey and Watson, 1975

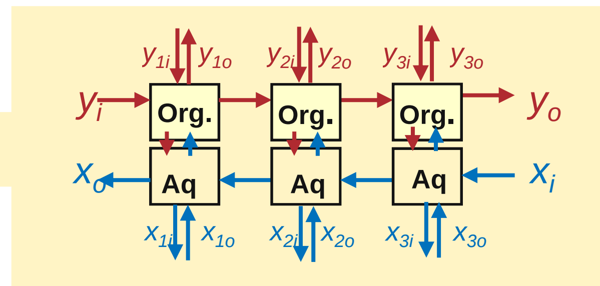


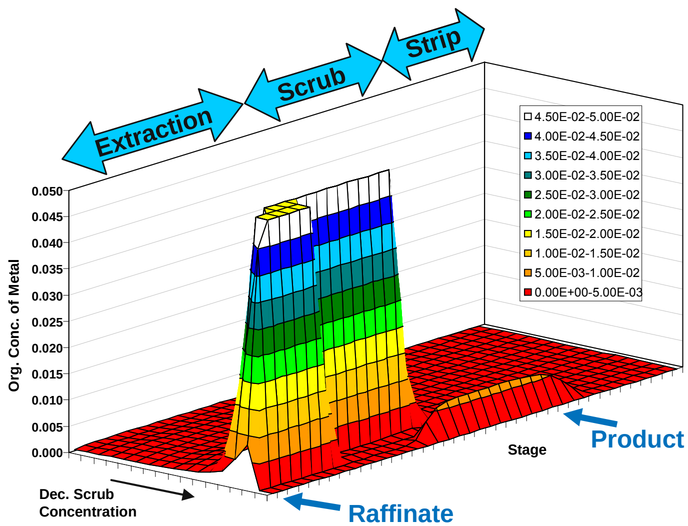
With good input data, good predictions are obtained – within conditions of fit

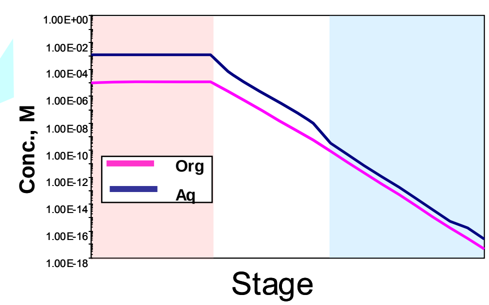
AMUSE Models Solvent Extraction







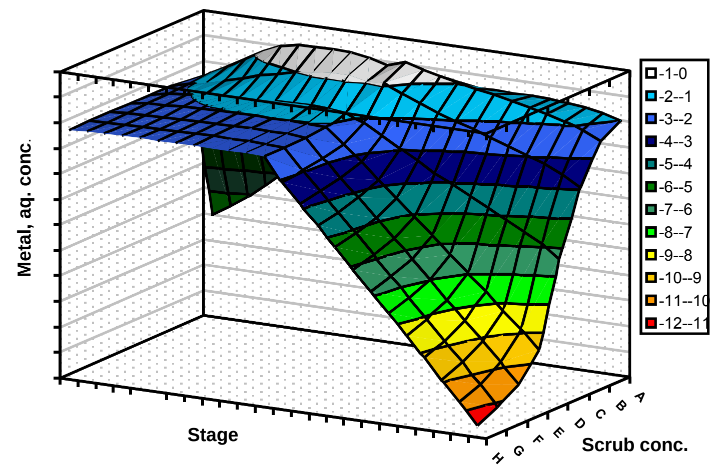


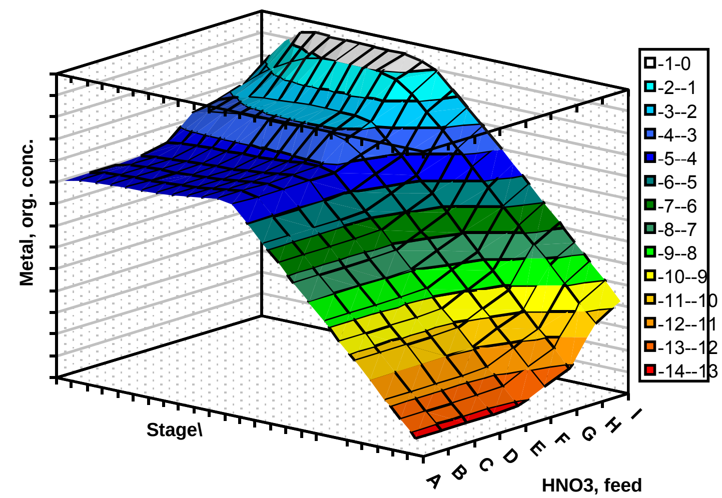


M. Regalbuto and C. Pereira, ANL

AMUSE has been used for process upset and product diversion analysis

- AMUSE was used to bracket the operational window for a plant conceptual design
  - Four fuel compositions were used as the initial process feed
    - *High and low burn-up; long- and short-cooled fuels*
  - Results showed little difference with cooling time but stronger effect due to burnup differences
- More recently AMUSE has been used to examine the effect of changing specific process parameters on the behavior of different elements
  - Design of instrumentation to track material
  - Process control
  - Product purity determination
  - Product diversion detection





Changes in feed composition lead to changes in the concentration profiles in the aqueous and organic phases

Current work – Linkage of AMUSE to plant-scale flowsheet in ASPEN

M. Regalbuto and C. Pereira, ANL

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  - Plant-level modeling
    - 1980’s example
    - Current efforts
  - Agent design
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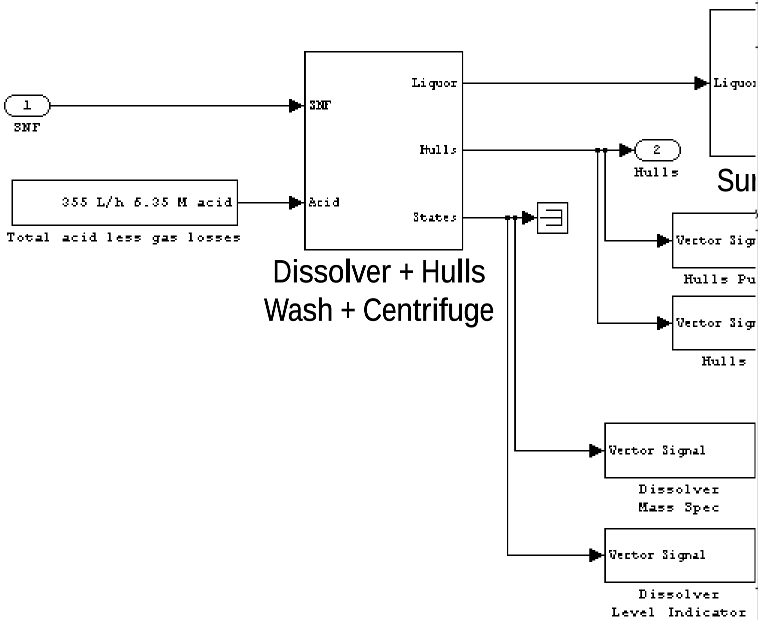
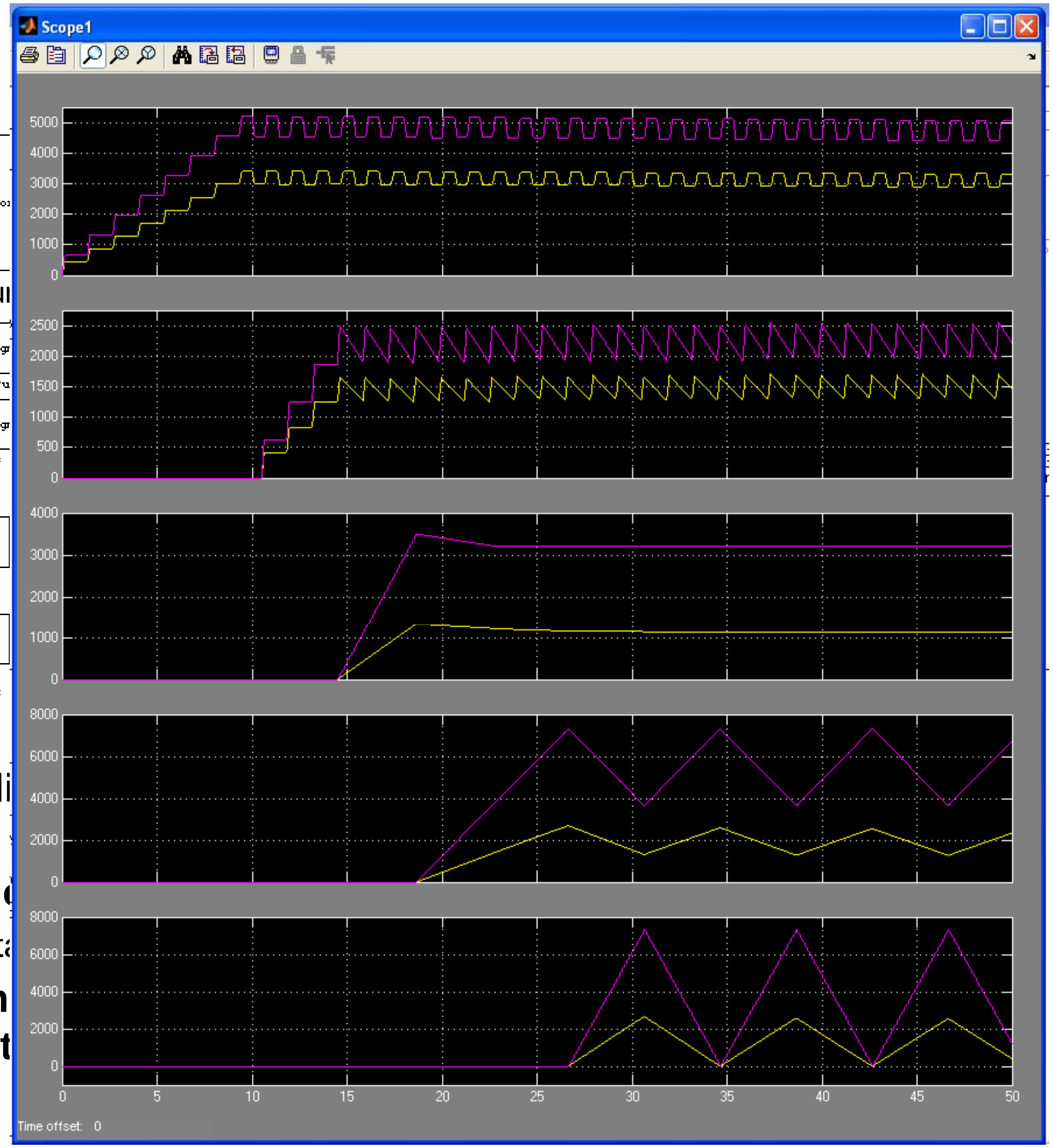
1980's – a full plant model

- **Consolidated Fuel Reprocessing Program - a complete plant simulation run in the Advanced System for Process ENgineering (ASPEN) simulator**
- **52 components tracked throughout a preconceptual design of a plant containing 32 systems and approximately 700 streams, including:**
  - **fuel cleaning and storage**
  - **disassembly and shearing**
  - **dissolution and feed preparation**
  - **hulls drying**
  - **feed clarification**
  - **feed preparation and accountability**
  - **solvent extraction**
  - **solvent extraction ancillary systems (concentration, backcycle, storage, high-activity waste concentration, solvent recovery)**
  - **process support (acid and water recovery and recycle, process steam, and sump)**
  - **product conversion**
  - **cell atmosphere cooling and purification**
  - **process off-gas treatment**
  - **vitrification**
  - **vitrification off-gas treatment**
- **Large simulation for computers of the time**
  - **broken down into three segments that were executed separately to achieve a steady-state material balance for the complete plant.**

R. T. Jubin, ORNL

Sandia Safeguards Performance Model

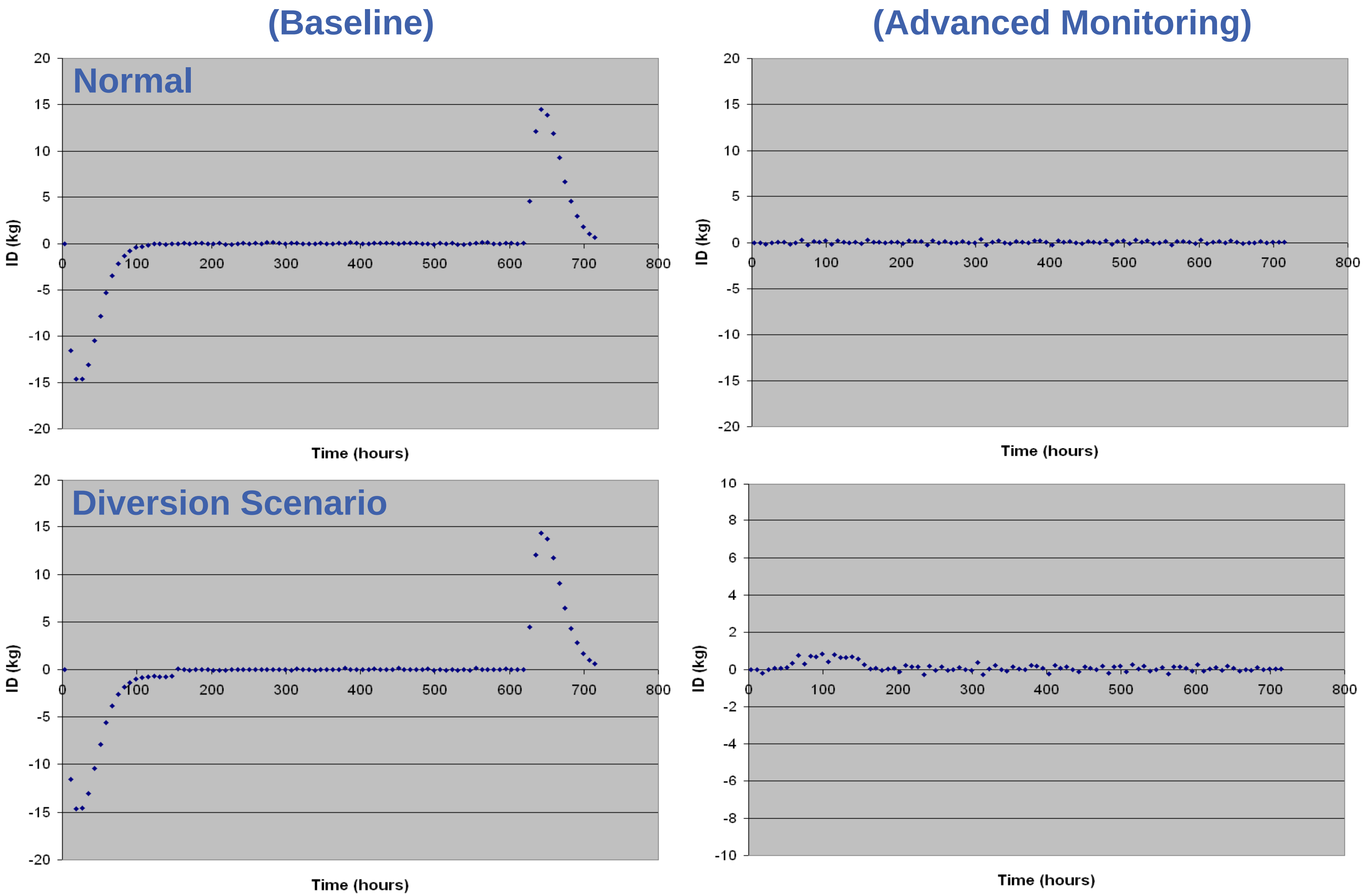




- The model uses the MatLab Simuli
  universities, and industry.
- The model tracks bulk flow rates,
  – Solvent extraction splits based on data
- Measurement blocks simulate a m
  tank or a mass spec measurement

B. Cipiti and N. Ricker, SNL

Pu Inventory Difference

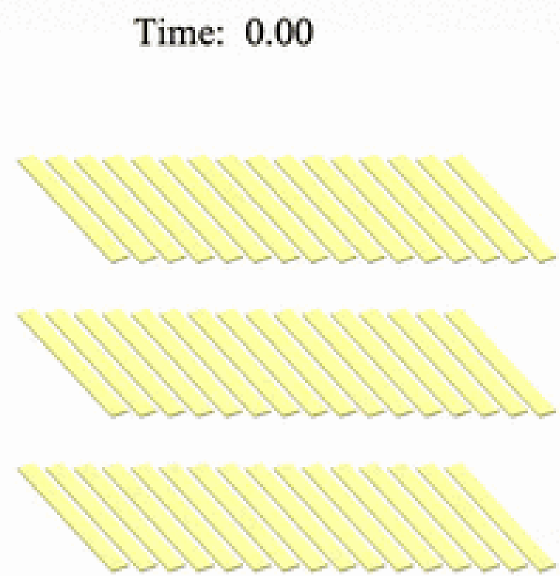


B. Cipiti and N. Ricker, SNL

Current state of separations process modeling

- **Solvent extraction most developed**
  - **Useful aid in process development and analysis**
  - **Semi-empirical fits**
  - **Many species not modeled well, or not at all**
  - **Leading codes use equilibrium stages**
  - **Current codes do not predict well:**
    - **Mass transfer and reaction kinetics effects**
    - **Effects of micellization, third-phase formation, radiolysis, etc.**
  - **Few transient codes**
- **Other important processes not well modeled**
  - **Legacy modules for some important unit operations are available**
    - **e.g., dissolver, acid recovery**
- **Full plant models are crude**
  - **Simple descriptions of important unit operations**
  - **Not fully transient**

Example of transient output from SEPHIS process model for U/Pu solvent extraction step.



Height of bars indicates concentration of uranium in organic (top) and aqueous (bottom) phases in a 48-stage mixer settler bank. Time indicates the time in minutes from the start of operation with zero concentration throughout the system.

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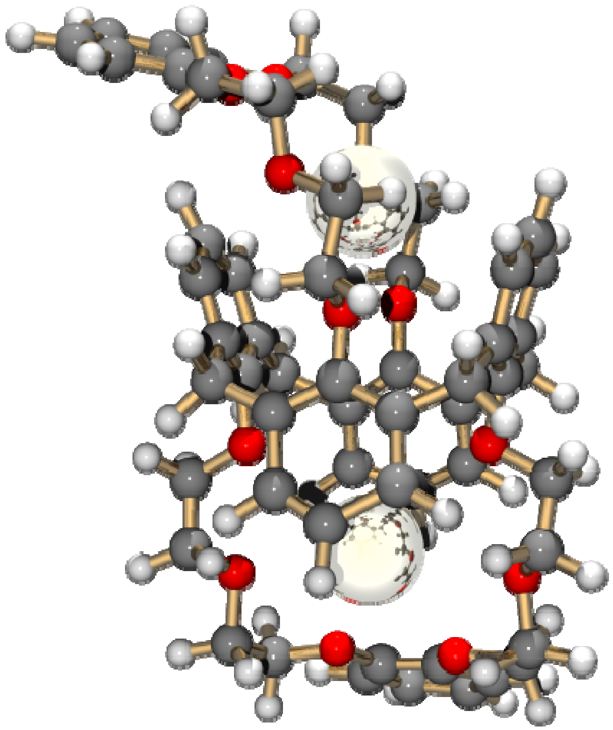
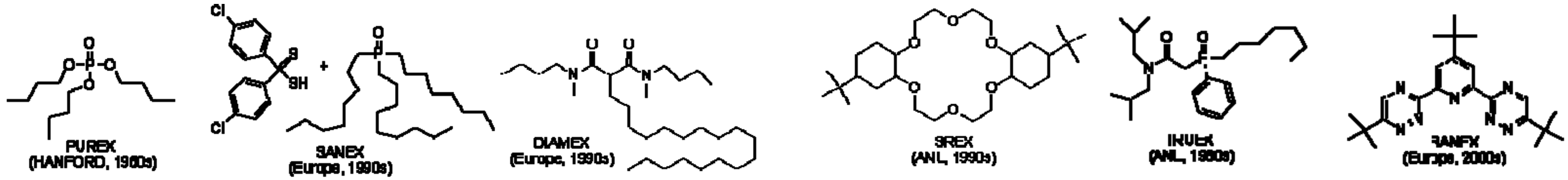
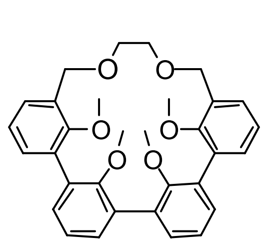


Sequestering agents are the basis for separations

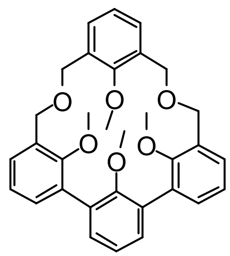


Influence of ligand architecture

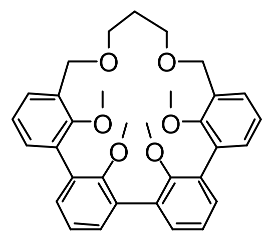
Large effects on binding affinity:



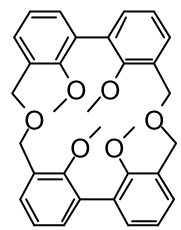
10^{10}



10^{6}

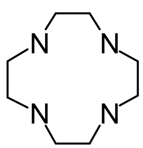


10^{5}

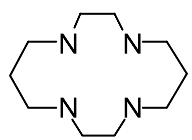


10^{3}

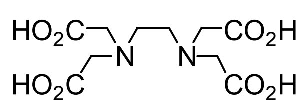
and significant impacts on selectivity:



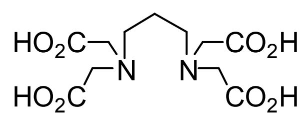
$Hg^{2+}/Cu^{2+} = 5$



$Cu^{2+}/Hg^{2+} = 10^4$



$Eu^{3+}/Al^{3+} = 13$

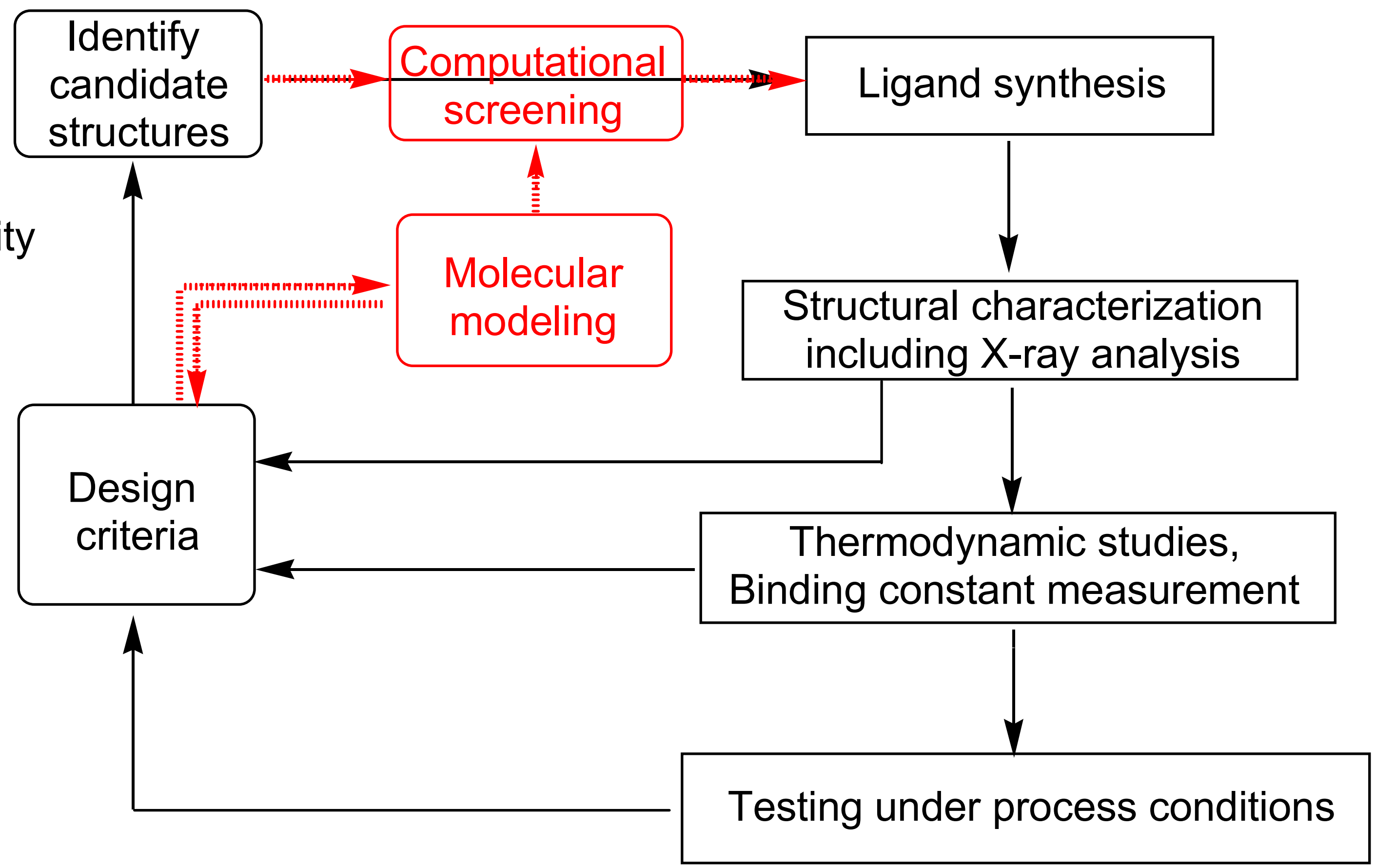


$Al^{3+}/Eu^{3+} = 500$

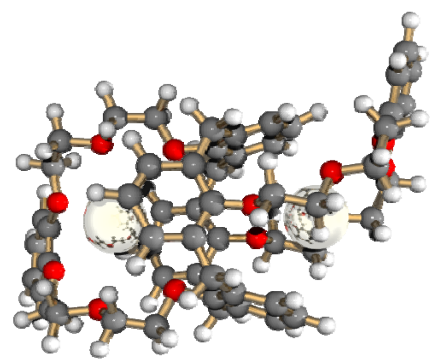
B.Hay, ORNL

Experimental development is slow and expensive

Optimize:
- binding affinity
- selectivity
- solubility
- stability
- cost



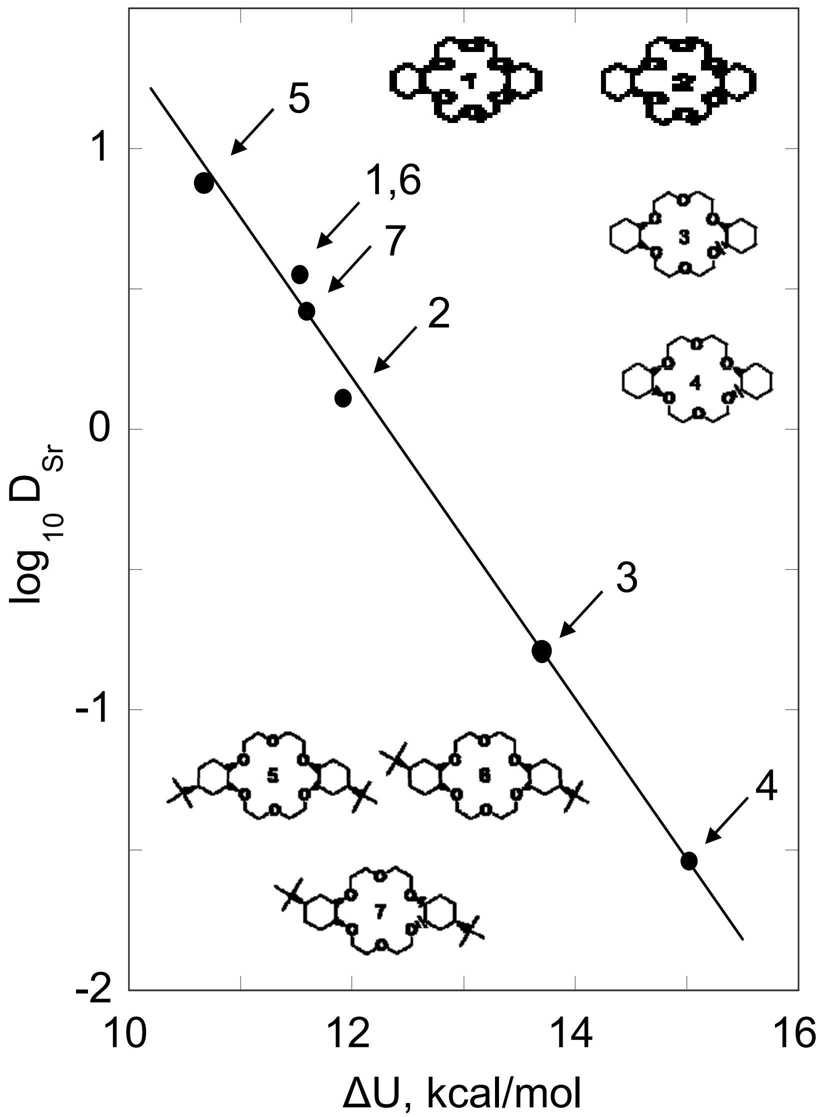
Computer-aided ligand development can acclerate progress



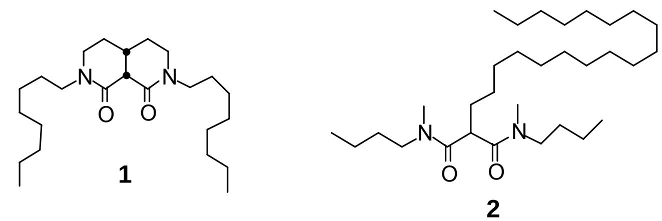
B.Hay, ORNL

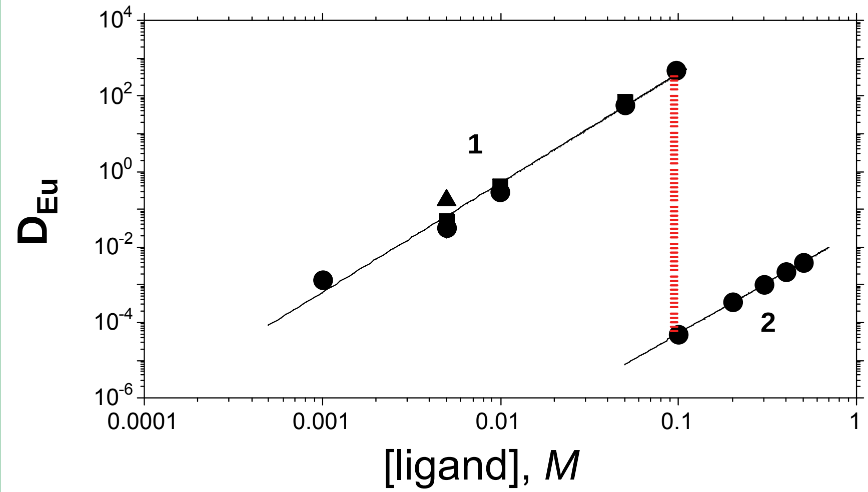
Experimental validation

Extraction of Sr^{2+} from 1M HNO_3 using 0.1 M ligand in n-octanol, 25 °C



Extraction into t-butylbenzene from aqueous solution containing 1 M $NaNO_3$, 1.5 mM HNO_3, 0.1 mM $Eu(NO_3)_3$, and 1-μL of ^{155}Eu tracer solution.





10 million times more effective

Lumetta, G. J.; Rapko, B. M.; Hay, B. P.; Gilbertson, R. D.; Weakly, T. J. R.; Hutchison, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 5644.

B.Hay, ORNL

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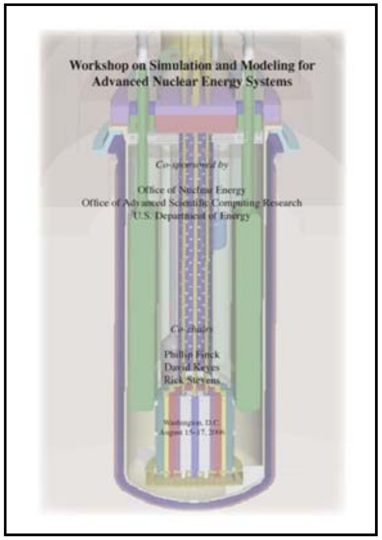
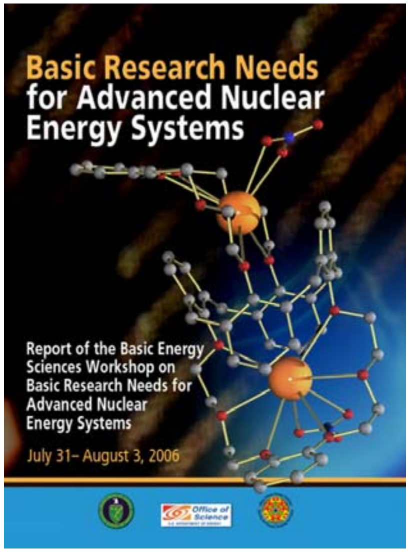
Recent workshops have identified key needs for contributions by modeling and simulation

- **Separations Challenges**
  - **Plant-scale simulation**
    - integrated toolset to enable full-scale simulation of a plant – chemistry, mass transport, energy input, and physical layout
    - dynamic plant models
  - **Computational fluid dynamics**
    - Multiple fluid phases, fully developed turbulence, non-Newtonian flows, interfacial phenomena, radical chemical processes due to the presence of ionizing radiation
  - **Predictive methods for thermodynamics and kinetics data as input to process simulators**
    - extend currently limited thermodynamics data reliably into broader ranges of parameter spaces
    - incorporate limited experimental data and use computational chemistry approaches
  - **Rational design of the separations system from first-principles physics and chemistry**
    - predict what molecules will have the desired properties and can be synthesized
    - reliably predict the properties of liquids, solvation, and kinetics in solution
  - **Connecting/crossing time and length scales, with uncertainty quantification**
    - access longer times without dramatic changes in theoretical and algorithmic approaches
    - span spatial regimes; critical regime is the mesoscale (1 nm-1 μm)
      - Below 1 nm, computational chemistry; above 1 μm, continuum approaches
  - **Data management and visualization**
    - Data must be captured, managed, integrated, and mined from a wide range of sources to enable the optimal design and operation of separation processes
    - Computer resources and access
    - Export control issues



http://www-fp.mcs.anl.gov/anes/SMANES/gnep06-final.pdf



http://www.sc.doe.gov/bes/reports/abstracts.html#ANES

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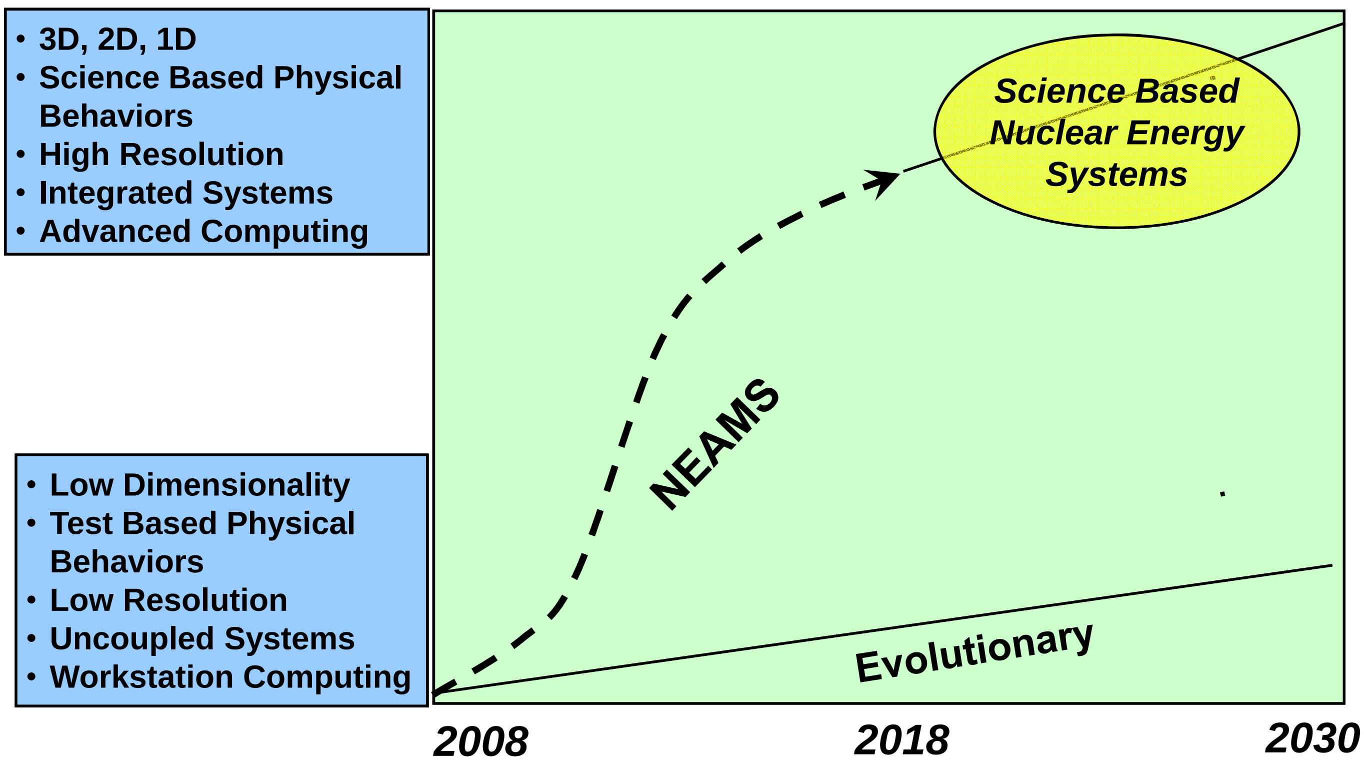
Stepping Up to the New Level of Understanding!

NEAMS Vision

To rapidly create, and deploy next generation, verified and validated nuclear energy modeling and simulation capabilities for the design, implementation, and operation future nuclear energy systems to improve the U.S. energy security future.



A. Larzelere, DOE-NE

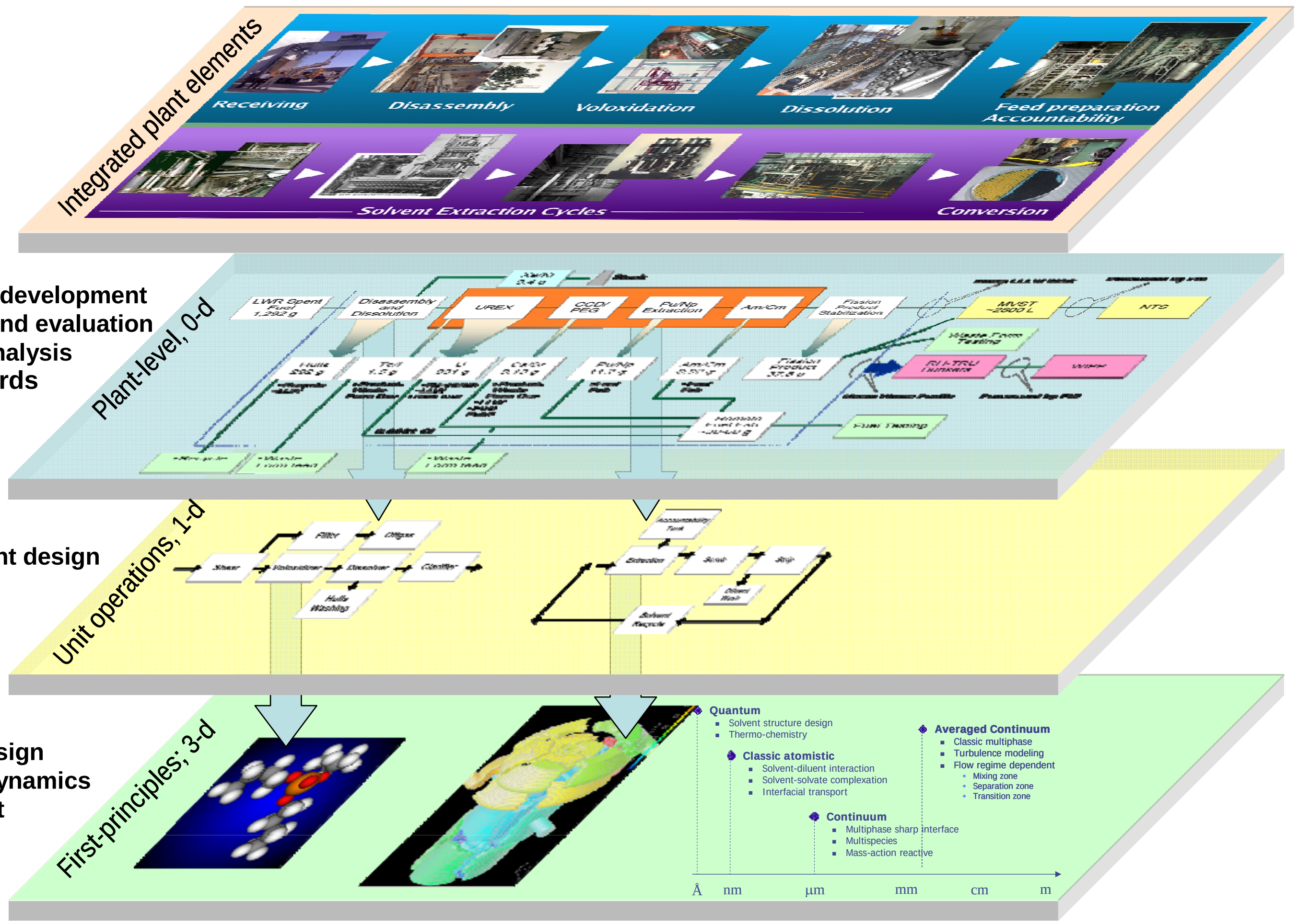
Separations M&S development

A primary goal is the development of an integrated plant model that allows dynamic simulations of the operation of separations plants of various configurations and operating conditions. Subscale models to provide required fidelity in chemical and physical processes.

Process development
Design and evaluation
Safety analysis
Safeguards

Equipment design
Safety
Cost

Agent design
Thermodynamics
Transport



Needs

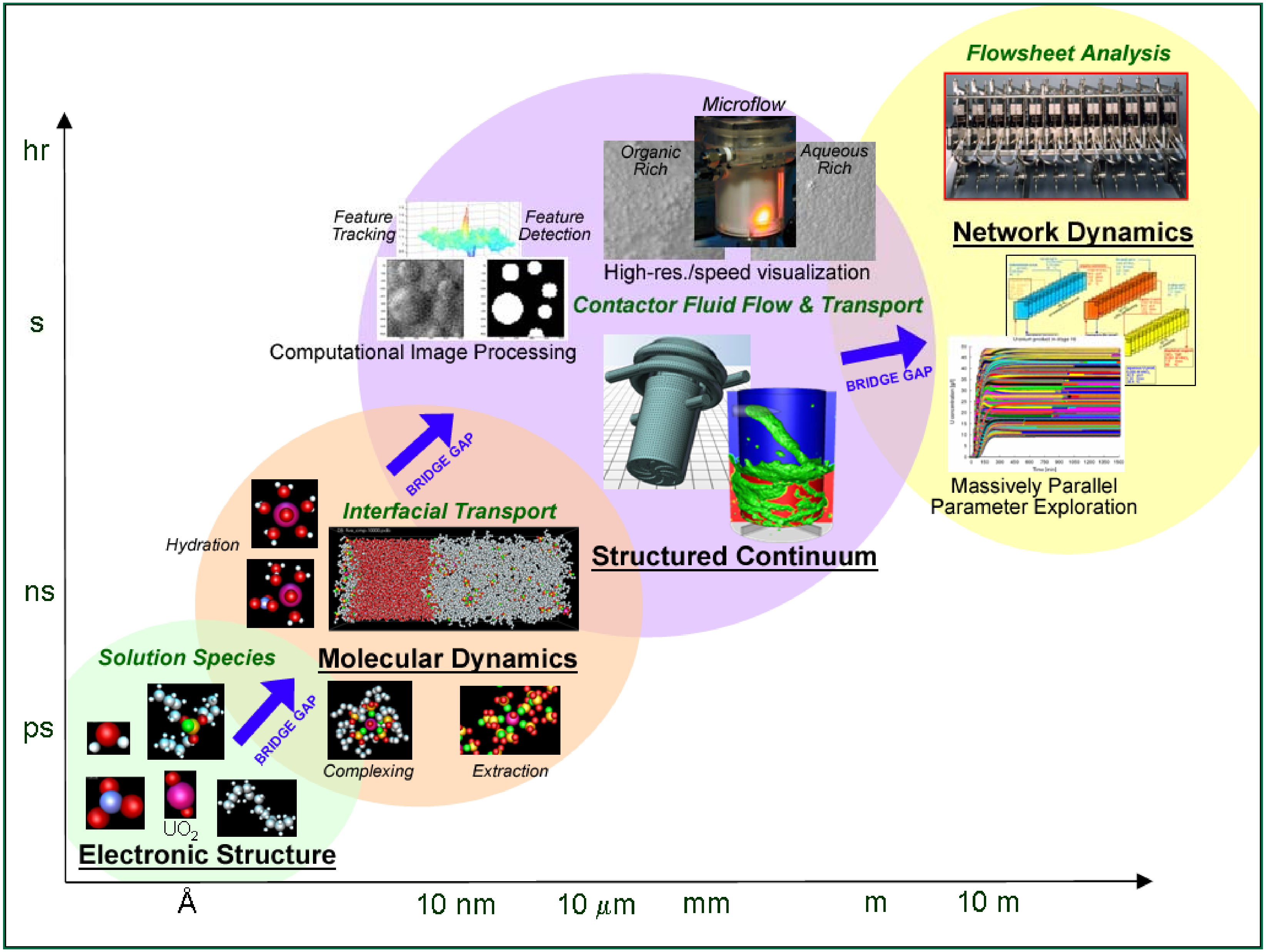
Requirements at plant level drive development of unit operations and subscale models

Integrated, transient plant simulator
Modern, expandable architecture
Bridging to detailed models

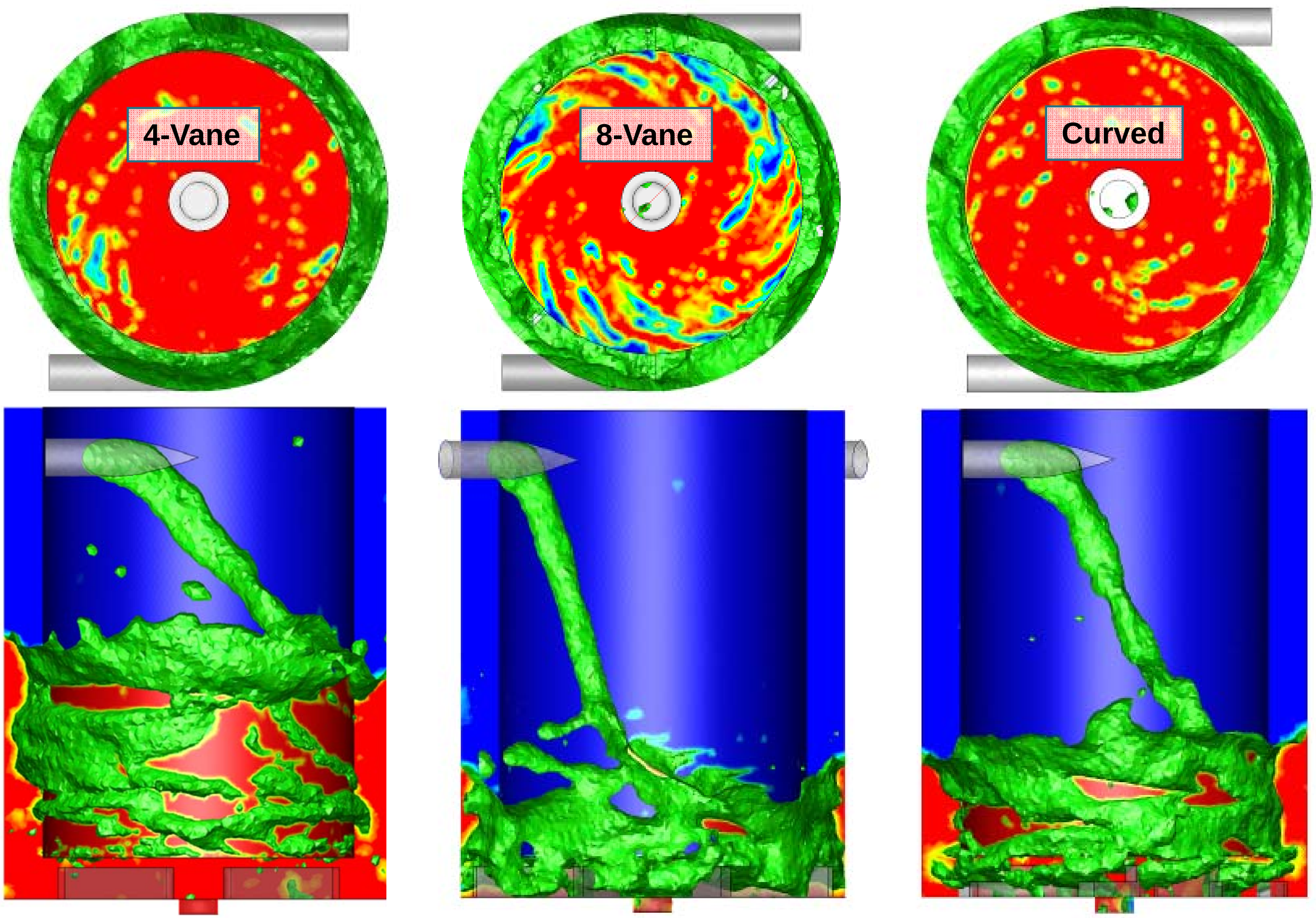
Improved models of multicomponent, multiphase unit operations
- Solvent extraction contactors, dissolvers, etc.
- Electrochemical separators
- Voloxidizers, calciners, etc.

Detailed models
- Thermodynamic and physical properties
- Chemistry fundamentals
- Transport in multiphase, reactive flows

Modern M&S for Solvent Extraction



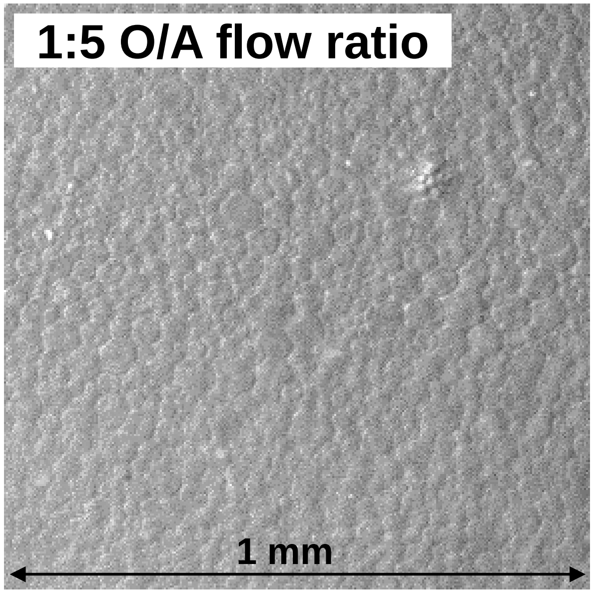
Comparison of effect of vane geometry on mixing



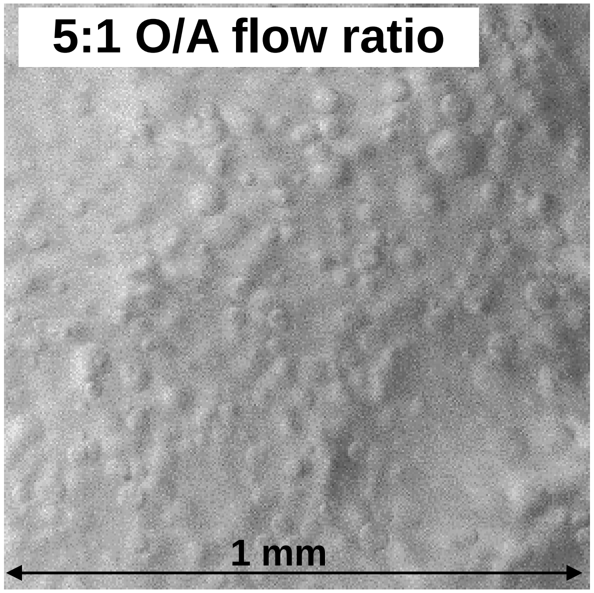
K. Wardle, ANL

Flow Regime Visualization

- **State-of-the-art high-speed digital video imaging, solid-state light, and optics provide needed insight**
- ***Sub-millimeter flow regime never seen before***
- ***Reveals significant time and length scales under realistic system and operating conditions***

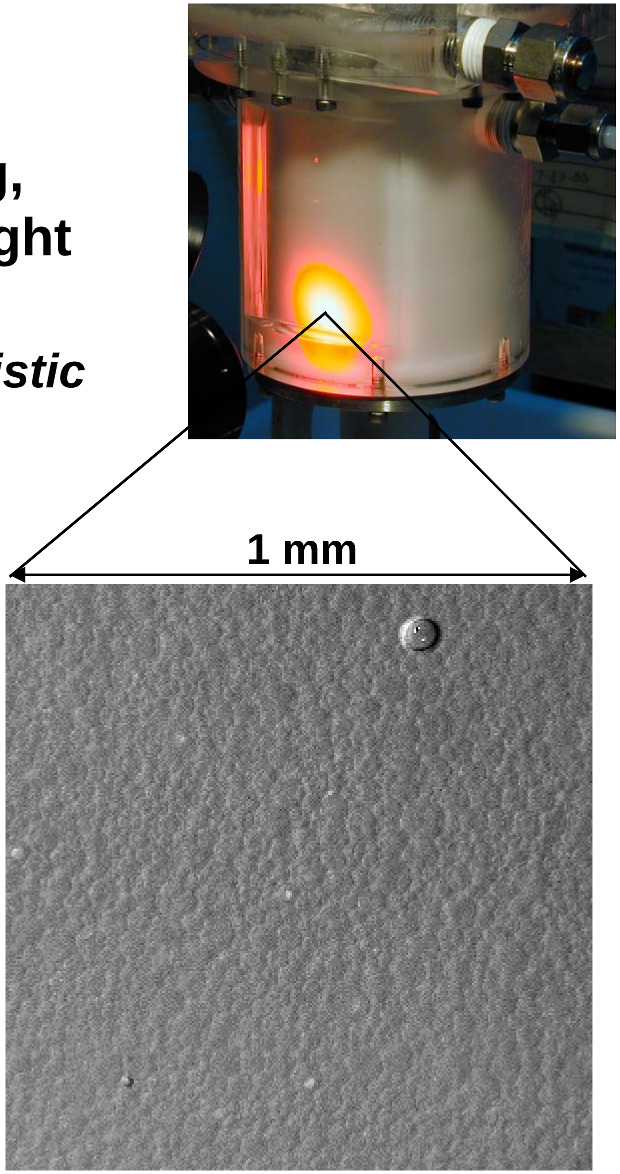


- **Elapsed time:** 37 ms



- **Elapsed time:** 18.5 ms

Organic-rich flow regimes possess greater air entrainment

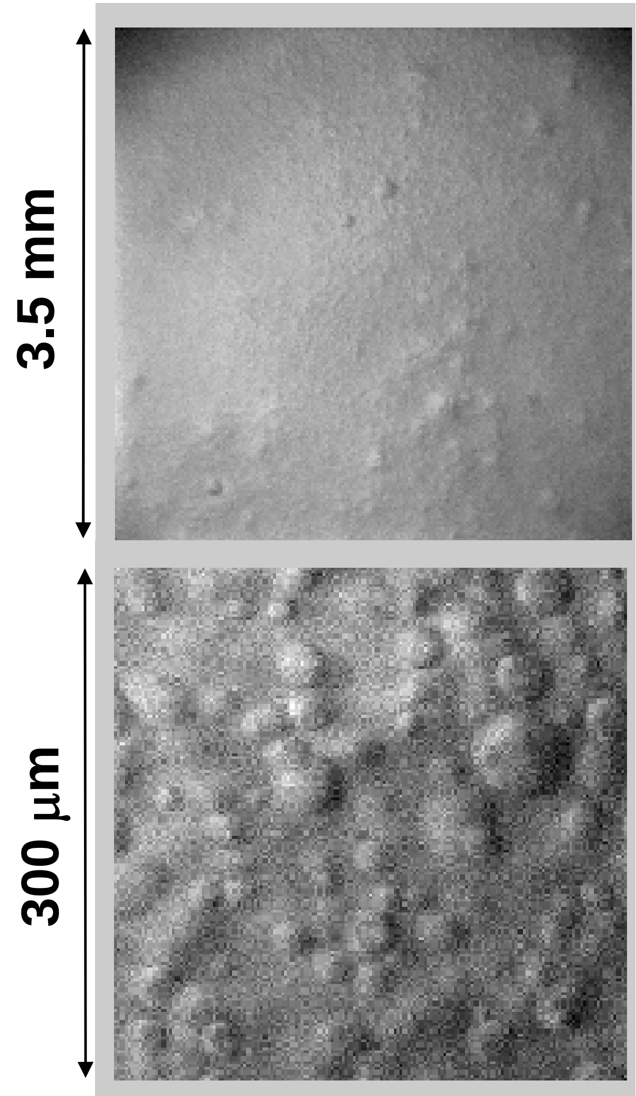


- ***These videos provide more than insight for modeling . . .***

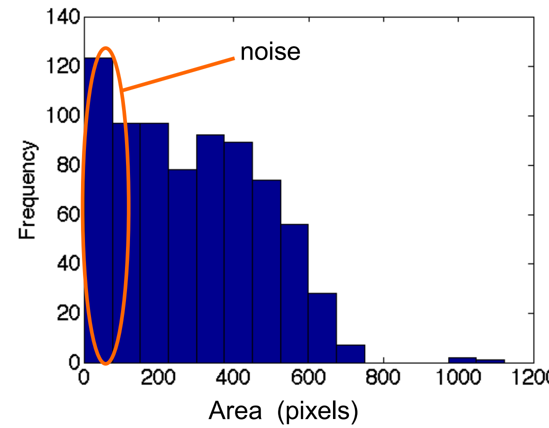
V. de Almeida, ORNL

Computer-Aided Image Analysis

- **Large data sets are obtained (8 GB for 1-s elapsed time)**
- **Can utilize powerful tools of computer image analysis (machine vision)**
- **Computing intensive – need to inspect every pixel and its vicinity**
- **Parallel computing can process large data sets on modest clusters**



Generate data useful for model development



- **Drop and bubble size distribution**
- **Velocity tracking**
- **Calibration of phase mixture turbulent momentum balance**

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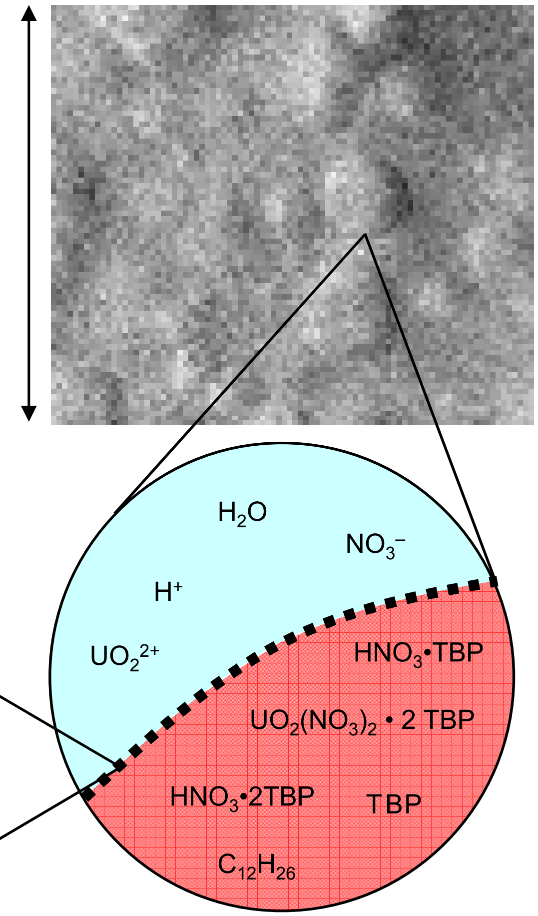
Chemical Transport

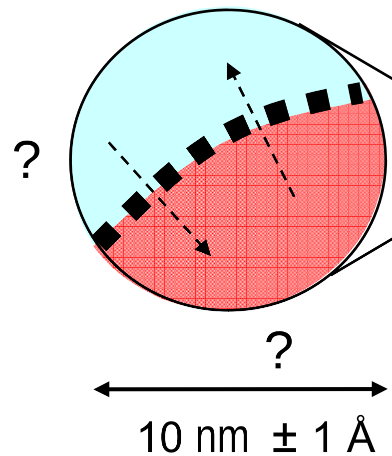
- Important chemical reactions occur at the interface

Challenges

- Lack of basic understanding of how species move across interfacial "region"
- Strongly coupled physical and chemical processes

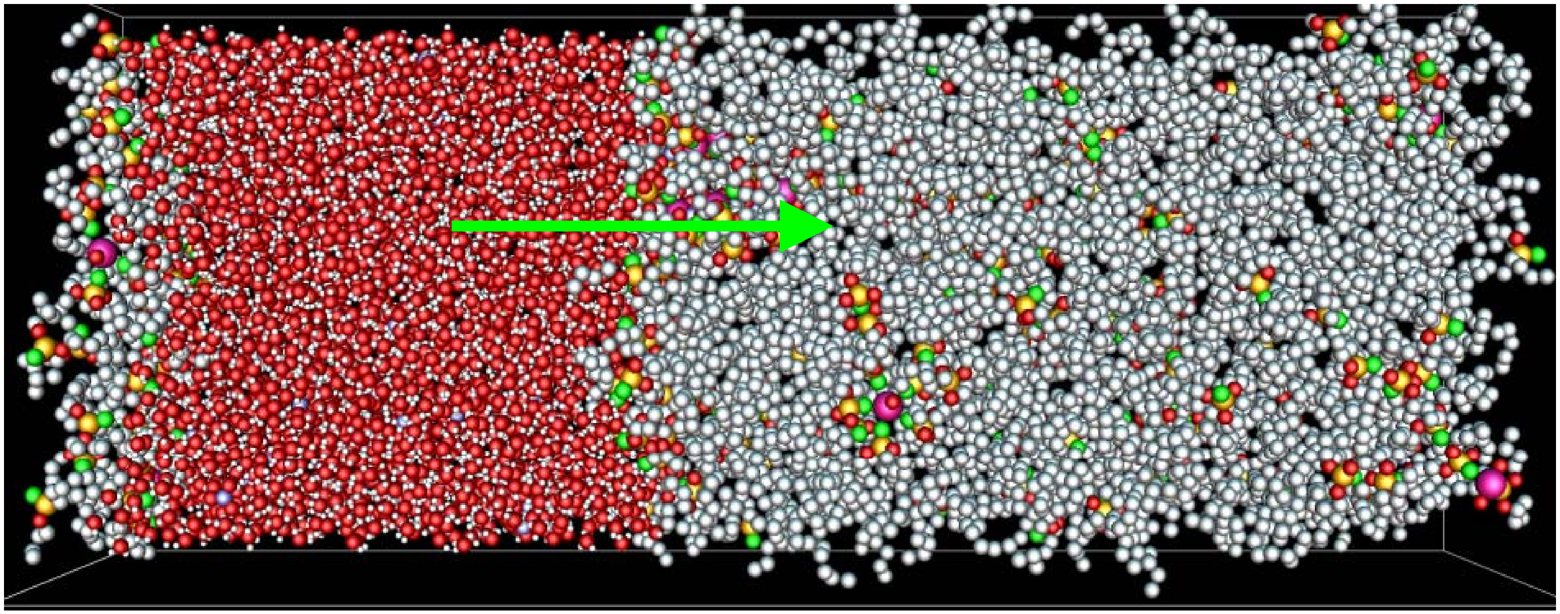


An approach to understand solvent extraction

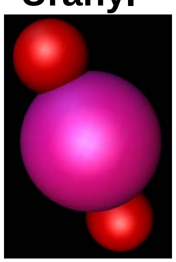


- Molecular dynamics simulation
- Calibration from experimental data
- Insight from molecular quantum chemistry calculations when experimental data are not available

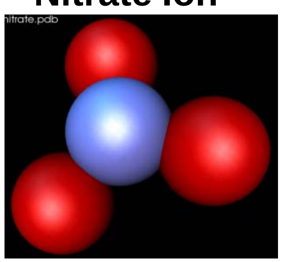
Interfacial Transport "Visualization" by Molecular Dynamics Simulation



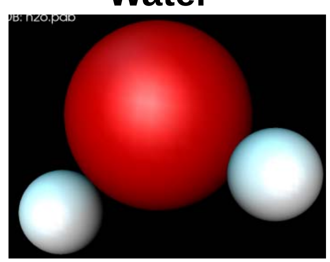
Uranyl



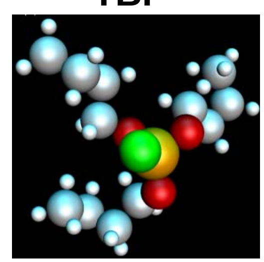
Nitrate Ion



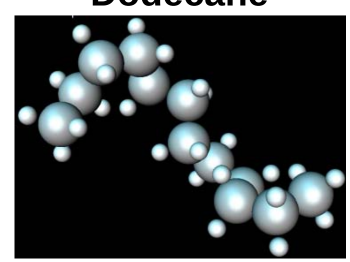
Water



TBP



Dodecane



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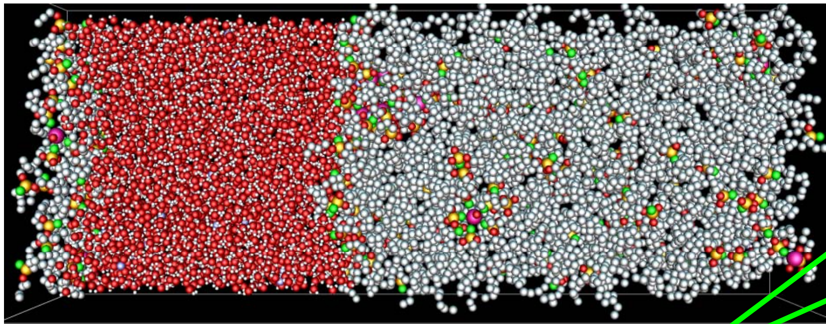
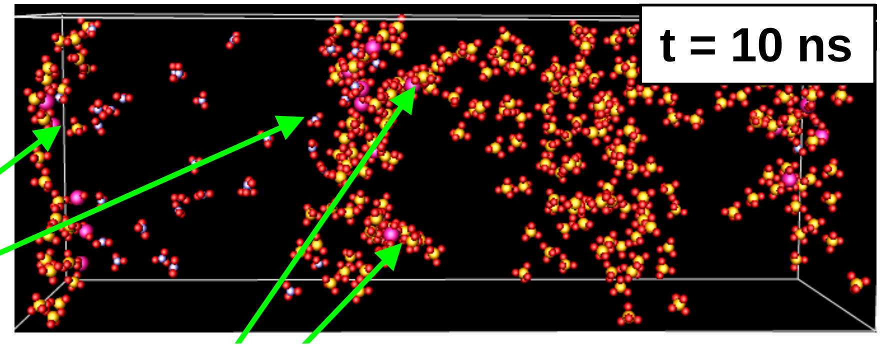
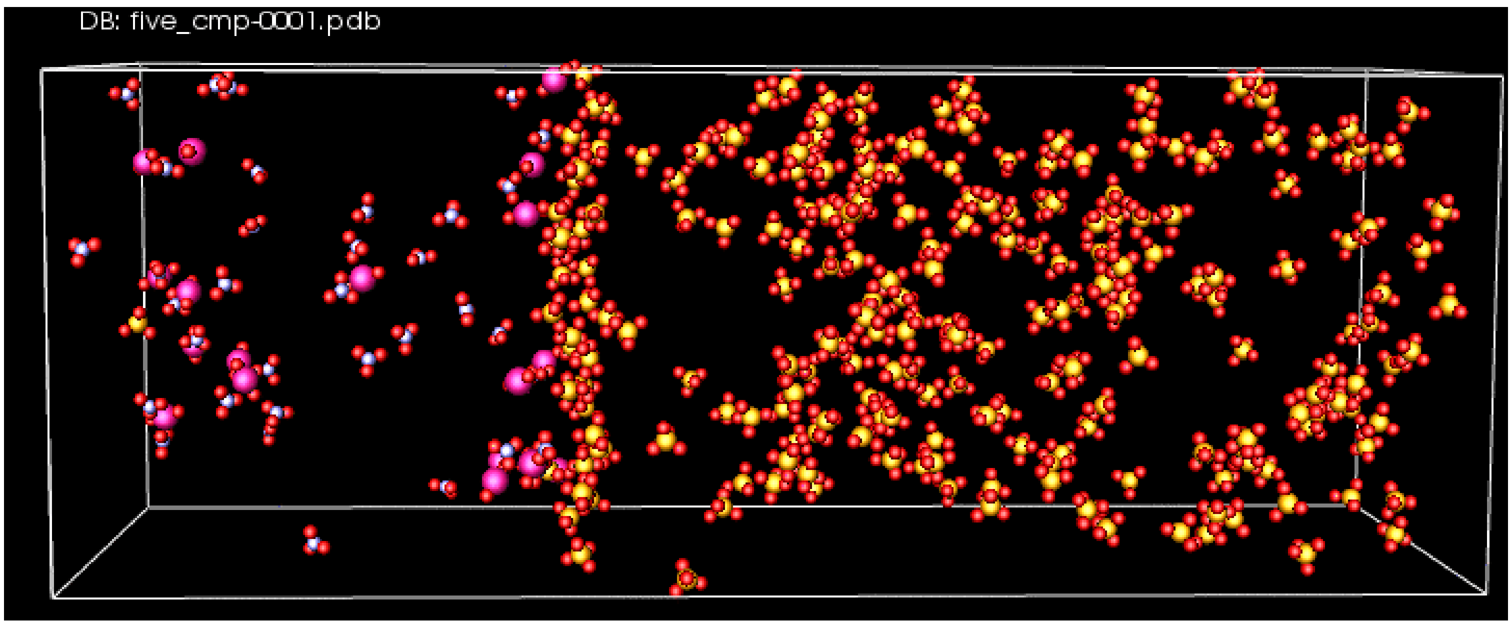
Interfacial Transport "Visualization" by Molecular Dynamics Simulation

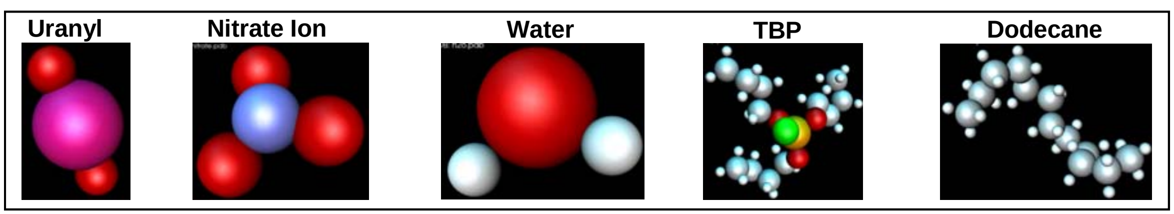


- All uranyl adsorbed on interface
- Some nitrate ion also adsorbed



- Onset of extraction of UO_2^{2+} , NO_3^- , H_2O
- Species have crossed the TBP surfactant layer





- H_2O and organic hidden; TBP butyl tails hidden

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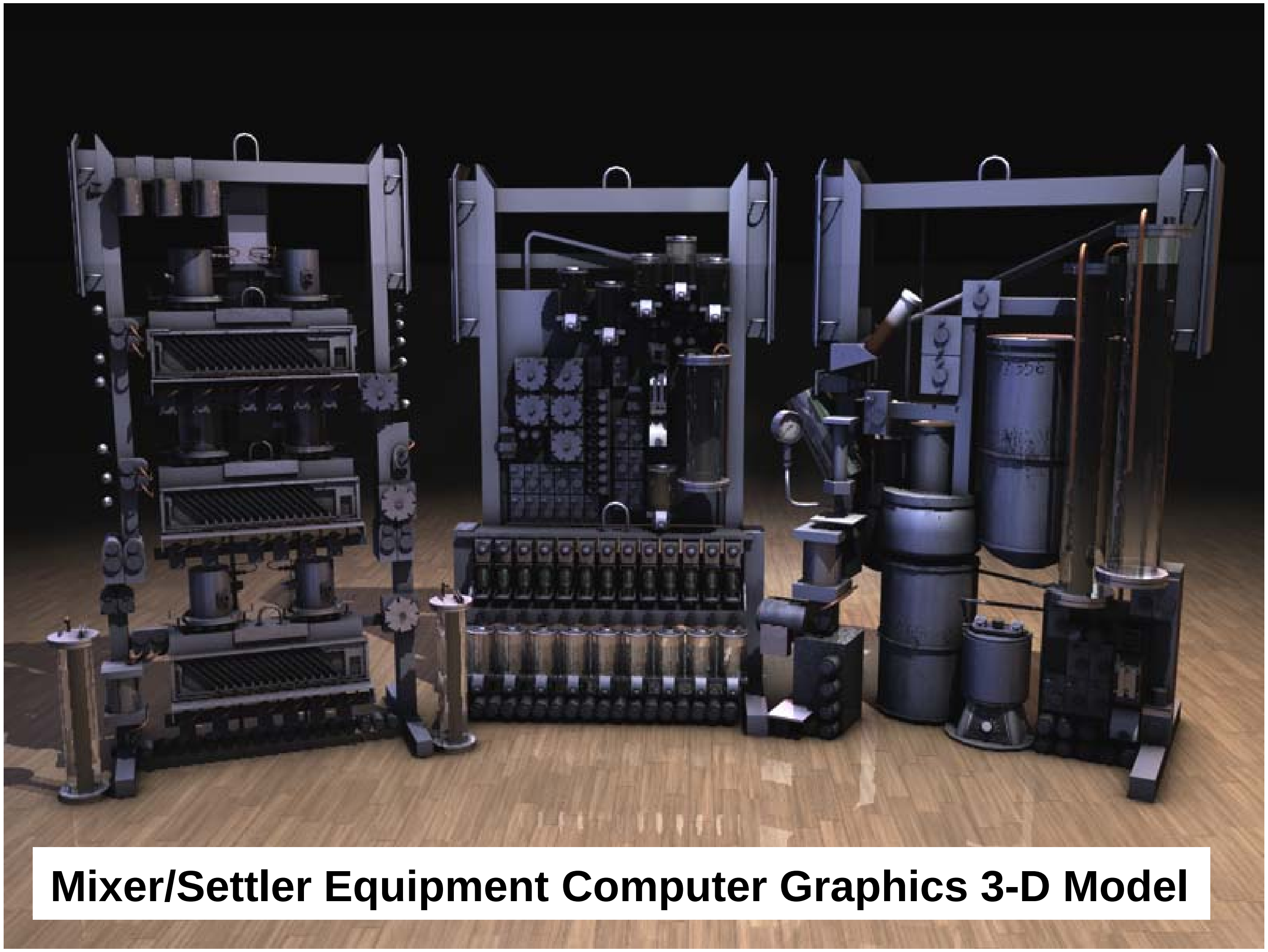
Photorealistic and Physics-Realistic Interactive Models for Test, Evaluation and Analysis



Mixer/Settler Equipment Computer Graphics 3-D Model

- Model built and textured from scratch in 1.5 work days by the Los Alamos National Laboratory VISIBLE development team, using only photos of the original equipment.
- Each part of the modeled equipment can be manipulated and custom programmed for behavior.

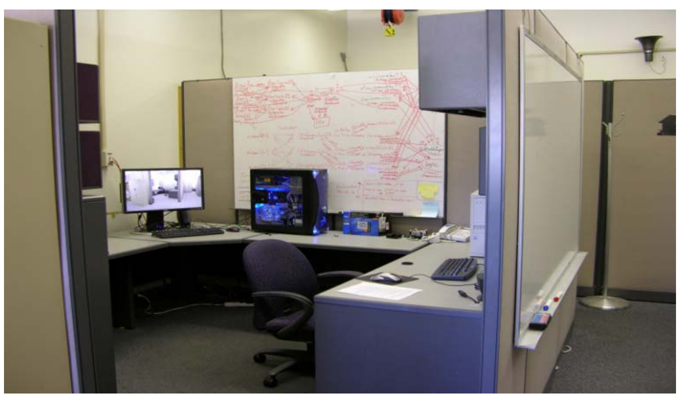
K. Michel, LANL

Visualization in Separations and Safeguards

- 3-D models already employed in safeguards
  - Experiments, micro scale - High Performance Computing
    - Power walls
  - IAEA Training
    - Mock Inspection exercises
- Visual models could provide a cost-effective safeguards design and test of a facility design
  - Drop-in toolkit for safeguards implements
  - Integrate numeric models that characterize materials, chemical processes, instruments, detectors
  - Challenge safeguards in virtual environment
    - Where are the planned safeguards weak or effective?
    - Where should the safeguards be improved?
    - Multi-player engagement in an integrated virtual computer locale
- Broader Application
  - Process design
    - Integrated process simulation with imagery
    - Utilize existing process simulation codes from across DOE complex in a virtual modeled framework
  - Training

K. Michel, LANL

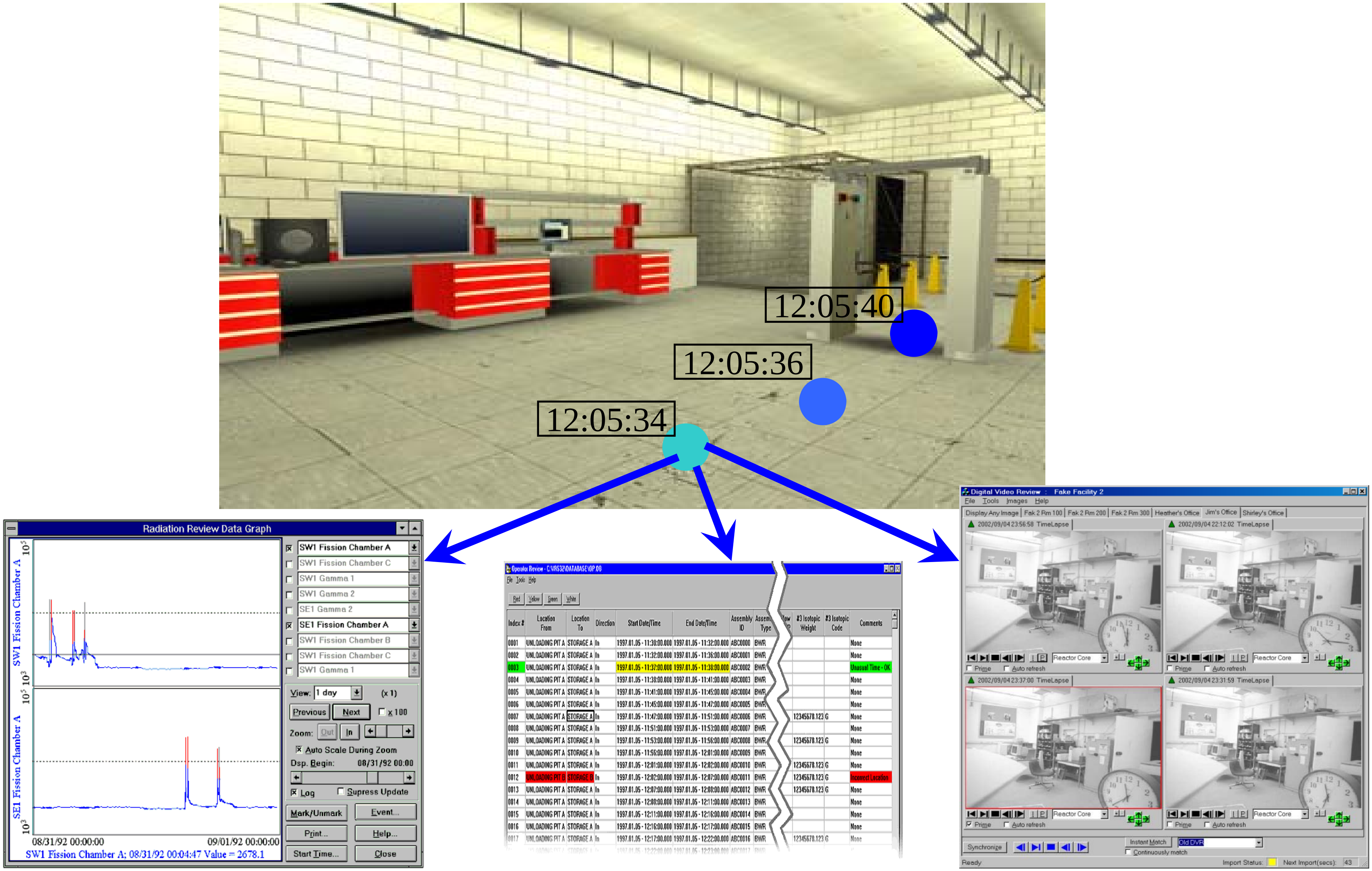
Real-world vs. Virtual World



- A virtual model can have as much, or as little detail as needed.

K. Michel, LANL

Future Safeguards Data Review Interface: Safeguards Data Shown in Context for Evaluation and Analysis of Events



Summary

- **Modeling and simulation have provided useful input to the development of fuel cycle separations over the past several decades**
- **With significant scientific advancements and vast increases in computational power, modeling and simulation can play an increasing role in solving the complex challenges to be overcome in developing advanced nuclear energy systems.**

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