

Milestone Letter Report

Status of Safeguards and Separations Model Development at Plant and Molecular Levels

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Work Package OR0915090201 – “Modeling and Simulation Support - ORNL”

FY09 Milestones:

No. M3509020106 – Report on CCA framework for plant-level simulation

No. M3509020107 - Demonstrate parallelized version of HostDesigner

1. OVERVIEW

A primary goal of the Safeguards and Separations IPSC effort is the development of process modeling tools that allow dynamic simulations of separations plant operations under various configurations and conditions, and integration of relevant safeguards analyses. A requirement of the effort is to develop codes on modern, expandable architectures, with flexibility to explore and evaluate a wide range of process options.

During FY09, efforts at ORNL have been focused on two priority tasks toward achieving the IPSC goal:

- a top-down exploration of architecture – Subtask 1: Explore framework for code development and integration for plant-level simulation
- a bottom-up fundamental modeling effort– Subtask 2: Development of molecular-level agent design code

Subtask 1 is important because definition and development of architecture is a key issue for the overall effort, as selection of an overall approach and code/data requirements is a necessary first step in the organization, design and development of separations and safeguards codes that will be incorporated.

The agent design effort of Subtask 2 is a molecular-level modeling effort that has a direct impact on a near-term issue of the Separations and Waste Forms Campaign. A current focus of experimental efforts is the development of robust agents and processes for separation of Am/Cm. Development of enhanced agent-design codes will greatly accelerate discovery and experimental testing.

Progress on these two Subtasks is described in the sections below, comprising the milestones M3509020106 – Report on CCA framework for plant-level simulation, and M3509020107 - Demonstrate parallelized version of HostDesigner.

2. SUBTASK 1: INTEGRATED PLANT-LEVEL TOOLKIT

2.1 Background

An integrated reprocessing plant is envisioned as a collection of all physico-chemical processes needed to transform spent nuclear fuel into new fuel and waste forms matching the stringent specifications of the product and waste processes. While existing reprocessing technology options deliver high quality products efficiently and robustly, they do not meet the challenges of minimizing waste, effluents, proliferation risk, environmental impact, and cost. Hence here lies the opportunity for modeling and simulation to play a role in the future design of a US reprocessing plant.

The 10-year vision for this IPSC is the development of a fully integrated, dynamic, plant-level simulator able to design, optimize, control, operate, and safeguard a reprocessing plant in a similar way flight simulators operate in the aircraft industry. That is, a digital reprocessing plant.

In view of the breadth of processes involved in a reprocessing plant it is advantageous to begin the task of implementing integrated performance and safety codes (IPSC) by considering a dynamic plant-level simulation capability that spans the entire plant. This capability would enable early feasibility analysis of existing and emerging reprocessing technology, and more importantly would help identify areas of research and development needed to improve the simulation tool. To assure the longevity of the simulation capability, models should be modular, extensible, hierarchal and aligned with a long term vision to operate, control, and protect the reprocessing plant. In order to help prioritize and organize the task of designing modules and implementing corresponding codes, a plant can be viewed as a three-tier set of modules (fig. 1).

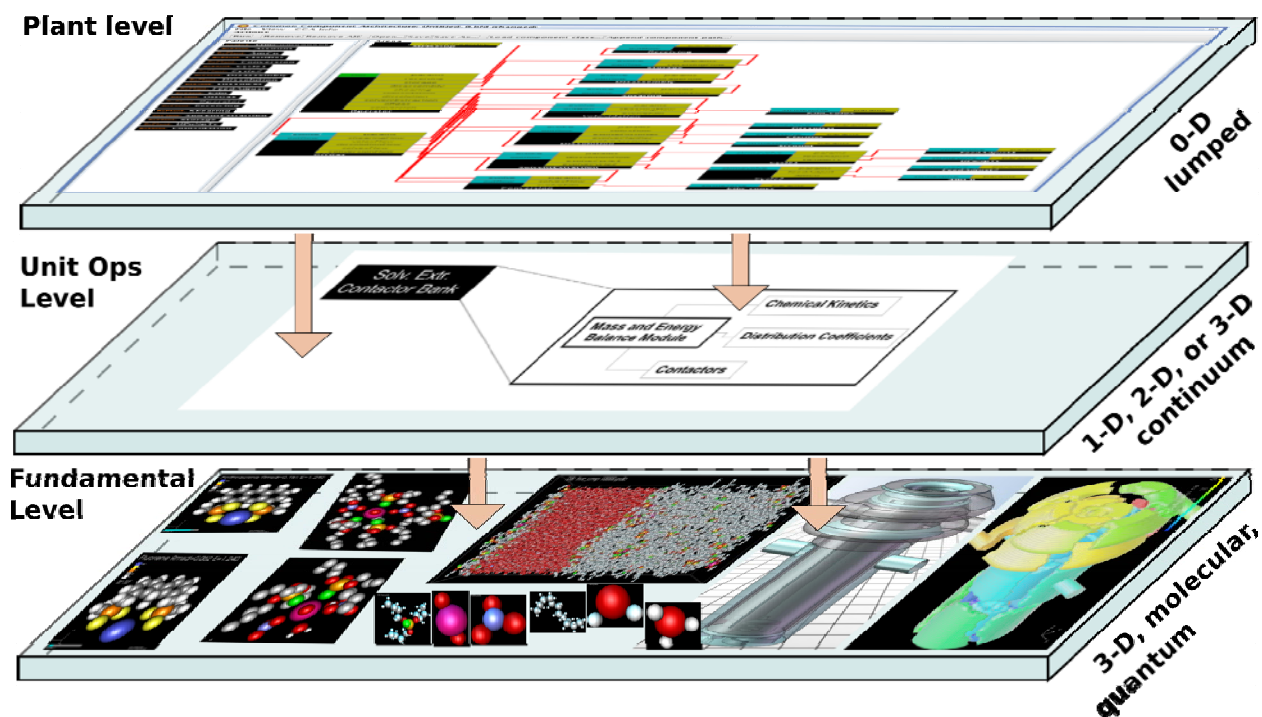


Figure 1. Tiered grouping of models and codes for a reprocessing plant. Top-down implementation approach guides development and determines research priority on lower tiers.

The top tier is a collection of discrete event models that provides throughput analysis, scheduling impacts, and output compositions. Models at this level generally summarize significant sections of the separations plant or collection of sections. These high-level models (i.e. zero-dimensional models for which elapsed time is the principal variable) can use the simulation environment to call supporting simulations at other levels of (finer) detail not captured in discrete event simulations, such as those described by rigorous chemical process models. Depending on the level of detail in the submodels selected, discrete event models require the least amount of computer cycles from the pool of computers attached to the problem-solving environment; say a few processors to several dozens of processors.

In the middle tier, macroscopic process models are designed to represent a specific unit operation or group of operations within the facilities. Models at this level are modular and may actually consist of several interchangeable models for the same separations plant section at varying levels of detail. For instance, modules for a space-time averaged one-dimensional versus a two-dimensional fluid flow model of a chemical reactor. The models are typically based on well-founded physical approximations that meet the accuracy requirements of the analysis. For example, a well-mixed chemical reactor might be represented by a point calculation to determine output composition. Macroscopic models can also use decision logic in the simulation environment to call other process models or models at other levels of detail. The requirement for computing power at this level may be on the order of tens to hundreds or thousands of processors depending on the submodels chosen.

In the bottom tier, first-principles models can be developed to address specific computer-intensive calculations needed to accurately describe time-dependent, three-dimensional (or higher dimensional) systems. For example, these models could include solid thermo-mechanics with microstructure, turbulent fluid flow, micro-nano flows, molecular dynamics, molecular mechanics, quantum mechanics calculations, and radiation transport if it is necessary to adequately model the system of interest. Computing power requirements at this level could be the highest available; up to hundreds of thousands of processors.

2.2 Technical Objectives

The foregoing prompts a natural *top-down* approach to initiate design and implementation of codes and modules. Therefore the purpose of this FY's work was to initiate the development of a realistic, flexible, and effective simulation capability for spent nuclear fuel reprocessing facility that can be used to evaluate the performance of alternative process flow sheet options based on characteristics such as throughput, nonproliferation metrics, environmental and economic impact, and public policy and regulatory compliance. The models in the simulation will provide engineering solutions at the appropriate level of detail for the design and implementation of a separations plant, including experimental support, process and equipment design and engineering, safety analysis, and material accountability.

The effort was aimed at establishing the structure for the evolution of a dynamic simulation of a full separations plant which is detailed, modular, and multiscale. The simulation was structured to utilize existing information, models, and codes developed over the past several decades throughout the DOE complex, while enabling the incorporation of advanced models as they are developed. The work was implemented in concurrent stages, namely, *assessment*, where existing codes and modules are evaluated by separations and simulations experts, *integration*, where a modular software integration architecture is developed to allow for efficient use of legacy codes and incorporation of new advanced codes, and *advanced modeling* where detailed models of processes for which improved accuracy is necessary are created.

The objective of the work was to use an existing framework environment to compose a preliminary plant-level simulator. In this activity, several unit operation modules needed to be implemented either by newly developed but simple codes, or by leveraging legacy codes. Both scenarios needed to be explored to fully evaluate the capability of the plant-level simulator in terms of flexibility and extensibility.

2.3 Progress

The viability of the Common Component Architecture (CCA) [1] approach was evaluated by implementing examples of major sub-systems of a reprocessing plant. The CCA tools used (Bocca, Ccaffeine, CCA specification, Babel, and SIDL) supported the following initial requirements: a) use existing framework for software composition, b) leverage of legacy software in open and close source code modes, c) support of all major programming languages, d) enable parallel computing, and e) use of

open source tools. The following strategic decisions were made: CCA components should wrap legacy software to minimize code modification, newly developed plant modules should be functional as stand-alone, further modifications to the initial design should be made in consultation with the ECT (Enabling Computational Technology) element of the NEAMS program and users of the FCR&D Separations and Waste Forms and MPACT campaigns.

The initial component design was based on the major sub-systems of a reprocessing plant, namely, head-end, separations, back-end, and auxiliary systems. Within each sub-system a set of components were implemented for the major operations as algorithm logics component and a holder of the material streams for the operation. The collection of components is called a toolkit and can be assembled in different ways. The initial toolkit was used to illustrate the concept and consists of a portion of the expected sub-systems of a plant-level model, as follows:

A) Operators

1. Operator. This is a component that evolves the plant by time-advancing other components that provide a time-evolution port.

B) Head-End (all first-level components in this sub-system control algorithm logic and retain the material stream data for the operation)

1. Receiving.
2. Storage.
3. Disassembly.
4. Shearing.
5. Voloxidation.
 - a) Kiln. This component is configured for the voloxidation process.
6. Dissolution.
 - a) Dissolver.
 - b) Clarifier.

C) Separations

1. Solvent Extraction
 - a) Cycle#1.
 - i. Feed adjustment. This generic component is configured for this particular cycle.
 - ii. Solvent extraction (U-Pu-Np-Tc).
 - b) Cycle#2.
 - i. Feed adjustment. Similarly this component is a second instance properly configured.
 - ii. Solvent extraction (Am-Cm).

D) Back-End

1. Conversion.
 - a) Kiln. This component is configured for the relevant material product.

E) Auxiliary.

1. Offgas.

The connectivity of the workflow is provided in Figure 2.

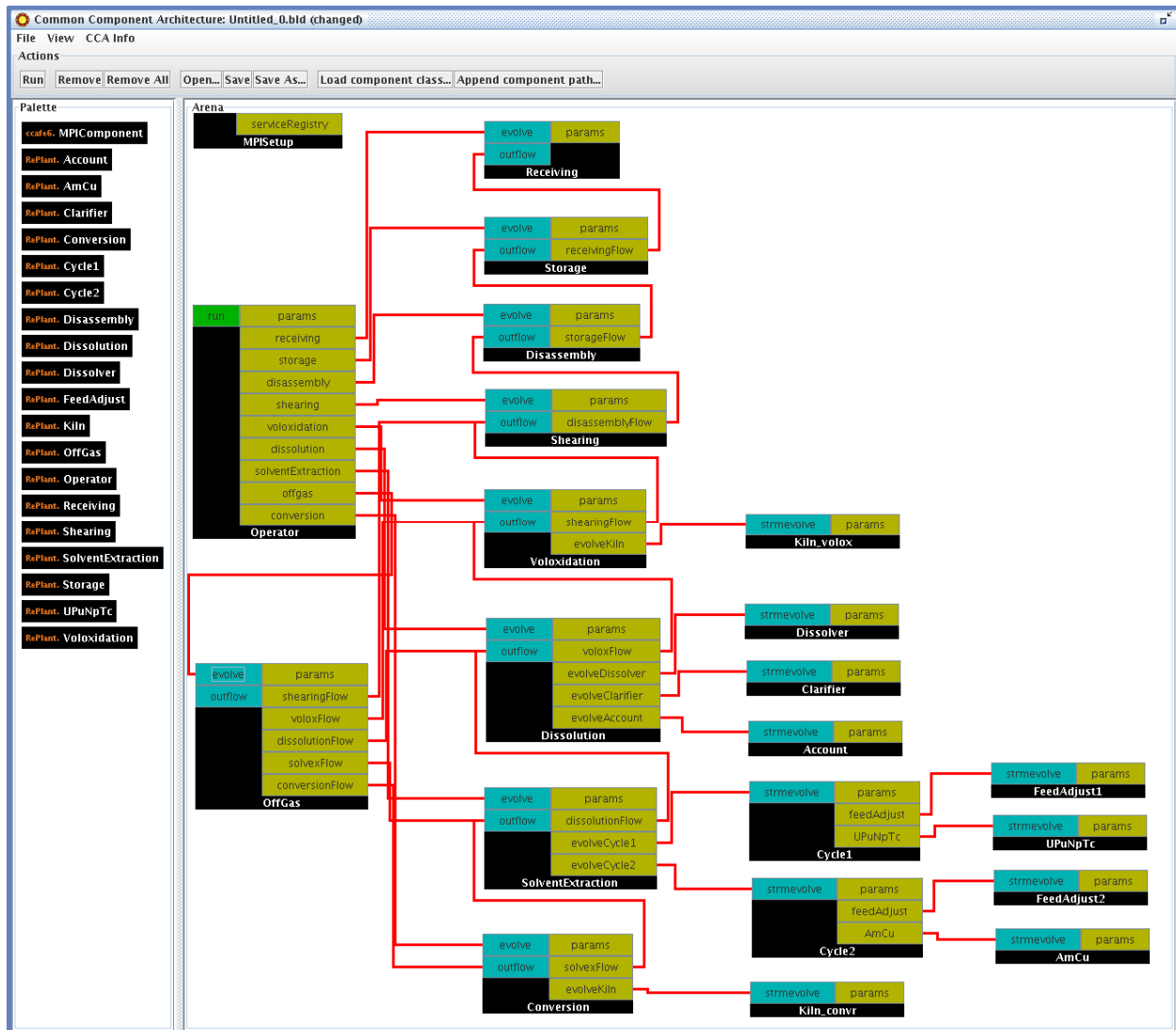


Figure 2. CCA-based initial plant design. The toolkit has 19 components, 3 ports, and 1 interface.

In this initial effort, simple implementation of unit operations were made wherein material streams are simply split on an artificial basis so the flow of material throughout the plant can be correctly verified. The initial design assumed that some basic device functionality can be captured by a single component. For example, a rotary kiln and/or a feed adjust tank components can be instantiated multiple times in the plant application and configured accordingly to the particular upstream process to which they are connected. This framework has many desirable properties. For example, components can be connected and disconnected to explore different layouts or flowsheet configurations. Different versions of the same component can be used for verification and validation purposes. Alternatively, different implementations of a unit operation component can coexist in the application for testing purposes. For example, a dissolver code provided by developer A can be substituted for, and tested against, another dissolver provided by developer B.

In this preliminary design a material stream was conceptualized as an abstract data type (SIDL interface) from which real material streams are derived. This interface is perhaps the beginning of a plant-level interface to be further elaborated with participation of users and developers.

To prove the concept of re-use of legacy codes, the ORNL SEPHIS (Solvent Extraction Process Having Interacting Solutes; written in Fortran 77 in the 70's) was wrapped and used to simulate a PUREX separation process [2]. The CCA wrapper component, namely U-Pu-Np-Tc was written (C++) to call a time integration method and data exchange methods on a modified version of the underlying SEPHIS code. The modifications were those sufficient to re-package the code as a library and create the aforementioned methods. The SEPHIS library was linked to the CCA plant application, and an LWR spent fuel shipping cask mass was entered in the Receiving component. The application was run to simulate the evolution of the digital plant long enough to allow for the production of the solvent extraction raffinate (Fig. 3).

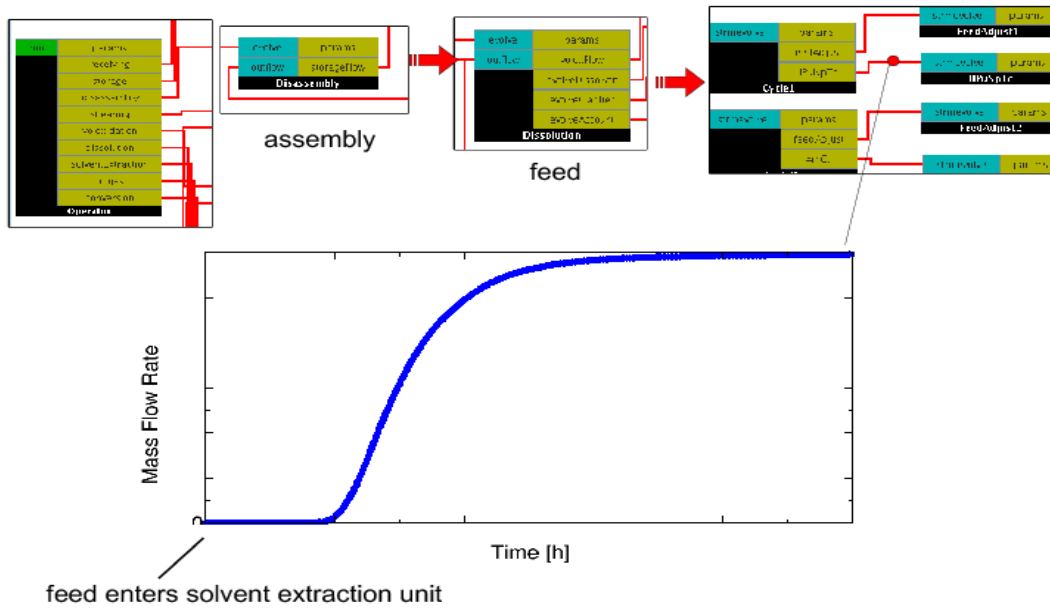


Figure 3. Time evolution of a specie of interest in the solvent extraction simulation component. The result is correct when compared to the stand-alone SEPHIS library code.

To demonstrate the promise of the plant-level simulation application, a diversion scenario was also simulated (Fig. 4). Here the feed to the solvent extraction unit is diverted for a short time during the start-up transient. The results showed the capability to employ existing codes to generate transient simulations. To further illustrate the advantage of wrapping new and legacy code as libraries linked to a CCA component, additional work was done in providing the same solvent extraction simulation library to a different framework, namely Simulink (on top of MATLAB) [3]. This work required extensions and improvements of the underlying library (Fig. 5) which were made readily available to the CCA plant application since the wrapper does not intrude into the library. Alternatively, with minor coding necessary to create a MATLAB interface for the library, the Simulink framework was able to take advantage of the library. A shortcoming of the Simulink approach is the lack of support for multi-language programming. Therefore unlike the CCA framework, there was no direct link between the solvent extraction unit library and Simulink, and the exchange of data was made through input/output to hard disk.

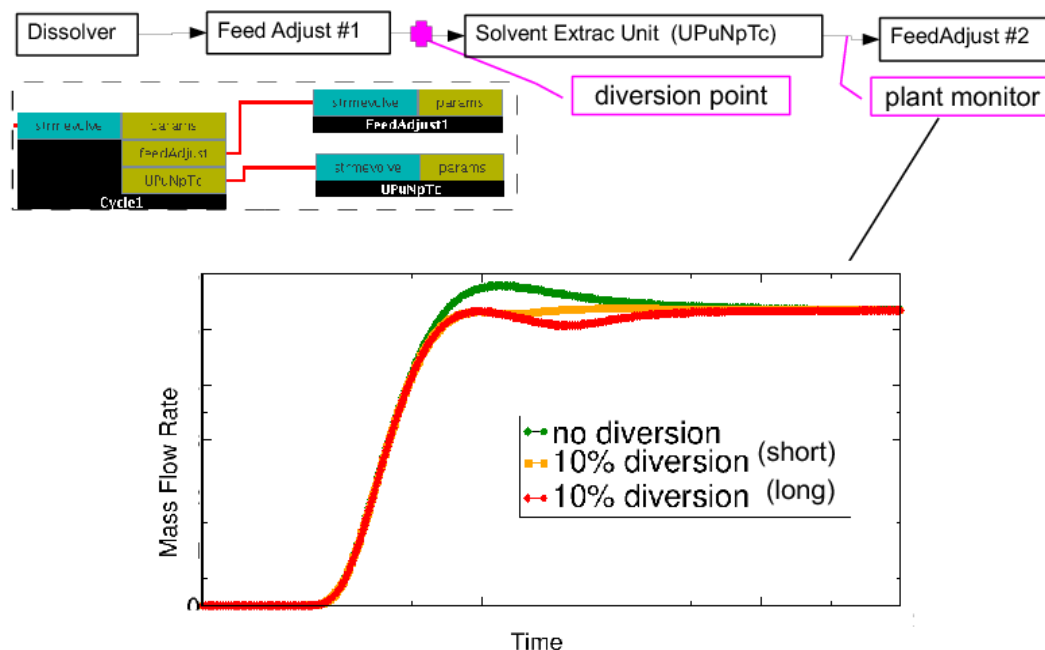


Figure 4. Diversion simulation. Results were verified against the stand-alone SEPHIS library code.

2.4 Conclusion and Future Work

The experience with the CCA-based plant application was positive and, in the short term, will provide a template for developing and testing the concepts for achieving the digital plant vision.

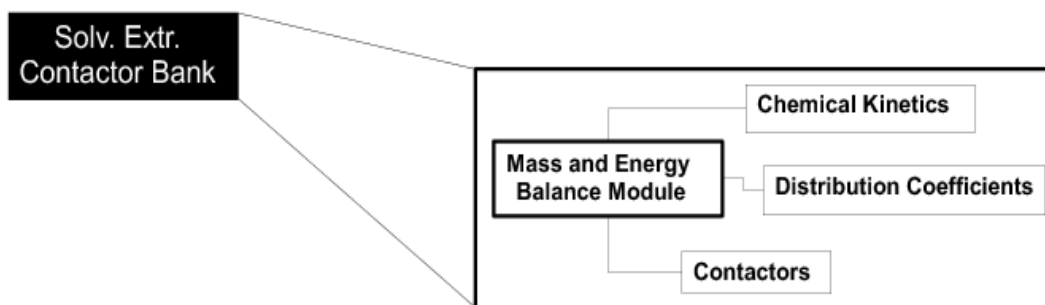


Figure 5. New functionality for the library of a solvent extraction (CCA) component. Sub-modules will allow for calibration from 2nd tier modules in the areas of chemical kinetics, distribution coefficients and contactor hydraulics. The mass and energy balance module will be time-dependent in all quantities.

The follow-on work will focus in extending the design of the plant interface by engaging the user community and potential library developers. In addition, work towards refining the definition of components and the development and maintenance of the plant interface will be pursued.

2.5 References

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3. SUBTASK 2 – SOLVENT EXTRACTION LIGAND DESIGN AND PERFORMANCE

3.1 Background

Selective separations are essential for reprocessing of spent nuclear fuels. Increases in the efficiency of liquid-liquid extraction processes would conserve both materials and energy, reduce the footprint of expensive facilities, and lessen concern about nuclear waste. Engineering the required level of performance, however, has long been a challenge. The development of computational tools that would enable the design of new reagents and processes would shorten process development time, reduce secondary waste, improve the efficiency of separation reactions, and enable completely new capabilities in spent fuel partitioning.

The ten-year vision for this IPSC is the molecular design of solvent extraction processes of interest to spent fuel reprocessing. This includes the molecular solvent agent design taking into consideration its performance in solution and interfacial regions during non-equilibrium processes.

The greatest justification for this vision lies in shortening the development time for new separation systems, optimizing performance, and reducing technical risk. Current experimental approaches to process development consume 15-20 years in basic discovery, development, and implementation of full-scale plants. Nearly half that time involves risky and expensive testing of many candidate extractants, and progress tends to stop with the first usable candidate rather than the optimum one. Empirical searches for new extractants for An separation from Ln and Cs+Sr separation, currently underway in multiple labs, would greatly benefit from the accelerated and improved ability to design successful candidates prior to undergoing the expense of synthesis and testing.

Because organic sequestering agents (hosts) with a high degree of recognition for specific ions (guests) provide the basis for most solvent extraction processes, there has been large effort expended to design effective and selective hosts for targeted ionic species. Simple extractants bearing one or two donor groups exhibit relatively weak binding and selectivities limited by intrinsic binding affinities [1,2]. As demonstrated by research on Cs⁺/Na⁺ separation [3], truly remarkable recognition for specific ions can be achieved using hosts that contain multiple binding sites arranged in a constrained configuration. The design of such hosts involves selecting the set of binding sites and then choosing the connecting geometric structure that ties them together, in other words, the molecular architecture. To achieve strong complexation with a specific guest, the host architecture must satisfy two conditions [1,2,4]. First, the host must be able to adopt a conformation in which all binding sites are positioned to structurally complement the guest. Second, the host should exhibit a limited number of stable conformations, the binding conformation being low in energy relative to other possible forms.

Whereas criteria for selecting the number and type of binding sites are well established [1,2,4], the identification of optimal host architecture remains a challenge. The deliberate design of host structures by assembling sets of disconnected binding sites in three dimensions is not a trivial task. Until recently, we could only generate trial structures by hand with a graphical user interface, an extremely time-consuming

process. Often, it is not readily obvious which linkage structures might be best used to connect the binding sites to obtain a host cavity that is organized for guest coordination. To address the problem of how to identify new host molecules that recognize and bind strongly to specific guests, we have adopted a computational approach pioneered by the pharmaceutical industry to develop a *de novo* structure-based design software, HostDesigner (HD), specifically created to identify host architectures that are organized for the complexation of small ions [5,6]. HD generates and evaluates millions of candidate structures and rapidly identifies 3D architectures that position binding sites for optimal interaction with the guest. As implied by the term *de novo*, molecules are assembled from molecular fragments. The building algorithms combine user-input host-guest fragments with linking fragments taken from a database. The host-guest fragments define the optimal geometry for one or more binding sites interacting with the guest. The linking fragment database, originally consisting of 10,000 hydrocarbons, recently has been expanded to over 900,000 structures by the addition of ether, amine, and amide functionality. During the building process, all possible connectivities, stereochemistries, and conformations are constructed, which generates large numbers of structures. After evaluation and ranking (*vide infra*), cartesian coordinates for the top candidates are output to a file.

Deliberate host design requires the ability to distinguish a good architecture from a poor architecture. Various scoring approaches can be used to evaluate the degree of binding site organization offered by a host structure. Because of the large number of structures being generated HD uses very fast methods for accomplishing these evaluations. This is achieved by using geometric factors to rank structures on the basis of how well their binding sites correspond to those of the guest [5,6]. In addition, conformational energy increments, based on potential surfaces for simple hydrocarbon analogs, are used to estimate the conformational stability of the host structures, allowing them to be ranked on the basis of their degree of preorganization [6]. Although approximate in nature, these methods provide a rapid, initial means of selecting a list of the best candidates from a large group of potential structures. This list can subsequently be reprioritized using more accurate evaluation methods.

In prior design applications [7,8], subsequent ranking of candidate structures from HD was accomplished in an automated two-step process using molecular mechanics (MM) models. Such models provide a computationally efficient tool to evaluate the degree to which a host is structurally organized for guest complexation. MM models partition the steric energy into stretching, bending, torsion, and non-bonded (van der Waals, electrostatics, hydrogen bonding) interactions.

The first step of the MM scoring process is a determination of how strongly the binding conformation of the host binds the guest. This is measured by the binding energy or, alternatively, by the induced strain in the host [9]. In either case, the calculations involve optimization of the host-guest complex followed by the optimization of the host and guest after they have been separated. This step is relatively inexpensive and can be applied to thousands of structures within a few hours time, resulting in a list that is reprioritized with respect to how strongly the host can bind the guest.

The second step of the MM scoring process is the determination of the conformational stability of the host binding conformation, in other words, the degree of preorganization. Calculations involve analysis of the host molecule to locate all low lying conformations and determining the stability of the binding conformation relative to the global minimum conformation. This step is much more expensive and, depending on the size of the molecules under consideration, can take hours per structure. In prior work, we have limited conformational analysis to ≤ 500 of the top candidates from the first step. The final output is a list of structures ranked with respect to the degree of binding site organization.

Although fast and effective, the existing MM scoring modules necessarily neglect other factors of concern in sequestering agent design. These factors include the influence of electronic structure and solvation on radionuclide binding affinity. Physical models that account for these factors (quantum mechanics,

molecular dynamics) exist and software that performs these calculations could be coupled with the existing design code to improve the fidelity and accuracy of the scoring process. Because such models are computationally expensive, coupling HostDesigner with additional scoring modules necessitates further developing the code to take advantage of parallel computing architectures.

It is important to emphasize that current molecular design approaches of solvent extraction agents do not take into account the real environment in which the agent will operate. For instance, the interactions between the agent and the organic diluent phase is not taken into consideration. The interaction between the agent and the interfacial region between the organic and aqueous phases is not considered either. More importantly, effects of oxidation, hydrolysis, and radiolysis of the agent are not part of a systematic design criterion. Therefore the design of a solvent extraction agent by current methods is a first step towards the optimal candidate.

To realize the vision of a molecular designed solvent extraction process, improvements need to be made in scoring candidates with better methods including resolving the electronic structure, and simulating the effects of solvation at the quantum level of theory. In addition, a simulation of the molecular dynamic process of extraction needs to be carried out to investigate the performance of the agent. This entails a large molecular dynamics simulation contacting the organic and aqueous phases to predict the complexation reactions at the molecular level. The benefit of this undertaking is the prediction of speciation, reaction mechanisms, and associated quantities of interest to process modeling such as equilibrium constants, distribution coefficients, and separation factors.

3.2 Technical Objectives

The aforementioned issues led us to work towards two objectives to make progress in realizing the vision of simulating an extraction process at the molecular level. The first objective is related to the need to improve the design of agents by incorporating better scoring methods, which make simulations more expensive. Specifically, one objective was to modify the HD code to run on parallel machines, which will reduce the computational time/cost. The second objective is related to the simulation of the extracting performance of an agent candidate. Here we have expanded on force field calibrations needed to obtain the first simulation to demonstrate extraction of acidic uranyl nitrate into a mixture of tributylphosphate and dodecate.

3.3 Progress:

3.3.1 HD parallelization

In the linking mode, the builder stage of HD searches for a link fragment from a library that bridges the user complex fragment. This search can be efficiently parallelized since no communication is needed between processors once the computational load is distributed. Similarly the following two stages of MM analysis can be carried out in parallel without any communication between processors until the final step where the candidates are scored. Therefore, the objective of the FY 09 efforts was to implement a master-slave approach to balance the computational load and parallelize the HD code using the MPI (message passing interface) library. This also required modifications needed to prepare the code for current and future changes, such as, version control, code building macros, and reorganization so that the parallel programming mode chosen is generic and usable by all stages of the HD code.

The builder stage of the HD code was parallelized using a master-slave approach, that is, one process handles the distribution of trial fragments to the slave processes. When a slave process is done with one fragment it requests additional work from the master (Fig. 6). This way, the work load among processes is automatically balanced (Table 1; results of parallel code correctly reproduce the results of the original sequential code; Fig. 7). However, each process reads the actual fragment data from a library file and

therefore I/O (input/output) becomes an issue and interferes with the speed-up results. In particular, since multiple processes may compete for the I/O service in a given machine, a racing condition may arise and the speed-up result is not linear. In the FY 09 work, parallel I/O issues were not addressed since they require further analysis of how to handle the HD fragment library which at the moment is kept out of core; analysis of this issue will be carried out in the FY 10 effort.

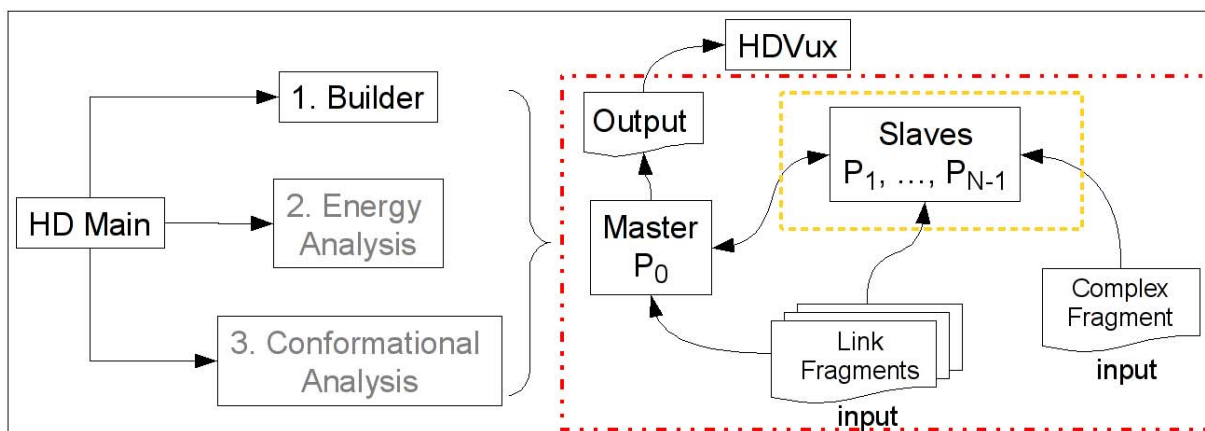


Figure 6. Parallelization of the HD code. Master-slave approach to balance the load of processing link fragments from the HD library; I/O optimization not implemented yet.

Table 1. HD speed-up results for example case. A lithium di-methyl-ether complex fragment. (Trial links are the number of links from the library used to build a host. Trial hosts are all the configurations tried with the trial links. I/O issues prevent linear speed up; these issues will be resolved in FY10.)

Library: 966 418 Links				
# Proc's	Build [s]	Speedup	# Trial Links	# Trial Hosts
1	108.4	-	39 685	1 960 568
2	55.2	2	19 842	980 284
4	38.6	3	9 921	490 142
8	24.2	4	4 961	245 071
16	13.4	8	2 480	122 535
32	7.1	15	1 240	61 267
64	3.5	31	620	30 633

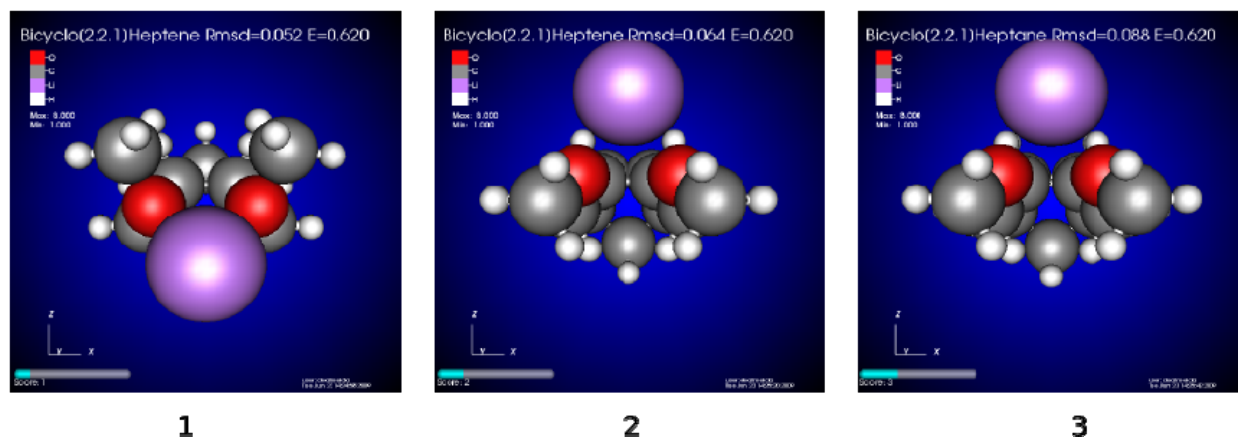


Figure 7. First three HD builder candidates for a lithium dimethyl ether complex fragment.

3.3.1.1 Conclusion and Future Work in HD parallelization

A first parallel version of the code has been implemented successfully and the infrastructure for further work has been put in place. The improvements in the code will make it amenable to coupling with other parallel modules such as a computational quantum chemistry library to be used as an enhanced scoring method. Efforts will continue in this activity to define requirements for future code enhancements by coordination with the Fuel Recycle R&D Separations and Waste Forms Campaign Sigma Team for minor actinides separation. In particular, continued collaborations will be aimed at verifying the parallel HD code results against results obtained for realistic synthesis of agents under the Sigma Team program using original sequential version of the code (Fig. 8). We aim to facilitate use by the Sigma Team of improved versions of the HD code.

In addition, this implementation will facilitate code development efforts under an ASCR project “Accelerating de novo design of separations agents” funded in FY10 to support an existing ORNL BES project “Principles of chemical recognition and transport in extractive separations”. The overarching goal of this ASCR project is aimed toward advancing scoring capability for anion receptors by coupling HostDesigner with the quantum mechanics program, NWChem. Although geared toward agents that bind simple inorganic anions, such as chloride, nitrate, and sulfate, the capability developed under this effort

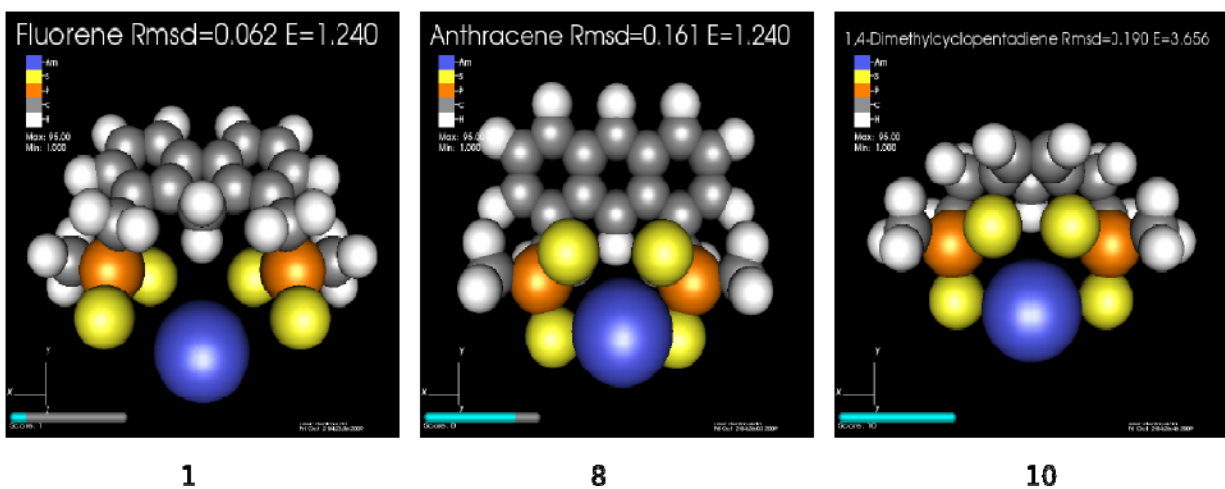


Figure 8. Candidates for an americium sequestering agent with a dimethylphosphinate chelate binding group. The complex fragment was chosen by the minor actinide Sigma team as the basis for designing a new host. Pictures show candidates 1, 8 and 10 on the HD builder list. These results obtained with the parallel HD match those obtained with the original sequential version of the code.

should be readily extended to problems of interest to the Office of Nuclear Energy.

3.3.2 Molecular Dynamics of Solvent Extraction

Recent work [10,11] on the simulation of interfacial molecular dynamics of uranyl nitrate led to the observation that extraction into the bulk of an organic phase containing tributylphosphate (TBP) is limited and does not reproduce the complex $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ commonly used in empirical stoichiometry of solvent extraction for this system. The closest structure observed in the simulations was $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP} \cdot 2\text{H}_2\text{O}$ (Fig. 9, left) which exists at the interface but not in bulk. Furthermore, indications that a modified force field, based on quantum calculations for the complexes formed at the interface involving TBP, uranyl nitrate, and water could alter the interactions qualitatively to a point where extraction into bulk was obtained (Fig. 8, right); however in the form of $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{TBP}$ [11].

The objective of this FY 09 effort was to collect the results of these recent computational experiments and further evaluate the total energy of surrogate complexes in gas phase via computational quantum mechanics. The results of this investigation [12] firmly demonstrate the need for future studies of coupled molecular dynamics and quantum mechanics before a realistic assessment of the performance of a solvent extraction agent in solution can be made. Another objective of this sub-task was to generate initial molecular dynamics configurations for a two-phase system similar to the acidic composition in [10] on the order of 1 million of atoms for future scale-up simulations. This entailed equilibrating an aqueous phase and an organic phase individually and then bringing both systems into close contact in order to form an interface. This initial configuration will be used in the future for further numerical convergence results and improved modeling of the aqueous-organic interfacial region.

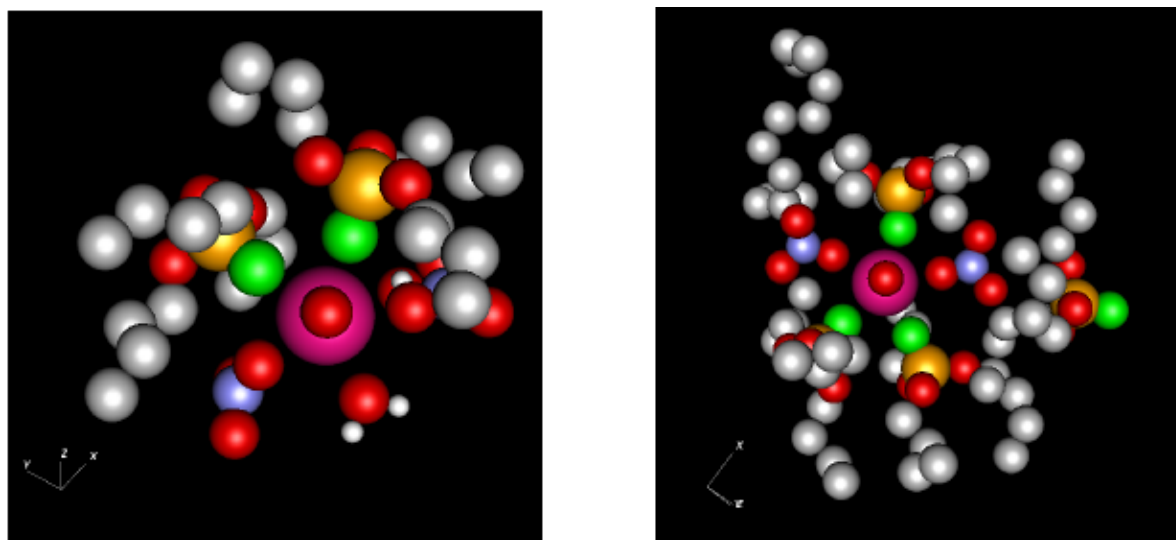


Figure 9. Uranyl nitrate TBP complexes. **Left:** interfacial complex closest to experimentally inferred compound; does not extract into the bulk region of the organic phase. **Right:** extracted compound into the organic phase after adjustment of point charges guided by fitting an electrostatic potential from quantum calculations. Compared with the left compound the extraction replaced one molecule of H_2O by one TBP

3.3.2.1 Conclusion and Future Work in Molecular Dynamics of Solvent Extraction

The work referred above has been instrumental in significant ways. First, it has shown that molecular solvent extraction phenomena can be captured qualitatively by modeling in the classical limit when properly calibrated. Second, there exists knowledge to consider fairly realistic systems including realistic diluents and acidic conditions; reference [10] was the first publication in the open literature to consider a realistic organic mixture and dissociated nitric acid for the TBP-dodecane, uranyl nitrate extraction problem. It remains to be explored whether the approach can be used to provide quantitative estimates of

the rates of extractions, and corresponding speciation details. Follow-on work examining these issues will be conducted in a newly funded NEUP project, “Quantifying Water Extraction by TBP/Dodecane via Molecular Dynamics Simulations” (NEUP 09-430. PI – B. Khomami, University of Tennessee-Knoxville). The overall scope of the work is the development and testing of a molecular dynamics simulation code for water extraction into tributylphosphate/dodecane. ORNL will carry out molecular quantum mechanics simulations on tributylphosphate/dodecane to generate force field parameters for the molecular dynamics simulation and provide support in adapting the molecular dynamics simulation code to run on massively parallel machines.

3.4 References

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