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Requirements for a Dynamic Solvent Extraction Module to Support Development of Advanced Technologies for the Recycle of Used Nuclear Fuel

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June 2011

Idaho National Laboratory

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FIGURES

TABLES

ACRONYMS

ACC	Annular Centrifugal Contactor
AFCF	Advanced Fuel Cycle Facility
AMUSE	Argonne Model for Universal Solvent Extraction
ANL	Argonne National Laboratory
CCD-PEG	Chlorinated Cobalt Dicarbollide – Polyethylene Glycol
CFD	Computational Fluid Dynamics
COEX	CoExtraction
DOE-NE	Department of Energy – Nuclear Energy
FCR&D	Fuel Cycle Research and Development
FPEX	Fission Product Extraction
GWd/MT	Giga-Watt days per MetricTon
IAEA	International Atomic Energy Agency
INL	Idaho National Laboratory
IPSC	Integrated Performance and Safety Codes
NEAMS	Nuclear Energy Advanced Modeling and Simulation
NPEX	Neptunium Extraction
ODE	Ordinary Differential Equation
PDE	Partial Differential Equation
PUREX	Plutonium and Uranium Reduction Extraction
QA	Quality Assurance
QAPD	Quality Assurance Program Document
SafeSeps	Safeguard and Separations
SX	Solvent Extraction
TALSPEAK	Trivalent Actinide - Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes
TBP	Tributyl Phosphate
TRUEX	Transuranic Extraction
UREX	Uranium extraction
VU	Validation and Uncertainty

NEAMS CAMPAIGN/SAFESEPS IPSC
REQUIREMENTS FOR A DYNAMIC SOLVENT EXTRACTION MODULE TO SUPPORT DEVELOPMENT OF ADVANCED TECHNOLOGIES FOR THE RECYCLE OF USED NUCLEAR FUEL

1. BACKGROUND

The Department of Energy's Nuclear Energy Advanced Modeling and Simulation (NEAMS) Program has been established to create and deploy next generation, verified and validated nuclear energy modeling and simulation capabilities for the design, implementation, and operation of future nuclear energy systems to improve the U.S. energy security. As part of the NEAMS program, Integrated Performance and Safety Codes (IPSC's) are being produced to significantly advance the status of modeling and simulation of energy systems beyond what is currently available to the extent that the new codes be readily functional in the short term and extensible in the longer term. The four IPSC areas include Safeguards and Separations, Reactors, Fuels, and Waste Forms.

As part of the Safeguards and Separations (SafeSeps) IPSC effort, interoperable process models are being developed that enable dynamic simulation of an advanced separations plant. A SafeSeps IPSC "toolkit" is in development to enable the integration of separation process modules and safeguards tools into the design process by providing an environment to compose, verify and validate a simulation application to be used for analysis of various plant configurations and operating conditions. The modules of this toolkit will be implemented on a modern, expandable architecture with the flexibility to explore and evaluate a wide range of process options while preserving their stand-alone usability. Modules implemented at the plant-level will initially incorporate relatively simple representations for each process through a reduced modeling approach. Final versions will incorporate the capability to bridge to subscale models to provide required fidelity in chemical and physical processes.

A dynamic solvent extraction model and its module implementation are needed to support the development of this integrated plant model. As a stand-alone application, it will also support solvent development of extraction flowsheets and integrated safeguards approaches within the Fuel Cycle Research and Development (FCR&D) Program. The purpose of this document is to identify the requirements for this dynamic solvent extraction model to guide process modelers and code developers to produce a computational module that meets anticipated future needs.

2. SCOPE OF DYNAMIC SOLVENT EXTRACTION MODELING AND SIMULATION EFFORT

The scope of this effort is to develop, as part of the NEAMS SafeSeps IPSC, dynamic solvent extraction simulation software that can be seamlessly incorporated into an overall dynamic plant-level application as well as to function as a stand-alone solvent extraction module. The term "dynamic" refers to the fact that the underlying model is not limited to steady-state operations nor batch processes but generates and requires time-dependent (input/output) data in a continuous operation mode. The goal is to develop an IPSC solvent extraction module that is not uniquely developed by any single National Laboratory or entity but is instead the result of a collaborative DOE-NE effort managed by the NEAMS SafeSeps IPSC. The underlying computer code, and input/output parameters, can be modified or expanded by the wider user community as necessary to meet DOE goals.

The developed module must be sufficiently flexible to allow for the representation of solvent extraction processes that are currently under development, for which data may be limited, as well as those that may be developed in the future. Specific data needs to support modeling of a process are specified in Section 5. In addition, the developed model must be capable of integration with other components of the plant level model through the plant level toolkit and system architecture being developed by the SafeSeps program.

The dynamic solvent extraction model should be configurable (possibly via composition) for simulation of multi-cycle solvent extraction unit operations that may comprise an advanced used nuclear fuel recycling scheme, as shown in the example in Figure 1.[1] This figure also shows the required interfaces with other unit operations (i.e., head end, conversion, and support systems). Note that the head-end, conversion, and support operations identified in the figure, which are integrated into an overall separations process flowsheet, are outside of the scope of the solvent extraction modeling effort.

The intent of this document is to identify scope and requirements for this modeling and simulation effort with the input and agreement of the Separations Technology Development team prior to the initiation of significant advanced model development. A proposed approach for the modeling and simulation effort, an evaluation of currently available dynamic models/codes, a preliminary evaluation of data needs to support this effort, and a proposed path forward are identified below.

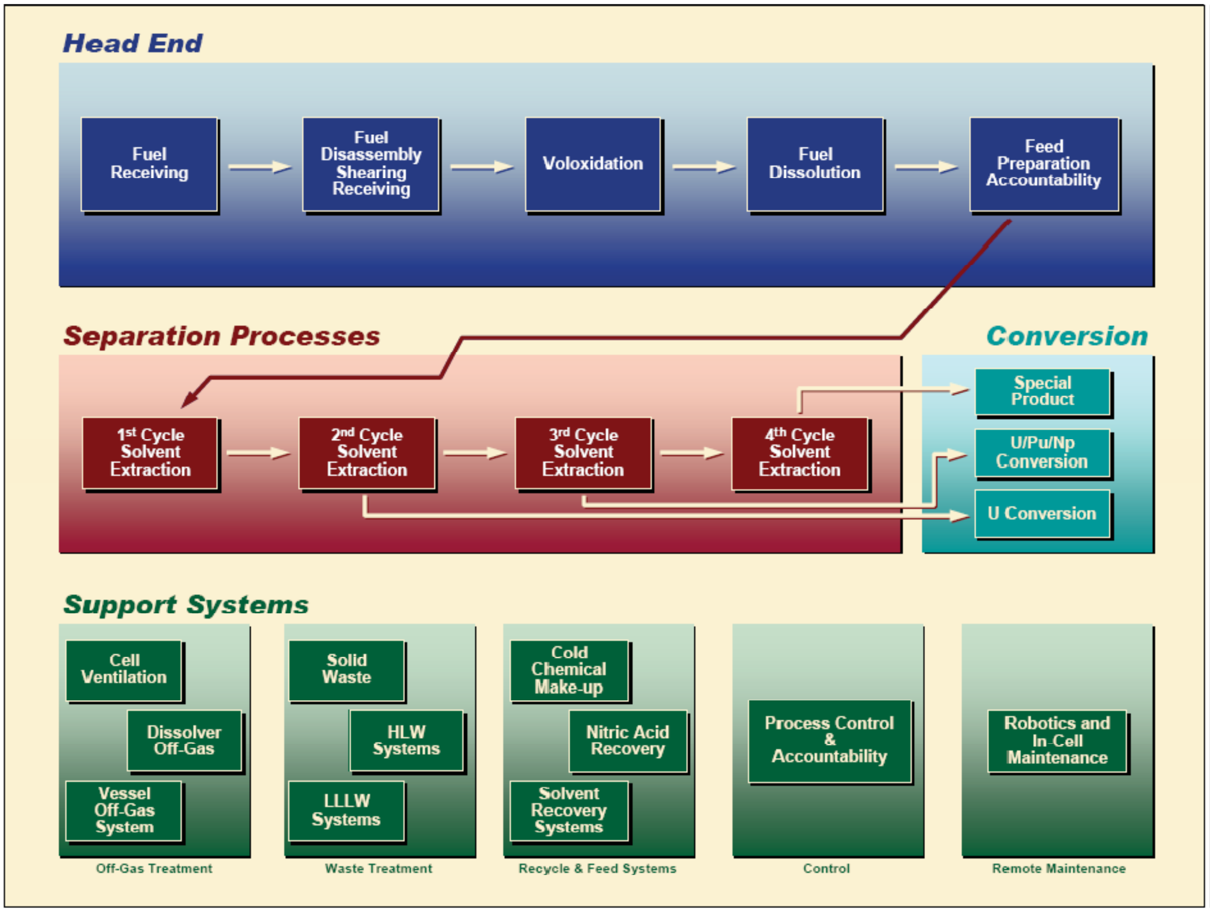


Figure 1. Aqueous Processing Block Diagram

3. MODELING REQUIREMENTS

The modeling requirements needed for the development of a software module are based on multiple anticipated uses of the simulation tool by NE and related stakeholders for advanced capability in solvent extraction simulation. A dynamic solvent extraction modeling capability is necessary to support research and development activities related to 1) processing of used nuclear fuel and radioactive waste treatment, 2) evaluation and analysis of newly developed separation processes, 3) design, operation, and operator training for future processing facilities, and 4) safeguards analyses to support facility design and operation. These potential uses drive the need for better predictions and dynamic process capability.

This section collects information to assist the development of modeling methods for solvent extraction and their corresponding realizations into simulation software. It is assumed that the effort of developing a model will entail the application of a rigorous uncertainty quantification approach which will be an integral part of the model. Therefore the recommendations below are not meant to be sufficient but judged to be minimal to advance beyond the current state of modeling. Extensions of the model to allow for validation and uncertainty quantification will be addressed by future efforts.

3.1 Desirable Model Quantities

The input variables for the dynamic solvent extraction model should include:

- Dissolved used fuel composition, either input directly or tied to the output of a front end (dissolution) model. This topic is discussed further in section 3.2.5.
- Process flowsheet design details including
    - Compositions of feed solutions, including solvent, scrub, strip, solvent wash, and diluents wash
    - Absolute feed solution flowrates and step changes or variable flowrates
    - Location of all feed and effluent streams within the flowsheet
    - Recycle streams and routing of effluent streams
    - Feed solution temperatures and relevant temperatures in the process equipment
    - Distribution ratios, if user-defined
    - Thermodynamic and kinetic parameters
    - Time-dependent, flow-rate dependent, material holdup in stages
- Specific equipment parameters (such as number of stages in each section), as detailed in Section 3.3

Based on the user-defined input variables, the following output, as a function of time, are required.

- Effluent stream flowrates, concentrations of tracked species, and solution densities
- Concentrations exiting and entering stagewise contactors (such as mixer-settlers and centrifugal contactors), and at specified points in differential contactors (such as pulsed columns)
- Distribution ratios
- Hold up of material throughout the system
- Temperature of effluent solutions and solutions within the equipment

- Energy input requirements for cooling or heating to achieve desired temperature profiles

Additionally, the following output may be included based on prioritization efforts.

- Chemical speciation, e.g. oxidation state of components
- Degradation product concentrations
- Gross alpha and beta/gamma dose throughout the processes if isotopic feed concentrations are provided

3.2 Chemical Components

The specific components that need to be included in the dynamic solvent extraction model include 1) those components of used nuclear fuel that are the target of separation and recycle, 2) the species that could potentially adversely impact fabrication of fuel, 3) the species that could potentially adversely impact waste form integrity, 4) the components introduced in the various solvent extraction processes that impact chemistry (e.g., nitric acid, reductants, complexants, solvents) and 5) components that can co-extract and impact process performance Specific elements and compounds in each of these categories are detailed below. In addition, the model should be extensible to allow for the addition of other components of interest as data become available.

3.2.1 Elements targeted for separation

The non-volatile and semi-volatile elements typically targeted for separation with advanced aqueous separation processes are shown in Figure 2 and include the actinide elements from Th through Cm, the lanthanide elements through Gd, Cs, Sr, Tc, and tritium. Volatile species, such as Kr and Xe are not included since they will be released to the offgas in the head end processes. The model should predict the elemental concentrations of these components and calculate activities of specific isotopes based upon the isotopic distribution of the elements in the feed solution. In addition, the model should allow for the user to input the valence state of several actinides including Pa(IV), Pa(V), U(IV), U(VI), Np(IV), Np(V), Np(VI), Pu(III), Pu(IV), Pu(V), Pu(VI), Am(III), and Am(VI). Prediction of valence states of the actinides is also desired.

3.2.2 Fuel Fabrication Impurities

Numerous elements have been identified as impurities or suspected impurities in the fabrication of fuel.[2] As the limits for these elements have been defined for specific fuel types, these elements should be explicitly included in the developed models if feasible. Specific elements are shown in Figure 3.

3.2.3 Waste form impurities

There are several elements that significantly impact waste form performance and should therefore be included in the modeling efforts. These elements are primarily the transition metals. The transition metals of particular interest that were not previously identified as fuel fabrication impurities include Sc, Y, Zr, Nb, Tc, Rh, Pd, Re, Os, Ir, Pt, Au, and Hg.

3.2.4 Process specific components

Each individual separations process targets a specific element or group of elements. To accomplish these separations, it often requires the introduction of unique chemicals that can potentially impact the downstream separations chemistry and post-separations processing. It is impossible to identify all chemicals which may be used, but several compounds routinely used in aqueous separations processes need to be included. These compounds include nitric acid, sulfate, phosphate, fluoride, chloride, oxalate, acetohydroxamic acid, ferrous sulfamate, carbonate, lactate, citrate, and DTPA. The components could comprise individual cases within the code structure that can be called if required and omitted if not. However, the code must be flexible enough to accommodate novel extractants and additives for which detailed chemical models do not yet exist. These could be handled by generic archetypes with user defined parameters or as simple stoichiometric species. As these processes are characterized by concentrated non-ideal solutions whose density and concentration vary throughout the system, inclusion of an overall water balance will yield more accurate flows and concentrations.

For any particular process being modeled, one must account for the solvent components and any known degradation products arising from these components. There are several processes which are actively being used industrially or are under development for used fuel recycle for which data to support modeling efforts are available. These processes and the associated solvent components are summarized in Table 1. Although there are standard compositions for some systems, new processes may require alternate concentrations in order to achieve specific objectives. Consequently, and as suggested for the solution models, handling these as standard solvent systems but with user defined compositions is likely the optimal course because the quality and quantity of the data varies widely. As a significant fraction of process development has been focused on implementing wholly novel extractants or combinations of extractants, a generic solvent case with user-defined inputs should be developed to provide feedback to process developers. While the overall code needs to be flexible enough to allow any process to be modeled if sufficient data are available, the processes listed in Table 1 currently have a significant amount of data available and, therefore, any could serve as the focus of initial model development efforts.

3.2.5 Components that may interfere with processes

Certain undesirable chemical components may be co-extracted in a solvent extraction process and interfere with the extraction of components that are the target of separation. While these are process dependent, several metals are typically of concern including Zr, Mo, Na, and K. These components, along with others identified as new processes are developed, should be included and the model should predict the mass transfer of these components and the impact on process performance.

3.2.6 Range of Feed Concentrations

The dynamic solvent extraction model should be capable of modeling a wide variety of potential feed compositions. This would include feeds resulting from dissolution of various used fuel types resulting from current reactor operation as well as future fast reactors. In a previous DOE-NE conceptual design activity for an Advanced Fuel Cycle Facility (AFCF)[3], bounding feed compositions were established based on the dissolution of (1) 25 GWD/MT, 5-year cooled fuel, (2) 25 GWD/MT, 50-year cooled fuel, (3) 100 GWD/MT, 5-year cooled fuel, and (4) 100 GWD/MT, 50-year cooled fuel. It is possible that longer-cooled fuel may be processed but it is not expected that this would cause any issues as the changes in feed composition would be small.

Additionally, the model should allow for feed compositions to be directly input so individual processes can be modeled. For example, it may be desired to model an actinide/lanthanide separation process (TALSPEAK) individually. The ability to directly input the feed composition to this process, independent of the prior processes, is necessary.

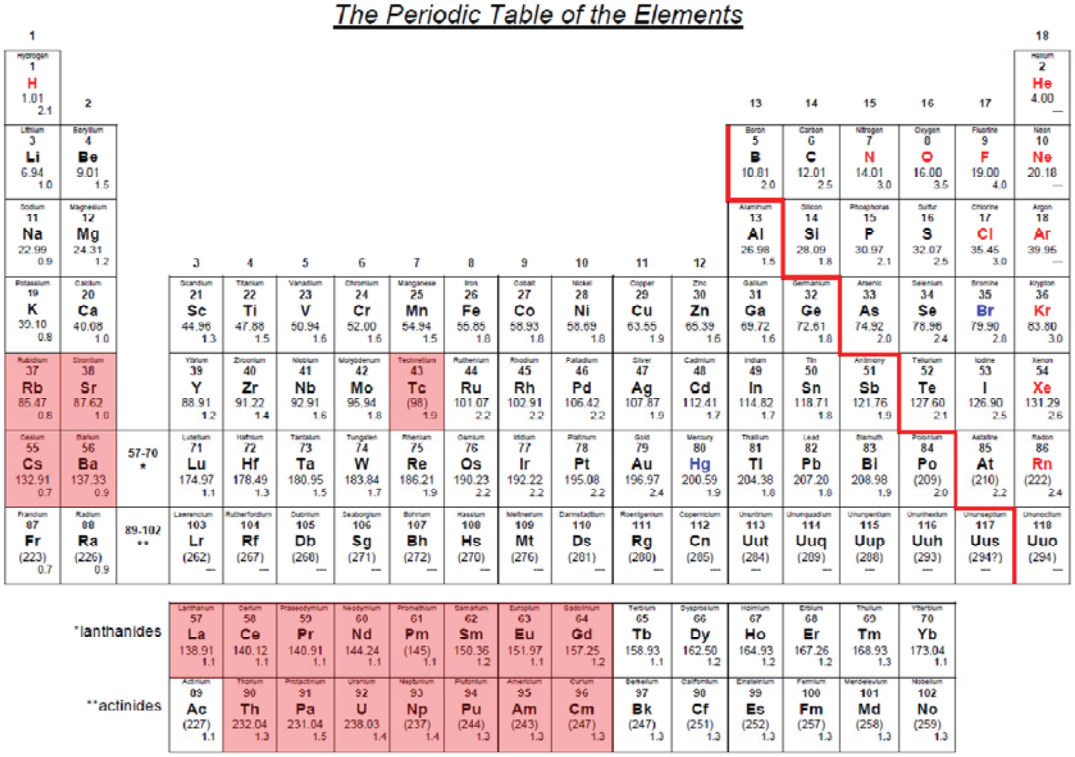


Figure 2. Elements typically targeted for separations

Table 1. Solvent components for potential advanced aqueous processes

Solvent Extraction Technology	Solvent Components
PUREX/UREX/COEX/NPEX	Tributyl phosphate, n-dodecane or Isopar-L
TRUEX	PUREX solvent components plus CMPO
FPEX	DtBu18C6, MAXCalix, TBP, Isopar-L
CCD-PEG	CCD, PEG-400, FS-13
TALSPEAK	HDEHP, dodecane

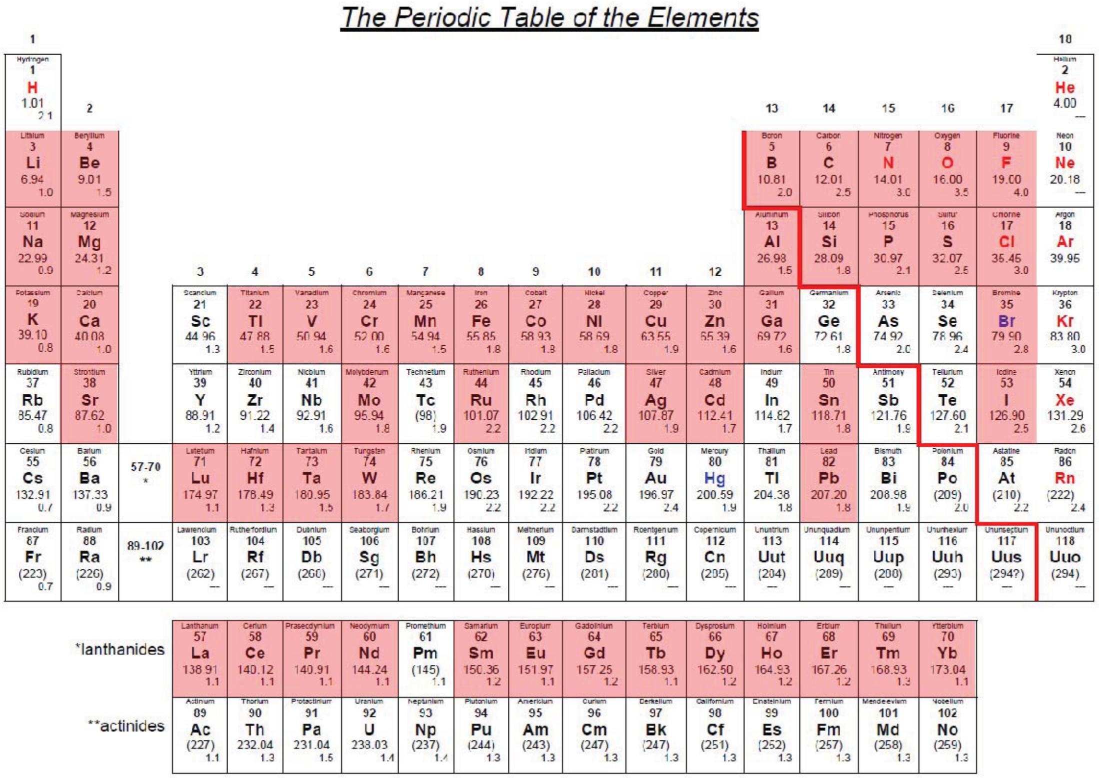


Figure 3. Potential Fuel Fabrication Impurities of Concern

3.3 Equipment

Three types of solvent extraction contacting equipment are typically used in the nuclear industry: pulsed columns, centrifugal contactors, and mixer-settlers (See Figures 4 through 6).[4] Therefore, the code should allow for the use of each of these types of equipment or a combination. All of these equipment models need to support prediction of the variables identified earlier (e.g., component concentrations, flowrates, and temperature). The design of the solvent extraction equipment and the method of operation have significant impact on the performance of the process. This includes the hydrodynamics of the solutions during phase contact and disengagement which impact other-phase carryover and the contact time of the phases as related to the kinetics of the process which impacts mass transfer. The sections below identify equipment-specific parameters that are important in the performance that are relevant to development of improved models and their code implementation.

3.3.1 Pulsed Columns

The following equipment parameters are relevant to hydrodynamic and mass transfer performance of pulsed columns, and should be included in the pulsed column model, regardless of the method chosen to model the system.

- Mode of operation: aqueous or organic continuous

- Active column diameter and length
- Disengagement head volumes
- Feed locations (column fraction or physical position)
- Sampling locations

The following parameters will be necessary if mass transport models are developed

- Pulse frequency and amplitude
- Type of pulse generator (i.e. mechanical or pneumatic pulser/pulse leg)
- Plate type – choice of several standard plate types depending upon data availability. Should include nozzle plates
- Plate spacing
- Fractional air entrainment

The capability to input the following equipment/process related parameters should also be included. It should be noted that it is anticipated that a sub-scale predictive capability will ultimately be developed for these parameters; meanwhile, specific experimental measurements can be made and used as calibration parameters.

- Other-phase carryover either directly input or calculated from variables listed above.
- Height equivalent to a theoretical stage or height of transfer unit
- Mass transfer coefficients
- Holdup of phases per theoretical stage or height of transfer unit as a function of flow rates

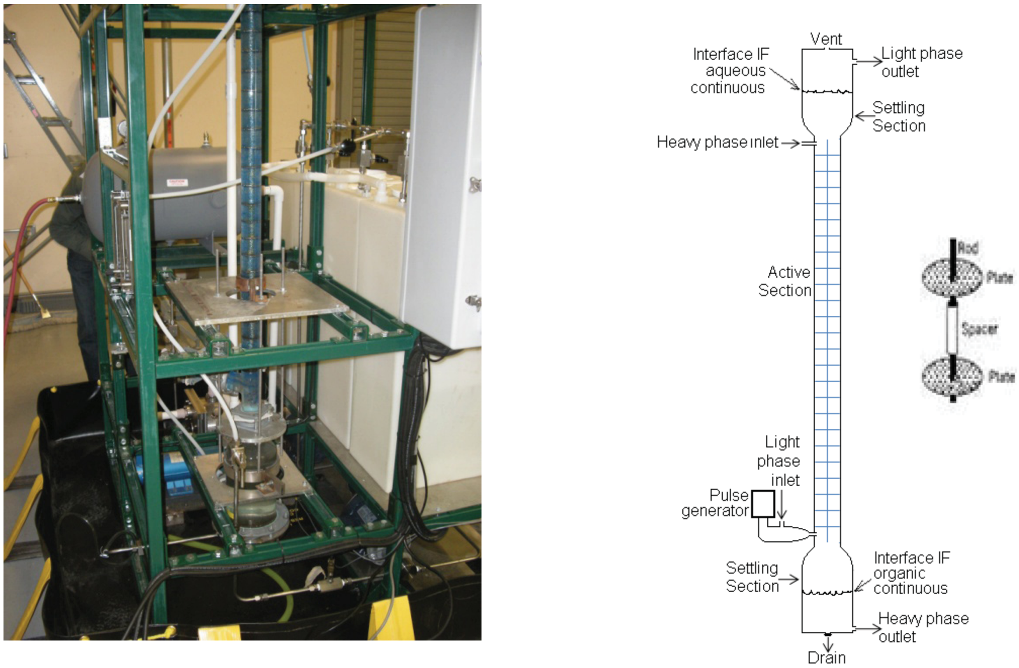


Figure 4. Pulsed column and schematic

3.3.2 Centrifugal Contactors

The following equipment parameters are relevant to prediction of performance of centrifugal contactors, and should be included to develop an annular centrifugal contactor model.

- Number of stages
- Feed and effluent locations
- Recycle, bypass, and sampling streams
- Rotor diameter
- Rotor speed
- Contactor dimensions to determine solution holdup and residence time in the mixing zone and separating zone
- Vane type
- Inclusion of a heating/cooling capability (either as user input parameter or as a jacketed heat exchanger on the centrifugal contactor housing included in energy balances. Required fluid flows and surface areas can be user defined or calculated based on heat loads.

The capability to input the following equipment/process related parameters should be included. It should be noted that it is anticipated that a sub-scale predictive capability will ultimately be developed for these parameters.

- Chemical equilibrium efficiency, either directly input or calculated
- Other-phase carryover either directly input or calculated

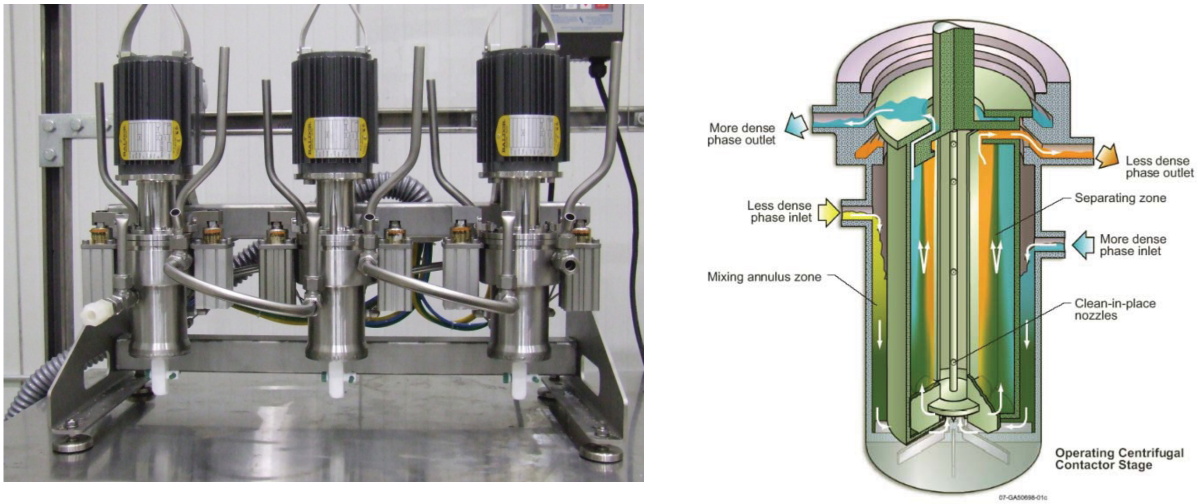


Figure 5. 5.5-cm centrifugal contactor and schematic

3.3.3 Mixer-Settlers

The following equipment parameters are relevant to prediction of the performance of mixer-settlers, and should be included to develop a mixer-settler model.

- Number of stages
- Feed and effluent locations
- Recycle, bypass, and sampling streams
- Mixing zone dimensions/volume to determine holdup and residence time
- Settling zone dimensions/volume to determine holdup and residence time
- Mixer speed, blade types, and dimensions (determine mixing intensity)

The capability to input the following equipment/process related parameters should be included. It should be noted that it is anticipated that a sub-scale predictive capability will ultimately be developed for these parameters.

- Chemical equilibrium efficiency either directly input or calculated
- Other-phase carryover either directly input or calculated

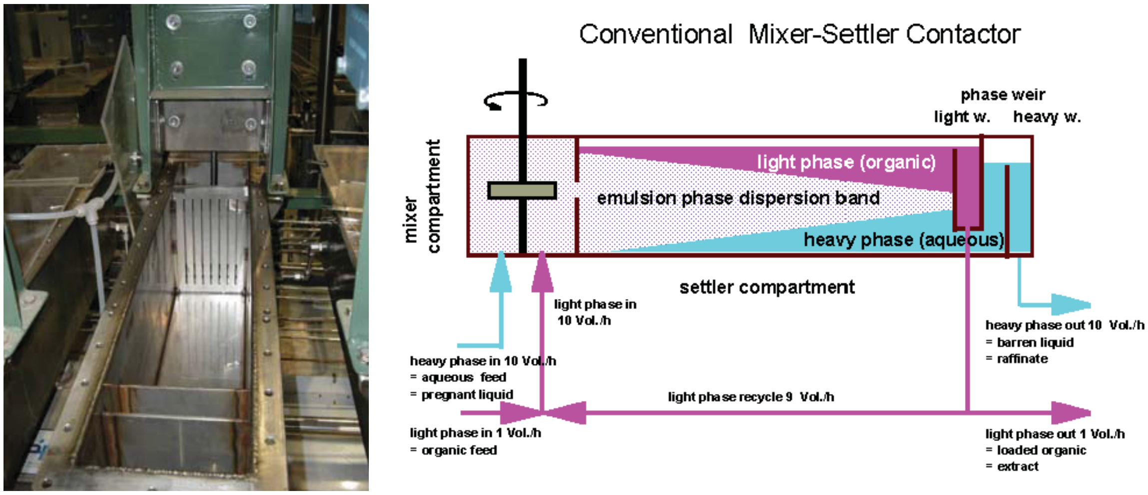


Figure 6. Mixer-settler and schematic

3.3.4 Tankage and Ancillary Equipment

A typical separations facility will include equipment other than the specific separation equipment. While other major units of operation (e.g., evaporators, ion exchange) are outside of the scope of this effort, process surge vessels and feed/product tanks are an integral part of the dynamic process and should be included in the model. These tanks are particularly important in determining hold-up, for carrying out feed adjustments, and to buffer plant operations that have differing time constants. In a detailed model, they provide a potentially more accurate representation of normal and off-normal operations. As such, the following parameters should be included.

- Number of tanks
- Location of tanks within processes
- Tank volumes and dimensions
- Parameters of heat exchanger equipment (can be user specified or calculated).
- Feed adjustment chemicals, volumes, rates of addition, and reaction times
- Residence times
- Liquid transfer mechanisms (steam jets, air lifts, etc.) and fill rates
- Amount of heels and precipitates (formation chemistry)
- Carryover (from contacting equipment)

4. MODELING APPROACH

Existing dynamic modeling capabilities have previously been researched. Based upon these efforts and the knowledge and experience of modelers within the SafeSeps IPSC, a recommended approach has been developed to achieve the goals of this modeling effort. Data needs to support model development have also been identified.

4.1 Existing Dynamic Simulation Capabilities

4.1.1 Literature Survey

A survey of existing dynamic solvent extraction modeling capabilities has recently been performed by Krebs and these capabilities are summarized in Tables 2 and 3.[5] Specific references for each of these processes are also provided. This literature review was conducted as a precursor to implementing time-dependent equations in the Argonne Model for Universal Solvent Extraction (AMUSE) code in order to better ascertain the state of the art in solvent extraction process models. Of particular interest were the forms of the time-dependent differential equations and the solution techniques employed. Although several different codes have been used to simulate the PUREX process, none appear to have been kept current, with the exception of AMUSE. More importantly, none is as flexible as AMUSE as the majority focused on either recovery of U and Pu using PUREX or the industrial separation of the rare earth elements. In some instances copies of the models in the form of computer codes are available in the reports: SEPHIS, ICPSEF, PUBG, CUSEP, and MIXSET. The details on some of the codes, particularly those developed in other countries, are very limited. Of the numerous models/codes, three are worthy of note: SEPHIS, PUBG, and MIXSET.

Groenier first reported on the SEPHIS code in 1972.[6] It was designed to model PUREX flowsheets run with mixer-settlers. Mixers were modeled using the assumption of intense, perfect mixing. It was assumed that all mass transfer between the two phases occurred in the mixers and complete separation was obtained in the settlers. Watson and Rainey reported on their modification of the SEPHIS code.[7] The distribution coefficients are calculated using empirical fits to experimental data. In 1979 Mitchell reported on further modifications of the SEPHIS code.[8] Species followed by SEPHIS-MOD4 included U(VI), Pu(IV), Pu(III), HNO_3, and a Pu(IV) reductant. Time-dependent differential equations are used to calculate the concentration profiles during transient and steady-state conditions. SEPHIS-MOD4 uses the Runge-Kutta method to numerically integrate the differential equations describing the mixer. A second, faster integration method using the finite difference form of the mixer differential equations was implemented for calculating steady-state conditions directly. Time-dependent differential equations were developed for the settlers, but were subsequently reduced to the finite difference form and solved using iterative methods. Chemical reactions are handled in a separate subroutine, but are not directly included in the mass balance equations. Three different methods are offered to the user to reduce Pu(IV) to Pu(III). Many heat effects, other-phase carryover (back-mixing), and phase entrainment were neglected. Bendixsen later adapted SEPHIS-MOD4 for simulating the first-cycle uranium extraction system, conducted on sieve-plate pulse columns, at the Idaho Chemical Processing Plant (ICPP).[9] SEPHIS modules have been written for THOREX, BUTEX, and a process for co-extraction of plutonium and neptunium; in addition, preliminary blocks have been added to calculate extraction coefficients or provide coefficient data bases for UREX, TRUEX, FPEX, and TALSPEAK.

Beyerlein and Geldard developed PUBG for the IAEA.[10-12] They used a modified version of the Richardson total nitrate salting strength equation to calculate distribution coefficients of the species. Time-dependent differential equations were used to describe the settlers and were numerically integrated using the fourth-order Runge-Kutta method. The time-dependent, mass balance differential equations were developed for the mixers, but were reduced to coupled polynomial equations for steady-state conditions. The coupled polynomial equations were then solved iteratively. A time-dependent differential equation is used to describe heat transfer in the settlers.

MIXSET was developed to simulate solvent extraction processes using mixer-settlers. Known reports for MIXSET describe the 1977 and 1979 versions, and the more recent MIXSETX.[13-15] The 1977 version, written in FORTRAN IV, handled H^+, U(IV), U(VI), Pu(III), Pu(IV), NH_2OH, and N_2H_4. Distribution coefficients could be provided by the user as either a third order polynomial or in tables. The 1979 version included two groups of reaction models. The first included reduction of Pu(IV) by U(IV), oxidation of Pu(III) by HNO_3, oxidation of U(IV) by NO_3^- or O_2, and decomposition of HNO_2. The second included reduction of Pu(IV) by hydroxylamine nitrate (HAN), oxidation of Pu(III) by HNO_3, decomposition of HNO_2. The last published version of MIXSET-X handles HNO_3, U(IV-VI), Pu(III-VI-V-VI), Np(IV-V-VI), Am, Cm, Zr, Tc, HNO_2, Sr, Ru, Cs, Ce(III), and Gd(III) species. Overall it includes distribution coefficients for 31 constituents including actinides and fission products (FPs), and 45 chemical reactions. Users select any distribution coefficients and chemical reactions to be tracked, and adjust reaction rate constants via the data they input. Recycle flow through a buffer tank and TBP degradation calculations are also available. The authors state that MIXSET-X can simulate the solvent extraction processes at the Tokai reprocessing plant in one calculation run. The authors also state that the program structure and mathematical modeling of the system have been entirely changed to obtain numerical stability and program readability.

4.1.2 Time-dependent AMUSE Code development

The AMUSE code is an up-to-date steady-state modeling tool developed by Argonne National Laboratory (ANL) for numerous solvent extraction processes including PUREX, UREX, NPEX, COEX, TRUEX, FPEX, and CCD-PEG.[16] The distribution coefficients (D-values) used in AMUSE can be user defined or calculated using thermodynamically-based equations as opposed to empirical polynomial equations fitted to sets of experimental data. ANL recently initiated the implementation of time-dependent differential equations into AMUSE code. Initial development of time-dependent AMUSE was done in the MATLAB® environment. A two-phase, three section, 20 stage countercurrent centrifugal contactor flow model was created that initially used fixed D-values. The model calculates the mass balance for each phase at each stage resulting in two time-dependent differential equations per stage. The 4th-order Runge-Kutta method is then used to obtain a solution. The time-dependent mass balance equations have been modified to accommodate user specified number of sections and stages per section. The time-dependent equations have been linked to the FORTRAN version of SASPE, within the MATLAB® environment, allowing the D-values to be updated during the course of the calculation.

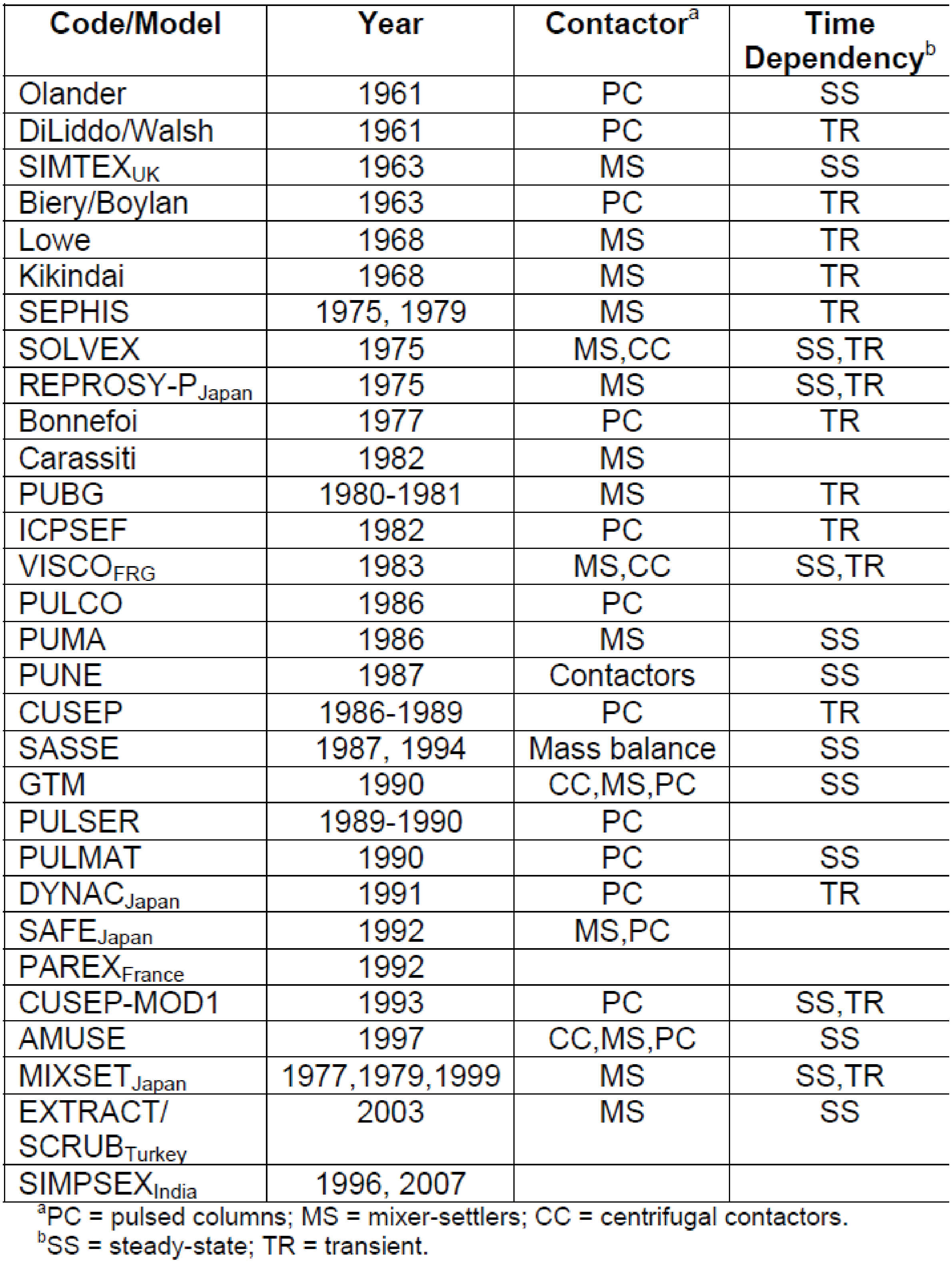
4.1.3 INL dynamic solvent extraction model development

The Idaho National Laboratory, through a Laboratory Directed Research and Development (LDRD) project, has recently initiated development of a dynamic solvent extraction model. An executable model was developed initially to simulate dynamic conditions in a PUREX-type flow sheet using conventional mixer-settler solvent extraction equipment. This model was then expanded to simulate the time-dependent changes, from startup to steady state, in a 30-stage annular centrifugal contactor bank (ACC) running a TRUEX flow sheet. A pilot scale demonstration was performed and the results compared to the model simulation. The centrifugal contactor model was developed using a simplified combination of continuity and momentum conservation terms from the Navier-Stokes equations. Work has recently focused on further refinement to model concentration transients in a centrifugal contactor. Systems with forced convection terms (i.e., mass flow) are often modeled adequately by considering spatial gradients only in the direction of flow. Effects from flow vectors in other directions, i.e. mixing, are approximated by an overall dispersion coefficient. This approach is not technically correct in terms of modeling the real physics; however, it is common in engineering practice and has provided levels of fidelity that are adequate for research and development support. The ACC model uses three well mixed volume elements to simulate the concentration changes in each phase occurring in the mixing zone, and a continuous dispersed plug flow volume element to model concentration changes occurring in the rotor. The model provides reasonable predictions of the extractable metal as compared to the experimental data. The simulation predicts dynamic and steady-state concentration profiles that agree quite well with expected system behavior, which indicates the structure and numerical solution of the model equations are correct. It was also shown that the model simulation converges to a solution quite rapidly. All modeling work was conducted using the gPROMS® software package for solving the differential equations.

4.1.4 ORNL dynamic solvent extraction model development

Oak Ridge National Laboratory, through a Laboratory Directed Research and Development project, and later with interactions with other sponsors, has been developing a time-dependent plant level solvent extraction module based on non-equilibrium multi-stage cascade of contactors. The approach has been modular for stand-alone and integration modes. Initial experiments with this module as integrated into a third-party plant-level simulator were recently reported.[18] The implementation has followed a componentized approach wherein no approximation is made on the time-dependent terms of the balance equations, and a fully implicit and coupled solution of the resulting differential algebraic equations (DAE) is obtained with direct use of DAE solvers (at the moment DASPK). Past time-dependent solvent extraction codes have spent much of the implementation effort in solving uncoupled equations iteratively and proved to be a fragile numerical scheme. The current code uses a rigorous assembly of equations and a robust time adaptive solution method suitable for sensitivity analysis using the existing Jacobian matrix of the non-linear system of algebraic equations. Past work with the current code has also invested in an external adapter code to perform massive parameter studies via parallel computing. An example with results was recently reported.[19] More recent work has focused in developing components in the solvent extraction code that fit a generic separations process so that integration with other processes designed and implemented in the same fashion allows for the composition of an entire plant simulation application via the SafeSeps tookit.[20-21] The current solvent extraction module has the ability to leverage reaction mechanisms if available; at the moment the SEPHIS fit to distribution coefficients for the PUREX process is used. The resulting code is prototyped with the open source Octave m-language which provides a C++ API for incremental transformation into a compiled future code. Demonstration of the capability to incorporate F-SASPE into the module is a planned SafeSeps activity for FY11.

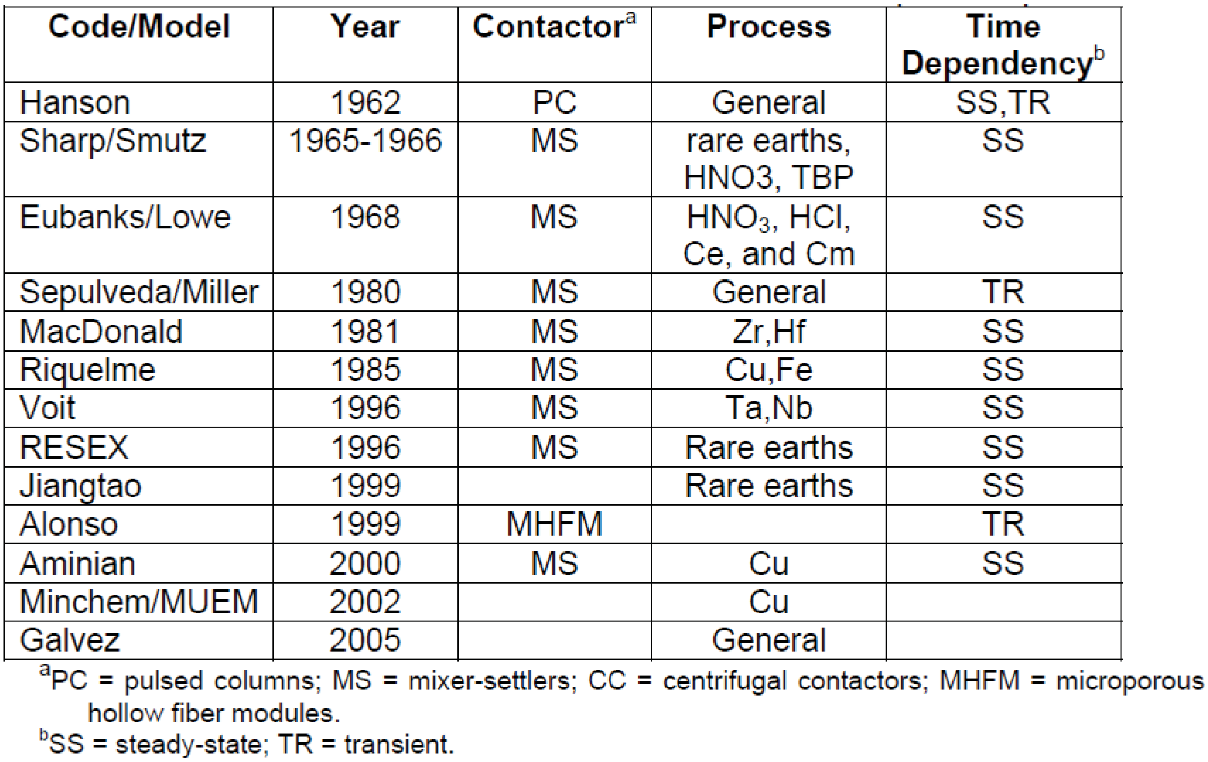
Table 2. Previously developed solvent extraction models for PUREX processing



Code/Model	Year	Contactor[a]	Time Dependency[b]
Olander	1961	PC	SS
DiLiddo/Walsh	1961	PC	TR
SIMTEX$_{\text{UK}}$	1963	MS	SS
Biery/Boylan	1963	PC	TR
Lowe	1968	MS	TR
Kikindai	1968	MS	TR
SEPHIS	1975, 1979	MS	TR
SOLVEX	1975	MS,CC	SS,TR
REPROSY-P$_{\text{Japan}}$	1975	MS	SS,TR
Bonnefoi	1977	PC	TR
Carassiti	1982	MS	
PUBG	1980-1981	MS	TR
ICPSEF	1982	PC	TR
VISCO$_{\text{FRG}}$	1983	MS,CC	SS,TR
PULCO	1986	PC	
PUMA	1986	MS	SS
PUNE	1987	Contactors	SS
CUSEP	1986-1989	PC	TR
SASSE	1987, 1994	Mass balance	SS
GTM	1990	CC,MS,PC	SS
PULSER	1989-1990	PC	
PULMAT	1990	PC	SS
DYNAC$_{\text{Japan}}$	1991	PC	TR
SAFE$_{\text{Japan}}$	1992	MS,PC	
PAREX$_{\text{France}}$	1992		
CUSEP-MOD1	1993	PC	SS,TR
AMUSE	1997	CC,MS,PC	SS
MIXSET$_{\text{Japan}}$	1977,1979,1999	MS	SS,TR
EXTRACT/ SCRUB$_{\text{Turkey}}$	2003	MS	SS
SIMPSEX$_{\text{India}}$	1996, 2007		

[a] PC = pulsed columns; MS = mixer-settlers; CC = centrifugal contactors.
[b] SS = steady-state; TR = transient.

Table 3. Solvent extraction models for other separation processes



Code/Model	Year	Contactor[a]	Process	Time Dependency[b]
Hanson	1962	PC	General	SS,TR
Sharp/Smutz	1965-1966	MS	rare earths, HNO3, TBP	SS
Eubanks/Lowe	1968	MS	HNO_3, HCl, Ce, and Cm	SS
Sepulveda/Miller	1980	MS	General	TR
MacDonald	1981	MS	Zr,Hf	SS
Riquelme	1985	MS	Cu,Fe	SS
Voit	1996	MS	Ta,Nb	SS
RESEX	1996	MS	Rare earths	SS
Jiangtao	1999		Rare earths	SS
Alonso	1999	MHFM		TR
Aminian	2000	MS	Cu	SS
Minchem/MUEM	2002		Cu	
Galvez	2005		General	

[a] PC = pulsed columns; MS = mixer-settlers; CC = centrifugal contactors; MHFM = microporous hollow fiber modules.

[b] SS = steady-state; TR = transient.

4.2 Recommendations for Feature Requirements

The NEAMS SafeSeps IPSC should develop a dynamic solvent extraction model that seamlessly integrates with an overall dynamic plant level architecture, and that can function as a stand-alone solvent extraction application. This is the current approach for designing and implementing the SafeSeps IPSC modules of the plant toolkit.[19-21] The goal is to develop an IPSC solvent extraction model through a collaborative DOE-NE effort managed by the NEAMS SafeSeps IPSC. Recommendations are provided for an approach to achieve this goal.

This document will not attempt to detail internal features of the models and software to be developed but it does provide a list for considerations of desired features. Features will be determined by the modeling and developers teams that will work from a set of usage requirements to be provided in a later document. Specific features of concern are:

1. The programming language must be flexible to allow for modification and expansion of the code. It also must be able to interface with other models and sub-models in the overall plant level model architecture.
2. The final software program should not utilize commercial software requiring licensing. It is acceptable to utilize commercial software to support programming or solving of differential algebraic equations to facilitate model development or to verify the mass transfer and thermodynamic equations that are developed. These initial modeling efforts will ultimately require conversion to platforms that do not require licensing.

3. Existing data and models, primarily those developed at ANL, ORNL and INL, including the PUBG, MIXSET, and PULCO/PULSER/PULMAT models, should be used to advance development of the IPSC model where appropriate. The wide variety of equilibrium data from the AMUSE code should initially be utilized for development of dynamic models. In the longer term, it will be desirable to transition to equilibrium and non-equilibrium models based on thermodynamics and kinetics of the system.
4. For most processes, centrifugal contactors and mixer settlers can be treated as a series of stages with perfect mixing and separation.
5. Terms for efficiency and other-phase carryover (either user specified or calculated (from higher fidelity models) may often be used to account for deviations from ideal behavior.
6. It may not be necessary to model the mass transfer within a contactor stage. This will reduce the complexity of the differential equations and the necessary solvers. Notable exceptions include systems where reaction kinetics and/or mass transfer are slow relative to residence time, such as systems with redox reactions or complexation reactions in centrifugal contactors.[22]
7. Plant-level solvent extraction models should be built from mathematically reduced models of the underlying continuum level. In this approach an extensible model is derived and its implementation into software will inherit the capability for future fidelity improvement.
8. A dynamic pulsed column model will likely require modeling of the mass transfer along the column in order to predict concentrations at any given point along its length.
9. The overall model should incorporate equilibrium and non-equilibrium models (See Figure 7) as needed to describe the extraction chemistry. As only certain complexes or species of a given metal are extracted, the relative quantities of the extractable and in-extractable species and their inter-conversion must be controlled to achieve the desired separation. Modeling in-process speciation (e.g., Np in nitric acid) may require describing both the final equilibrium state and/or the kinetics of conversion from one species to another.
10. The overall model should incorporate component-specific kinetic models (See Figure 7) as needed. It is known from the literature that some metal components extract at different rates at different solution conditions. In some instances kinetic models could be favored over equilibrium models for a given component.[22]
11. An energy balance should be included in order to predict temperature profiles throughout the process. This will also allow the user to determine the energy needs for the process within the plant. The calculation will depend upon the equipment type, solution flowrates and process chemistry.
12. The model must include a GUI to allow use by non-expert customers.
13. The model must be fully documented and developed in accordance with the FCR&D QAPD, and Verification and Validation Plan.

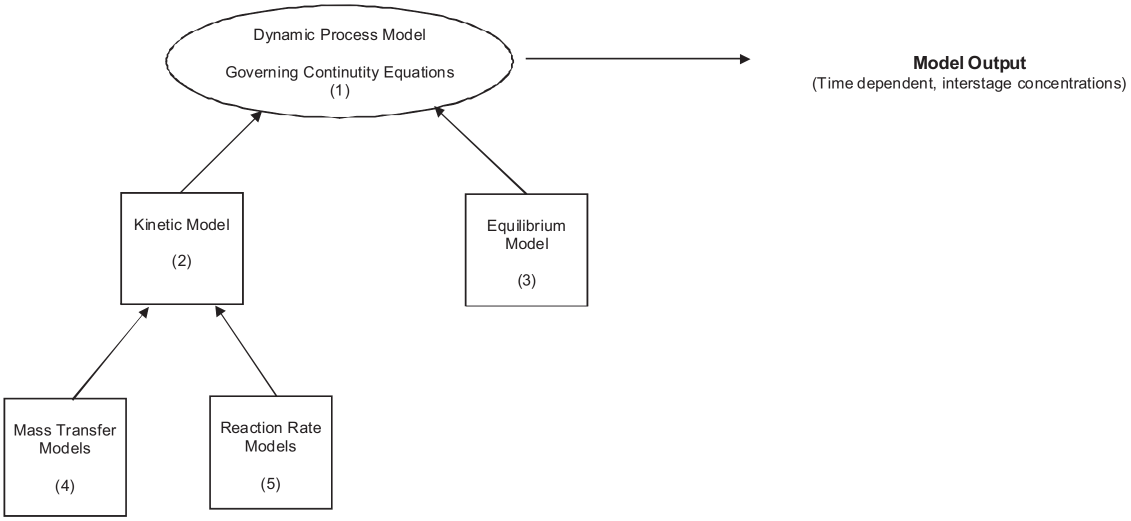


Figure 7. Schematic of modeling approach

5. DATA NEEDS

Considerable data are available for many solvent extraction processes including PUREX, UREX, COEX, NPEX, TRUEX, TALSPEAK, FPEX, and CCD-PEG. All of these systems, with the exception of FPEX, are currently available within the AMUSE code, and these data should be available for use in this effort. However, additional experimental data will be needed to expand the number species which are followed, and to model both evolutionary advances in these processes and more advanced solvent extraction separations as they are developed. Dynamic models will require data that can be used to predict the evolution of processes, while most available data have been collected for equilibrated systems. This will include considerable thermodynamic data as the models transition from the experimentally determined component-based equilibrium models in the AMUSE code to equilibrium models based on the thermodynamics of the system. A focused experimental program will be required to generate the data required to support this modeling effort. This experimental program needs to be tightly coupled with the modeling and simulation development of the solvent extraction software to ensure the experimental data are obtained for a given model and aimed at a given computational validation procedure. Specific data requirements are listed below.

1. Equilibrium distribution data on many relevant components are available in the current literature[17]. Additional data will be required to incorporate all of the elements and compounds of interest identified in section 3. To illustrate this point, the PUREX, UREX, and NPEX models as currently implemented in AMUSE have D-value equations for H^+, Ag^+, Bi^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, MoO_2^{2+}, Pd^{2+}, Rh^{3+}, $Ru(NO)^{3+}$, VO^{2+}, VO_2^+, Y^{3+}, ZrO^{2+}, La^{3+}, Ce^{3+}, Ce^{4+}, Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Th^{4+}, UO_2^{2+}, Np^{4+}, NpO_2^+, NpO_2^{2+}, Pu^{3+}, Pu^{4+}, Am^{3+}, Cm^{3+}, F^-, Cl^-, PO_4^{3-}, SO_4^{2-}, TcO_4^-, AHA, acetic acid, and HNO_2. The following components have fixed D-values as they do not appreciably extract: Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Cr^{3+}, Cs^+, Li^+, Mg^{2+}, Na^+, Rb^+, $Ru(NO)(NO_3)_x^{3-x}$ (for x=1,2), Sr^{2+}, $C_2O_4^{2-}$, ClO_4^-, boric acid ($B(OH)_3$), and I_2. Conversely, the CCD-PEG model currently implemented in AMUSE only has D-value equations for Cs, Sr, Eu, and Am. The other components, comprised of transition metals and other lanthanides and actinides, use the D-values of these four components as the basis for

their D-values. Finally, at the other end of the spectrum there are no TALSPEAK or FPEX models currently implemented AMUSE, calculations involving these process use known fixed D-values. Hence entire model needs to be developed for the TALSPEAK and FPEX processes.

2. Current models[16] describe distribution coefficients as functions of concentrations and activities. More robust models (i.e., system thermodynamics) use models of activity coefficients for all components. Chemical potentials derived in this manner would then reproduce the experimental distribution coefficients, but also tend to be more robust and accurate in extrapolations to data-poor operating conditions. The program SXFIT in one such model being currently being developed.[23]

3. Dynamic behavior requires knowledge of holdup, mass transfer rates and interfacial areas. Initial approximations may substitute overall measures of efficiency for these data, but more detailed descriptions would be preferred. In particular, mass transfer coefficients for species of interest (e.g., uranium and plutonium), as functions of extraction process and temperature would be very useful. The variation of interfacial area with process parameters (e.g., rotor speed or pulse rate) is also needed.

4. Kinetic rates for reactions of interest (e.g., redox, metathesis, solvent degradation) are needed to describe system behavior as well as identify which reactions are appropriate to represent using equilibrium relationships.

5. Dynamic energy balances require knowledge of heat transfer rates, heats of reaction, and heat capacities. Heat transfer rates for most common process equipment are available from commercial vendors. For many components and processes it is expected that heats of reaction will not contribute significantly, although sufficient data should be gathered to validate this assumption. Heat capacities will tend to reflect the values of the continuous pure phase components, but will deviate significantly at higher loadings. Accurate heat capacities are particularly important at production scales where surface to volume ratios can be significantly lower than at laboratory and pilot scales.

6. A standardized procedure needs to be established for collecting batch scale distribution coefficient data. This is envisioned as some of the data may be used for validation purposes. With respect to batch scale validation studies one needs to know both sources of and magnitudes of error associated with the data set being collected. Examples of error that would be used in a propagation of error analysis would be the error of the pipette used for transfers, the error on the gamma spectrometer for counting the isotopic tracer used, and the error of the temperature bath used. The procedure should *not* specify acceptance criteria for a target level of error. The sole purpose is to ensure that *all* necessary data are collected at the time the experiments are conducted. A standardized format for the reporting of the batch scale data should be provided.

7. A standardized procedure needs to be established for collecting lab-scale validation data. One needs to know both sources of and magnitudes of error associated with the data set being collected. Examples of error that would be used in a propagation of error analysis would be the error of pumps used to deliver solutions to the equipment, the error of the gamma spectrometer used for counting the isotopic tracer used in the experiment, and the error of the of the temperatures as measured by a multiplexing data acquisition system. The procedure should *not* specify acceptance criteria for a target level of error. The sole purpose is to ensure that *all* necessary data are collected at the time the experiments are conducted. Additional data that could be recorded are the model numbers of pumps and characteristics of the data acquisition system, for example.

8. A repository needs to be established for the data used in model development and in validation studies. A strong recommendation is that all data be stored both electronically and in tabular form. All <u>raw</u> data should be deposited in the data repository. The purpose of the repository is to ensure that model developers are using well known, documented data sets. Requiring that the raw data be stored allows for later analysis using mathematical techniques that have not been developed, or envisioned, at the time the data were collected. A very important feature of a central data repository is that it would facilitate data compilation from multiple data sources. One source of data that is available is from the open literature, much of which would need to be digitized. As the population of the central data repository grows, analysis of the repository could be used to demarcate targeted experimental data collection.

9. There are a limited number of components for which kinetic data are available. For the PUREX process most components extract quickly, it may be easier to focus on those components that are known or expected to extract slowly.

10. Predictive capability for temperature dependency of distribution coefficients is currently limited. For example, in AMUSE only U, Th, and Bi have temperature dependency incorporated into their D-value equations.

11. Potential contributors to thermal effects in addition to process heating/cooling and mixing energy should be considered. For example, enthalpy of extraction may be important, particularly for components with the largest concentrations. Decay heat may also be important to the contribution of heat to the system and should be investigated.

12. On-line analytical and process data measurements are needed from engineering-scale equipment to track concentrations of multiple species in real time. For components which online measurement is not feasible, sample data as a function of time during transient conditions are needed. These data are necessary to support model validation.

6. PATH FORWARD

Development of the SafeSeps IPSC dynamic solvent extraction model to meet the requirements detailed in this document will be a very complex, multi-year process. There are numerous requirements identified in this document (e.g., equipment types, components of interest, solvent systems of interest, desired output). A prioritization of the needs is necessary to ensure the development effort most effectively meets the customer needs. The following path forward to development of the model and its corresponding software implementation is the recommended starting point for this prioritization activity.

1. Start the modeling effort with a process that is well understood and for which substantial data exist. It is recommended that the initial focus be for TBP-based solvent extraction processes (PUREX, UREX, COEX and NPEX). This will also support the SafeSeps IPSC plant level modeling goal of developing a plant-level model based on the PUREX process.

2. Utilize existing equilibrium solution data initially. Because the transition to equilibrium models based on system thermodynamics will require a sizeable, organized data collection and reconciliation effort, the initial focus of that effort should be on capability development rather than deployment. There are ongoing efforts in the DOE NE FCR&D to generate applicable thermodynamic data as well as develop a predictive modeling capability incorporating non-idealities of aqueous-based separation processes using the computer program SXFIT.[23] This effort will provide the basis for the transition to equilibrium models based on system thermodynamics.

3. Initial modeling should focus on systems utilizing stage wise contactors, because their physical compartmentalization enables straightforward comparison to equilibrium-stage models. Priority is given to centrifugal contactors because of their efficient fluid dynamics; they are compact and relatively easy to operate. Numerous data are available and can be collected from centrifugal contactor experimental setup across the complex. Consequently, validation tests can be performed with existing equipment. Through addition of equipment-focused modules, the code can be expanded to include mixer-settler and pulse column models, as well as models of other contactor types, while employing common chemistry modules.
4. Focus on the components that are targeted in the separations process initially (see Section 3.2.1). Considerable data are currently available for these elements. Co-extraction of other components of interest will likely require support of an experimental program and can be added at a later date. The code should readily accommodate addition of species as data come available or through user-defined properties.
5. Incorporate an approach that decomposes the solvent extraction model into four modeling sub-components, namely, mass and energy balances, chemical thermodynamics, chemical kinetics, and contacting operations[19]. The modeling approach would employ general stage-wise cascade arrangements of either physical or logical stages (or both) to be exercised by the developer of the module. The mass and energy balances will be implemented to allow for generality of the model and enable interoperability of different contacting devices. This decomposition will eliminate a common implementation problem of past codes which intertwined all elements and therefore had no natural extensibility property. For example, a change in kinetics or contacting device typically leads to a total overhaul of the code.
6. Define usage requirements for the software based on the previous recommendations to aid in the design of the initial product.
7. Involve the NEAMS VU Program right from the start of this effort. Work with QA personnel to ensure all modeling and data generation/validation experiments are performed within the requirements of the FCR&D QAPD.
8. Work closely with SafeSeps personnel to ensure that the model is compatible with the overall IPSC modeling architecture being developed and interfaces with other unit operations models.

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