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# Nuclear Energy Advanced Modeling and Simulation (NEAMS) Waste Integrated Performance and Safety Codes (IPSC): Gap Analysis for High Fidelity and Performance Assessment Code Development

Yifeng Wang, J. Guadalupe Argüello, Geoff Freeze, Harold C. Edwards, Thomas Dewers, Timothy J. Fuller, Carlos Jove-Colon, Joon H. Lee, Paul Mariner, Malcolm Siegel, and Stephen Webb

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## Abstract

This report describes a gap analysis performed in the process of developing the Waste Integrated Performance and Safety Codes (IPSC) in support of the U.S. Department of Energy (DOE) Office of Nuclear Energy Advanced Modeling and Simulation (NEAMS) Campaign. The goal of the Waste IPSC is to develop an integrated suite of computational modeling and simulation capabilities to quantitatively assess the long-term performance of waste forms in the engineered and geologic environments of a radioactive waste storage or disposal system. The Waste IPSC will provide this simulation capability (1) for a range of disposal concepts, waste form types, engineered repository designs, and geologic settings, (2) for a range of time scales and distances, (3) with appropriate consideration of the inherent uncertainties, and (4) in accordance with rigorous verification, validation, and software quality requirements.

The gap analyses documented in this report were are performed during an initial gap analysis to identify candidate codes and tools to support the development and integration of the Waste IPSC, and during follow-on activities that delved into more detailed assessments of the various codes that were acquired, studied, and tested. The current Waste IPSC strategy is to acquire and integrate the necessary Waste IPSC capabilities wherever feasible, and develop only those capabilities that cannot be acquired or suitably integrated, verified, or validated.

The gap analysis indicates that significant capabilities may already exist in the existing THC codes although there is no single code able to fully account for all physical and chemical

processes involved in a waste disposal system. Large gaps exist in modeling chemical processes and their couplings with other processes. The coupling of chemical processes with flow transport and mechanical deformation remains challenging. The data for extreme environments (e.g., for elevated temperature and high ionic strength media) that are needed for repository modeling are severely lacking. In addition, most of existing reactive transport codes were developed for non-radioactive contaminants, and they need to be adapted to account for radionuclide decay and in-growth. The accessibility to the source codes is generally limited. Because the problems of interest for the Waste IPSC are likely to result in relatively large computational models, a compact memory-usage footprint and a fast/robust solution procedure will be needed. A robust massively parallel processing (MPP) capability will also be required to provide reasonable turnaround times on the analyses that will be performed with the code.

A performance assessment (PA) calculation for a waste disposal system generally requires a large number (hundreds to thousands) of model simulations to quantify the effect of model parameter uncertainties on the predicted repository performance. A set of codes for a PA calculation must be sufficiently robust and fast in terms of code execution. A PA system as a whole must be able to provide multiple alternative models for a specific set of physical/chemical processes, so that the users can choose various levels of modeling complexity based on their modeling needs. This requires PA codes, preferably, to be highly modularized. Most of the existing codes have difficulties meeting these requirements.

Based on the gap analysis results, we have made the following recommendations for the code selection and code development for the NEAMS waste IPSC: (1) build fully coupled high-fidelity THCMBR codes using the existing SIERRA codes (e.g., ARIA and ADAGIO) and platform, (2) use DAKOTA to build an enhanced performance assessment system (EPAS), and build a modular code architecture and key code modules for performance assessments. The key chemical calculation modules will be built by expanding the existing CANTERA capabilities as well as by extracting useful components from other existing codes.

# ACKNOWLEDGEMENTS

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# 1.0 INTRODUCTION

The U.S. Department of Energy (DOE), Office of Nuclear Energy (NE) Advanced Modeling and Simulation Campaign, co-ordinates the development of Integrated Performance and Safety Codes (IPSCs) in four technical areas: Fuels, Reactors, Safeguards and Separations, and Waste. Within the DOE-NE Advanced Modeling and Simulation (NEAMS) Campaign, these four IPSCs are supported by four cross-cutting elements: Fundamental Methods and Models (FMM), Verification and Validation and Uncertainty Quantification (VU), Enabling Computational Technologies (ECT), and Capability Transfer (CT). The goal of the NEAMS Waste IPSC is to develop an integrated suite of computational modeling and simulation capabilities to quantitatively assess the long-term performance of a disposal (or a storage) system in an engineered/geologic environment. The Waste IPSC will provide this simulation capability (1) for a range of disposal concepts including various waste form types, engineered barrier designs, and geologic settings, (2) for a range of temporal and spatial scales, (3) with appropriate consideration of the associated uncertainties, and (4) in accordance with rigorous verification, validation, and software quality requirements.

To achieve this goal, the Waste IPSC will incorporate three levels of model fidelity: (1) constitutive relationships derived from mechanistic sub-continuum processes; (2) high-fidelity continuum models; and (3) moderate-fidelity performance assessment (PA) continuum models. The integration of modeling and simulation capabilities at these three levels of fidelity will derive from a combination of existing code acquisition and new code development. These multi-fidelity modeling and simulation capabilities must be supported by efficient frameworks and enabling tools/infrastructure, also derived from a combination of existing and new codes.

The development of the Waste IPSC will be an iterative process over the multi-year duration of the project. In fiscal year 2010 (FY10), activities within the Waste IPSC included: (1) specification of a challenge problem and associated milestones to demonstrate proof of concept; (2) development of a verification and validation (V&V) plan; (3) a preliminary gap analysis of thermal-hydrologic-chemical-mechanical-biological-radiological (THCMBR) code capabilities; and (4) initial development and integration of frameworks and enabling tools/infrastructure. These activities build upon the Waste IPSC system design specifications outlined in SNL (2009). The specifications of the challenge problems and associated milestones, designed for testing and tracking the progress of the IPSC code development, are documented in Freeze et al. (2010a). The V&V plan is documented in Edwards et al. (2010) and the preliminary THCMBR code gap analysis is summarized in Freeze at al. (2011, Section 4.3 and Appendix A). In fiscal year 2011, an activity was initiated to refine the existing code capability gap analysis and to expand it to include a more detailed hands-on assessment of a series of codes that were acquired, studied, and tested. These codes were chosen on the basis of the preliminary assessment that was initially performed.

This report documents the refined gap analysis performed for the development of both high fidelity and PA continuum codes. Section 2.0 summarizes the technical requirements for the high-fidelity and PA code development. Section 3.0 describes relevant THCMBR processes and the corresponding mathematical formulations. Section 4.0 summarizes the gap analysis of a selected set of existing THCMBR codes and tools as compared to the code requirements described in Section 3.0. Section 5.0 provides the recommendations for bridging the identified gaps. Section 6. summarizes the overall Waste IPSC gap analysis progress to date.

The Waste IPSC gap analysis is a continuing process and the analysis documented in this report serves only as a starting point for subsequent analysis planned to be conducted throughout future years. Therefore, the list of codes examined in this report is by no means exhaustive. Further development and integration of code capabilities, frameworks, and tools will be documented in future reports.

# 2.0 TECHNICAL SPECIFICATIONS FOR HIGH FIDELITY AND PERFORMANCE ASSESSMENT CODE DEVELOPMENT

## 2.1 Objectives and Intended Uses of NEAMS Waste IPSC

As mentioned in Section 1.0, the overarching goal of the Waste IPSC is to develop an integrated suite of modeling and simulation capabilities to quantitatively assess the long-term performance of a radioactive waste disposal (or storage) system in an engineered/geologic environment (SNL 2009, Section 1). This requires the simulation of the coupled THCMBR processes that govern radionuclide (or other hazardous constituent) movement from the waste forms through the engineered components and the geosphere for a range of alternative disposal system designs (e.g., disposal concepts, waste emplacement geometry, waste form types, engineered component designs, geologic settings) and conditions (e.g., saturated vs. unsaturated flow, boiling vs. non-boiling temperature, reducing vs. oxidizing chemistry). Accurate simulation of a disposal system requires modeling the coupled THCMBR processes over a broad range of time scales (nanoseconds to millions of years) and distances (angstroms to kilometers). The broad range of time scales and distances further requires the application of uncertainty quantification (UQ) techniques to the models and their inputs. Depending on their different uses, the set of codes and tools developed under the NEAMS Waste IPSC will be subjected to various levels of code verification & validation and quality assurance.

The waste IPSC has several intended uses (Edwards et al., 2010, Section 2.2):

- Performing analyses to support decision-making and prioritization of disposal options;
- Designing waste forms and engineered barrier systems (EBS);
- Performing analyses to support site selection, characterization, and licensing for a selected disposal system, and;
- Providing a working example for meeting the requirements of the waste IPSC challenge problem.

There will be multiple users for the waste IPSC in the foreseeable future. In the next few years, development efforts and challenge-problem milestones could provide insights on the modeling of disposal systems to the DOE-NE Nuclear Energy Used Fuel Disposition (UFD) Campaign. This campaign may, in turn, provide information to the Secretary of Energy’s Blue Ribbon

Commission (BRC) on America's Nuclear Future. The waste IPSC will also be used by the DOE-NE Waste Form (WF) Campaign in evaluating the interplay between waste-form durability and disposal system performance for various waste forms and disposal-system environments. In the next 5 to 10 years, the capabilities of the waste IPSC will be needed by the DOE-NE UFD to inform implementation of the BRC's recommendations and evaluate the relative performance and long-term safety of alternative radioactive-waste disposal or storage concepts and designs. The Waste IPSC will also inform the DOE-NE WF Campaign about the potential benefits of high-performing waste forms for selected waste streams in specific disposal system environments. In that same time frame, simulations enabled by the waste IPSC capabilities may provide input and insights to the Nuclear Regulatory Commission (NRC) as that agency considers revisions to the federal regulations governing the disposal of radioactive waste. The waste IPSC will be needed by the DOE to support site selection and to prepare a defensible technical basis (i.e., a performance assessment) for a license application for selected disposal alternatives.

The entire waste IPSC will be subjected to a high level of scrutiny by stakeholders. The public will be the first and foremost of stakeholders, although indirectly, through the policy makers, regulators, licensing authority, advocates, and interveners. It is anticipated that policy makers and regulators will use the waste IPSC to support decision-making and prioritization among various options for waste disposal. A second set of stakeholders will be the scientific community (including those contributing to the development of the waste IPSC) who will be asked to critique and evaluate the scientific adequacy and merit of the product. It is anticipated that the scientific community will use the developed modeling and simulation capabilities to design waste forms and engineered barrier systems for long-term disposal systems. Finally, another important set of stakeholders will be the users of the waste IPSC to run analyses to support licensing. It is anticipated that these stakeholders will be interested in system-level performance analyses with quantified uncertainties that will place strong demands on the tool set.

## 2.2 Conceptualization of Generic Waste Disposal Systems

A generic representation of a waste disposal system is shown in Figure 1. The system includes components, domains, and phenomena common to most nuclear waste geologic disposal systems. The top half of Figure 1 shows the physical domains of the system: engineered barrier system (EBS), geosphere, and biosphere. The terms near field (or near-field environment) and far field (or far-field environment) are also commonly used to describe the physical domains of a disposal system. The near field encompasses the EBS and the adjacent portion of the host rock that experiences durable (but not necessarily permanent) changes due to the presence of the repository (e.g., hydro-mechanical alteration due to tunnel excavation, thermal-chemical alteration due to waste emplacement). The far field encompasses the remainder of the geosphere and the biosphere.

The bottom half of Figure 1 shows the phenomena that can affect each of these domains. These phenomena include, at a high level, the coupled THCMBR processes that control:

1) Radionuclide Source Term – which includes degradation of the waste form, degradation of the waste package, interaction with the EBS environment, and radionuclide dissolution and precipitation,
2) Radionuclide Transport through the EBS – which includes advection, diffusion, and sorption of dissolved and colloidal radionuclides and interaction with the EBS environment,
3) EBS Environment - which includes thermal evolution, fluid movement, fluid chemistry evolution, degradation of EBS components (e.g., waste form, waste package, buffer materials, backfill, liner, seals),
4) Radionuclide Transport through the Geosphere (the host rock and surrounding geologic units) - which includes advection, dispersion, and sorption of dissolved and colloidal radionuclides and interaction with the geosphere environment,
5) Geosphere Environment - which includes temperature variation, fluid movement, fluid-water interaction, and mechanical and chemical alteration of the host rock and surrounding geologic units,
6) Radionuclide Transport in the Biosphere – which includes radionuclide movement, uptake, and human health effects, and
7) Biosphere Environment and Dose Factors - which includes THCMBR processes that affect radionuclide movement and uptake and the characteristics of receptor.

These high-level phenomena are represented and described in additional detail by a set of potentially relevant features, events, and processes (FEPs). The identification of a preliminary set of 208 Waste IPSC FEPs broadly applicable across different disposal alternatives is described in Freeze et al. (2010b, Section 2.3).

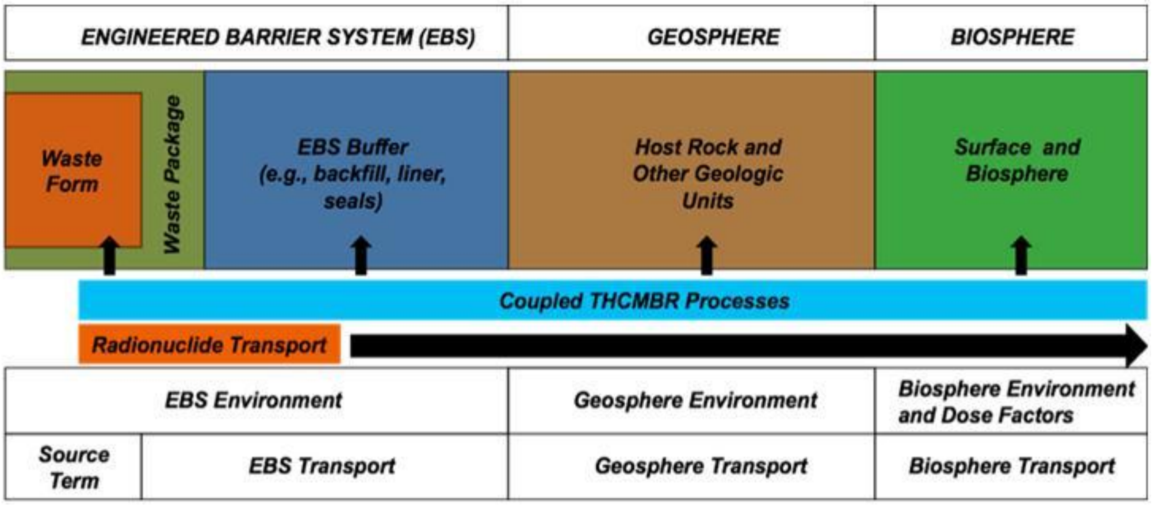


**Figure 1.** Components of a generic disposal system

A set of 6 potential waste form type groupings (Table 1) and 8 potential disposal concept/geologic setting groupings (Table 2) were identified to define the expected range (based on current knowledge) of disposal system concepts, designs, settings and conditions (Freeze et al. 2010a, Section 2.1; Freeze et al. 2010b, Section 2.1). These groupings result in 35 combinations (ignoring the placeholder "Other" groups) of waste form types and disposal concepts/geologic settings that broadly define the range of potential alternative disposal system designs that might need to be evaluated using the Waste IPSC. Within any single alternative disposal system design there may be important sub-designs (e.g., waste emplacement geometry, thermal loading, engineered component (waste form, waste package, backfill, etc.) design and materials) and/or conditions (e.g., saturated vs. unsaturated flow, boiling vs. non-boiling temperature, reducing vs. oxidizing chemistry) that may further delineate the range of technical capabilities required of the Waste IPSC. As technologies and socio-political drivers evolve, the relevant waste form groupings, concept/setting groupings, disposal system domains, and phenomena may all evolve, which may in turn lead to evolving code requirements.

**Table 1.** Groupings of Potential Waste Form Types

| Group Number | Waste Form Type | Description |
|---|---|---|
| 1 | Used Nuclear Fuel (UNF) | e.g., Commercial, DOE-Owned, HTGR |
| 2 | High-Level Waste (HLW) Glass | Current (e.g., borosilicate) and future (e.g., no minor actinides) |
| 3 | High-Level Waste (HLW) Glass Ceramic / Ceramic | Current (glass bonded sodalite) and future (e.g., from electrochemical processing) |
| 4 | High-Level Waste (HLW) Metal Alloy | From electrochemical or aqueous reprocessing, cermets |
| 5 | Lower Than HLW (LTHLW) | Class A, B, and C, and GTCC |
| 6 | Other | Molten salt, electro-chemical refining waste, etc. |

Note: HTGR = High-temperature gas-cooled reactor; GTCC = Greater than Class C.

The technical scope of the Waste IPSC must be broad enough to represent the range of potentially relevant THCMBR processes (and associated time- and length-scales) captured by these 7 high-level phenomena for a range of disposal system alternatives encompassed by the 35 combinations of concepts/settings and waste form types.

**Table 2.** Groupings of Potential Disposal Concepts and Geologic Settings

| Group Number | Disposal Concept / Geologic Setting | Description |
|---|---|---|
| 1 | Surface Storage | Long-term interim storage at reactors or at centralized sites |
| 2 | Shallow Disposal | e.g., near-surface disposal, LTHLW sites (Depths <= 100 m) |
| 3 | Mined Geologic Disposal (Hard Rock, Unsaturated) | Granite/crystalline or tuff (Depths > 100 m) |
| 4 | Mined Geologic Disposal (Hard Rock, Saturated) | Granite/crystalline or tuff (Depths > 100 m) |
| 5 | Mined Geologic Disposal (Clay/Shale, Saturated) | Clay/shale (Depths > 100 m) |
| 6 | Mined Geologic Disposal (Salt, Saturated) | Bedded or domal salt (Depths > 100 m) |
| 7 | Deep Borehole Disposal | Granite/crystalline (Depths~ 1000 m) |
| 8 | Other | Sub-seabed, carbonate formations, etc. |

## 2.3 Probabilistic Performance Assessments of Waste Disposal Systems

Due to the inherent uncertainties associated with the simulation of long-term performance of radioactive waste disposal systems, the capabilities to perform probabilistic assessments will be a key aspect of the Waste IPSC. The intent of a probabilistic PA is to provide stakeholders with a risk-informed decision analysis regarding the performance of the disposal system. Such an assessment is designed to answer four key questions related to the waste isolation capability of the disposal system (Helton et al. 1999; Pilch, Trucano, and Helton 2006):

I Scenario identification – What can happen?
II Likelihood of scenarios – How likely is it to happen?
III Consequences of scenarios – What are the consequences if it does happen?
IV Credibility – How much confidence do we have in the answers to the first three questions?

The performance of a disposal system is generally described with prespecified metrics, such as the peak or cumulative dose that a hypothetical receptor can potentially receive within a regulatory time frame, typically ranging from 10,000 to 1 million years. The dose is estimated by accounting for the release rates of all radionuclides at a specified disposal-system boundary and the associated health effects of the released radioisotopes. In a PA, the projected dose is compared to a performance metric (e.g., for a license application, the performance metric is a dose standard defined by a regulatory agency). Figure 2 shows an example of the output from a probabilistic PA from the Waste Isolation Pilot Plant (WIPP) for comparison.

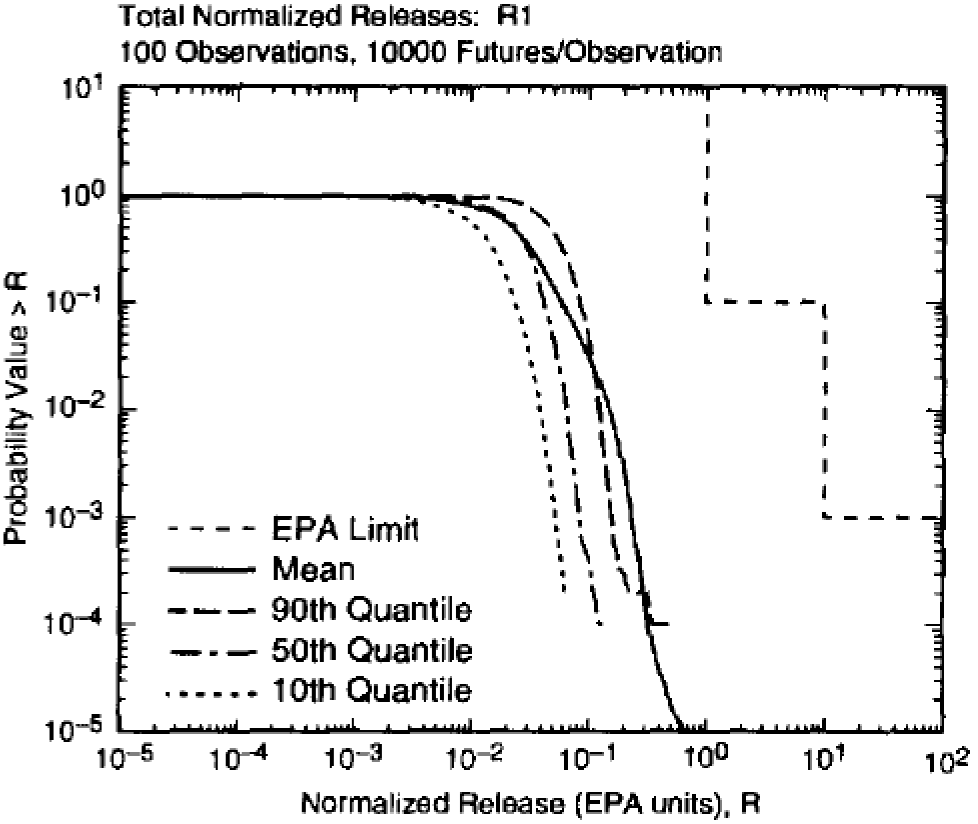


**Figure 2.** Example from Helton et al. (1999) comparing normalized release with Environmental Protection Agency (EPA) limit for WIPP.

The safety margin of a disposal system is defined as the difference between the regulatory standard, denoted, for example, by the dashed "EPA Limit" line in Figure 2 and the projected value of the performance metrics, denoted, again for example, by the solid "Mean" line in the figure. In a probabilistic PA it is also necessary to quantify the uncertainty associated with the projected safety margin. The safety margin analysis and uncertainty quantification (UQ) are thus an integral part of the performance assessment of a nuclear-waste disposal system. For instance, the EPA specifically dictates the PA for WIPP in 40 CFR 194. The following are examples of these requirements:

a) The results of performance assessments shall be assembled into "complementary, cumulative distribution functions" (CCDFs) that represent the probability of exceeding various levels of cumulative release caused by all significant processes and events.
b) Probability distributions for uncertain disposal system parameter values used in performance assessments shall be developed and documented in any compliance application.

c) Computational techniques, which draw random samples from across the entire range of the probability distributions developed pursuant to paragraph (b) of this section, shall be used in generating CCDFs and shall be documented in any compliance application. (EPA 1998).

It is worth noting that in items (b) and (c) above, the EPA specifically requires the careful evaluation of probability distributions for uncertain model input parameters and the appropriate propagation of uncertainties through PA calculations. Performance assessments for the waste IPSC will also have to produce data that meet similar regulatory agency requirements.

For the Yucca Mountain project, the National Regulatory Commission (NRC) defines a similar probabilistic PA methodology and requirements in 10 CFR 63, although specific details and standards differ from WIPP. It is anticipated that similar methodologies will be adopted for future performance assessments of radioactive-waste disposal systems.

## 2.4 Functional Requirements for NEAMS Waste IPSC Development

The Waste IPSC will incorporate three levels of model fidelity: constitutive relationships derived from mechanistic sub-continuum processes; high-fidelity continuum models; and moderate-fidelity PA continuum models. The integration of modeling and simulation capabilities at these three levels of fidelity will derive from a combination of existing code acquisition and new code development. These multi-fidelity modeling and simulation capabilities must be supported by efficient frameworks and enabling tools/infrastructure, also derived from a combination of existing and new codes. Waste IPSC technical requirements are described in Freeze et al. (2010a, Section 2) and Freeze et al. (2011), use cases are identified in SNL (2009, Section 5) and Freeze et al (2010a, Section 3), and computational requirements are outlined in Edwards et al. (2010, Sections 3 through 6).

The high-level functional requirements for the waste IPSC are documented as use cases in SNL (2009, Section 5 and Appendix B) and Freeze et al. (2010a, Section 3). The requirements are developed according to a top-down approach that starts with the top-level requirements for a performance assessment system and then propagates these requirements down scale to the high-fidelity continuum and sub-continuum models. The development of functional requirements is an iterative process, with high-fidelity continuum and sub-continuum models influencing performance assessment. These requirements will be revised and refined as the project progresses.

### 2.4.1 Functional Requirements for Performance Assessment Codes

Long-term performance assessments of waste isolation in geologic repository environments require consideration of coupled THCMBR processes that span multiple spatial and temporal scales. A PA calculation generally requires a large number (hundreds to thousands) of model simulations to quantify the effect of model parameter uncertainties on the predicted repository performance. A PA model – a simplified version of the corresponding high fidelity model - is designed to speed up PA calculations while still capturing the essential behavior of the high-fidelity model. For this purpose, a PA model must be sufficiently robust and fast in terms of code execution.

A PA model can be as simple as a response surface (e.g., look-up table or neural network) or can be a model with reduced dimensionality and couplings among different processes. It is perceived that PA models combined with appropriate integration/analysis tools will ultimately constitute a PA system, in which self-contained PA models (or code modules) will be linked with high flexibilities to accommodate specific repository concepts (Figure 3). A PA system constructed in this manner will be sufficiently flexible to handle different disposal environments (e.g., bedded salt, volcanic tuff, clay, granite, deep borehole disposal, etc.) and various waste forms (e.g., glasses, metallic alloys, ceramics, etc). This PA system will provide multiple alternative models for a specific set of physical/chemical processes, so that the users can choose various levels of modeling complexity based on their modeling needs.

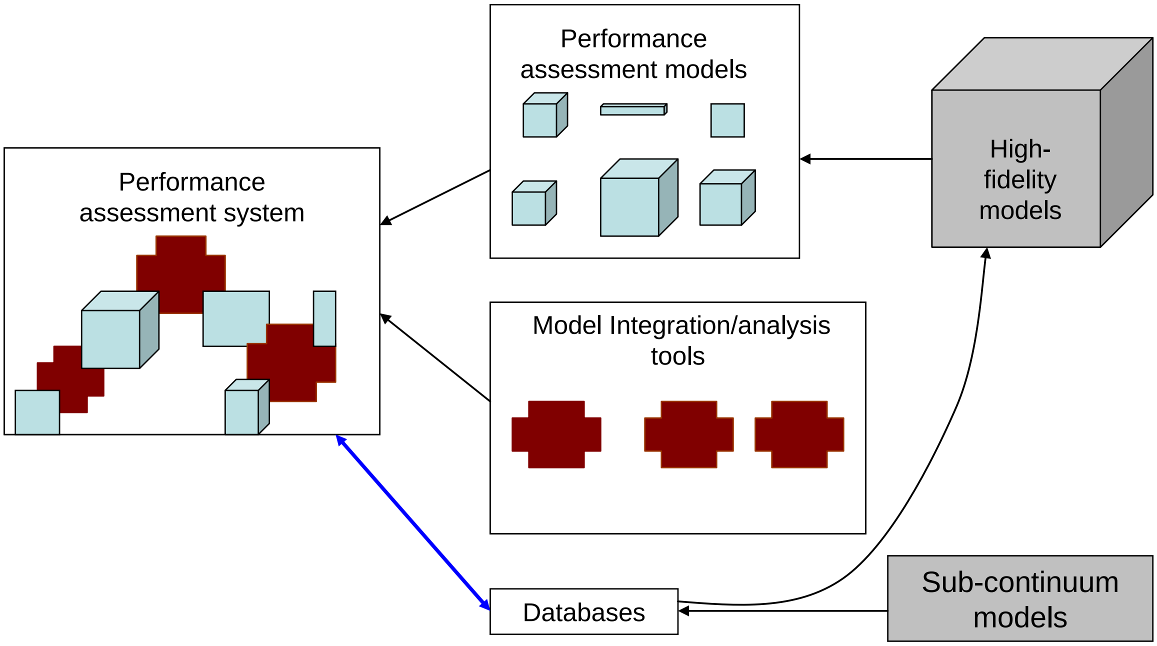


**Figure 3.** Construction of a performance assessment (PA) system from PA models. The relationship of PA models to high-fidelity and sub-continuum models are also indicated. The PA system repeatedly reads the input parameter values from and saves the simulation results to the databases during a PA calculation (SNL, 2009).

Different from the high-fidelity model, a PA system will be mainly limited to handling unidirectional linking among code modules at each time step (i.e., there will be no iterative feedback between processes) and it will run model simulations on coarse grids. In each code module, however, full couplings among various physical/chemical processes are expected; therefore, the degree of model granulation is a key factor that must be considered in PA model development. Finally, for regulatory compliance applications, the PA system must be designed to ensure the transparency, traceability, reproducibility, and retrievability of simulation results.

The requirements for a PA system are grouped into two general categories: the system level and the subsystem level. At the system level, a series of use cases describe possible scenarios for the application of a PA system:

- Set up access permissions for various categories of users.
- Define simulation domains for a disposal system (e.g., waste panels or drifts, radionuclide release pathways, etc).
- Define the types of waste forms, the types of waste containers and their distributions in the disposal system.
- Define state variables of each simulation domain and associate each simulation domain with a set of model operations (i.e., process models or code module).
- Determine model parameters by fitting a model to experimental data.
- Determine the statistical properties of the parameter distribution or probability density function to be used in the simulations.
- Run multiple independent codes (or modules) sequentially according to a specified data flow among them.
- Run a deterministic calculation, if needed, by using the means, medians, specified constants (or flow fields), or specified percentile values for the model parameters.
- Perform multiple realizations for a given scenario.
- Perform uncertainty analyses and construct statistical results for regulatory compliance.
- Identify important parameters that control total system performance through sensitivity analyses.
- Determine the uncertainty related to the PA model abstraction and simplification.
- Verify and validate a code module or a linked set of code modules against a set of testing cases.
- Perform regression tests against a set of established testing cases.
- Visualize the temporal evolution of the state of each individual simulation domain the user selects.
- Provide a graphic interface to wrap and execute a self-contained code.

A performance assessment system constructed from PA models consists of six subsystems. The requirements of the subsystem level are formulated according to the functionalities of each subsystem:

- Basic model linking/integration tools: Provide miscellaneous functions and tools for model linking.
- Thermal processes: Provide necessary code modules for modeling heat generation and conduction in the near-field environment of a disposal system.
- Hydrologic/transport processes: Provide necessary code modules for calculating flow fields and the related radionuclide transport in the disposal system.
- Mechanical processes: Provide necessary code modules for simulating rock damage and deformation around the excavation of the repository and their impacts on the integrity of an engineered barrier system.
- Chemical processes: Provide necessary code modules for modeling the chemical evolution of both the near-field and the far field environments.

- Databases: Provide a data warehouse for storing input parameter data, PA results, and the other data supporting the derivation of the input parameter values and PA calculations.

### 2.4.2 Functional Requirements for High Fidelity Codes

High-fidelity models—that range from waste forms, to waste packages, to the EBS buffer/ emplacement drift, and to the far-field domain—are designed to evaluate the integrated coupled THCMBR processes involved in waste isolation. Simulations of these processes typically involve large three-dimensional meshes, simulate time periods of tens of thousands of years, and require explicit coupling between the processes. The coupling between THCMBR processes may be fully integrated, two-way coupling contained in a single code, or one-way coupling that requires periodic communication between codes developed to model the different processes. Additionally, the high-fidelity models must be sufficiently flexible to handle different geologic disposal environments (e.g., salt, clay, granite, deep borehole, etc.), engineered barrier design options (e.g., waste forms and waste package types, backfill, etc.), and various waste forms (e.g., glasses, metallic alloys, ceramics, etc). For a regulatory compliance application, this system must be designed to ensure the transparency, traceability, reproducibility, and retrievability of simulation results.

The requirements for the high-fidelity models are focused on the couplings among different physical/chemical processes. The requirements are categorized into the following three groups of use cases:

*Thermal-Hydrological Processes:* Two use cases are formulated for the continuum (or high-fidelity) models for thermal-hydrological processes. The first use case assumes that the simulation domain geometry is fixed and the only necessary coupling is to the chemistry code. This coupling can be one-way, for which a flow field is given from the thermal-hydrological code and radionuclide release and transport are modeled accordingly. Two-way coupling is included as a possibility, for which the geochemical evolution in the domain could affect the flow field via thermo-physical property changes. The second use case captures the first, but also includes the effects of evolving domain geometry from various processes such as drift collapse, precipitates affecting pore openings, rock falls, waste package corrosion breach and degradation, flow through breach openings, etc. This use case requires coupling of the thermal-hydrological code to both the chemistry and mechanical codes. Again a variety of coupling procedures will need to be available from one-way coupling to two-way coupling, either loosely or tightly. In the far-field, the thermal-mechanical coupling with hydrological processes become less important. Accordingly, the modeling of hydrological processes will focus on the representation of flows in spatial heterogeneous (e.g., fractured) media.

*Mechanical Processes:* All the mechanical cases at the continuum model level have direct input into one of the following processes critical to waste isolation:

- Mechanical failure of the waste form or waste package - such a failure would introduce water or contaminants to the waste form;

- Mechanical change to the porosity or permeability of the host rock - such a change would affect the hydrologic flow and transport of radionuclides from the near field to the far field environment.

The use cases in this group describe the requirements for modeling mechanical processes related to:

- Closure of the drift around the waste package due to salt creep or clay deformation;
- Thermal-mechanical behavior of the drift and the potential for rock fall event with sufficient energy to cause mechanical failure in the waste package or waste form;
- Thermal-mechanical behavior of the drift and the change in fracture apertures and permeability in the near field;
- Hydroscopic swelling of bentonite backfill and the resulting stress changes on the WP/WF and closure of fractures/interfaces in backfill (i.e., change in permeability);
- Effect of seismic events on waste form and waste package (mechanical failure);
- Closure of the drift around the waste package due to salt creep, and the effect of that creep on the salt backfill around the waste package and waste form.

*Chemical/transport Processes:* Use cases for chemical processes at the continuum level are focused on the couplings among various chemical reactions in waste forms, waste packages and the near field environment as well as the couplings of these reactions with thermal, hydrological, and mechanical processes. These use cases describe the requirements for simulating the following processes:

- Evolution with time of (1) waste form composition and (2) radionuclide isotopic composition and distribution within the waste form and inside the waste package;
- Chemistry of incoming water into the emplacement drift;
- Evolution of water chemistry from interaction with ground support and other introduced materials in the emplacement drift;
- Evolution of water chemistry from interaction with backfill around the waste package in the emplacement drift;
- Evolution of water chemistry from interaction with rock fall rubble around the waste package;
- Uniform corrosion process and penetration of waste package wall;
- Localized corrosion (pitting and crevice corrosion) process and penetration of waste package wall;
- Stress corrosion cracking (SCC) process and penetration of waste package wall;
- Corrosion degradation of waste package internal structural materials upon initial breach of the waste package;
- Corrosion degradation of waste form canisters upon initial breach of waste package;
- Waste form degradation, radionuclide release and mobilization from the waste form, and in-package chemical environment inside breached waste package;
- Radionuclide release from breached waste package and transport in the EBS;
- Radionuclide transport from the EBS to the far field;

- Reactive transport of radionuclide in the far-field, including radionuclide sorption/desorption and colloid-facilitated transport and accounting for the effect of chemical and physical heterogeneities in geologic media.

### 2.4.3 Functional Requirements for the Challenge Problem

The waste IPSC challenge problem and associated milestones were defined to demonstrate progress in the development of modeling and simulation capabilities, the deployment of frameworks, and the implementation of code verification and validation practices (Freeze et al., 2010a). The challenge problem focuses on a specific type of waste form from Table 1, i.e., high-level-waste borosilicate glass, and a specific disposal concept and geologic setting from Table 2, i.e., mined geologic disposal in salt. The problem includes the coupled THCMBR processes that describe (1) waste form degradation and the associated mobilization of radionuclides, i.e., the radionuclide source term, and (2) radionuclide transport through the near field. The challenge problem also includes the effects of coupled THCMBR processes on the physical and chemical environment in the EBS. The performance measures for the challenge problem include radionuclide mass flux and cumulative release (out of the EBS and across subdomain boundaries); radionuclide mass in place (within the waste form, waste package, and EBS); and spatial distributions of various physical and chemical properties in the EBS, e.g., pH, temperature, fluid saturation, and glass degradation rate.

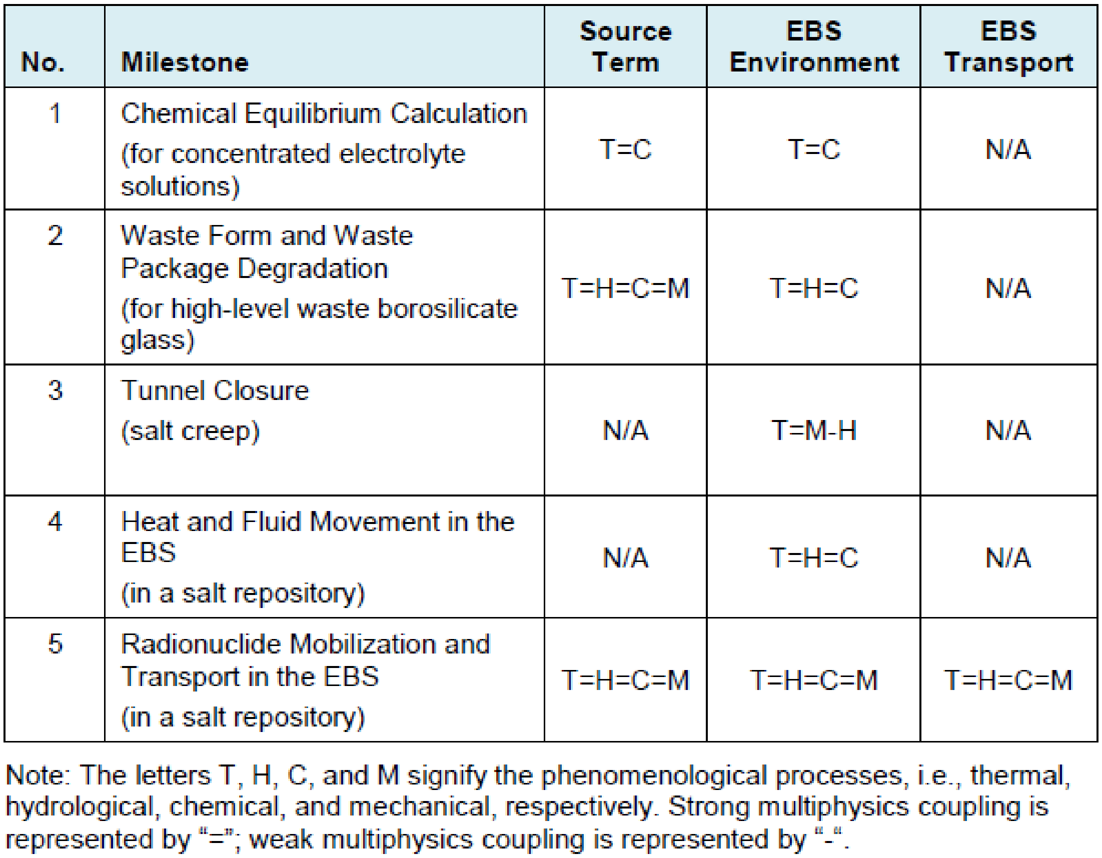
Five milestones are formulated for the waste challenge problem (Table 3) (Freeze et al., 2010a). The specific requirements for each milestone are summarized as follows (Freeze et al., 2010):

1) *Chemical equilibrium calculations:* In both the high fidelity and PA models, the chemical equilibrium calculation will be implemented in a self-contained code module, which will calculate the concentration of each dissolved or gaseous species and the amount of each mineral precipitated from the solution for a specified pressure and temperature condition, given the total mass of each chemical component. For a concentrated electrolyte solution, the activity of each dissolved chemical species will be calculated with a Pitzer or specific ion interaction formulation. This code module must be robust so that a solution can be obtained at each spatial node and each time step in the calculation. A key issue is the completeness and self-consistency of the thermodynamic database. A large gap exists in data availability, especially at high temperatures for some important radionuclides. For the PA model, the module will be used to systematically evaluate the impact of the uncertainties in the thermodynamic data on radionuclide solubility calculations.

2) *Waste form and waste Package degradation:* In the high-fidelity model, the waste package will be represented using a 3-D high resolution mesh to capture the spatial heterogeneity of the materials inside the waste package. Detailed waste package failure mechanisms (e.g., stress corrosion cracking) will be included in the model. These high-fidelity simulations will invoke constitutive models with associated material property databases, founded on chemical processes that have been identified and quantified by atomistic-scale simulations and experiments. These atomistic chemical processes, including reactions and diffusion, will be aggregated to derive averaged rate laws for glass dissolution, with a process and dataflow that is verified and validated (V&V) and that propagates uncertainties. In the PA model, the

waste package will be represented as a well-mixed cell or a small number of physically connected compartments. The PA model will be focused on uncertainty quantification through stochastic sampling of input parameter distributions and multiple realizations of waste package degradation.

**Table 3.** Milestones for Waste IPSC Challenge Problem



| No. | Milestone | Source Term | EBS Environment | EBS Transport |
|---|---|---|---|---|
| 1 | Chemical Equilibrium Calculation<br>(for concentrated electrolyte solutions) | T=C | T=C | N/A |
| 2 | Waste Form and Waste Package Degradation<br>(for high-level waste borosilicate glass) | T=H=C=M | T=H=C | N/A |
| 3 | Tunnel Closure<br>(salt creep) | N/A | T=M-H | N/A |
| 4 | Heat and Fluid Movement in the EBS<br>(in a salt repository) | N/A | T=H=C | N/A |
| 5 | Radionuclide Mobilization and Transport in the EBS<br>(in a salt repository) | T=H=C=M | T=H=C=M | T=H=C=M |

Note: The letters T, H, C, and M signify the phenomenological processes, i.e., thermal, hydrological, chemical, and mechanical, respectively. Strong multiphysics coupling is represented by “=”; weak multiphysics coupling is represented by “-“.

3) *Tunnel closure:* Both the high-fidelity and the PA models will calculate the large deformations and closure of the tunnel and the thermal transfer in the tunnel and surrounding rock as a function of water content in the various materials, the geologic stratigraphy, boundary conditions, any potential gas generation, and the physical configuration of the waste packages. In the high-fidelity model, the tunnel and a representative extent of material (including other geologic strata) above and below the excavation, any backfill, and a representation of the waste packages will be modeled with a 3-dimension high resolution mesh to capture the heterogeneity of the materials in the tunnel and surrounding rock. The high fidelity model will be intended to capture detailed spatial and temporal evolution of deformation and thermal transfer in the tunnel. In the PA model, the tunnel closure will be implemented with a simplified, reduced-resolution representation based on the high-fidelity

continuum model. The PA model will also focus on uncertainty quantification through input parameter sampling and multiple model calculations.

4) *Heat and fluid movement in the near field:* Both the high-fidelity and the PA models will calculate heat and fluid movement in the EBS as a function of water chemistry, degradation kinetics of waste form and waste package materials and any accompanying gas generation, and the physical configuration of the waste packages. In the high-fidelity model, the EBS (potentially including the excavation disturbed zone) and a representation of the waste packages will be modeled with a 3-dimension high resolution mesh to capture the heterogeneity of the materials in the bear field (including any air gap). The high-fidelity model will be intended to capture detailed spatial and temporal evolution of heat and fluid flow within the EBS. In the PA model, the EBS components will be treated as coarsely gridded compartments derived from the high-fidelity continuum model representation. The PA model will be focused on uncertainty quantification through input parameter sampling and simulation of multiple realizations.

5) *Radionuclide mobilization and transport in the near field:* In the high-fidelity model, the tunnel and a representative extent of material surrounding the tunnel, the salt backfill, and a representation of the waste forms and waste packages will be modeled with a 3-dimension high resolution mesh to capture the heterogeneity of the materials in the tunnel and surrounding rock. Three-dimensional multiphase flow and transport simulations will be performed with high spatial resolution, sufficient to capture the individual waste packages. The high-fidelity model will be intended to capture detailed spatial and temporal evolution of deformation, heat and fluid movement, chemical reactions, and radionuclide transport occurring in the near field. In the PA model, the EBS will be represented by a set of coarsely divided compartments, and waste packages will be grouped according to their failure modes and breach times. The representation of the coupled THCM processes governing deformation, heat and fluid movement, chemical reactions, and radionuclide transport will be informed by the high-fidelity model simulations. The PA model will be focused on quantifying the uncertainty for the data transfer from the high-fidelity model to the PA model.

This set of specific requirements for the challenge problem milestone constitutes a subset of overall functional requirements for the waste IPSC.

# 3.0 RELEVANT PROCESSES AND MATHEMATICAL FORMULATIONS

This section describes THCMBR processes relevant to the waste IPSC and their mathematical formulations. This section, together with the functional requirements in the previous section, provides a reference framework for the gap analysis of existing THCMBR codes, with an emphasis on the couplings of multiple processes. The coupled multi-physics described here combines conservation laws for mass, momentum and energy, together with phenomenological or experimentally based equations of state, kinematic conditions, transport laws, rate expressions, and other constitutive relations that express the linkages or couplings between processes.

## 3.1 Thermal-Hydrologic-Chemical Processes

Conservation or continuity relations for mass or energy density of a component *i* in a phase *j* can be written generally as (e.g., Martinez and Stone 2008):

$$\frac{\partial d_j^i}{\partial t} + \vec{\nabla} \bullet \vec{\mathbf{q}}_{\mathbf{j}}^{\mathbf{i}} - Q_j^i \qquad (1)$$

where d is the mass or energy density, q is the flux density with respect to a reference coordinate system, and Q is a source term. Section 3.1.1 discusses applications of Equation 1 to thermal modeling; Section 3.1.2 describes hydrologic modeling and thermal-hydrologic couplings as well as applicable codes. Section 3.1.3 discusses chemical and reactive transport modeling and codes.

### *3.1.1 Thermal Modeling*

Thermal modeling stemming from Equation (1) can be treated in a strict thermodynamic sense (with internal energy as the conserved variable) or, with assumptions, temperature can be assumed to be the conserved variable for heat transport. In the first case, a general expression for multiphase deformable fractured or porous media with saturations *S* is (e.g., Martinez et al. 2001):

$$\frac{\partial}{\partial t}\left[(1-\phi)\rho_s e_s + \phi(\rho_l S_l e_l + \rho_g S_g e_g)\right] + \vec{\nabla} \bullet \vec{\mathbf{q}}_e = Q_e \qquad (2)$$

where $\phi$ is porosity, $\rho$ is density, *e* is internal energy, and the subscripts *s*, *l* and *g* refer to solid, liquid, and gas respectively. The heat flux vector q can include terms for heat conduction, convection, and heat transport. The source term *Q* can include heats of reaction, condensation and evaporation, and radioactive decay.

Common codes for heat transport in porous materials are discussed in the next section, as they are relevant to both heat and fluid flow.

### *3.1.2 Hydrologic Modeling*

Similar to Equation (2), conservation laws can be written for aqueous, gaseous, and supercritical fluids (solutions) occupying intergranular pores in a deformable porous media. This requires specifying the flux density q in Equation (1) in terms of a fluid flux relative to the moving solid, and a solid phase velocity. The resulting terms couple directly to mechanics considerations of stress and deformation discussed in Section 3.2, such as solid phase compressibility, and elastic or elastic plastic deformation of the porous media. This is discussed in detail by Martinez and Stone (2008); Rutqvist et al. (2002) and Lo et al. (2002) among others. Ignoring these terms for simplicity, mass transport equations can be written for components *i* (here in the form of mass fractions *Y*) in the intergranular phases as:

$$\frac{\partial}{\partial t}\phi(Y_{il}\rho_l S_l + Y_{ig}\rho_g S_g) + \vec{\nabla}\bullet(Y_{il}\rho_l \vec{\mathbf{v}}_l + Y_{ig}\rho_g \vec{\mathbf{v}}_g - \vec{\mathrm{J}}_{ig}) = Q_i \tag{3}$$

Here $J_{ig}$ is the gas phase flux, which can include multicomponent diffusion. The Darcy flux $v$ for phase $j$ is given by (Martinez et al. 2001):

$$\vec{\mathbf{v}}_j = -\frac{k_{rj}}{\mu_j} k \bullet (\vec{\nabla} P_j + \rho_j \vec{\mathbf{g}}) \tag{4}$$

where $k_r$ are the relative permeability for phases $j$, $\mu$ is viscosity, $k$ is the permeability tensor, and intrinsic property of the porous media, $P$ is pressure and g is gravitational acceleration. The set of Equations (3) and (4) are supplemented by expressions relating capillary pressure $P_c = P_g - P_l$ and relative permeability as a function of saturations. There are numerous models for these (see for example Pruess et al. 1999 or Martinez et al. 2001) or van Genuchten (1980). Equations (3) and (4) can be cast in a variety of forms, depending on the choice of primary variables (i.e. saturations, densities or pressures).

### *3.1.3 Multicomponent Multiphase Reactive-Transport Modeling*

Geochemical reactive transport modeling for subsurface systems needs to include a lengthy list of processes including aqueous speciation, dissolution/precipitation, redox processes (as mediated by microbiological processes), ion-exchange between solutions and minerals, surface chemical reactions occurring at phase interfaces (i.e. surface complexation, sorption), the effects of these processes on porosity and permeability, coupling with mechanical effects (e.g. water-assisted creep and crack growth; fracture healing, clay mineral swelling) as well as transport (advective, dispersive and multicomponent diffusion, osmotic potentials) and multiphase flow and reaction. The mathematical formulations described here focus on spatio-temporal continuum scales. Recent reviews on reactive transport modeling have been performed by Crawford (1999), Steefel et al. (2005) and MacQuarrie and Mayer (2005).

Geochemical reactive transport models can be classed variously as inverse or forward; batch or transport; equilibrium, non-equilibrium, or “partial local equilibrium”. All reaction-transport codes in use today for multicomponent spatial-temporal modeling use the partial local equilibrium approach, wherein homogeneous reactions such as aqueous speciation [most of which occur with rates faster than milliseconds (Brezonik 1994)] are assumed to be at equilibrium, and heterogeneous reactions such as mineral-water dissolution/precipitation are kinetically mediated. This is by no means exclusive; for example, rates of aqueous conversion of gas phases like hydrogen, carbon dioxide or methane can occur on the time scale of hours. Biogeochemical cycling of sulfur in the aqueous phase at methane/brine seeps involves microbially-mediated homogeneous reactions that can occur on a similar time scale (Senko et al. 2004).

One source of debate is the question of metastability and the role of kinetics in subsurface processes. No one argues that diamonds occur metastably at surface conditions (the stable equilibrium phase under surface conditions would be graphite; diamonds persist due to large activation energy barriers). Some would argue that clay minerals, for example, are metastable precursors to equilibrium phyllosilicates such as micas. Important clay mineral transformations in the subsurface such as smectite-illite are interpreted in the context of the Ostwald step-rule (Morse and Casey 1988). Other workers assign thermodynamic properties to clays as distinct phases, with mixed results. These separate views impact modeling methodologies, i.e. local equilibrium versus a kinetic approach.

Thus users of a multicomponent, multiphase geochemical simulator must keep several questions in mind – what are the time and length scales under consideration; what is the reactive buffering capacity (e.g. of gases and minerals); what are the limitations on thermodynamic and kinetic data for the system in question; what are the options for model validation; what are the (geo) chemical and biological processes that must be included; and most importantly, what processes can be excluded from consideration.

*Speciation/Solubility Modeling:* At its simplest, geochemical modeling of multicomponent systems calculates the speciation of an interstitial solution at equilibrium and determines the saturation state of a suite of minerals and/or gases with respect to that solution. In other words, given an analytical suite of concentrations of elements, speciation/solubility codes distribute moles or masses of the elements amongst discrete chemical species existing in solution at equilibrium at the temperature, pressure, and chemical conditions of interest.

For a chemical system involving N species $A_i$ and $N_r$ chemical reactions, any chemical reaction can be expressed as:

$$0 = \sum_{l=1}^{N} \upsilon_{lr} A_l, \quad (r = 1,....,N_r) \tag{5}$$

where the $\nu_{lr}$ is a stoichiometric coefficient, defined to be <0 for reactant species and >0 for product species. In all geochemical models, a discernment is made between basis species (the minimum set of species required to describe all species in a phase such as an aqueous solution, gas, or mineral). These are termed by various authors as "master", "component" or "primary" species and need not necessarily reflect actual species (Reed 1982). All chemical models (e.g., Wolery 1979) use an alternative description wherein all reactions involving secondary species (aqueous complexes) are written as [termed the canonical form; here we follow notation given in Lichtner (1996)]:

$$A_i \Leftrightarrow \sum_{j=1}^{N_c} \tilde{\upsilon}_{ji} A_j \tag{6}$$

Here, the new stoichiometric matrix is found from:

$$\tilde{\upsilon}_{ji} = -\sum_{r=1}^{N_R} \upsilon_{jr} (\upsilon^{-1})_{ri} \; (j = 1,..., N_c); (i = N_c + 1,...., N) \tag{7}$$

where $N_c$ is the number of primary species ($N_c = N\text{-}N_R$). Various geochemical databases express reaction sets in a given canonical form which is beneficial for retrieval, but also this form is necessary for solution. Speciation/solubility codes all involve a choice of components, a reduction of the system of equations to a minimum number (and a method of selecting stable mineral and gas phases at the conditions of interest). These models solve a set of nonlinear algebraic conditions including $N_c$ mass balance constraints, and $N_R$ mass action equations for the secondary species *i*, which take the following general form (Reed 1982):

Mass-balance:

$$M_{i}^{tot} = n_W [m_i + \sum_i \tilde{\upsilon}_{ji} m_i] \tag{8}$$

Mass action:

$$K_i = \frac{\prod_j m_j^{\tilde{\upsilon}_{ji}} \gamma_j^{\tilde{\upsilon}_{ji}}}{m_i \gamma_i} \tag{9}$$

Here $M^{tot}$ is total number of moles, $n_w$ = number of kilograms of solvent phase, $m_i$ is the molality of the $i^{th}$ species, and $\gamma_i$ is the activity or fugacity coefficient of the $i^{th}$ species in solution. Substituting the mass action equations into the mass balance equations yields a set of $N_c$ nonlinear algebraic equations that can be solved directly, for example using Newton-Raphson methods to determine the equilibrium state in terms of components. These are substituted back into the mass balance expressions to obtain the set of N species concentrations.

The same speciation/solubility problem can be equivalently formulated as a problem of minimizing the total Gibbs free energy (*G*) of the chemical system (Karpov et al. 1997; Kulik 2006):

$$\underset{i}{Min} \quad G(n) = \sum_i n_i \mu_i, \qquad An = M^{tot} \quad and \quad n \geq 0 \tag{10}$$

where ***n*** is the vector of the moles of chemical species in the system; A is the matrix of stoichiometric coefficients of chemical species; $\mathbf{M}^{tot}$ is the vector of total amounts of independent components; and $\mu_i$ is the chemical potential of the *i-th* species. Equation (10) can then be solved using a convex programming algorithm [e.g., an interior point method or the Villars-Cruise-Smith (VCS) approach (Smith and Missen 1982)].

For aqueous solutions, the activity coefficients, reflecting the difference between activities (a thermodynamic model quantity) and concentrations (actual entities in a solution, at least in some statistical sense), are found from two distinct methods (see Bethke 1996 for a concise summary). In part, these differences reflect parallel views of aqueous electrolyte solutions as being completely dissociated, partly dissociated, totally associated, or ignoring disassociation altogether. The first apply some form of the Debye-Hückel equation that takes into account long range ion interactions, and is dependent on the solution's ionic strength, ionic radii, and dielectric properties of the solvent. These include the original and extended Debye-Hückel equations, the Davies equation, and the B-dot model, variously applicable to solutions of increasing salinity or ionic strength, defined as:

$$I = \frac{1}{2}\sum_{i} m_i z_i^2 \qquad (11)$$

where m is concentration in molality and z is ionic charge. The B-dot method is routinely used to calculate activity coefficients for solutions of ionic strength up to one molal, or just slightly more concentrated than seawater. Care must be taken when applying models for activity coefficients to not mix activity coefficients derived from different conventions and assumptions, and not to confuse models that use "true" ionic strength, which accounts for complexation reactions, and stoichiometric ionic strength, which assumes complete dissociation.

The second method can be termed the virial coefficient method, or "Pitzer" method [after the chemist who largely championed the method (Pitzer 1979)]. This method is different from the Debye-Hückel methods in that little or no speciation of the solution need be accounted for, although some complexation is assumed, especially for solutions at elevated temperature. In part this is because short range interactions become prominent as a solution increases in ionic strength, so what constitutes an actual species becomes blurred. As such this method is used exclusively for solutions of high ionic strength. These would include any aqueous solutions in salt repositories and in contact with crushed salt backfill, most oil field waters, waters deriving from evaporation or boiling, waters in pore spaces that "dry out" as may occur during heating or in disturbed zones surrounding tunnels, and groundwater in contact with evaporative minerals. There is much attention paid to expanding the range of applicability of Pitzer-type models to increasingly more complex solutions in the fields of nuclear-waste performance assessment, oil field reservoir quality, and subsurface carbon storage (e.g., Moffat and Jove-Colon 2009).

*Continuity Equations:* There are many excellent publications devoted to spatio-temporal reactive transport modeling. The formulations here are given by Lichtner (1996). In general, conservation of mass for the $i^{th}$ aqueous or gaseous solute mass (in moles/volume) in a phase $\pi$ with saturation $s$ and porosity $\phi$ is given by:

$$\frac{\partial}{\partial t}\left(\phi s_{\pi_i} c_i\right) + \vec{\nabla}\cdot\vec{J}_i = \sum_{r=1}^{N_r} \upsilon_{ir} I_r \quad (i = 1,\ldots N) \qquad (12)$$

with flux *J*. The sum on the right hand side is over the total possible $N_r$ homogeneous and heterogeneous reactions $I_r$ in $\pi$, where $\upsilon_{ir}$ are the stoichiometric coefficients (number of moles of *i* participating in the *r*th reaction). Application to modeling chemical reaction and transport would require simultaneous numerical solution of *N* partial differential equations (PDEs).

In practice solving the problem is a difficult task for several reasons including the lack of knowledge of aqueous speciation kinetics; the disparate time scale between homogeneous and heterogeneous reaction kinetics; and the orders of magnitude difference in the molar densities of solid and aqueous species (leading to "stiff" solutions and slow time stepping). Because of this, models for multicomponent reaction-transport all make certain simplifying assumptions that reduce the number of PDE’s or otherwise simplify the numerical solution.

*Local Equilibrium:* One simplification that is in use (if not commonly) is to assume local equilibrium. Reeves and Kirkner (1988) discuss several methods for transport and reaction assuming local equilibrium. Analogous to the batch equilibria treatment, these authors separate aqueous (and gaseous) species between primary (component) and secondary species, and also include sorption and mineral precipitation/dissolution. While this is strictly for a single phase pore fluid, the method can be extended to include additional pore phases. Letting $L$ represent the transport operator, their equations are:

$$\frac{\partial \phi c_j}{\partial t} + L(c_j) = r_j^c \quad j = 1, \ldots\ldots, N_c \tag{13}$$

$$\frac{\partial \phi x i}{\partial t} + L(x_i) = r_j^x \quad i = 1, \ldots\ldots, N_x \tag{14}$$

where $c_j$ is component $j$ concentration, $x_i$ is secondary species $i$ concentration, and the r are reaction rates where ($aq$ denotes aqueous reactions, $c$ denotes sorption, and $p$ denotes precipitation)

$$r_j^c = r_j^{c(aq)} + r_j^{c(s)} + r_j^{c(p)} \tag{15}$$

The Reeves and Kirkner (1988) treatment continues by specifying the $x$ in terms of the $c$ in canonical form:

$$x_i = \gamma_i^{-1} K_i \prod_{j=1}^{N_c} a_j^{\tilde{\upsilon}_{ij}} \quad (i = 1, \ldots, N_x) \tag{16}$$

and defining a total species concentration $u_j$ in terms of the $c$ and $x$:

$$u_j = c_j + \sum_{i=1}^{N_x} \tilde{\upsilon}_{ij} x_i \tag{17}$$

Multiplying Equation (14) by the stoichiometric matrix and summing over $i$ to $N_x$ allows one to eliminate the homogeneous reaction rates, and to express reaction and transport in terms of the $u_j$ to obtain:

$$\frac{\partial}{\partial t}(\phi u_j) + \frac{\partial}{\partial t}(\phi f_j^{su}) + \sum_{k=1}^{N_p} B_{kj} \frac{\partial}{\partial t}(\phi p_k) + L(u_j) = 0 \quad j = 1, \ldots, N_c \tag{18}$$

Here the $f$ are functions resulting from expressing the sorbed concentrations $s$ in terms of the $u$ (nonlinear mass-action expressions for equilibrium between solution concentrations and surface complexes), $B$ is a stoichiometric matrix for mineral dissolution/precipitation reactions, the p are moles of precipitate per volume of pore fluid, and Np is the number of solid phases. This method reduces the number of unknowns from $2N_c + N_x + N_p$ to $N_c$ PDE's plus $N_p$ mass action equations (relating $p_k$ to the $u_j$) (in reality, one would likely need to include $N_c$ additional equations to solve for the sorption terms).

Reeves and Kirkner (1988) also suggest an alternative method (first introduced apparently by Walsh et al. 1984) by using the total concentration of component j (aqueous + sorbed + solid), $w_j$, as:

$$w_j = u_j + s_j + \sum_{k=1}^{N_p} B_{kj} p_k \quad j = 1,\dots,N_c \tag{19}$$

in which case Equation (18) becomes:

$$\frac{\partial}{\partial t}(\phi w_j) + L[f_i^{uw}(w_1,\dots,w_{N_c})] = 0 \quad j = 1,\dots,N_c \tag{20}$$

a system of $N_c$ PDE's, $N_p + N_x$ mass action equations, and $N_c$ equations of the form of Equation 4.1.18. The algebraic expressions are directly related to the batch equilibrium relations in Equations 4.1.8 and 4.1.9, and so the method basically consists of solving batch equilibrium at every node coupled to a transport equation (Equation 4.1.19). The local equilibrium assumption should be used when the transport time over a length scale of interest is much longer than the time scale for equilibration (Steefel and Van Cappellan 1990).

*Local Partial Equilibrium:* The previous time-scale issues do not hold for many problems of interest and so many surface and subsurface chemical problems are critically dependent on the kinetics of reactions. Widely popular is the assumption of local partial equilibrium, or fast and slow reactions (Lichtner 1996), in which fast reactions like most homogeneous reactions are taken at equilibrium, while slow reactions (including many mineral-water reactions) are kinetically mediated (Lichtner 1985; Ortoleva et al. 1986; 1987a; 1987b; Yeh and Tripathi 1989; 1990). This method is covered in detail in the summary text by Lichtner et al. (1996) and follows much of the derivation in the previous section. In the case where all mineral reactions are treated kinetically, and where mass diffusion of components is species-independent, Lichtner (1996) showed that a description of local partial equilibrium involving mineral-solution reactions can be expressed as:

$$\frac{\partial}{\partial t}(\phi \Psi_j) + \vec{\nabla} \cdot \vec{J}_j = -\sum_{m=1}^{N_{\min}} \tilde{\upsilon}_{jm} I_m + \sum_{r=1}^{N_R^{ke}} \upsilon'_{jr} I_r^{ke} \tag{21}$$

$$\frac{\partial \phi_m}{\partial t} = \bar{V}_m I_m \tag{22}$$

$$\phi = 1 - \sum_m \phi_m \tag{23}$$

where:

$$\Psi_j = c_j + \sum_{i-1}^{N_{aq}} \tilde{\upsilon}_{ji} c_i \tag{24}$$

$$\vec{J}_j = (-\tau\phi D\vec{\nabla} + \vec{v})\Psi_j \tag{25}$$

$$\upsilon'_{jr} = \upsilon_{jr}^{ke} + \sum_{i=N_c^{le}+1}^{N_{le}} \tilde{\upsilon}_{ji} \upsilon_{ir}^{ke} \tag{26}$$

where $N_{aq}$ is the number of aqueous species, $N_{min}$ is the number of minerals, $N_R^{ke}$ is the number of kinetically-controlled reactions, $N_{le}$ is the number of reactions at local equilibrium (i.e. complexation reactions), $N_c^{le}$ is the number of components or primary species, $\tilde{\upsilon}_{ji}$ is the stoichiometric coefficient defined in Equations (6) and (7), $\upsilon_{jr}^{ke}$ is the stoichiometric coefficient kinetic reactions, $\tau$ is the formation factor of the geologic medium, $D$ is the diffusion coefficient in bulk water, $c_i$ is the concentration of species i, $I$ is the reaction rate, $V_m$ is the molar volume of solid $m$, and $\phi_m$ is the mass fraction of solid $m$, and $\vec{v}$ is the flow velocity. The spatial and temporal changes in rock porosity can be calculated from Equation (23). These changes can potentially impact hydrological (and possibly mechanical) properties of a geologic medium, as captured by Equations (3) and (4).

Mineral rate laws give the reaction rate in terms of reactive surface area and solution and sorbed species concentrations. At the very least these are generally nonlinear functions of the primary species concentrations $c_j$. A review of mineral-water reaction rate laws and associated parameters is found in Palandri and Kharaka (2004). Also of interest for coupling to geomechanical codes, in an Eulerian frame, Equations (21) and (22) can be modifiable to account for solid matrix deformation (Dewers and Ortoleva 1990).

One problem with the above approach is that in many subsurface systems, mineral-water reaction kinetics for common mineral types occurs on widely disparate time scales (e.g. carbonates and sulfates equilibrate with aqueous solutions on the order of days or months at surface conditions, while silicates can take tens to hundreds of thousands of years). Ranges in reaction rate time scales can produce very stiff numerical solutions.

*Quasi-Stationary State:* For a particular system, if the time scale for substantial reaction involving a solid phase is orders of magnitude greater than the time scale for solute reaction and transport to reach a steady state, then a viable approximation for the reaction transport equations (i.e. Equation 21) is the quasi-stationary state approximation (Ortoleva et al. 1986; 1987a; 1987b; Lichtner 1988; Dewers and Ortoleva 1990; 1992) which amounts to ignoring the time derivative in Equations (12) and (21). This approach is valid for long (geologic) time scales and has been shown useful in describing zonation associated with reaction fronts and chemical waves, and in coupled mechanical-chemical formulations describing basin evolution and rock lithification patterns.

*Kinetics of mineral-water reactions:* A geochemical reaction is described as an overall stoichiometric reaction, with little known about its elementary reaction steps. In this sense, all rate expressions used in geochemical modeling are empirical. Partly based on the transition state theory, these empirical expressions can be formulated in the following general form (e.g., Lichtner, 1996):

$$I_m = s_m k_m \prod_i a_i^{\beta_i} f(\Omega_m) \tag{27}$$

where $k_m$ is the reaction rate constant; $s_m$ is the surface area of mineral *m*; $a_i$ is the activity of species *i*; and $\Omega_m$ is the saturation degree of the solution with respect to mineral *m*. In general, the reaction rate is a nonlinear function of the concentrations of dissolved species.

For a microbially mediated reaction, the reaction rate can be described by a dual Monod expression (Wang and Papenguth, 2001):

$$I_m = I_{\max}\left(\frac{C_D}{K_D + C_D}\right)\left(\frac{C_A}{K_A + C_A}\right) \tag{28}$$

where $C_D$ and $C_A$ are the concentrations of electron donor and acceptor respectively; and $K_D$ and $K_A$ are the half-saturation constants for electron donor and acceptor respectively.

*Radionuclide Decay and Retardation:* A simplified reactive transport formulation for a radionuclide species with first order decay and adsorptive retardation can be set forth as follows (e.g., Hansen et al. 2010, p. 44). Conservation of mass for the $i^{\text{th}}$ aqueous or gaseous solute mass ($c_i$ is the molar concentration) in a phase $\pi$ with saturation *s* and porosity $\phi$ is given from Equation (18) by:

$$\frac{\partial}{\partial t}\left(\phi s_{\pi_i} c_i\right) + \vec{\nabla} \cdot \vec{J}_i = \sum_{r=1}^{N_r} \upsilon_{ir} I_r \quad (i = 1, \ldots N) \tag{29}$$

The sum on the right hand side is over the total possible $N_r$ homogeneous and heterogeneous reactions $I_r$ in $\pi$, where $\upsilon_{ir}$ are the stoichiometric coefficients (number of moles of *i* participating in the *r*th reaction, Lichtner 1996; see Martinez et al. 2001 for similar treatment). Let us consider only a single solute species, *c*, in a liquid phase, and account for advective and diffusive flux, wherein Equation (29) becomes:

$$\frac{\partial}{\partial t}(\phi s_L c) + \vec{\nabla} \cdot (\vec{v}_L c) = \vec{\nabla} \cdot (\phi s_L D \vec{\nabla} c) + \phi R \tag{30}$$

Here $v_L$ is the liquid Darcy velocity and *D* is an effective mass diffusion coefficient which includes a tortuosity, i.e. $D = D_m \tau$. *R* is the net molar production rate of *c*, which accounts both for first order radioactive decay and a term accounting for sorption. Following the treatment by Schwartz and Zhang (2003, their Equation 23.12), Equation (30) becomes:

$$\frac{\partial}{\partial t}(\phi s_L c) + \vec{\nabla}\cdot(\vec{v}_L c) + \frac{\partial}{\partial t}(s a_m) = \vec{\nabla}\cdot(\phi s_L D \vec{\nabla} c) + r \tag{31}$$

The third term on the left-hand-side is the time rate of change of the product of an areal molar concentration s and the specific surface area of mineral per unit bulk volume, $a_m$ (Tompson and Jackson 1996), and r accounts for any other chemical reaction rate.

When sorption reaction rates are considered rapid relative to transport rates, s will approach a local equilibrium with the local bulk fluid concentration *c*, and thus can be represented by a sorption isotherm. Using a linear sorption isotherm, one defines the commonly used retardation factor $R_f$ in Equation (31):

$$\frac{\partial}{\partial t}(\phi s_L c R_f) + \vec{\nabla}\cdot(\vec{v}_L c) = \vec{\nabla}\cdot(\phi s_L D \vec{\nabla} c) + r \tag{32}$$

where $R_f = 1 + a_m k/\phi s_L$ with k the isotherm constant. Usually retardation is defined in terms of an apparent distribution coefficient (as a means of relating sorption behavior to experimental measurement) $K_d$, which relates the total contaminant mass adsorbed per total solid mass to the bulk aqueous concentration (Tompson and Jackson 1996). With $K_d = a_m k/\rho_b$ with $\rho_b$ the bulk mass density, $R_f = 1 + \rho_b K_d/\phi s_L$, i.e. Equation 23.14 of Schwartz and Zhang (2003), here modified for partially saturated media. For a solute species undergoing first order radioactive decay, $r = -\phi s_L R_f \lambda c$, where $\lambda$ is the decay constant, related to radionuclide half-life by $t_{1/2} = ln(2)/\lambda$ (Schwartz and Zhang 2003).

The $K_d$ approach does not, however, explicitly account for changes in groundwater chemistry or mineralogy that may occur along the transport pathway. If such changes are considered possible or likely, $K_d$ values must be spatially varied or assigned appropriate uncertainties. Temporal changes in groundwater chemistry may also occur due to changes in groundwater flow in future climate states. Degradation of engineered barriers and subsequent downstream movement of the chemically altered water (carrier plume) may also induce chemical changes.

An alternative to the $K_d$ approach is the surface complexation modeling (Dzombak and Morel 1990; Davis and Kent 1990; Goldberg et al. 2007), which represents surface species equilibria using mass action equations corrected for changes in electrostatic energy (e.g. electrical double layer theory). Surface complexation modeling and the supporting thermodynamic data have reached a level of maturity that makes incorporation into transport models feasible, at least for simple systems (see, e.g. Davis and Curtis 2003). Unlike the simple $K_d$ approach, surface complexation modeling can explicitly account for spatial and temporal changes in groundwater chemistry, including the effect of a carrier plume, albeit with increased computational burden.

*Colloidal transport:* Colloids are small particles in the 1 nm to 1 mm size range that are mobile in groundwater. They can be inorganic or organic and are formed by rock weathering/erosion processes, precipitation of mineral phases from supersaturated solutions, degradation of organic materials (including microbes), or, in the case of repository systems, by corrosion/degradation of anthropogenic materials such as waste forms and engineered barriers (Painter et al. 2010).

The primary concern with colloids is that they provide mobile surface area onto which radionuclides can attach and thus effectively "hitch a ride" through the hydrogeologic system (Painter et al. 2010). Parameters that affect colloid-facilitated transport include colloid concentration, partitioning coefficient of radionuclides to colloids (especially relative to partition coefficients to immobile surfaces), rates of desorption of radionuclides from colloids, retardation rates factors for colloids, and rates of permanent immobilization of colloids (filtration). The filtration coefficient ε can be calculated by (Harvey and Garabedian 1991):

$$\varepsilon = 1.5\frac{1-\phi}{d_m}\alpha_c\eta_c \tag{33}$$

with

$$\eta_c = 0.9\left(\frac{k_B T}{\mu d_c d_m q}\right) + 1.5\left(\frac{d_c}{d_m}\right)^2 + (\rho_c - \rho)\frac{g d_c^2}{18\mu q} \tag{34}$$

where $d_m$ is the particle size of the medium grains; $\alpha_c$ is the collision efficiency factor; $\eta_c$ is the single collector efficiency; $d_c$ is the colloid diameter, $k_B$ is the Boltzmann constant; T is the absolute temperature; $\rho_c$ is the colloid density; ρ is the water density; μ is the water viscosity; q is the Darcy velocity; and g is the gravity constant.

*Texture Distributions and Population Balance Approach:* The treatment of solid phase and pore texture in the above examples of systems of equations is seen to be based on "average" properties (porosities, volume fractions, mean crystal sizes) which are at best a crude description of a reacting porous media. While pore scale methods can treat such variations explicitly, at the continuum scale, a better description of a reacting porous media takes explicit account of mineral grain and pore-size distributions. Sometimes termed "particulate" or "population" dynamics, this approach has been popularized by chemical engineers [a classic text is by Randolph and Larson (1988)] applied to, e.g. industrial scale batch crystallization (Ramkrishna 2000), but is rarely used in treatments for subsurface reactive transport (Eberl et al. 1990; Steefel and Van Cappellan 1990; Dewers and Reches 2004). Including a complete size and/or pore distributions can be critical in accurately describing water-rock interaction, as mineral grain sizes in the lower tail of a crystal size distribution may have minimal volume, but possess the bulk of reactive surface area.

A population balance equation for crystal growth invokes the population distribution of crystal sizes or particulates *L*, *n(L)*, as (Randolph and Larson 1988):

$$\frac{\partial n}{\partial t} = \vec{\nabla} \bullet (n\vec{u}) + B - D \tag{35}$$

where u is the particulate velocity vector in "phase space" which includes spatial coordinates and non-spatial internal coordinates which can include particulate size. In this case u, for size-independent growth, is equal to the crystal growth rate. *B* and *D* are the so-called "birth" and "death" functions which can include physics such as nucleation, agglomeration, aggregation, fracturing and healing of grains, etc. Ostwald ripening, in which case the growth velocity depends on L or size-dependent growth, is a special case of Equation (35) (Eberl et al. 1990). Approaches like Equation (30) are common in studies of microbial population dynamics (for example, see Lauffenberger 1991).

A similar population equation could be constructed for porosity, for example, and could include coupled physics like pore collapse through grain crushing, in which the pore size distribution and grain size distribution are coupled through '*B*' and '*D*' terms. Other examples of coupling include hydrologic - permeability is often as a function of the pore size distribution, and mechanical - recent "creep laws" for geomaterials, for example, are often expressed as a function of the crystal size distribution. Combining the above within a full reactive transport methodology has rarely if ever been attempted (with time and three spatial dimensions, this would require numerical solutions in a five dimensional space and codes simply aren't set up for that). One simplification in common use is to express Equation (30) in terms of the moments of distribution. In this case, ignoring transport, the single PDE in Equation (30) is reduced to four coupled ordinary differential equations (ODEs) for particle number density, average size, surface area, and volume fraction.

Finally, population balance-like methods may be a viable alternative to upscaling methods like homogenization, in which case upscaled physics can include aspects like distribution tail-dependent physics, chemical microenvironments, and pore-scale heterogeneity, which are lost by averaging techniques.

## 3.2 Mechanical Processes and Code Capabilities

### *3.2.1 Governing Mechanical Equations*

For mechanical (geo-mechanical) systems, there are three basic sets of equations that govern the description of a system deforming under a given load. The first is the set of equations of motion:

$$\sigma_{ij,j} + \rho b_j = \rho a_j \tag{36}$$

or, for the case when the processes are very slow such that inertia ( $\rho a_j$ ), may be neglected, these equations become the equilibrium equations:

$$\sigma_{ij,j} + f_i = 0 \tag{37}$$

where $\sigma_{ij}$ are the components of the stress tensor and $f_i = \rho b_i$ are the body forces. The second set is the set of strain-displacement relations:

$$e_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i} + u_{k,j}u_{k,i}) \tag{38}$$

where $e_{ij}$ is the strain tensor and $u_i$ is the displacement vector.

The third set of equations, the so-called constitutive equations, relates the equilibrium equations to the strain-displacement relations through the material (constituent) response of the material that is undergoing the deformations. This third set of equations can take on many forms depending on the material that is being modeled, ranging all the way from a simple elastic material that could be used to model, say a granitic material, to materials such as clay and rock salt, with significantly more complicated behaviors that require significantly more sophisticated and involved material descriptions.

As an example of this third set of equations, consider a constitutive model for the latter material above, rock salt (Krieg 1984). It is one of the materials of interest for Waste IPSC applications and is a creeping material with a creep rate that is highly temperature-dependent. Its overall strain rate can be characterized by the equation:

$$\dot{e}_{ij} = -\frac{\nu}{E}\dot{\sigma}_{kk}\delta_{ij} + \frac{1+\nu}{E}\dot{\sigma}_{ij} + \dot{e}^{C}_{ij} + 3\alpha\dot{T}\delta_{ij} \tag{39}$$

where $\sigma_{ij}$ are the components of the stress tensor, $\nu$ is the Poisson's ratio, $E$ is Young's Modulus, $T$ is temperature ($^{\circ}K$ ), $\alpha$ is the coefficient of linear thermal expansion, and $\delta_{ij}$ is the Kronecker Delta.

The creep strain rate, $\dot{e}^{C}_{ij}$, is given by:

$$\dot{e}^{C}_{ij} = \left|\dot{e}^{C}_{kl}\right| \frac{\sigma'_{ij}}{\left|\sigma'_{ij}\right|} \tag{40}$$

where $\sigma'_{ij}$ are the components of the deviatoric stress tensor. If one takes the simplest constitutive model for rock salt mechanical behavior in which only secondary creep (steady-state) is considered, the magnitude of the creep rate can now be expressed in terms of the effective creep strain rate, $\dot{\mathbf{e}}$, or the effective stress, $\bar{\sigma}$, as follows (Herrmann, et al. 1980):

$$\left|\dot{e}^{C}_{ij}\right| = \sqrt{1.5}\,\dot{\mathbf{e}} \tag{41}$$

$$\dot{\mathbf{e}} = D\bar{\sigma}^{n} \exp\left(-\frac{Q}{RT}\right), \tag{42}$$

where $\dot{\mathbf{e}}$ is defined as:

$$\dot{\mathbf{e}} = \left(\frac{2}{3}\dot{e}^{C}_{ij}\dot{e}^{C}_{ij}\right)^{1/2} \tag{43}$$

while $\bar{\sigma}$ is:

$$\bar{\sigma} = \left(\frac{3}{2}\sigma'_{ij}\sigma'_{ij}\right)^{1/2} \tag{44}$$

$D$ and $n$ are constants determined from data analysis (typically from laboratory-scale creep tests), and $T$ is the temperature ($^{\circ}K$), $Q$ is the effective activation energy (cal/mole), and $R$ is the universal gas constant (1.987 cal/mole-$^{\circ}K$).

While the secondary creep constitutive model for rock salt described above is a simple example of a basic model for rock salt, there are a variety of other constitutive models for rock salt that may be needed to better describe its response. Those could range from models like the Unified Creep-Plasticity model (Aubertin et al. 1991) to the Multi-mechanism Deformation (Munson et al. 1989) and the Multi-mechanism Deformation Coupled Fracture (MDCF) (Chan et al. 1999) models of Munson and co-workers. The latter two models have been extensively used at the Waste Isolation Pilot Plant (WIPP) because they can model a wider range of rock salt behavior (including primary, secondary, and tertiary creep, for the case of the MDCF model).

In a similar vein and because there are materials that may comprise different geologic repository settings, other constitutive models of interest for this application may be needed. These might include the following:

- clay materials models (e.g., Alonso, et al. 1990; Wheeler and Sivakumar 1995),
- plasticity models (e.g., Krieg 1978; Sjaardema and Krieg 1987) for the various components in the EBS, and,
- other generalized cap-plasticity models (e.g., Fossum and Brannon 2004; Brannon et al. 2009) that could be used for a range of different geo-materials that may characterize the repository geosphere.

### 3.2.2 Mechanical Modeling

The three sets of equations, described above, that govern mechanical (geomechanical) response have been implemented in computer codes using different discretization and solution techniques. However, the most common implementations are those that use the finite element method as the discretization technique and an implicit solver as the solution technique. The resulting finite element codes themselves can range from:

- individual stand-alone applications for addressing a specific class of problems (e.g., implicit, small strain, linear elastic material response);
- to more general implementations typically derived for a broader class of problems such as is typical of many DOE codes aimed at the broader class of national laboratory applications, e.g., explicit, large deformation, inelastic material response (Lin 2005; Maker 1995; Taylor and Flanagan 1989; Blanford et al. 2001; SIERRA Mechanics Team 2010a, 2010b),

- to the most general implementation that addresses broad classes of problems such as is typical of commercial codes, e.g., implicit/explicit, small/large deformation, general material response (ANSYS 2010; SIMULIA 2007).

For the Waste IPSC, the mechanical code capability most likely to be of importance to address the broader range of waste forms, engineered barrier systems, and repository settings is the ability to model large strain/deformation. This is needed for the large deformations anticipated to occur in some disposal system settings. Similarly, a robust and efficient contacting surface capability will also be needed to complement these large deformations, as these may lead to surfaces that develop contact interactions as they deform toward each other, although originally they may not have been in contact with each other. Also needed is the ability to model general inelastic response, to be able to model the behavior of the various materials like rock salt, clay, crushed rock, etc., that might comprise the various disposal system components. Hence, a robust constitutive model interface will be needed to be able to supplement the material library that exists in a code.

## 3.3 Numerical Methods

The simplest and most direct method for reactive transport modeling, but not always the most numerically efficient and subject to convergence problems for especially non-linearly coupled sets of partial differential equations s is the “One-step” or global implicit approach (Steefel and Lasaga 1994; Steefel and MacQuarrie 1996) – this involves solving a fully coupled system with a large Jacobian matrix for typical Newton method. Similar but newer and more efficient approaches use a modified Newton method (Steefel and MacQuarrie 1996). These include solving for mixed differential-algebraic equations solving for the $\psi_i$ or $u_i$ (Lichtner 1985) or direct substitution of mass action expressions into PDE’s and solving for the $c_j$ (Steefel and Van Cappellan 1990). While this is the simplest and most direct approach, it can be slow. Thus many workers employ some sort of operator split which include:

- Sequential non-iterative approach (SNIA) in which a single time step consists of transport step followed by reaction step using transported equations; generally simple and robust but problems occur at boundaries; it also tends to overestimate reaction amounts in problems where concentrations are continually decreasing (i.e. decay reactions; Steefel and MacQuarrie 1996);
- Strang splitting – similar to SNIA but centers the reaction step in middle of two transport steps;
- Sequential iterative approach (SIA) (recommended by Yeh and Tripathi 1989; 1990); several schemes are in use but involves iterating between reaction and transport within a single time step. One method involves alternating reaction and transport terms as a source term from the previous iteration; this has shown convergence problems for some types of reaction schemes.

Jacobian-free Newton-Krylov methods are gaining popularity and need mentioning (Hammond et al. 2007, based on Hammond’s thesis and work on core PFLOTRAN). Jacobian-free Newton-Krylov was developed to avoid the need for a Jacobian matrix, which is computationally expensive to compute and store. Jacobian-free Newton-Krylov involves computing the matrix-vector products of a Krylov solver (e.g., conjugate gradient (CG), generalized minimum residual (GMRES), bi-conjugate gradient stabilized (Bi-CGSTAB), available in Sandia National Laboratories TRILINOS; Heroux et al. 2005) by employing a numerical approximation to the Jacobian-Krylov vector product. It can be computationally efficient in memory and processing. However, it requires specific preconditioning and a large number of Krylov solver iterations.

# 4.0 GAP ANALYSIS OF EXISTING CODE CAPABILITIES

Gaps can exist in the necessary phenomenological expressions, the degree of coupling necessary between multi-physics, or in the numerical methods used for solution. As described in Section 2.0, the gap analysis of code capabilities for Waste IPSC continuum processes, for both high-fidelity-scale and PA-scale models, was focused on four high-level THCM phenomena: EBS Environment, EBS Transport, Geosphere Environment, and Geosphere Transport. For the purposes of gap analysis, code capabilities were evaluated with respect to thermal-hydrologic-chemical (THC) phenomena and mechanical (M) phenomena. Within each of these gap analyses (THC and M), code capabilities to simulate the four high-level phenomena were considered collectively (e.g., the processes for EBS transport and geosphere transport are not significantly different). Additionally, each of the gap analyses considered code capabilities to simulate phenomena relevant to saturated hard rock, clay/shale, and salt geologic settings.

This gap analysis is a follow-up to a preliminary code capability analysis performed in fiscal year 2010 (FY10) (Freeze et al. 2011). The preliminary analysis was focused on the identification of relevant codes (mostly thermal-hydrologic-chemical codes) and the evaluation of each code based exclusively on the information available in open literatures. The list of the identified codes and their key features are described in Appendix A. From this list, 14 codes (EQ3/6, Cantera, PHREEQC, GEM-Selektor, HYDROGEOCHEM, PFLOTRAN, FEHM, TOUGH2, TOUGHREACT, CORE$^{2d}$, MODFLOW/MT3DMS/RT3D and PHT3D) were selected for further examination. The codes were selected based on the consideration of their functionalities and the availability of the codes. The list of the codes examined is not exhaustive and will be updated as needed as the waste IPSC project proceeds. The selected codes were obtained, recompiled and tested using example test problems provided with the codes to the extent possible. In particular, each code was evaluated against the functional requirements for addressing challenge problem milestones 1 and 2 (in some cases also milestone 3). The relevance of each code to other milestones will be evaluated in the future.

This section documents the result of the gap analysis for each code considered. The codes analyzed can be grouped into four categories: (1) chemical equilibrium/reaction path calculation codes, (2) thermal-hydrologic-chemical (THC) codes, and (3) thermal-hydrologic-mechanical (THM) codes. Two additional codes were also evaluated: WAPDEG - a model for waste package degradation; and DAKOTA - a system optimizer that can potentially be used as a performance assessment driver.

## 4.1 Chemical Equilibrium/Reaction Calculation Codes

### 4.1.1 EQ3/6

EQ3/6 is a software package utilized to perform geochemical modeling computations encompassing fluid-mineral interactions and/or solution-mineral-equilibria in aqueous systems. The software package is composed of two major components: EQ3NR, a speciation-solubility code; EQ6, a reaction path modeling code to simulate water/rock interaction or fluid mixing in either a pure reaction progress mode or a time-dependent or kinetic mode. Supporting software includes EQPT, a data file preprocessor, along with several supporting thermodynamic data files, as well as file converter programs to update old input files. The software can model thermodynamic equilibrium, irreversible mass transfer, and reaction kinetics. The supporting thermodynamic data files contain both standard state and activity coefficient-related data that allows the use of activity models such as Davies, B-dot, or Pitzer's equations for calculating activity coefficients.

**Physical basis/mathematical model**

- Aqueous
    - Solvent is water but allows for other phases such as solids and gases to be present
- Chemical equilibrium
    - Mass action law equations:
        - Algebraic treatment: *n* equations with *n* unknowns
        - Each reaction is mass and charge balanced
        - Each equation is nonlinear and a function of chemical species activities, reaction stoichiometries, and corresponding equilibrium constants
        - Assumes constant temperature and pressure
        - Data inputs for log K values of mass action reactions are constrained at the liquid-vapor saturation curve of $H_2O$. That is, there is no correction for pressure.
- Conservative
    - Mass balance
        - Mass balance is maintained through prescribed mass action equations
        - Total mass conservation is constrained through elemental abundance balances among all species present in the system
    - Charge balance
        - Charge balance is maintained through prescribed mass action equations
        - Charge balance is maintained throughout the speciation iteration
        - Option customarily used for an initial "uncharged" aqueous solution by allowing the code to adjust initial pH or an initial elemental concentration.

  - Corrections for nonideality
    - Corrections in concentrated electrolytes are done through the Pitzer approach and through Debye-Hückel methods, such as the B-dot approach by Helgeson et al. (1981) and the Davies equation.
  - Unique solution
    - Constrained by a set of *n* equations with *n* unknowns

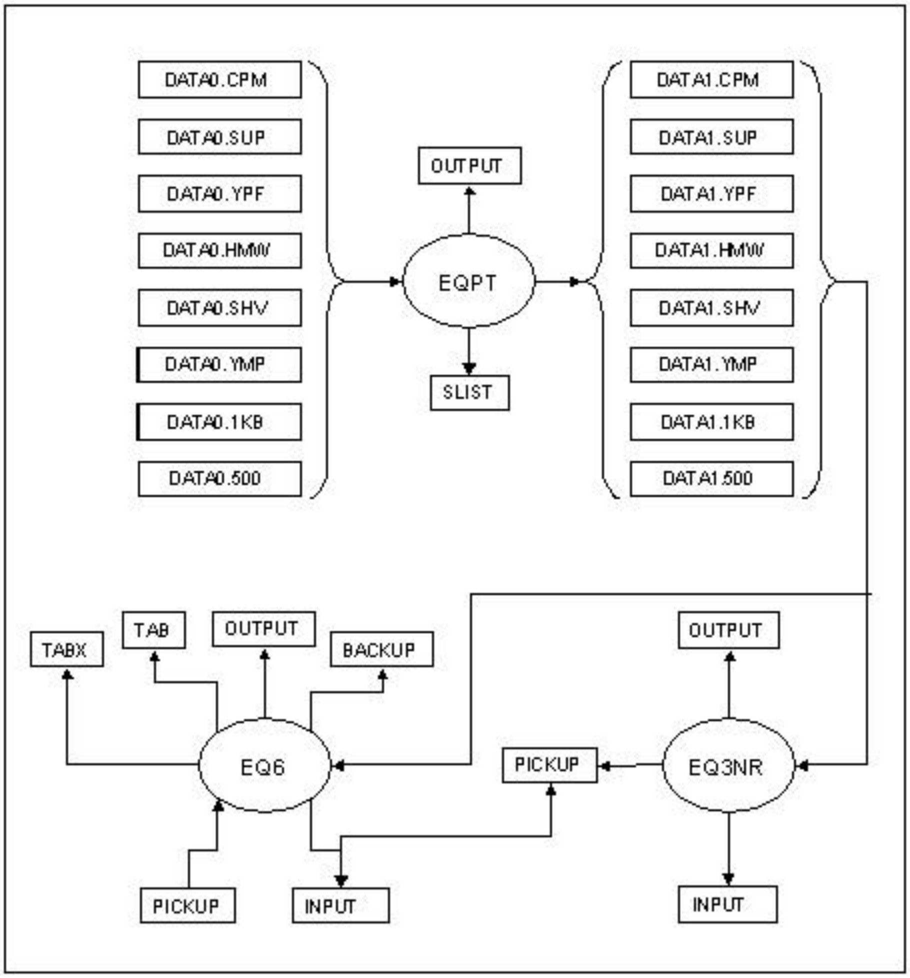
**Functionalities**

Table 4 lists the relevant code functionalities along with their description for the challenge milestones.

**Code structures**

- Fortran 90 programming language.
  - Currently release of the EQ3/6 only provides executables (i.e., no source code) for Windows platforms. Availability for use in other platforms is uncertain.
- File Types
  - *.exe (Code executables)
    - RUNEQ3NR.EXE (Runs EQ3NR equilibrium speciation code)
    - RUNEQ6.EXE (Runs EQ6 eaction path modeling code)
    - RUNEQPT (Runs EQPT database file pre-processor – reads a data0.* file and produces data1.* file readable by EQ3/6)
    - XCIF3.EXE (EQ3 input file format converter from versions 7.0 and 7.2 to version 8.0)
    - XCIF6.EXE (EQ6 input file format converter from versions 7.0 and 7.2 to version 8.0)
  - Data0.dat (ASCII input data files – “dat” stands for specific data type)
  - Data1.dat (Binary input data files readable by EQ3/6)
  - Slist –file generated by RUNEQPT.EXE that list all chemical species in the used database file
  - Output – file generated by RUNEQPT.EXE that summarizes the contents and potential error messages in the database file
  - Pickup file – generated by EQ3NR that serves as input to EQ6
  - TAB and TABX – Tabulated total mass data generated by EQ6
  - Backup – backup files of input EQ3/6 problem

- Generalized code structure:



Source: EQ3/6 SOFTWARE USER'S MANUAL, Version 8.0 (Wolery and Jarek 2003)

**Figure 4.** Code structure of EQ3/6

## Numerical algorithms

- Chemical equilibrium:
  - EQ3NR: Pre-Newton-Raphson optimization method for rapid convergence far from the solution and the hybrid Newton-Raphson method for rapid convergence close to the solution. Both methods are applied to the solution of non-linear set of algebraic equations.
  - EQ6: Newton-Raphson algebraic equations solver as in EQ3 plus a Gear predictor-corrector method of backward differences for "stiff" ODE systems
  - Provides equilibrium compositions of aqueous species and gases

    - Allows for chemical equilibria computations between aqueous solution and ideal gases
- Transport: Not explicitly implemented except for the fluid-centered, flow-through open system option. This option mimics a packet of aqueous fluid flowing through a reactive medium where product phases are left behind. However, these product phases can no longer further interact with the passing fluid packet. There are no explicit transport parameters used in this calculation.

- Kinetics:
    - Rate laws programmed in EQ6:
        - Relative rate equation
        - Transition State Theory (TST) rate equation
        - Linear rate equation
- Robustness
    - Generally robust even for highly concentrated solutions and reaction path problems
        - Convergence problems may occur near concentration limits of activity coefficient models particular in strong electrolytes,
        - There may be phase appearance/disappearance problems in solubility calculations as a function of temperature,
        - Convergence problems can be caused by ill-defined initial conditions.

**Databases**

- Databases developed and/or compatible with EQ3/6 version (8.0+) composed of data blocks with logK values of mass action reactions up to 300°C:
    - YMP thermodynamic databases (only source data0.* files listed):
        - data0.ymp.R# (# equals 2 through 5): data blocks containing thermodynamic data for minerals, aqueous species, and gases
        - data0.ypf.R2: Pitzer binary and ternary temperature-dependent parameters for a large set components common to many salt systems
        - Thermodynamic databases included with the code package:
            - data0.sup (based on standard SUPCRT92 database)
            - data0.hmw (Harvey-Moller-Weare database of Pitzer parameters)
            - data0. com (known as the “combined” database – large set of parameters from various sources)
            - data0.500 (based on SUPCRT92 log K isobaric calculations at 500 bars)
            - data0.1kb (based on SUPCRT92 log K isobaric calculations at 1000 bars)
        - The code SUPCRT92 along with the SPEQ06.dat database is used to generate the log K values for the mass action reactions contained in the EQ3/6 databases.

**Demonstrated applications**

- Relevant thermodynamic test problems provided with software:
    - Several test problems that include cases for solubility, testing of activity coefficients options, kinetic rate laws, and reaction path calculations involving titration
    - Many other test cases (not included in the LLNL code distribution) are available from YMP calculations such as salt solubilities, evaporation calculations, and dust deliquescence
    - Test cases (not included in the LLNL distribution) involving coupling with the code DAKOTA for optimization of log K values for a specific reactions

**Accessibility of source codes**

- Code is distributed by the LLNL Industrial Partnership Office (IPO) for a fee.
- License: End-user license agreement with Lawrence Livermore National Security, LLC

**Other unique features**

- Long usage history by many users worldwide on various types of geochemical calculations
- Coupling of EQ3/6 with other codes such as DAKOTA to perform parameter optimization and sensitivity analysis
- Ability to expand the thermodynamic database data blocks to include new phases
- Multiple activity coefficient models for aqueous species (e.g., Pitzer, b-dot, Davies)
- Capability for fixing the amount of buffer mass, say for redox dependent calculations
- Reaction path modeling can evaluate mass transfer and mineral phase stability during hydrothermal alteration of a mineral assemblage. This type of modeling can be done as open and closed system modes, as a function of the reaction progress variable (i.e., the extent of a chemical reaction), and as a function of temperature.
- Titration type calculations as a function of increasing temperature – useful to map solubility surfaces
- Basis aqueous species switching
- Two choices of ion exchange models: Gapon and Vanselow

**Limitations**

- Equilibrium constants are fixed for a given pressure range (LVP for $H_2O$) and are not corrected by the code for changes in pressure.
- In some cases there is lack of numerical stability for problems involving strong electrolytes.
- Rate laws only apply to mineral phases.
- Limited (if not functional) capability to model solid solutions.

- No adsorption modeling capabilities

**Table 4.** Chemical Functionality Needs versus EQ3/6 Capabilities

| **Functionality** | **High-Fidelity Model** | **PA Model** | **Code Capability** | **Comments** |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | Yes | |
| Mineral equilibration | Yes | Yes | Yes | |
| Solid solutions | Yes | Yes | Yes | Largely untested and maybe not even fully functional |
| Gas species equilibration | Yes | Yes | Yes | |
| Gas phase modeling | Yes | Yes | No | Liquid solvent $H_2O$ is required |
| Temperature corrections | Yes | Yes | Yes | |
| Pressure corrections | Yes | Yes | No | |
| Pitzer equations | Yes | Yes | Yes | |
| Ion exchange | Yes | Yes | Yes | Gapon and Vanselow models |
| Surface complexation | Yes | Yes | No | |
| Uncertainty propagation | No | Yes | No | EQ3/6 lacks this capability but it can be coupled with DAKOTA for this purpose for certain case of parameter study |
| Uncertainty evaluation | No | Yes | No | See above |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

| | | | | |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Yes | Apply only to solids |
| Flow-through | Yes | Yes | No | However, EQ3/6 mimics reactive flow through the fluid-centered, flow-through open system option |
| 3-D mesh | Yes | No | No | |
| Stress corrosion cracking | Yes | Yes | No | |
| Radiolysis | Yes | Yes | No | Except maybe for the thermodynamic treatment of radiolytic species at equilibrium |
| Reactive transport | Yes | Yes | No | EQ3/6 mimics reactive flow through the fluid-centered, flow-through open system option |
| THC reactive transport | Yes | Yes | No | |
| Uncertainty propagation | Yes | Yes | No | EQ3/6 doesn't have this capability but it can be coupled with DAKOTA for this purpose for certain case of parameter study |
| *Other Potentially Important Chemical Functionalities* | | | | |
| Colloids | Yes | Yes | No | |
| Solution density calculation | Yes? | No? | No | |
| Decay and ingrowth | Yes | Yes | No | |

## 4.1.2 CANTERA

Cantera is a general purpose object-oriented constitutive modeling package capable of performing thermodynamic, chemical kinetics, and transport calculations involving equilibrium aqueous speciation and solubility between solution, solid, and gas. This modeling package has interfaces to C++, FORTRAN, Python, and Matlab. Its origins lie in modeling combustion systems and allied chemical vapor deposition processes (Moffat and Jové-Colón 2009). Some of the features include the ability to conduct kinetics simulations with large reaction mechanisms, to compute chemical equilibrium, to evaluate thermodynamic and transport properties of mixtures, to evaluate species chemical production rates, to conduct reaction path analysis, to create process simulators using networks of stirred reactors, and to model non-ideal fluids. Cantera has been built into the SIERRA framework, and SNL is actively expanding the capabilities of this code.

**Physical basis/mathematical model**

- Aqueous
    - Solvent is water but allows for other phases such as solids and gases to be present. There is kinetic treatment of liquid phase reactions. Transport methods for aqueous and other solvent systems is under construction. Activity coefficient corrections in concentrated electrolytes are calculated through the Pitzer approach. Other corrections are possible through Debye-Huckel methods, including the b-dot approach by Helgeson et al. (1981). Although largely untested, the presence of ion-pair species could capture non-ideal effects.

- Gas
    - Cantera originated in the combustion and CVD communities. It has a full range of kinetics, thermodynamics, and transport capabilities for ideal gases.
- Solids and solid/fluid interactions
    - There is thermodynamic and kinetic treatment of solid/fluid interactions at between multiple phases including surface phases (e.g., adsorbed species).
- Particle Methods
    - Particle balance equations are solved using a sectional-modeling capability
- Chemical thermodynamic equilibrium
    - Minimize Gibbs free energy using the Villars-Cruise-Smith (VCS) algorithm (Smith and Missen 1981)
        - Thermodynamic equilibrium is attained by minimizing the total Gibbs free of the system
        - VCS algorithm can be used to find the equilibrium solution of a set of species in multiple phases
        - Assumes constant temperature and pressure
        - Charge and mass balance is maintained through VCS iteration
        - Since this approach does not depend on prescribed mass action law reactions along a certain P-T range, pressure corrections are captured implicitly in the Gibbs free energy minimization computation.

        - Minimize Gibbs free energy using the BNR formulation of element potentials (Smith and Missen 1982)
    - Conservative Formulations for transport and reaction in 0D and 1D systems.
        - 0D Formulations
            - Total mass conservation is constrained from kinetic equations for elemental abundance balances among all species present in the system, using an ordinary differential equation (ODE) solver.
            - Simulate the evolution of 0D network of reactors using continuous stirred-tank reactor (CSTR) flow/pressure controllers, moving/reacting walls and valves.
            - Include Routines to print out tables of thermodynamic and transport properties including standard state and open circuit voltages.
        - 1D Methods
            - Simulate opposing flow flames, rotating disks, and burner-stabilized flames.

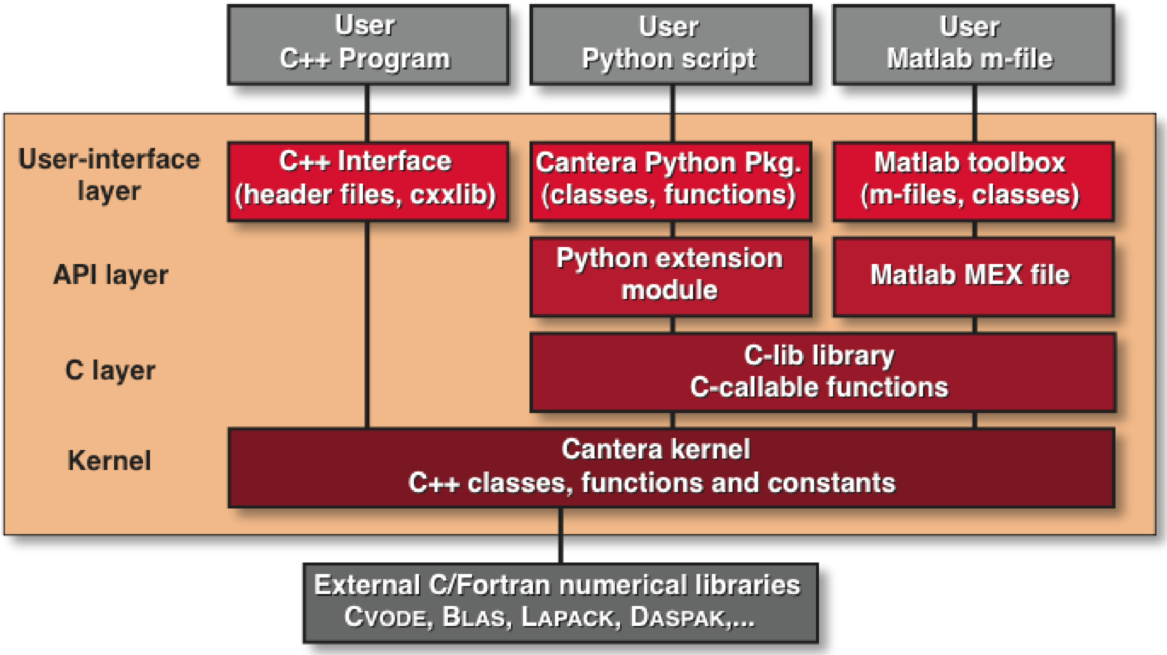
**Functionalities**

Table 5 lists the relevant code functionalities along with their description for the challenge milestones.

**Code structure**

- C++ programming language. Most of the development is carried out in Linux platforms but there may be some development for Windows environment using Microsoft Visual Studio C++ .
- File Types
    - *.cpp
    - *.h
    - Makefiles
    - *.xml (XML input data files)
    - *.cti (ASCII input data file)
    - *.html (Doxygen-type documentation from source code)
    - *.d (C++ dependency file)
    - *.o (C++ object file)
    - *.ctt (ASCII file describing problem input constraints)

- Generalized code structure:



Source: http://www.nsf-combustion.umd.edu/presentations/dgoodwin_speech.pdf

**Figure 5.** Code architecture of Cantera

## Numerical algorithms

- Chemical equilibrium:
    - VCS approach uses the Newton-Raphson method
    - Provides equilibrium compositions of aqueous species and gases
    - Allows for chemical equilibrium computations between aqueous solution and ideal gases
- Transport: In Cantera this is called the Liquid Transport Branch. This branch is an attempt to formulate transport parameters for liquid systems. Currently, Cantera has a solid representation of transport within dilute gas systems using the Dixon-Lewis multi-component gas formulation and within porous flow of gases using the dusty gas approximation. The existing implementations include the Stefan-Maxwell equations for liquids, specifically molten salts, which have been validated against experimental data. It also has an implementation of general liquid transport using simple functional formulations for the transport parameters. Class “Transport” includes eight daughter classes. The “functional” relationships of these classes are shown in Figure 6.

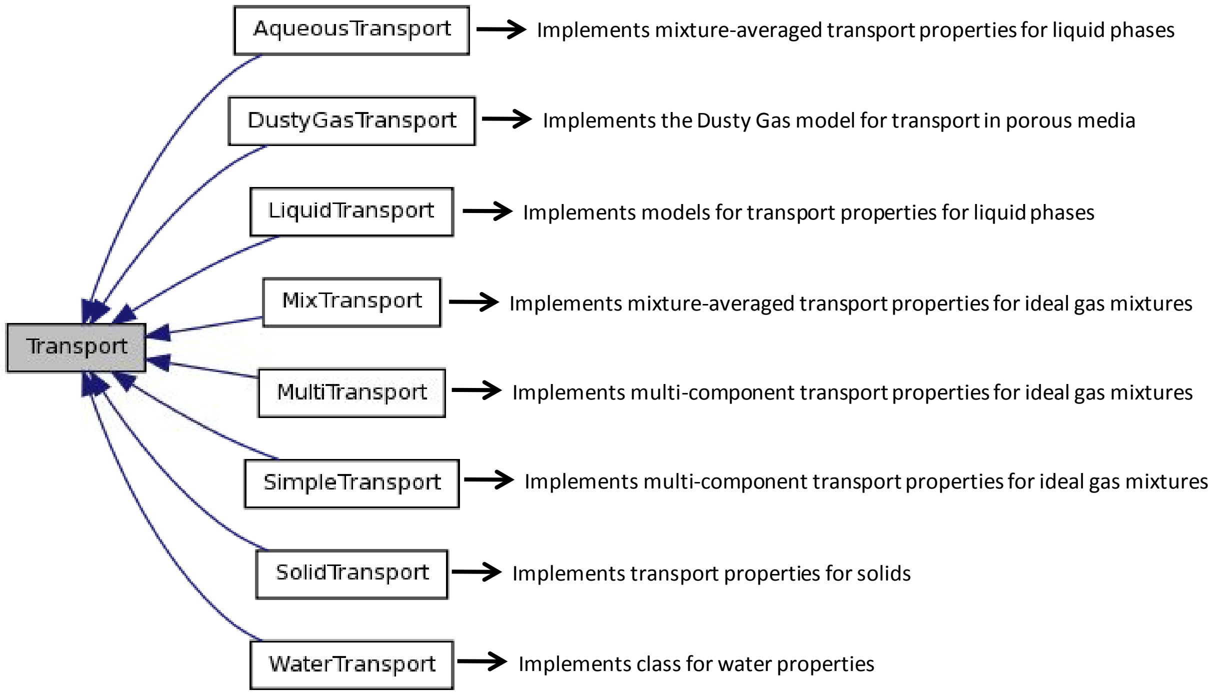


**Figure 6.** Inheritance diagram for the transport class in Cantera

- Kinetics:
  - C++ class **kinetics** manager to implement a kinetic model:
    - Expressions valid for elementary reactions in ideal gas mixtures
    - Satisfy mass balance requirements for backward/forward reaction rates
    - Heterogeneous chemistry at interfaces (empirical reaction orders, TST-type)
  - Compatible with CVODE (now SUNDIALS) differential/algebraic equation solvers
- Robustness
  - Cantera is generally robust, but more test cases are needed to better assess code performance on various geochemical problems.
    - Convergence problems may occur for certain multiphase equilibria.
    - There are phase appearance/disappearance problems in phase equilibrium calculations

## Database

- Databases developed and/or compatible with current Cantera version 1.8
  - YMP thermodynamic databases:
    - data0.ymp.R# (# = 2 - 5): data blocks containing thermodynamic for minerals, aqueous species, and gases were converted to XML format

        - data0.ypf.R2: Pitzer binary and ternary temperature-dependent parameters for a large set components common to many salt systems
        - SPEQ06.dat SUPCRT92 database: Cantera can read HKF EoS parameters. Can read Maier-Kelley Cp parameters for temperature extrapolations of solid thermodynamic properties.
    - NASA and NIST thermodynamic databases:
        - Large set of data for solids and gases
        - Parameterization consistent with NASA polynomial parameterization readable by Cantera. It should be noted that Cantera can read other data parameter formats.

**Demonstrated applications**

- Relevant thermodynamic test problems provided with software:
    - Five test problems using the implemented forms of the Debye-Hückel equation for activity coefficients
    - Eight test problems using the Pitzer formulation to compute the thermodynamic properties of simple electrolytes
    - One test problem to compute the thermodynamic properties of an ideal aqueous solution
    - One test problem to compute the thermodynamic properties of an ideal solid solution
    - Two test problems to compute the thermodynamic properties of a stoichiometric solid
    - Six test problems to compute the thermodynamic properties of $H_2O$
    - One Villars-Cruise-Smith (VCS) problem to compute the solubility of NaCl in the presence of several gases.
    - Other test cases are available for other types of transport, surface kinetics, and combustion problems in the Cantera test problems suite.

- Equilibrium problems recently developed in Cantera (not included in the distribution):
    - Calcite solubility as a function temperature and NaCl ionic strength for a fixed $CO_2$ gas concentration.
    - Quartz solubility and Gibbs energy optimization using DAKOTA.
    - $CO_2$ gas solubility in aqueous solutions as a function of pressure and temperature
    - Computation of mean activity coefficients and osmotic coefficient for NaCl and a function of solute concentration.
    - Computation of $\Delta G^{\circ}_{rxn}$ for the reaction $NaCl_{(s)} \rightarrow Na^{+} + Cl^{-}$ as function of temperature
    - Computation of aqueous solution densities (in the dilute range) as a function of pressure, temperature, and composition
    - Calculation of excess enthalpy for a NaCl solution as a function of temperature and concentration

### Accessibility of source codes

- Open source Berkeley Software Distribution (BSD) license
- Code download and other types of information are available through Google Code (http://code.google.com/p/cantera/)
- Google Code site provides for submittal of issues

### Other unique features

- Flexibility and agility to compose various types of problems exploiting the capabilities to extract thermodynamic properties of fluid phases.
- Coupling of Cantera with other codes such as DAKOTA to perform parameter optimization and sensitivity analysis
- Ability to expand the thermodynamic database data blocks to include new phases
- Various options of activity coefficient models for aqueous species (e.g., Pitzer, Debye-Hückel)
- Representation of solid solutions through a Margules-type parameterization
- Capability for modeling aerosol kinetics and transport (CADS – Cantera Aerosol Dynamics Simulator) for particle transport. This feature allows for the thermodynamic treatment of particle nucleation (through condensation of gas species) and surface growth.
- Molten salt phase equilibria

### Limitations

- Potential numerical instability for certain type of problems.
- The user must develop the problem by writing C++ code. This is not a pre-packaged plug-and-play type of software tool and some programming skill is necessary.
- Limited number of developers and slow turnover rates for further improvements.

**Table 5.** Chemical Functionality Needs versus Cantera Capabilities

| Functionality | High-Fidelity Model | PA Model | Code Capability | Comments |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | Yes | |
| Mineral equilibration | Yes | Yes | Yes | |
| Solid solutions | Yes | Yes | Yes | |
| Gas species equilibration | Yes | Yes | Yes | |
| Gas phase modeling | Yes | Yes | Yes | |
| Temperature corrections | Yes | Yes | Yes | |
| Pressure corrections | Yes | Yes | Yes | |
| Pitzer equations | Yes | Yes | Yes | |
| Ion exchange | Yes | Yes | No | Currently not implemented but it could be developed in the future |
| Surface complexation | Yes | Yes | No | Currently not implemented but it could be developed in the future. For example, in the form of Kulik approach |
| Uncertainty propagation | No | Yes | No | Cantera itself doesn't have this capability but it can be coupled with DAKOTA for this purpose |
| Uncertainty evaluation | No | Yes | No | See above |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

| | | | | |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Yes | Needs to assess form of desired rate laws |
| Flow-through | Yes | Yes | No | However, Cantera has 1-D liquid transport capabilities. Needs to assess if conforms to “flow-through” transport through porous media |
| 3-D mesh | Yes | No | No | |
| Stress corrosion cracking | Yes | Yes | No | However, Cantera has the capability for modeling electrode reactions that are relevant to electrochemical processes in corrosion |
| Radiolysis | Yes | Yes | No | Except for the thermodynamic treatment of radiolytic species at equilibrium |
| Reactive transport | Yes | Yes | Limited | 1-D only – Cantera provides constitutive models for 2D and 3D codes like Sierra |
| THC reactive transport | Yes | Yes | Limited | Code does not simulate heat transfer at phase boundaries nor convection in response to temperature gradients. |
| Uncertainty propagation | Yes | Yes | No | Cantera itself doesn’t have this capability but it can be coupled with DAKOTA for this purpose |
| *Other Potentially Important Chemical Functionalities* | | | | |
| Colloids | Yes | Yes | No | Code can model particle transport but it’s developed for aerosols including kinetics. Not sure if this can be expanded to colloids |
| Solution density calculation | Yes? | No? | Yes | |
| Decay and growth | Yes | Yes | No | |

### 4.1.3 GEM-Selektor and GEMIPM2K

GEM-Selektor (GEMS) and GEMIPM2K are codes that perform thermodynamic modeling of heterogeneous aquatic (geo)chemical systems by Gibbs energy minimization (Karpov et al. 1997). GEMS uses an efficient interior points method (IPM) numerical module to compute equilibrium phase assemblage and speciation from a total system bulk elemental composition over a wide range of temperature and pressure. GEMS can also be used to simulate irreversible mass-transfer from principles of local and partial equilibrium. Two solutions are solved in each GEMS application, a primal solution (equilibrium chemical speciation) and a dual solution (equilibrium chemical potentials of the elements).

GEMIPM2K is a standalone GEM solver used in coupled reactive transport modeling. GEMIPM2K is not available except on collaborative projects. These codes are developed and supported by a team led by Dmitrii A. Kulik at the Paul Scherrer Institute in Villigen, Switzerland. Although there is no published user's manual, there is a web site (http://gems.web.psi.ch/) that contains much useful documentation, references and links for related publications, and an in-depth tutorial. The reference version for this analysis is 2.3.1-PSI, released 8/24/2009.

**Physical basis/mathematical model**

Unlike most geochemical codes, existing phases (including aqueous) are not predetermined. Mass balance is conserved for each element or chemical component across all potential phases. Each mass balance equation is linear and is simply a sum-product of the concentrations of the various species of the element and its stoichiometry within the species.

GEMS minimizes the Gibbs energy of all elements in the system to determine a heterogeneous system of species and phases. The system Gibbs energy is a function of temperature, pressure, species stoichiometry, Gibbs energy of formation of each species at standard state, and species activity coefficients.

These set of chemical relationships define a system such that there are an equal number of equations and unknowns. The most important unknowns in this case are the phases present, the amount of each phase, and the various species concentrations in each phase. These unknowns can then be solved by numerical iteration to obtain a unique solution that satisfies all equations simultaneously.

**Functionalities**

Table 6 lists the relevant chemical functionalities for the challenge milestones and indicates which functionalities are included in the code.

**Code structures**

GEMS is written in ANSI C/C++ programming language. Cross-platform software is used to allow use on any common platform.

The calculation sequence is as follows:

- Stage 1
    - Scaling numerical controls to the size of the system
    - Simplex calculation (for initial approximations only; otherwise use previous calculation as initial approximation)
    - FIADE procedure for adjusting mass balance deviations
    - Main IPM Descent procedure (energy minimization)
    - Selekt-2 procedure to evaluate and adjust phase assemblage if necessary
    - If new phase assemblage, return to FIADE procedure
- Stage 2
    - Modified FIADE-2 procedure for stricter mass balance
    - Main IPM Descent procedure
    - Modified Selekt-2 procedure
    - If new phase assemblage, return to FIADE-2 procedure
    - Dual solution check
    - If convergence not yet achieved, return to FIADE-2 procedure

### Numerical algorithms

To solve the chemical equations GEMS performs an interior points method (IPM) non-linear minimization of total Gibbs energy of the heterogeneous multi-phase chemical system. For transport: GEMIPM2K uses the "operator splitting" approach to provide a module for coupling with reactive fluid mass transport models. There is no documentation currently available for solving kinetic problems.

The code documentation asserts that the code is "fast and robust." Convergence problems may occur, however, when the geochemical setup is inconsistent or when the transport equations solver introduces numerical oscillations into the chemical system. It is also noted that complex geochemical problems can be slow for non-ideal solutions and sorption phases.

### Database

The default database distributed with GEMS is composed of three parts: 1) kernel, 2) complementary, and 3) specific. The kernel part is imported from the "Nagra/PSI chemical thermodynamic database 01/01." It also includes a subset of SLOP98.DAT and has been reviewed by the GEMS developers. This part can be used at temperatures up to 150-200 $^{o}$C at saturated vapor pressures. The complementary part contains SLOP98.DAT data, which allows calculations up to 1000C and pressures up to 5 kbar. This part has a much broader range of elements and species than the kernel part but has not been reviewed by the GEMS developers. The specific part has not been released yet. It will contain additional data for minerals, solid solution end-members, and surface complexes.

The default GEMS database (DB.default) distributed with the software is write-protected. Changes and additions to the DB.default data are saved in separate modeling project files.

## Demonstrated applications

Test problems provided with the software include chemical equilibrium speciation, system phase equilibration with speciation within phases (in this case, aqueous, gas, and mineral phases), redox reaction path, solid-solution equilibration, and surface complexation. A test problem involving kinetic reactions was not included.

Documentation of several aspects of the code is provided in pdf format at the home web site. The topics include:

- temperature and pressure corrections
- calculation of activity coefficients for aqueous species and solid-solution end-members
- surface complexation modeling
- chemical equilibrium partitioning with reference to two solid-solution aqueous solution systems relevant to nuclear waste disposal.

Publications on the following GEMS applications are also listed at the web site:

- Adsorption applications for actinides
- Solid solutions in presence of Eu(III)
- Cementitious waste stabilization systems
- Fe-Cr-Ni spinel formation for light-water reactor conditions
- Adsorption under hydrothermal conditions
- Diagenetic solid-solution aqueous-solution equilibria under anoxic conditions

## Accessibility of source codes

Currently, GEMS version 2 is available for download but not the source code. Version 2 of GEMIPM2K is currently only available on collaborative projects. The following restrictions apply to version 2:

- No fee if used for educational and academic research purposes only
- No registration
- Source code by special request
- Terms and conditions of use
    - Acknowledge the authors (http://gems.web.psi.ch/teamhist.html) and the PSI in publications and products
    - Modification of the software must include a notice stating its purpose, author, and date.
    - Application of the software in any other activities except education and academic research requires a written agreement with the vendor (Paul Scherrer Institute).

Version 3, which is not yet released, will involve the following changes and restrictions:

- GEMIPM2K code name will change to GEMS3K and will be included in the release.
- Algorithmic framework will be published (possibly by September 2011), after which the source code will be released under LGPL or similar license.

- Any modifications/improvements/extensions of the GEMS3K source code performed by third parties would need to be communicated to the developers in a form sufficient for potential integration into the next 'official' GEMS3K version.

**Other unique features**

Potentially useful features and capabilities of the code that are relatively uncommon, unique, or noteworthy include:

- The ability to determine which phases (aqueous, gas, mineral, solid-solution, etc.) are present and the composition of those phases from a bulk recipe of elements, temperature, and pressure
- Modular format
    - Unlike most other geochemical modeling codes, GEMS has an interactive modular package that shares data objects in memory.
- Redox
    - Certain problems that are hard for other geochemical codes to solve, such as redox equilibrium in solid solution-aqueous solution systems, can be easily and directly solved in GEMS.
- A graphical user interface for
    - predicting consistent standard molar properties (e.g., standard Gibbs energy, heat capacity, and entropy) for the thermodynamic database from a simple reaction with a log K value. These molar properties can be used to predict Gibbs energy values over a temperature interval of 0 to 50 $^{o}$C.
    - predicting molar properties of ideal and non-ideal solid solutions
    - adding predefined composition objects (e.g., steel and HLW glass)
    - graphically checking calculations over ranges of pressures and temperatures
    - plotting results and developing scripted formats for these plots
    - plotting speciation and solubility pH diagrams and experimental data points
- Rate equations can be defined using math script programming within the input file, i.e., the user is not limited to a specific set of rate models.
- Has the ability to simulate sorption isotherms
- Calculation of solution density from aqueous concentrations
- Sequential batch reaction mode (fluid-centered flow-through)
- Inverse modeling

**Limitations**

Table 6 indicates functional limitations with regard to Challenge Milestones 1 and 2. Relative to other geochemical codes evaluated in this exercise, this code is new and not widely tested. In addition, help files and documentation are missing for some features.

**Table 6.** Chemical Functionality Needs versus GEM Codes Capabilities

| Functionality | High-Fidelity Model | PA Model | Code Capability | Comments |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | Yes | |
| Mineral equilibration | Yes | Yes | Yes | |
| Solid solutions | Yes | Yes | Yes | |
| Gas species equilibration | Yes | Yes | Yes | |
| Gas phase modeling | Yes | Yes | Yes | |
| Temperature corrections | Yes | Yes | Yes | |
| Pressure corrections | Yes | Yes | Yes | |
| Pitzer equations | Yes | Yes | No | Pitzer capability is under development. Projected release in Ph.D. thesis in 2012. Code uses extended Debye-Hückel activity model. |
| Ion exchange | Yes | Yes | Yes | |
| Surface complexation | Yes | Yes | Yes | |
| Uncertainty propagation | No | Yes | No | |
| Uncertainty evaluation | No | Yes | No | |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

| | | | | |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Yes? | Apparently added in version 2.2 but no documentation currently available |
| Solid-centered flow-through mode | Yes | Yes | Yes | Must use GEMIPM2K, which is currently available only on collaborative projects |
| 3-D mesh | Yes | No | No | |
| Stress corrosion cracking | Yes | Yes | No | |
| Radiolysis | Yes | Yes | No | |
| Reactive transport | Yes | Yes | Yes | Must use GEMIPM2K, which is currently available only on collaborative projects |
| THC reactive transport | Yes | Yes | No? | Must use GEMIPM2K, which is currently available only on collaborative projects |
| Uncertainty propagation | Yes | Yes | No | |
| *Other Potentially Important Chemical Functionalities* | | | | |
| Colloids | Yes | Yes | No | |
| Solution density calculation | Yes? | No? | Yes | |
| Decay and ingrowth | Yes | Yes | No | |

### 4.1.4 PHREEQC

PHREEQC is a U.S. Geological Survey computer program developed by D.L. Parkhurst and C.A.J. Appelo to perform a wide range of ion-association aqueous geochemical calculations including chemical equilibrium, kinetic reaction, and one-dimensional transport through porous media. Phases modeled include aqueous, mineral, gas, solid-solution, and sorption. Sorption can be modeled as ion exchange or surface complexation. Special features include the ability to model kinetic reactions with user-defined rate expressions, perform activity corrections using extended Debye Huckel or Pitzer equations, allow the number of surface or exchange sites to change as a function of dissolution or precipitation, calculate solution density, and simulate isotope equilibrium and fractionation.

The reference version of PHREEQC for this analysis is 2.17.5-4799, released 9/7/2010. The primary user's guide is Parkhurst and Appelo (1999). Much documentation can also be found at the home website: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.

**Physical basis/mathematical model**

The mathematical model for the chemical system is based on the presence of an aqueous solution. Other phases may be present, but the chemical potentials are determined based on the aqueous composition.

Mass balance is conserved for each element or chemical component. Each mass balance equation is linear and is simply a sum-product of the concentrations of the various species of the element and its stoichiometry within the species.

Chemical equilibrium reactions are represented in this model by mass action equations. There is one mass action equation for each chemical reaction. Each reaction is mass balanced and charge balanced. The mass action equations are nonlinear and are a function of chemical species activities, reaction stoichiometry, and equilibrium constants. The unknown values in these equations are the equilibrium species concentrations and their activity coefficients.

Activity coefficients are needed to correct for non-ideal conditions resulting from ion interactions. These coefficients can be estimated from ion-association or ion-interaction equations as a function of ionic strength or the concentrations of individual ions.

Charge balance is either implicitly maintained by the balanced mass action laws or optionally achieved in the initial solution by allowing the code to adjust initial pH or an initial elemental concentration.

Heterogeneous reactions, such as gas dissolution/exsolution, mineral dissolution/precipitation, and surface adsorption/desorption, may also be included in the system by providing an additional mass action expression for each new species or pure phase. Additional constraints on these reactions may be provided by additional mass balance equations for total quantities (e.g., sorption sites or total initial quantities of gases or minerals), fixed fugacities (e.g., gases), and saturation constraints (e.g., minerals).

Ultimately, a set of chemical relationships is defined such that there are an equal number of equations and unknowns. The most important unknowns in this case are the concentrations of each species in each phase. These unknowns can then be solved by numerical iteration to obtain a unique solution that satisfies all equations simultaneously.

### Functionalities

Table 7 lists the relevant chemical functionalities for the challenge milestones and indicates which functionalities are included in the code.

### Code structures

PHREEQC is written in ANSI C programming language. A Makefile is also provided for compiling the program under Linux.

The calculation sequence, as noted in the model.c file, is as follows:

- residuals – calculate residuals, if small calculation is done
- sum_jacobian – calculate Jacobian
- ineq – call inequality solver
- reset – revise estimates of unknowns
- gammas – calculate new activity coefficients
- molalities – calculate molalities
- mb_sums – calculate mass-balance sums
- mb_gases – determine whether gas_phase exists
- mb_s_s – determine whether solid_solution(s) exist(s)
- switch_bases – determine whether new basis species is needed
- reprep – rewrite equations with new basis species if needed
- revise_guesses – revise unknowns to get initial mole balance
- check_residuals – check convergence
- sum_species – calculate sums of elements from species concentrations
- An additional iteration may be needed if unstable phases still exist in the phase assemblage.

### Numerical algorithms

The nonlinear chemical equilibrium reactions in PHREEQC are solved by Newton-Raphson iteration. Transport is simulated by an explicit finite difference model. For kinetic reactions, a 5th order Runge-Kutta integration method is used. Unacceptable numerical dispersion is prevented when simulating kinetic reactions by a subroutine that automatically reduces time steps when necessary to limit moles of reaction within a time step.

PHREEQC has been found to be relatively robust. Occasionally, adjusting scaling features in KNOBS may be needed to achieve convergence. Adjustments are sometimes necessary when total dissolved concentrations fall below 1e-15 mol/kgw.

Convergence problems have been noted when charge balancing is enforced and the element used to charge balance is used up, the wrong titrant is used to attain a desired parameter value (e.g., an acid is used to adjust pH when the pH is already too low), and noncarbonate alkalinity exceeds the entered total alkalinity.

## Database

Several databases are provided with version 2.17.5-4799. These databases demonstrate PHREEQC's ability to accommodate chemical reaction data compiled for other codes and to perform specialized calculations including those for SIT, Pitzer, surface complexation, ion exchange, and isotope models. Code documentation states, however, that log K values in the databases provided may not be internally consistent. The databases include the following:

- *Phreeqc.dat* – This database, generated 3/23/2009, is consistent with the database of WATEQ4F, another USGS code used to perform aqueous chemistry calculations. This database includes reactions for ion exchange and diffuse layer surface complexation. It also includes rate equations for K-feldspar, albite, calcite, pyrite, organic-C, and pyrolusite.
- *Wateq4f.dat* – This is the database of WATEQ4F, generated 8/23/2005. It includes revised arsenic data.
- *Minteq.dat* – This is the database of MINTEQA2, an EPA chemical equilibrium code. This database includes reactions for the diffuse layer surface complexation model reactions of Dzombak and Morel (1990) and a large number of organic acids and other organic species.
- *SIT.dat* – This database was developed by Amphos 21, BRGM and HydrAsa for ANDRA. Specific ion theory (SIT) implemented in this database in accordance with NEA TBD guidelines. The database includes the elements Rb, Cs, Ba, Ra, B, Sn, Pb, Sb, Se, Zr, Hf, Nb, Mo, Mn, Tc, Fe, Co, Ni, Pd, Ag, Cd, Sm, Eu, Ho, Th, Pa, U, Np, Pu, Am, and Cm.
- *Iso.dat* – This database was developed to demonstrate PHREEQC isotope capability. It includes $^{2}H$, $^{3}H$, $^{18}O$, $^{13}C$, $^{14}C$, $^{34}S$, and $^{15}N$ species, fractionation factors, and isotope-specific log K values
- *Llnl.dat* – This database is converted from 'thermo.com.V8.R6.230' prepared by Jim Johnson at Lawrence Livermore National Laboratory, in Geochemist's Workbench format. It has a date stamp of 2/9/2010. It includes temperature ranges of validity for reactions, though PHREEQC does not use this information.
- *Pitzer.dat* – This database contains Pitzer parameters for the following aqueous species: $H^+$, $OH^-$, $H_2O$, $Ca^{+2}$, $Mg^{+2}$, $Na^+$, $K^+$, $Fe^{+2}$, $Mn^{+2}$, $Ba^{+2}$, $Sr^{+2}$, $Cl^-$, $CO_3^{-2}$, $SO_4^{-2}$, $B(OH)_3$, $Li^+$, $Br^-$, $CO_2(aq)$, $HCO_3^-$, $HSO_4^-$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{-2}$, $CaB(OH)_4^+$, $MgB(OH)_4^+$, $CaCO_3(aq)$, $MgOH^+$, and $MgCO_3(aq)$. The database includes 47 minerals and gases, ion exchange, and the surface complexation model reactions of Dzombak and Morel (1990).

## Demonstrated applications

A total of 18 test problems are provided with software. These test problems include chemical speciation, equilibration with pure phases, mixing of solutions, evaporation with homogeneous

redox, irreversible reactions, reaction path calculations, gas phase calculations, surface complexation, kinetic oxidation, solid solution, transport and cation exchange, advective and diffusive flux of heat and solutes, dual porosity transport, and kinetic biodegradation.
PHREEQC has been widely used and accepted. A list of 36 reports and publications involving PHREEQC calculations is provided at the home web site: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/references.html

PHREEQC has also been tested and used on the Yucca Mountain Project. Applications include:

- Waste form degradation and release simulation, validation for EQ3/6 waste form cell model
- Surface complexation
- Langmuir competitive sorption and 1-D transport
- $UO_2$ drip test simulation

## Accessibility of source codes

The PHREEQC software and source code are made available by the USGS to be used in the public interest and in the advancement of science. This software may be freely used, copied, modified, and distributed, subject to the following restrictions and understandings briefly summarized here:

- The User's Rights Notice must be included in any distribution of the software
- Modifications must be clearly identified and include the author and date
- The user appropriately acknowledges the authors and the USGS in publications that result from the use of the software

## Other unique features

Potentially useful features and capabilities of the code that are relatively uncommon, unique, or noteworthy include:

- The ability to define practically any rate equation (using Basic programming) within the input file
- The ability to add new equilibrium reactions, elements, and species within the input file, and to supersede reactions in the database by modifying them in the input file
- The ability to simulate linear ($K_d$), Langmuir, and Freundlich adsorption (though a bit tricky)
- Calculation of solution density from aqueous concentrations
- SIT activity corrections
- Colloid transport
- Heat transport
- Dual porosity
- Isotope fractionation
- Inverse modeling

## Limitations

Table 7 indicates functional limitations with regard to Challenge Milestones 1 and 2. Operationally, the transport module of PHREEQC appears not to be optimized for simulating long periods of time, such as one million years. Time steps for transport (not kinetics) must be predetermined and constant (ANL-EBS-GS-000001 REV 01, Section 7.2.3.1).

**Table 7.** Chemical Functionality Needs versus PHREEQC Capabilities

| Functionality | High-Fidelity Model | PA Model | Code Capability | Comments |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | Yes | |
| Mineral equilibration | Yes | Yes | Yes | |
| Solid solutions | Yes | Yes | Yes | |
| Gas species equilibration | Yes | Yes | Yes | |
| Gas phase modeling | Yes | Yes | Yes | |
| Temperature corrections | Yes | Yes | Yes | |
| Pressure corrections | Yes | Yes | No | Equilibrium constants are not corrected by the code for changes in pressure. |
| Pitzer equations | Yes | Yes | Yes | Code capability also includes extended Debye- Hückel and SIT equations. |
| Ion exchange | Yes | Yes | Yes | |
| Surface complexation | Yes | Yes | Yes | |
| Uncertainty propagation | No | Yes | No | |
| Uncertainty evaluation | No | Yes | No | |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

| | | | | |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Yes | |
| Solid-centered flow-through mode | Yes | Yes | Yes | Not straightforward (see limitations) |
| 3-D mesh | Yes | No | No | |
| Stress corrosion cracking | Yes | Yes | No | |
| Radiolysis | Yes | Yes | No | |
| Reactive transport | Yes | Yes | Yes | 1-D only |
| THC reactive transport | Yes | Yes | Limited | Code does not simulate heat transfer at phase boundaries nor convection in response to temperature gradients. |
| Uncertainty propagation | Yes | Yes | No | |
| *Other Potentially Important Chemical Functionalities* | | | | |
| Colloids | Yes | Yes | Limited | Code can transport colloids with a diffuse double layer but not colloids related to equilibrium phases and kinetics. |
| Solution density calculation | Yes? | No? | Yes | |
| Decay and ingrowth | Yes | Yes | No | |

## 4.2 Thermal-Hydrologic-Chemical (THC) codes

### 4.2.1 HYDROGEOCHEM

HYDROGEOCHEM5 is a computer program developed over the last 2 decades by several generations of graduate students and collaborators led by Professor G.T. Yeh, currently at the University of Central Florida. The original version of the reactive HYDROGEOCHEMical transport model developed by the senior authors at Oak Ridge National Laboratory has evolved into a comprehensive model of coupled fluid flow, thermal, and reactive chemical processes. Input to the program includes the finite element numerical representation of the system, the properties of the media, reaction network, and initial and boundary conditions. Output includes the spatial distributions of pressure and total heads, velocity fields, moisture contents, temperature, and biogeochemical concentrations at user-specified times and locations (finite element nodes). The reference version for this analysis is described in ORNL/TM-2004/107 (Yeh at al 2004b).

**Physical basis/mathematical model**

Governing equations of the model include four types: flow, thermal transport, reactive transport, and reactive biogeochemical equations. In addition to initial conditions, four types of boundary conditions (Dirichlet, Cauchy, Neumann, and variable (inflow-outflow) are implemented in the model for the flow, thermal and species transport.

*Flow Equations:* A modified Richards equation describes density-dependent fluid flow in variably-saturated media. It is based on continuity of fluid, continuity of solid, motion of fluid (Darcy's law), consolidation of the media, and compressibility of water. The major factors controlling fluid flow are slight deformation of the media, pressure and gravity forces, capillary tension, evaporation, transpiration, infiltration, and artificial injections and pumping.

*Thermal Transport Equations:* The governing equations of thermal transport in a subsurface system are based on the principles of conservation of energy and the law of thermal flux.

*Species Transport:* The major transport processes are advection, dispersion/diffusion, and source/sinks. The partial/ordinary differential reactive transport equations are based on the conservation law of material mass stating that the rate of mass change is due to biogeochemical reactions and hydrologic transport.

*Biogeochemical Equations:* The biogeochemical module solves a system of mass balance equations (component equations and kinetic variable equations) and mass action equations. The model uses a reaction-based formulation, in which a reaction network is conceptualized as

$$\sum_{i\in\{M\}} \mu_{ik}\hat{C}_i \leftrightarrow \sum_{i\in\{M\}} \nu_{ik}\hat{C}_i, \;\; k\in\{N\} \qquad (45)$$

where $\hat{C}_i$ is the chemical formula of the *i*-th species, $\mu_{ik}$ is the reaction stoichiometry of the *i*-th species in the *k*-th reaction associated with the reactants, $\nu_{ik}$ is the reaction stoichiometry of the *i*-th species in the *k*-th reaction associated with the products, and $\{N\}=\{1,2,..N\}$ in which $N$ is the number of reactions. The production rate of any species is obtained based on the principle of reaction kinetics as

$$r_i = \sum_{k\in\{N\}} (\nu_{ik} - \mu_{ik}) R_k ,\ i \in \{M\} \tag{46}$$

where $R_k$ is the rate of the *k*-th reaction in moles of chemical per unit volume of water per unit time [M/L$^3$/T].

There are $N_E$ independent fast/equilibrium reactions and $N_K$ slow/kinetic reactions. For $N_K$ kinetic reactions, an explicit rate equation for each reaction is usually formulated. For every equilibrium reaction, an algebraic equation, i.e. a mass action equation is used to describe the corresponding fast/equilibrium reaction. Charge balance is maintained by the balanced mass action laws and conservation of charge.

Biogeochemical processes represented by the model include:

1. Aqueous speciation and complexation
2. Precipitation/dissolution
3. Ion exchange
4. Acid/base reaction
5. Redox reactions
6. Microbially-mediated reactions
7. Several sorption models including:
    a. Simple surface complexation (non-electrostatic)
    b. Double layer model
    c. Triple layer model

Kinetic models include: elementary rate laws, Monod kinetics, nth order reactions or empirical functions.

Aqueous species, NAPL, air and solid phase species are recognized. Species can be mobile or immobile; colloids can be transported as species that have surface areas and react with aqueous species.

Other features of the biogeochemical calculations include:

1) Corrections for nonideality: aqueous species activity can be calculated from concentrations using the Davies equation; activities can also be calculated at a user-specified constant ionic strength or not all. Activity coefficients of solids are assumed equal to 1.
2) Rate constants are calculated using activities rather than concentrations.
3) An automatic species switching scheme is used to solve stiff geochemical equilibrium problems. One set of components may be chosen at the start of a simulation but if the

concentration of a component drops below a certain limit, the matrix of equations is modified to allow another species for that component to be used.

*Coupled Processes:* The following coupled processes are represented:

1) Dependence of groundwater density and dynamic viscosity on species concentration and temperature from built-in theoretical functions or user-supplied empirical functions.
2) Effect of precipitation/dissolution on porosity, hydraulic conductivity, and water capacity using the moisture content and the amount and molar volumes of precipitated species.
3) Effect of precipitation/dissolution on hydrodynamic dispersion using a modification of Archie's Law.
4) Dependence of chemical reactions on temperature through use of the Van't Hoff relationship and calculated $\Delta H$ of reactions to adjust rate constants and mass action constants.

*Other features:*

1) Irregularly-shaped three-dimensional domains can be represented. HYDROGEOCHEM contains three types of elements: hexahedral, triangular prism, and tetrahedral elements.
2) Heterogeneity and anisotropy of the subsurface media can be taken into account. Material properties include: a) four or nine nonzero components of the saturated conductivity or permeability tensor in the Richards equation; b) user-defined values for bulk density, tortuosity, longitudinal and transverse dispersivities, specific heat, apparent thermal conductivity, and saturated moisture content.
3) Off-diagonal dispersion coefficient tensor components are included to deal with cases when the coordinate system does not coincide with the principal directions of the dispersion coefficient tensor.
4) The time step size can be reset when the boundary conditions and/or sources/sinks change abruptly. The time step size can be originally set small and then increased gradually to a desired extent. It can also be reset to the original small value as many times as needed.
5) An "in-element" particle tracking technique is used to accurately and efficiently perform particle tracking. The process of particle tracking is the principal issue of the Lagrangian step in the transient simulation of reactive chemical transport and thermal transport, but often can be very computationally intensive with other techniques.
6) Non-isothermal subsurface systems can be modeled.
7) Both steady-state and transient simulations can be conducted with either weak coupling or strong coupling of flow with thermal and reactive transport.
8) Both spatially and temporally distributed element and point sources/sinks can be considered, i.e. the source/sink intensity can be a function of time.

## Functionalities

Table 8 lists the relevant chemical functionalities for the challenge milestones and indicates which functionalities are included in the code.

## Code structures

*General solution method:* The general solution method is illustrated by the following flow chart (Yeh et al. 2011).

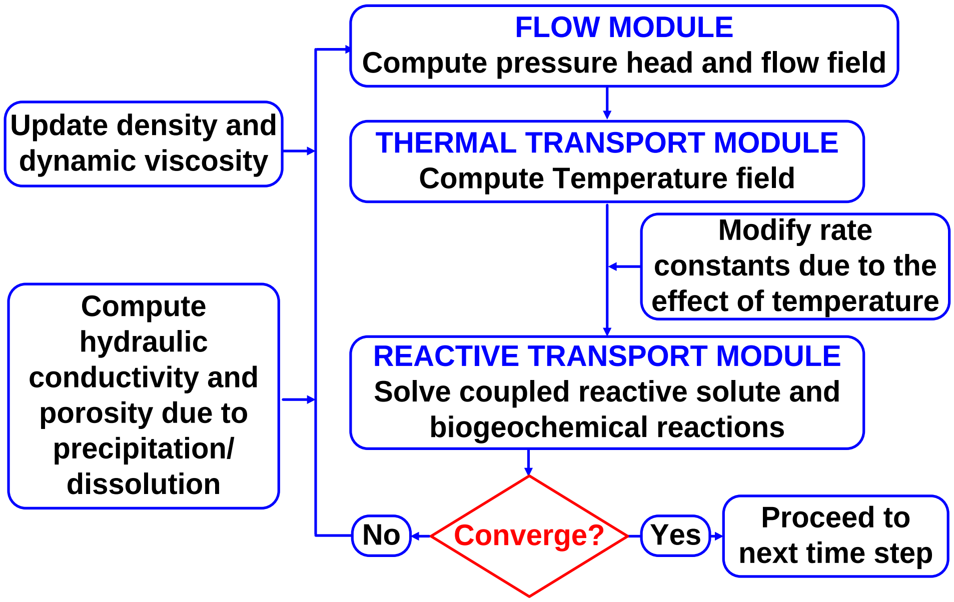


**Figure 7.** General flow chart of HYDROGEOCHEM

In each time step, an iterative procedure is used to solve the equations for coupled processes as follows:

1) The pressure head and flow field are obtained in the flow module with initial and boundary conditions.
2) The temperature field is obtained in the thermal transport module with initial and boundary conditions.
3) The reaction rate constants and parameters are updated to account for the effect of temperature.
4) The concentrations of all species and rates of all reactions are obtained in the reactive transport module.
5) Convergence of the solutions is checked. If solutions are convergent, the program proceeds to the next time step. If not, the fluid density and viscosity are updated then the program proceeds to the next non-linear loop of coupled processes. Once all species concentrations are obtained, posterior calculations of all rates of fast/equilibrium reactions are done.

*Code structures:* HYDROGEOCHEM 5.0 consists of a short MAIN routine, 191 subroutines, and 3 functions. The main functions are described below:

- MAIN module - specify the sizes of all arrays, read data file names, and open data files.
- Subroutine HGC50 - coupling of flow, heat transfer and biogeochemical transport and performance of the control and coordination activities.
- Subroutines HYDROS and HYDROT - steady state and transient simulations, respectively of fluid flow.
- Subroutines HEATS and HEATT - steady state and transient simulations, respectively of heat transfer.
- Subroutines CHEMIS and CHEMIT - linkage between the hydrologic transport model and reactive biogeochemical model for the steady state and transient simulations, respectively.

The remaining 184 subroutines can be classified into seven major categories with most important subroutines as described below:

- ***Fluid flow***: -14 subroutines: RHOMU0, SPROP, VELT, FQ468D, FBCMTRX, FSFLOWPRE, FSFLOW, FQ468TH, BCPREP, FASEMB, FQ468, FBC, FQ34R, FQ34S.
    - **Subroutine VELT** computes the Darcy's velocities.
    - **Subroutine FSFLOW** computes the fluxes through various types of boundaries and the increasing rate of water content in the region of interest.
    - **Subroutine FSFLOWPRE** computes the boundary flux based on pressure head.

- ***Hydrologic transport*** - 18 subroutines and one function: SROSTR, GRDROV, AFABTA, DISPC, MVELT, Q468D, SFLOW, Q34S, TACADC, WKTOTC, ASEMBL, Q468, TRANSP, EQNGEN_F, EQNGEN_P, BC, Q34CNV, CHKVBC.
    - **Subroutine MVELT** computes the material flux.
    - **Subroutine TRANSP** is called by Subroutines CHEMIS and CHEMIT to perform hydrologic transport computations of mobile components and mobile kinetic variables. Subroutine TRANSP calls Subroutine EQNGEN_F or EQNGEN_P to produce the matrix equation for each primary dependent variables (PDVs); Subroutine BC to implement the boundary conditions; and Subroutines BLKITR, PISS, PPCG, ILUCG, MICPCG, or SSORCG to solve the resulting matrix equations.

- ***Heat transfer*** - 15 subroutines and one function(EQ): DISPT, LANGVT, TASEMB, Q468T, KMATRIX, MATRIX, VMATRIX, VMATRIX1, TBC, Q34TB, TBC_1, Q34TB_1, ENTHA, ENTHABF, EKCONST, EQ.
    - **Subroutine DISPT** is called by Subroutine HGC50 to compute the thermal diffusion/dispersion/conductivity coefficients.
    - **Subroutine LANGVT** is called by HEATT to compute the Lagrangian tracking velocity for heat transfer when a transient simulation is performed.
    - **Subroutines ENTHA and ENTHABF** are called by MAIN to calculate the enthalpy of equilibrium and kinetic reactions, respectively.

- ***Solution of matrix equations for flow/transport /heat transfer simulations*** - 11 subroutines and one function (DOTPRD): BLKITR, SOLVE, PISS, PPCG, POLYP, ILUCG, LLTINV, MICPCG, MICP, SSORCG, SSORP, DOTPRD. The different subroutines are used for the different matrix solution techniques:
  - **Subroutine BLKITR**: block iteration methods.
  - **Subroutine PISS**: pointwise Gauss-Seidel iteration strategy
  - **Subroutine PPCG**: preconditioned conjugate gradient method
  - **Subroutine ILUCG**: incomplete Cholesky decomposition

- ***Computation of Lagrangian particle tracking*** - 44 subroutines and one function(FCOS): GNTRAK, REPLAS, ELENOD, WRKARY, ELTRK4, ELTRK6, ELTRK8, MMLOC, ONLINE, TRAK1T, TRAK2T, TRAK1P, TRAK2P, TRAK1H, TRAK2H, PLANEW, LOCQ3N, LOCQ4N, CHNGSN, SURE3D, LOCPLN, BASE2D, XSI2D, NEWXE, CKSIDE, CKCNEL, CKCOIN, ONPLAN, BDYPLN, BASE1, FIXCK, ALGBDY, INTERP1, BNDRY, LOCQ2N, SUR2D3, BASE, XSI3D, XSI3DP, CKBDY, ADVBC, Q34ADVB, TADVBC, Q34TADVB, FCOS.

- ***Biogeochemical equilibrium and kinetics***- 46 subroutines: OCSPIT, ARRVA, DERIV, LUDCMP, FUNCT, JACKR, BIOGEOCHEM, KIVRAT, KINEQL, TOTDNP, NPPT, MSP2EQ, ACOEF, MODIFK, MODBFK, RESIDU, RADC, USERMA, RIES, RKRXNS, RUSRLW, RATEL0, PRODBF, JACOB, JADC, JACKV1, JACKV2, JARXN, FBTERM, JOLAW, DERDRXN, DERXN, DERDEQ, DEREQ, DGELG, INDEXX, DISOLV, BASWIT, INVERSE, PREPOS, ERANK1, ERANK, KRANK, EKRANK, CPEQ, SPTYP.
  - **Subroutine OCSPIT**: called by Subroutines HGC50, CHEMIS, and CHEMIT to calculate the total dissolved concentrations, total sorbed concentrations, and total precipitated concentrations of all components and the negative logarithm of the concentrations of all component species by calling **Subroutine BIOGEOCHEM**. The inputs to Subroutine OCSPIT are the total analytical concentrations of all components and their identification numbers.
  - **Subroutine BIOGEOCHEM**: performs either the steady-state computation, a transient state computation using the steady-state solution as the initial conditions, or a transient computation using user supplied initial conditions. After initializing the concentrations of all product species given the estimate of component concentrations from Subroutine OCSPIT, BIOGEOCHEM calls **Subroutine KINEQL** to solve a set of mixed ordinary differential and algebraic equations governing mole balance, and biogeochemical kinetic and equilibrium reactions. It calls **Subroutine TOTDNP** to compute total dissolved, total sorbed, and total precipitated concentrations of all components after concentrations of all species have been found. Finally, it calls **LPOUT** to print biogeochemical species distributions.
  - **Subroutine ACOEF**: called by Subroutine KINEQL to compute ionic strength and activity coefficients of all species.

  - **Subroutine MODIFK:** called by Subroutine KINEQL to calculate the equilibrium constants for all equilibrium product species and the modified forward and backward rate constants for any basic kinetic reactions.
  - **Subroutine MODBFK**: called by Subroutine KINEQL to calculate the modified forward and backward rate constants for any mixed kinetic reactions.
  - **Subroutines RIES, RKRXNS, RUSRLW, RATEL0**: calculations of reaction rates,
- ***Utility functions*** - 36 subroutines: RDATIO, DATAIO, READR, READN, CONECT, SURF, PAGEN, LRL3D, LRN3D, FIDAT, IDAT, TIDAT, FSSDAT, SSDAT, TSSDAT, FBCDAT, BCDAT, TBCDAT, NODVA0, NODVA1, NODVA2, NODVA3, INTERP,ADVW3D, CALKD,FPRINT, PRINTT, TPRINT, FSTORE, STORE, TSTORE, LPOUT, TOTAL0, TOTAL1, TOTAL2, SHAPE.

## Numerical algorithms

*Numerical options for thermal and hydrologic transport equations:* Three numerical options are provided to solve the thermal and hydrologic transport equations:

1) Conventional FEM (finite element method).
2) Hybrid Lagrangian-Eulerian FEM
3) Hybrid Lagrangian-Eulerian FEM for interior and downstream boundary nodes plus FEM in advective form for downstream boundary nodes

The two optional hybrid Lagrangian-Eulerian FEMs are provided to solve transient advection-dominated transport problems and to avoid negative concentrations in computations of chemical equilibrium and/or kinetics under certain conditions.

*Numerical options for biogeochemical reactions and hydrologic transport equations:* Three schemes are available for numerically couple hydrologic transport and biogeochemical reactions.

1) Fully implicit iteration approach,
2) Operator splitting approach
3) Predictor-corrector approach.

*Methods to achieve convergent solutions for non-linear reactive chemical transport systems:* Because reactive transport systems are often strongly nonlinear, many options are available to achieve convergent solutions. These include: (a) three options (under-, exact-, and over-relaxation) to estimate the matrix in the solute transport-biogeochemical reactions coupling loop in reactive chemical transport); (b) two options (consistent and lumping) to treat the mass matrix; and (c) six options (block iteration method, successive point iterations, and four preconditioned conjugate gradient methods) to solve the linearized matrix equations.

*Other features:*

1) Finite difference (FD) methods are employed for temporal discretization of the governing partial differential equations.

2) The Galerkin finite element method is employed for spatial discretization of the modified Richards equation governing the distribution of pressure fields.

3) Automatic grid generation capability.

**Database**

None available. All reactions must be entered into the input decks.

**Demonstrated applications**

The HYDROGEOCHEM family of codes includes: HYDROGEOCHEM (versions 1.0, 2.0, 2.1, 3.0, 3.1, 3.2, 4.0 and 5.0); LEHGC (versions 1.0, 1.1 and 2.0) and several geochemical codes that do not include transport (EQMOD, KEMOD, BIOCHEM AND BIOGEOCHEM). The Users Manuals for several of these codes contain sample problems that were not repeated in subsequent versions. Table 2 compares the coupled processes simulated by some of these code. Table 3 summarizes the demonstrations of various processes using different versions of HYDROGEOCHEM.

HYDROGEOCHEM 5.0 is the most recent version of the code in three dimensions, while HYDROGEOCHEM 4.0 is the most recent version of the code in two dimensions. There are 13 two-dimensional- sample problems for HYDROGEOCHEM 4.0 (see Table 6.1 in Yeh et al. 2004a) and 13 equivalent pseudo three-dimensional (a 2-D problem with a single element in the third dimension) and 2 fully three-dimensional sample problems for HYDROGEOCHEM 5.0 (see Table 6.1 in Yeh et al. 2004b.)

Sample problems 1 – 9 illustrate the ability of HYDROGEOCHEM 4.0 to simulate saturated and unsaturated fluid flow, conservative solute transport under steady state and transient conditions, and density driven flow without chemical reaction. Sample problems 10 – 17 in HYDROGEOCHEM 4 demonstrate the use of the code in simulations involving transport coupled with complexation, precipitation and adsorption in porous or fractured media. Problem 18 demonstrates coupling between precipitation, porosity and transport for reactive and nonreactive tracers. Sample problems 15 and 16 for HYDROGEOCHEM 5.0 describe 3-D flow and transport coupled with complexation, ion exchange and mineral dissolution in isothermal and nonisothermal systems, respectively. These problems are the most complex examples in the User's Manual and include both equilibrium and kinetic reactions. The chemical system is a complex reaction network involving dissolution of the sorbing sites to form aqueous species, surface ionization of a solid and changes in sorption equilibria due to thermal transport (Example 16). In addition to the sample problems in the manuals, two recent review papers (Yeh et al. 2009, 2011) provide examples of applications of HYDROGEOCHEM to chemical scenarios relevant to the waste IPSC.

HYDROBIOGEOCHEM (Yeh et al. 1998) was used to model systems in which biodegradation of an organic substrate is coupled to advection-diffusion, aqueous complexation, and adsorption (Sample problems 5, 6, 8) and partially benchmarked (Problem 5) against studies by Vallochi and Tebbe (1997). In Problem 8, the organic substrate is a sorption site for metals and microbes and is biodegraded. Microbes both in solution and adsorbed to the substrate are capable of degrading the organic substrate. Sample Problem 7 for the HYDROBIOGEOCHEM code is a simulation of in situ copper mining using an acidic injection solution. It is based upon a benchmark reactive transport problem developed by Lichtner (1997). This problem involves the kinetic dissolution and formation of ten solid phase species.

Several of stand-alone geochemical codes related to HYDROGEOCHEM were developed over the years. Some of the component codes might be used as modules in a more comprehensive simulator proposed for the waste IPSC. The geochemical modules include:

- EQMOD – equilibrium geochemical speciation calculations that simulates aqueous complexation, surface adsorption, ion-exchange, precipitation/dissolution, and redox reactions.
- KEMOD, KEMOD1-1, KEMOD 2: A series of chemical speciation codes in which every chemical species can be treated as either an equilibrium-controlled or kinetically-controlled species. The later versions have increasingly greater flexibility in simulating kinetically controlled reactions.
- EQPITZ: a geochemical equilibrium code based on EQMOD that uses the Pitzer equations to calculate activity coefficients up to 20M ionic strength. (Yan 1992).
- EQMODCP: a geochemical equilibrium modeling code that can simulate co-precipitation, in addition to the processes represented in EQMOD (Zhu 1995).
- BIOGEOCHEM 1.0, BIOGEOCHEM 1.1 (Yeh et al. 2005): both a chemical speciation code and a preprocessor for HYDROGEOCHEM simulations. This code is a descendant of the KEMOD code and includes additional features for simulation of microbial processes. It incorporates the "new paradigm of reaction-based approaches" to biogeochemical processes (Fang et al. 2003) which allows description of the reaction system on an ad hoc empirical basis or in terms of more fundamental basic reactions.

Many processes including complex microbial reaction networks have been simulated with BIOGEOCHEM (Yeh et al. 2005) and can also be modeled using HYDROGEOCHEM. Descriptions of such simulations are summarized in Yeh et al. (2009, 2011) and described in more detail in Scheibe et al. (2006) and Fang et al. (2009).

**Accessibility of source codes**

The source codes and documentation for different members of the HYDROGEOCHEM family are summarized below:

| | Fortran code available | Formal Permission to Release to NEAMS | Post-processor |
|---|---|---|---|
| LEHGC | Yes | Yes | No |
| HYDROBIOGEOCHEM | Yes | Yes | Yes |
| HYDROGEOCHEM 4/5 | Yes | Not yet | Yes |
| BIOGEOCHEM | Yes | Not yet | No |
| EQPITZ | Yes | Not yet | No |
| EQMODCP | Yes | Not yet | No |

**Limitations**

- No thermodynamic or kinetic data bases that can be read externally from code. All reactions must be entered into the input decks.
- Equilibrium constants are not corrected by the code for changes in pressure.
- Activity coefficients are modeled using the Davies equation and therefore are not accurate in high ionic strengths. The stand-alone geochemical section code EQPITZ was developed to deal with this limitation but has not been incorporated into HYDROGEOCHEM yet.
- Co-precipitation and solid solution are not modeled by HYDROGEOCHEM. The stand-alone geochemical code EQMODCP (Zhu, 1995) was developed to simulate co-precipitation but has not been incorporated into HYDROGEOCHEM yet.
- Applications are limited to single fluid phase flows.
- Dual-porosity media cannot be dealt with effectively.
- No mechanical effects modeled.

**Table 8.** Chemical Functionality Needs versus HYDROGEOCHEM Capabilities

| **Functionality** | **High-Fidelity Model** | **PA Model** | **Code Capability** | **Comments** |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | Yes | |
| Mineral equilibration | Yes | Yes | Yes | |
| Solid solutions | Yes | Yes | Likely | EQMODCP can model these |
| Gas species equilibration | Yes | Yes | Yes | |
| Gas phase modeling | Yes | Yes | No | |
| Temperature corrections | Yes | Yes | Yes | |
| Pressure corrections | Yes | Yes | No | Equilibrium constants are not corrected by the code for changes in pressure. |
| Pitzer equations | Yes | Yes | Likely | EQPITZ can model these |
| Ion exchange | Yes | Yes | Yes | |
| Surface complexation | Yes | Yes | Yes | |
| Uncertainty propagation | No | Yes | No | |
| Uncertainty evaluation | No | Yes | No | |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

|  |  |  |  |  |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Yes |  |
| Flow-through | Yes | Yes | Yes |  |
| 3-D mesh | Yes | No | Yes |  |
| Stress corrosion cracking | Yes | Yes | No |  |
| Radiolysis | Yes | Yes | Likely | Not demonstrated yet |
| Reactive transport | Yes | Yes | Yes | 3-D |
| THC reactive transport | Yes | Yes | Yes |  |
| Uncertainty propagation | Yes | Yes | No |  |
| *Other Potentially Important Chemical Functionalities* |  |  |  |  |
| Colloids | Yes | Yes | Limited | Colloids are treated as mobile surface species controlled by equilibrium/kinetics. Full capabilities including generation and capture not demonstrated yet. |
| Solution density calculation | Yes? | No? | Yes |  |
| Decay and ingrowth | Yes | Yes | Yes | Not demonstrated yet |

**Table 9.** Couplings Modeled in Different Members of HYDROGEOCHEM Family of Codes

|  | T | H | C | M | B | R |
|---|---|---|---|---|---|---|
| T | X |  |  |  |  |  |
| H | 1 | X |  |  |  |  |
| C | 1 | 1, 2 | X |  |  |  |
| M |  |  |  | X |  |  |
| B |  | 1, 3 | 1,3 |  | X |  |
| R |  |  | *1,2* |  |  | X |

Code Key: 1 = HYDROGEOCHEM4/5; 2 = LEHGC; 3 = HYDROBIOGEOCHEM
Italic font: *probable but not yet demonstrated*

Strong Couplings
T-H: changes in density and flow to due heat transfer and vice versa
T-C: effect of temperature on reaction rates and equilibrium constants
H-C: transport of species and effect of precipitation/dissolution on flow through changes on porosity, density and dispersivity.
C-B: effect of chemistry on bacterial growth and vice versa
B-H: transport of bacteria by flow
C-R: change in concentration by radioactive production and decay

In many cases, these couplings can be suppressed. This may facilitate the running of certain problems where data are available from other analyses. For example, the flow field can be calculated or a transient or steady state velocity and moisture content can be read from an external file.

**Table 10.** Reactive Geochemical Transport Processes Important to the Waste IPSC and Relevant HYDROGEOCHEM Sample Problems

| Biogeochemical Reactions or Transport Processs | HYDROGEOCHEM (HGC), LEHGC or Other Sample Problems |
|---|---|
| Adsorption | HGC4: 14-16; HGC5:15 |
| Precipitation | HGC4: 13; HGC5:15 |
| Complexation | HGC4: 13; HGC5:15 |
| Flow and transport | HGC4: 5-8, 13; HGC5:15 |
| Precipitation of carbonates, sulfate or amorphous phases | HGC4: 17-19 |
| Ion exchange | HGC5:15 |
| Co precipitation | EQMODCP: |
| Colloid transport | LEHGC1.1: 9 |
| Monod Kinetics | BIOGEOCHEM sample problems model these |
| Bacteria transport | |
| Density driven-flow | HGC4: 9-10 |
| Unsaturated flow | HGC4:1-4 |
| Adsorption | HGC4: 14-16<br>HGC5:15 |
| Oxidation/reduction | none |
| Speciation in brines | EQPITZ |

## 4.2.2 PFLOTRAN

PFLOTRAN is described by its authors' as a "next-generation reactive flow and transport code for modeling subsurface processes… designed from the ground up to run efficiently on machines ranging from leadership-class supercomputers to laptops" (Hammond et al. 2011). It is a finite volume code based on frameworks for high-performance computing. Features of the code include a modular input file, implementation of high-performance I/O, ability to perform multiple realization simulations with multiple processors per realization, and multiple modes for multiphase flow and multicomponent geochemical transport.

**Physical basis/mathematical model**

PFLOTRAN is divided into several flow modes including multiphase $CO_2$- $H_2O$, air-liquid water, thermal-hydrologic-chemical (THC), and Richards' equation for variably saturated porous media. The flow modes are coupled to a multi-component geochemical transport mode through temperature, pressure, flow velocity, and phase saturation state.

- Multiphase Flow Equations:
    - Local equilibrium is assumed between phases for modeling multiphase systems; multiphase partial differential equations for mass and energy conservation are solved.
    - Additional constitutive relations account for capillary pressure and changes in phase.
    - van Genuchten, Books-Corey and Thomeer-Corey relative permeability functions are supported for Richards' equation for variably-saturated single phase flow.
    - Burdine and Mualem saturation functions are used and water density and viscosity are computed as a function of temperature and pressure through an equation of state for water.

- Geochemical Transport
    - Chemical reactions include:
        - Homogeneous aqueous complexation reactions
        - Heterogeneous mineral precipitation/dissolution,
        - Ion exchange,
        - Surface complexation
        - Multirate kinetic models
            - Rates of reactions in gas phase based on local equilibrium assumption
            - Rates of homogeneous aqueous complexation and ion exchange reactions based on local equilibrium assumption
            - Mineral reactions are based on kinetic rate laws derived from transition state theory.
            - Surface complexation reactions treated either as intrinsically fast reactions in local chemical equilibrium or through a kinetic multirate model

    - Geochemical transport mode may alter the flow field through changes in porosity, permeability and tortuosity caused by chemical reactions.
        - Porosity changes as mineral volume fraction changes.

    - Permeability is calculated using a power law relation between permeability and porosity.
    - Mineral surface area can vary according to a power law relation involving initial mineral surface area and volume fraction.
- Corrections for nonideality: Debye Hückel equation

**Functionalities**

Table 11 lists the relevant chemical functionalities for the challenge milestones and indicates which functionalities are included in the code.

**Code structures**

The code is written in a modular manner facilitating the incorporation of new computational algorithms and scientific processes (see Figure 8).

- Written in object-oriented Fortran9X and can interface with C and C++ codes.
- Frameworks for high-performance computing [i.e. HDF5 (Hierarchical Data Format 5), and MPI (Message Passing Interface), PETSc (Parallel Extensible Toolkit for Scientific computing), SAMRAI (Structured Adaptive Mesh Refinement Application Interface)].
- Domain decomposition parallelism is employed, with the PETSc parallel framework used to manage parallel solvers, data structures and communication. The domain decomposition is used to distribute the problem domain, potentially, across thousands of processor cores.

Figure 8 illustrates PFLOTRAN's workflow and data dependence (figure and description below from Hammond et al. 2011). PFLOTRAN's highest level object is the simulation which contains pointers to two types of objects, the realization and the time-steppers for flow and transport. The realization object contains a hierarchy of data structures and objects that define the problem statement and scientific algorithms being employed to solve the mathematical/scientific equations that govern the problem statement. The time-stepper encompasses the nonlinear and linear solvers utilized to solve the systems of PDEs either for steady-state conditions or for an increment in time (i.e. a time step). The time-stepper utilizes the realization object to first determine which scientific processes are being simulated and then populate the system of equations being solved.

Numbers in Figure 8 refer to:

1. Multi-Realization Simulation object: Highest level data structure providing all information for running simulations composed of multiple realizations.
2. Simulation object: Data structure providing all information for running a single simulation.
3. Time-stepper object: Pointer to Newton-Krylov solver and tolerances associated with time stepping
4. Solver object: Pointer to nonlinear Newton and linear Krylov solvers (PETSc) along with associated convergence criteria.
5. Realization object: Pointer to all discretization and field variables associated with a single realization of a simulation

6. Level object: Pointer to discretization and field variables associated with a single level of grid refinement within a realization
7. Patch object: Pointer to discretization and field variables associated with a subset of grid cells within a level
8. Auxiliary Data object: Pointer to auxiliary data within a realization/patch.

**Numerical algorithms**

- Information is limited:
  - 2 types of function evaluations to solve Newton-Raphson method
  - nonlinear Newton and linear Krylov solvers
  - Scalar Nonlinear Equations Solvers with underlying KSP linear equation solver and preconditioner components.

**Databases**

- Thermodynamic data are read from a database for equilibrium constants over a range of temperatures from 0–300 $^oC$ and fixed pressure at 1 bar for temperatures below 100 $^oC$ and along the saturation curve for pure water for higher temperatures.
- Database also includes reaction stoichiometry, mineral molar volumes, species valence, and Debye-Hückel parameters.
- User may also use a customized database for higher temperatures.

**Demonstrated applications**

PFLOTRAN has been run on problems composed of up to two billion unknowns using up to 131,072 processor cores on Argonne National Laboratory's Blue Gene/P and Oak Ridge National Laboratory's Jaguar supercomputers. The code is currently being applied to simulate uranium transport at the Hanford 300 Area and $CO_2$ sequestration in deep geologic formations. These illustrate the use of complex time-dependent boundary conditions and multi-component chemistry coupled to variably saturated flow, and two-phase simulation of $H_2O$ and supercritical $CO_2$.

**Accessibility of source codes**

PFLOTRAN is licensed under an open source GNU Lesser General Public License (LGPL). Information is available at the code website: http://ees.lanl.gov/pflotran/.

**Other unique features**

PFLOTRAN is able to carry out Monte Carlo fully coupled reactive transport analyses.

- Multiple simulations of different realizations are carried out simultaneously, with each realization being executed across multiple processor cores.

- The authors claim that “the discharge of each in parallel through domain decomposition within a processor sub-communicator group is a novel feat within subsurface simulation. This ability will revolutionize Monte-Carlo style analyses”. (Hammond et al. 2011).
- Output for the stochastic simulation is written to files and user then employs scripts or codes to post process the results, computing statistical averages, sampling data, *etc*.
- This approach has been successfully demonstrated on stochastic simulations composed of hundreds of thousands of realizations and utilizing thousands of processor cores.

**Limitations**

- User may use a customized thermodynamic database for higher temperatures but pressure must be fixed.
- Hydrodynamic dispersion and molecular diffusion treated as a diagonal tensor. A full dispersion tensor is not currently supported to avoid oscillatory behavior and negative concentrations..
- Diffusion is species independent.
- Lack of colloid-facilitated transport,
- Pitzer activity coefficient model is not supported.

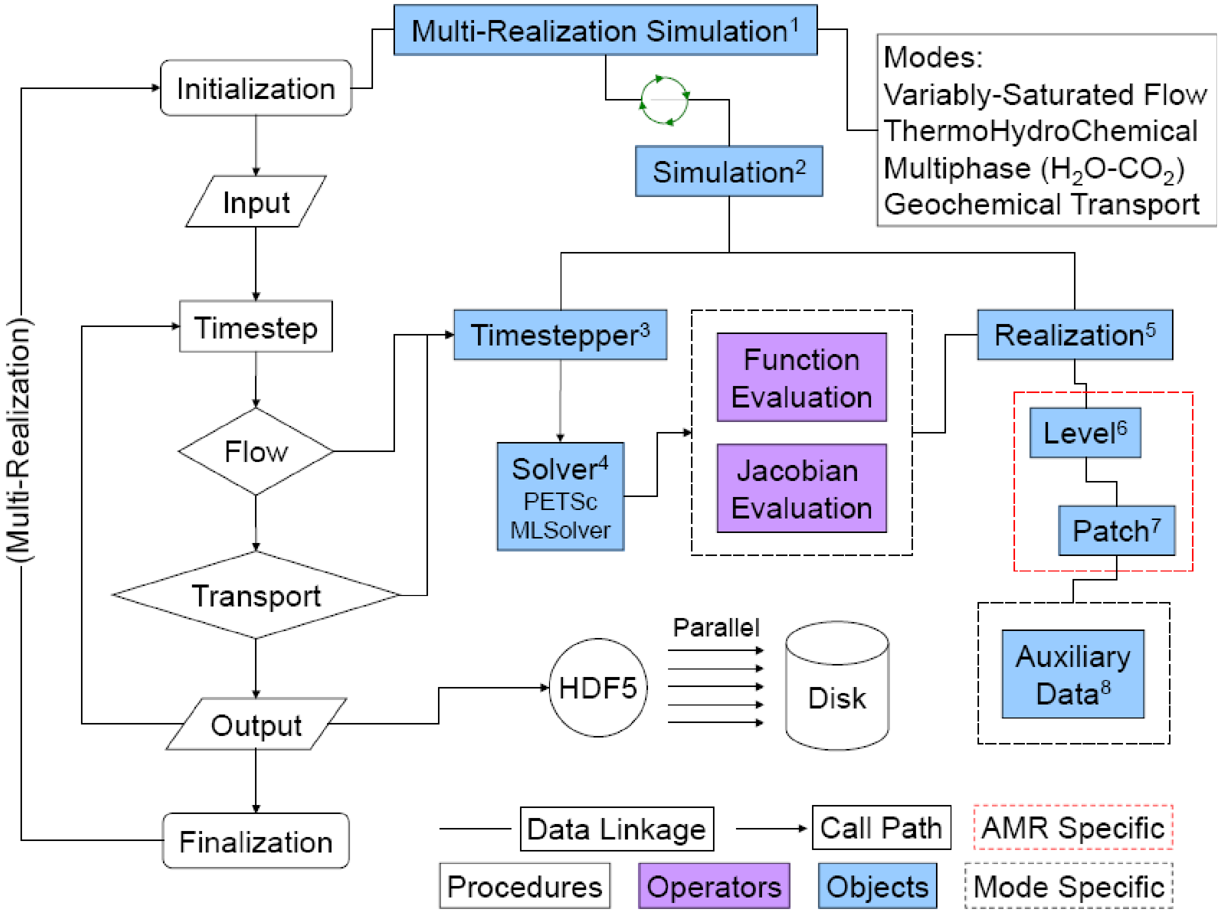


**Figure 8** Schematic of PFLOTRAN workflow and data dependence illustrating the use of procedures, operators, and objects within the code (see text for explanation of numbers) (Hammond et al. 2011).

**Table 11.** Chemical Functionality Needs versus PFLOTRAN Capabilities

| Functionality | High-Fidelity Model | PA Model | Code Capability | Comments |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | Yes | |
| Mineral equilibration | Yes | Yes | Yes | |
| Solid solutions | Yes | Yes | unknown | |
| Gas species equilibration | Yes | Yes | Yes | |
| Gas phase modeling | Yes | Yes | Yes | |
| Temperature corrections | Yes | Yes | Yes | |
| Pressure corrections | Yes | Yes | limited | Equilibrium constants are corrected by the code for changes in pressure up to 300 $^oC$ along saturation curve for pure water. At temperature below 100 $^oC$ pressure is fixed at 1 bar. |
| Pitzer equations | Yes | Yes | No | |
| Ion exchange | Yes | Yes | Yes | |
| Surface complexation | Yes | Yes | Yes | |
| Uncertainty propagation | No | Yes | Yes | When run in stochastic mode |
| Uncertainty evaluation | No | Yes | Yes | When run in stochastic mode |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

| | | | | |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Yes | |
| Flow-through | Yes | Yes | Yes | |
| 3-D mesh | Yes | No | Yes | Finite volume |
| Stress corrosion cracking | Yes | Yes | No | |
| Radiolysis | Yes | Yes | Limited | |
| Reactive transport | Yes | Yes | Yes | |
| THC reactive transport | Yes | Yes | Yes | |
| Uncertainty propagation | Yes | Yes | No | |
| *Other Potentially Important Chemical Functionalities* | | | | |
| Colloids | Yes | Yes | No | |
| Solution density calculation | Yes? | No? | Yes | |
| Decay and ingrowth | Yes | Yes | possibly | |

### 4.2.3 TOUGH2

TOUGH2 has been developed by Lawrence Berkeley National Laboratory for the nonisothermal flow of multicomponent, multiphase flow in porous and fractured media (Pruess et al. 1999). The reference version for this analysis is Version 2.0.

**Physical basis/mathematical model**

- Fluids
  - Fluid properties are described by Equation of State (EOS) Module.
  - Fluids are multiphase as appropriate.
  - Fluids can be in gas and liquid phases.
  - New equation of state modules can be added.
  - Current EOS modules include:
    - water, water with tracer
    - water, $co_2$
    - water, air
    - water, air with vapor pressure lowering
    - water, hydrogen
    - water, brine, air
    - water, brine, air, parent-daughter radionuclides
    - water, “dead” oil, non-condensible gas
    - water, passive air (richards’ equation)
    - water, nacl, non-condensible gas
- Conceptual Model
  - Mass continuity equations account for:
    - partitioning between gas and liquid phases by henry’s law
    - one eos module for liquid-solid sorption
    - constant pore compressibility and expansivity
  - Momentum equations account for:
    - Darcy’s law
      - special version available for forchheimer equation (turbulent flow)
    - principal axis permeabilities may be independent
    - numerous capillary pressure and relative permeability functions
    - new functions can be easily added
    - no coupling between fluid relative permeabilities
    - Klinkenberg effect included
    - dusty gas model available for gas diffusion
    - diffusion in liquid and gas phases
    - enhanced vapor diffusion
    - vapor pressure lowering for one EOS module
    - “random” grid permeability modifications
  - Energy equations account for
    - conduction and convection

            - thermal radiation boundary condition
        - TOUGH2 also includes a wellbore model:
            - limited wellbore coupling
            - additional development underway
    - Space and time discretization
        - Space discretization includes
            - integrated finite difference
            - no reference to global system of coordinates
            - mesh input that can be easily modified
            - dual porosity and dual permeability capability
            - limited mesh generation capability
            - interface weighing options user specified
                - upstream
                - harmonic
        - Time discretization includes
            - first-order
            - fully-implicit
    - Numerical solution algorithms include:
        - direct solvers
        - conjugate gradient solvers
        - automatic time step adjustment and fallback
    - Pre-processing includes
        - limited mesh generation capability
        - fixed field input format
        - some commercial programs available for pre- and post-processing
    - Post-processing includes
        - limited capabilities
        - some automatic routines available for use in tecplot
        - some commercial programs available for pre- and post-processing.

**Functionalities**

Table 12 lists the relevant chemical functionalities for the challenge milestones and indicates which functionalities are included in the code.

**Code structures**

- Fortran 77
- Different Equation of State (EOS) subroutines used for different eos modules
- Runs on PCs, workstations, and supercomputers
- Parallel version available (TOUGH-MP)
- Hydrate version available
- Inverse modeling version available (iTOUGH2)
- Limited coupling with mechanics codes (Stone et al., 2003; Leung et al. 2009)

**Numerical algorithms**

- Numerical evaluation of jacobian matrix elements and appropriate residual terms
- Newton-Raphson iteration procedure
- Automatic time step adjustment
- Re-execution of time advancement using smaller time step for convergence failure

**Database**

- Equation of state databases
    - Fluid properties calculated from detailed equation of state relationships

**Demonstrated applications**

- Test problems provided with software
    - heat pipe in cylindrical geometry
    - heat sweep in vertical fracture
    - five-spot geothermal production/injection
    - coupled wellbore flow
    - multiphase and nonisothermal processes in a system with variable salinity
    - thermal and tracer diffusion
    - contamination of an aquifer from VOC vapors in the vadose zone
    - flushing oil from a 1-D column by water injection
    - demonstration of gravity- capillary equilibrium
    - demonstration of permeability modification options
    - production from a geothermal reservoir with hypersaline brine and $CO_2$
- TOUGH2 symposium proceedings
    - Symposiums held every few years with numerous people attending and presenting applications

**Accessibility of source code**

- Standard versions available for small fee
- Additional fee for some versions ($CO_2$)

**Other unique features**

- Described above

**Evaluation**

- User input is often cumbersome but very flexible
- Automatic grid generation is very limited
    - May be able to use fehm mesh generation routine
- Post-processing is limited
- Good code flexibility

- Large world-wide user community
- Well respected computer program

**Table 12.** Hydrological Functionality Needs versus TOUGH2 Capabilities

| **Functionality** | **High-Fidelity Model** | **PA Model** | **Code Capability** | **Comments** |
|---|---|---|---|---|
| *Challenge Milestone 1: Chemical Equilibrium Calculation* | | | | |
| None | | | | |
| *Challenge Milestone 2: Waste Form and Waste Package Degradation* | | | | |
| None | | | | |
| *Challenge Milestone 3: Tunnel Closure (Salt Creep)* | | | | |
| Fluid Movement in Deforming Media | Yes | N/A | Needs to be Coupled to Mechanics Code | Some Limited Coupling has been done. |
| Simulation of fluid phase changes and binary diffusion in the gas phase | Yes | N/A | Limited | This functionality is available in TOUGH2 for porous and fractured media. This functionality is not available in TOUGH2 for open areas such as tunnels and other open spaces. |
| Simulation of heat transport in non-isothermal systems by convection, conduction, and radiation heat transfer | Yes | N/a | Limited | See above |

### 4.2.4 TOUGHREACT

TOUGHREACT is a three-dimensional non-isothermal multi-component reactive fluid flow, heat flow, and solute transport simulator for saturated and unsaturated porous media. Chemical reactions can be equilibrium, kinetic, and/or heterogeneous and can be applied over fairly broad ranges of pressure, temperature, and ionic strength. Sorption can be simulated by an ion exchange model or a linear adsorption isotherm. Changes to porosity and permeability are a function of precipitation and dissolution of minerals. TOUGHREACT is designed for a wide range of geologic applications including geothermal systems, diagenetic processes, subsurface waste disposal, and contaminant transport.

TOUGHREACT was developed at Lawrence Berkeley National Laboratory, was built from TOUGH2, a multi-phase fluid and heat flow code, by adding reactive geochemical capabilities. The user's guide for TOUGHREACT is Xu et al. (2004). Additional information on the code is provided at http://esd.lbl.gov/TOUGHREACT/index.html. The reference version for this analysis is version 1.2.

**Physical basis/mathematical model**

The physical basis and mathematical model is the same as that described for PHREEQC except that TOUGHREACT does not offer an ion interaction model for estimating species activity coefficients.

**Functionalities**

Table 13 lists the relevant chemical functionalities for the challenge milestones and indicates which functionalities are included in the code.

**Code structures**

TOUGHREACT is written in FORTRAN and accommodates all common platforms. A Makefile is provided for compiling the program under Linux. The code uses 64-bit arithmetic.

The calculation sequence is as follows:

- Initialize parameters
- Solve fluid and heat flow equations at current time step
- Solve solute transport of total dissolved components and transport of gas species, cell by cell
    - Compute any phase transfers
    - Iterate until convergence
- Update chemical state variables
- Go to next time step

## Numerical algorithms

The chemical equilibrium reactions in TOUGHREACT are solved by Newton-Raphson iteration. Transport is simulated by integrated finite difference (finite volume). Transport is solved separately from chemical reaction in a sequential manner by iteration.

Kinetics are also solved by Newton-Raphson iteration. When a mineral is exhausted, the time step may have to be limited manually to retain accuracy in rate law integration.

Convergence problems may occur when an initial guess for a water composition is inadequate or when transport causes an erroneous system composition at a grid block due to a large time step.

## Database

Several databases are supplied with the software. The largest databases are converted from an EQ3/6 database. They do not contain source references. The remaining databases are abridged for use in each sample problem.

The software includes a program for converting EQ3/6 databases to the required format. Also included is a program for switching basis species within the database.

## Demonstrated applications

An assortment of test problems is provided with software. Test problems include:

- Contaminant transport with linear adsorption and radioactive decay (1-D example compared to analytical solutions)
- natural groundwater chemistry evolution under ambient conditions
- assessment of nuclear waste disposal sites
- sedimentary diagenesis and $CO_2$ disposal in deep formations
- mineral deposition as in supergene copper enrichment
- mineral alteration and silica scaling in hydrothermal systems

Publications in which TOUGHREACT is used include the following topics:

- Supergene copper enrichment
- Hydrothermal systems
- $CO_2$ sequestration in saline aquifers
- Coupled thermal, hydrological, and chemical processes in boiling unsaturated tuff at Yucca Mountain
- Reactive transport in fracture-flow experiments under boiling conditions
- Calcite precipitation in the vadose zone
- Stable isotope fractionation in unsaturated zone pore water and vapor

## Accessibility of source codes

The source code and executable files for Version 1.2 are available subject to a license agreement with the following terms:

- Use only at the licensee’s site
- DOE-funded modifications, enhancements, or conversions of this package are subject to requirements of DOE O 241.1

### Other unique features

Potentially useful features and capabilities of the code that are relatively uncommon, unique, or noteworthy include:

- The ability to simulate fractured systems and dual permeability
- The adjustment of porosity and permeability resulting from mineral precipitation and dissolution
- An automatic time stepping scheme to recognize "quasi-stationary states" (QSS) and perform a “large” time step near the end of a QSS.

### Limitations

Table 3 indicates functional limitations with regard to Challenge Milestones 1 and 2.

**Table 13.** Chemical Functionality Needs versus TOUGHREACT Capabilities

| Functionality | High-Fidelity Model | PA Model | Code Capability | Comments |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | Yes | |
| Mineral equilibration | Yes | Yes | Yes | |
| Solid solutions | Yes | Yes | Yes | |
| Gas species equilibration | Yes | Yes | Yes | |
| Gas phase modeling | Yes | Yes | Yes | |
| Temperature corrections | Yes | Yes | Yes | |
| Pressure corrections | Yes | Yes | Limited | Code performs pressure corrections for gas species. |
| Pitzer equations | Yes | Yes | No | Under development. Uses extended Debye-Huckel activity model. |
| Ion exchange | Yes | Yes | Yes | |
| Surface complexation | Yes | Yes | No | Except for ion exchange, code can only simulate linear adsorption. |
| Uncertainty propagation | No | Yes | No | |
| Uncertainty evaluation | No | Yes | No | |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

| | | | | |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Yes | Code capabilities limited to mineral reactions and a general form of rate law, which can be a function of basis or non-basis species. |
| Solid-centered flow-through mode | Yes | Yes | Yes | |
| 3-D mesh | Yes | No | Yes | |
| Stress corrosion cracking | Yes | Yes | No | |
| Radiolysis | Yes | Yes | No | |
| Reactive transport | Yes | Yes | Yes | |
| THC reactive transport | Yes | Yes | Yes | |
| Uncertainty propagation | Yes | Yes | No | |
| *Other Potentially Important Chemical Functionalities* | | | | |
| Colloids | Yes | Yes | No | |
| Solution density calculation | Yes? | No? | No | |
| Decay and ingrowth | Yes | Yes | Yes | |

### 4.2.5 FEHM

FEHM (Finite Element Heat and Mass) is a code developed by Los Alamos National Laboratory for simulating heat transport, multi-fluid/multi-phase fluid flow, and contaminant transport in saturated and unsaturated porous media. This code is applicable to hydrogeologic, geothermal, and petroleum reservoir systems and can be used to predict the migration of aqueous and gas species in these systems. A dual-porosity and double-porosity/double-permeability component allows simulation of fractured media. Solute speciation and transport is simulated by a chemical equilibrium and reactive transport model and includes a particle tracking model.

Development of FEHM is led at LANL by George A. Zyvoloski (2007). A user's guide is not published but is available at the home web site (http://fehm.lanl.gov/) along with additional documentation. The reference version for this analysis is version 3.00.

**Physical basis/mathematical model**

- Fluids
  - Fluid properties are described by Equation of State (EOS) Module.
  - Fluids are Multiphase as Appropriate.
  - Fluids can be in Gas and Liquid Phases.
  - New EOS Modules can be added.
  - Current EOS modules include:
    - air, water
      - richards' equation option
    - gas, water, oil
    - $co_2$, water
- Conceptual Model
  - Mass continuity accounts for:
    - partitioning between gas and liquid phases by henry's law
    - solute transport
      - multiple solutes
      - chemical reactions
      - particle tracking
    - constant aquifer compressibility
  - Momentum equations account for:
    - Darcy's law
    - principal axis permeabilities may be different
    - numerous capillary pressure and relative permeability functions
    - no coupling between fluid relative permeabilities
    - Klinkenberg effect not included
    - diffusion in liquid and gas phases
    - vapor pressure lowering
  - Energy equation accounts for:
    - conduction and convection
  - Wellbore model is included:

        - embedded wellbore model
  - Space and time discretization
    - Space discretization incluides
      - control volume finite element
      - dual porosity and dual permeability capability
      - good mesh generation capability - LaGriT
      - interface weighing options user specified
        - upstream
        - harmonic
    - Time discretization includes:
      - first-order
      - fully-implicit
  - Numerical solution algorithms include:
    - conjugate gradient solvers
    - automatic time step adjustment and fallback
  - Pre-processing is included:
    - Good mesh generation capability - LaGriT
  - Post-processing is included:
    - Output for SURFER, Tecplot, GMV, and AVS

### Functionalities

Table 14 lists the relevant chemical functionalities for the challenge milestones and indicates which functionalities are included in the code.

### Code structures

- Fortran 90
- Runs on PCs, workstations, and supercomputers
- Parallel version in early stages
- Hydrate version available
- Inverse modeling available using PEST

The calculation sequence within the code is as follows:

- Initialize parameters;
- Calculate finite element coefficients;
- Compute flow and energy transport (if applicable);
- Compute reactive transport solution (if applicable);
  - Calculate solute reaction terms;
  - Form equations;
  - Solve Jacobian;
  - Iterate until convergence;
- Compute particle tracking solution (if applicable);
- Go to next time step.

## Numerical algorithms

The linear equations in FEHM are solved using a preconditioned conjugate gradient solution. Nonlinear equations, such as chemical equilibrium expressions, are solved by fully implicit, fully coupled Newton-Raphson iteration. When possible, the code will increase the time step by a user-supplied multiplication factor or decrease the time step if necessary for convergence.

Transport is simulated by a control volume finite element model. Numerical errors in reactive transport may result from the upwinding of the advection term. These errors are quantified by changing the grid size or comparing results to those of the particle-tracking module. Convergence problems may occur for nonlinear equations.

## Database

FEHM includes equation of state (EOS) databases and calculate fluid properties from detailed equation of state relationships. FEHM does not use a separate chemical database as an input file. Important reactions are entered directly into input files.

## Demonstrated applications

Following applications have been demonstrated for FEHM:

- Heat Conduction
- Temperature in Wellbore
- Hydraulic Head
- Pressure Transient Analysis
- Simplified Water Table Calculations
- Infiltration into a One-Dimensional, Layered, Unsaturated Fractured Medium
- Vapor Extraction from an Unsaturated Reservoir
- Barometric Pumping
- Dual Porosity
- Heat and Mass Transfer in Porous Media
- Free Convection
- Toronyi Two-Phase Problem
- DOE Code Comparison Project Problem Five, Class A
- Heat Pipe
- Dry-Out of Partially Saturated Medium
- One Dimensional Reactive Solute Transport
- Henry’s Law Species
- Fracture Transport with Matrix Diffusion
- Movement of a Dissolved Mineral Front
- Multi-Solute Transport with Chemical Reaction
- Three-Dimensional Radionuclide Transport
- Streamline Particle Tracking Model
- Cell-Based Particle Tracking Model

- Multiphase flow involving replacement of extracted ground water with cold recharge water, 2-D (results compared to results of other codes)
- Facilitated transport of radioactive cobalt by EDTA, 1-D (results to results of another code)
- Barometric pumping test - effects on volatile mass transfer
- Breakthrough curves for decay-chain case with sorption of intermediate species
- FEHM dissolution versus analytical solution
- Transport with matrix diffusion
- Henry's Law verification
- Check sorption isotherms

Additional demonstrated applications are provided in the literature. A list of 112 peer-reviewed publications using FEHM for simulation is provided at the FEHM website (http://fehm.lanl.gov), and a large number of these publications involve solute transport.

**Accessibility of source codes**

The source code and executable files for Version 3.00 are available subject to a license agreement with the following terms:

- The software is for research purposes only as allowed by the Los Alamos National Security (LANS) contract with DOE
- Software may not be duplicated, used, or redistributed without written permission from LANS
- DOE-funded modifications, enhancements, or conversions of this package are subject to requirements of DOE O 241.1
- User grants back to LANS the right to use any improvements made
- Improvements may be subject to export control

**Other unique features**

Potentially useful features and capabilities of the code that are relatively uncommon, unique, or noteworthy include:

- Documentation includes in-depth discussion for fluid flow and comparison of equations and solvers for fluid flow
- The ability to simulate colloid transport and contaminant sorption to colloids
- The ability to simulate fractured systems and dual permeability
- The ability to adjust porosity and permeability resulting from mineral precipitation and dissolution

**Evaluation**

TOUGH2 and FEHM each have their own advantages and disadvantages. TOUGH2 is superior in that the code is flexible, and it is well-respected and has a large world-wide user community. TOUGH2 also has additional versions including massively parallel and chemical reactions. FEHM has an advantage in pre-processing and post-processing and may have some advantages in solute transport. Coupling of the codes to structural programs is somewhat unknown at present. TOUGH2 has been coupled to some structural codes with some success. FEHM probably has an advantage in that it is based on a finite element formulation that is similar to structural programs.

Based on the above code comparison, TOUGH2 is recommended over FEHM for fluid flow and heat transport capabilities. An evaluation of the solute transport and chemical reaction capability should be conducted that is beyond the scope of the current comparison. In addition, coupling to structural programs needs to be further evaluated.

The pre-processing capability of FEHM (LaGriT) can probably be extended to TOUGH2. This capability should be evaluated against LBNL pre-processing capabilities in order to obtain a robust mesh generation capability. Post-processing can be improved without a large effort. This recommendation is subject to revision following the evaluations of the codes for solute transport and chemical reaction capability as well as coupling to structural programs.

## Limitations

Table 14 indicates functional limitations with regard to Challenge Milestones 1, 2 and 3. FEHM does not include an ion association or ion activity model to compute activity coefficients in saline waters.

**Table 14.** Chemical Functionality Needs versus FEHM Capabilities

| Functionality | High-Fidelity Model | PA Model | Code Capability | Comments |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | Yes | |
| Mineral equilibration | Yes | Yes | Yes | |
| Solid solutions | Yes | Yes | No | |
| Gas species equilibration | Yes | Yes | Yes | |
| Gas phase modeling | Yes | Yes | Yes | |
| Temperature corrections | Yes | Yes | Yes | |
| Pressure corrections | Yes | Yes | No | |
| Pitzer equations | Yes | Yes | No | Code does not calculate activity corrections. |
| Ion exchange | Yes | Yes | No | |
| Surface complexation | Yes | Yes | No | Code can simulate linear and nonlinear isotherms. |
| Uncertainty propagation | No | Yes | No | |
| Uncertainty evaluation | No | Yes | No | |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

| | | | | |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Yes | Governed by Arrhenius equation |
| Solid-centered flow-through mode | Yes | Yes | No | |
| 3-D mesh | Yes | No | Yes | |
| Stress corrosion cracking | Yes | Yes | No | |
| Radiolysis | Yes | Yes | No | |
| Reactive transport | Yes | Yes | Yes | |
| THC reactive transport | Yes | Yes | Yes | |
| Uncertainty propagation | Yes | Yes | No | |
| *Challenge Milestone 3: Tunnel Closure (Salt Creep)* | | | | |
| Fluid Movement in Deforming Media | Yes | N/A | Needs to be Coupled to Mechanics Code | Coupling may be easier than TOUGH2 due to Finite Element basis. |
| Simulation of fluid phase changes and binary diffusion in the gas phase | Yes | N/A | Limited | This functionality is available in FEHM for porous and fractured media. This functionality is not available in FEHM for open areas such as tunnels and other open spaces. |
| Simulation of heat transport in non-isothermal systems by convection, conduction, and radiation heat transfer | Yes | N/a | Limited. Thermal radiation is not available. | See above. |
| *Other Potentially Important Chemical Functionalities* | | | | |

| | | | | |
|---|---|---|---|---|
| Colloids | Yes | Yes | Yes | |
| Solution density calculation | Yes? | No? | No | |
| Decay and ingrowth | Yes | Yes | Yes | |

### 4.2.6 MODFLOW/MT3DMS/RT3D and PHT3D

MT3DMS: MT3D stands for the Modular 3-Dimensional Transport model, and MS denotes the Multi-Species structure for accommodating add-on reaction packages. MT3DMS is developed for use with any block-centered finite-difference flow model such as MODFLOW. MODFLOW/MT3DMS has been coupled with a number of different geochemical modules leading to a range of functionalities. This review focuses on 2 of these couplings: RT3D (Clement et al., 2011) and PHT3D (Prommer et al., 2003). RT3D is a finite difference, Fortran-based code for simulating three-dimensional, multi-species, reactive transport of chemical compounds in groundwater. RT3D solves the coupled partial differential equations that describe reactive transport of multiple mobile and/or immobile chemical species. RT3D can be linked to other codes to include porosity changes, interactions with the unsaturated zone, or full geochemistry. PHT3D is also a three-dimensional reactive transport model that couples the transport simulator MT3DMS to the geochemical modeling code PHREEQC-2. PHREEQC-2 includes a wide array of equilibrium and kinetic chemical processes, activity and temperature corrections. The version of MT3DMS reviewed was MT3DMS (v5.3) (2/10/2010). PHT3D version 2.10 (10/26/2010) which incorporates PHREEQC-2 version 2.17 was reviewed. RT3D version (RT3Dv2.5) was reviewed. Commercial third-party graphical user interface software is typically used to define simulation model systems and to visualize isosurfaces of results.

**Physical basis/mathematical model**

*Hydrologic/transport models and parameters:* MT3DMS, RT3D and PHT3D all inherit their transport model structure from MODFLOW, the finite difference model which used to calculate the flow fields used in transport simulations. Boundary conditions and model discretization are therefore similar. Three dimensional simulations require a finite difference grid, a temporal scheme, initial/boundary conditions, and associated property/parameter values. A rectilinear grid is supported; row, column, and layer spacing is allowed to vary; it is possible to use a deformed grid. A number of boundary concentrations (for mobile species) can be specified. These include: areal recharge, evapotranspiration, well, drain, river, general head-dependent boundary, and constant-head boundary (constant or time-varying) types of source/sink/boundary conditions. RT3D also provides a set of non-flow-related boundary condition/source types. These source types include constant concentration (for the duration of a simulation), specified concentration (stepwise transient), and exponentially decaying source. The MODFLOW LMT6 Package (operated in a “standard” mode) provides the linkage between flow and transport.

Aquifer-related parameters include porosity of the geological media and diffusion/dispersion parameters. RT3D allows the specification of longitudinal, transverse and vertical dispersivity coefficients. MT3DMSv5.3 has an optional dual-domain formulation for modeling mass transport where the porous medium consists of a mobile domain, where transport is predominately by advection, and an immobile domain, where transport is predominately by molecular diffusion. The exchange between the mobile and the immobile domains is specified by a mass transfer coefficient. This model is more appropriate for modeling transport in fractured media or extremely heterogeneous porous media than single-porosity advective-dispersive models. Component-dependent three-dimensional diffusion coefficients can be specified in the transport simulation.

***Geochemistry:*** The MT3DMS code is capable of handling:

- equilibrium-controlled linear or nonlinear sorption(Freundlich and Langmuir), which is incorporated into the transport model through the use of the retardation factor
- nonequilibrium (rate-limited) sorption
- first-order reaction
    - radioactive decay
    - biodegradation.
- kinetic mass transfer between the mobile and immobile domains in a dual-domain advection-diffusion model.

The basic chemical reaction package included in MT3DMS is intended for single-species systems. MT3DMS v5.3 incorporates a multicomponent program structure that can accommodate add-on reaction packages for modeling general biological and geochemical reactions. More sophisticated chemical reactions can be modeled through add-on reaction packages such as RT3D (Clement 1997) or PHT3D (Prommer et al., 2003).

RT3D can simulate:

- multi-species, 3-D reactive transport
- biodegradation kinetics
- inorganic reaction kinetics
- geochemical reactions
- NAPL dissolution
- dual porosity (mobile/immobile)
- colloid transport.

With additional programming, the following are also possible:

- virus transport
- heat transport
- risk analysis
- variable porosity over time
- interaction with vadose zone or surface water
- full geochemistry with speciation.

PHT3D couples MT3DMS with PHREEQC-2, a stand-alone geochemical code, which can solve equilibrium and user-defined kinetic controlled reactions. Total component concentrations are transported. The local redox state is modeled by transport of chemicals in different redox states [eg. Fe(II)/Fe(III)] separately; the pH is computed by charge balance. The version of PHT3D presented by Prommer et al. (2003) included a subset of processes (aqueous complexation, mineral precipitation/dissolution and ion exchange) and did not have the full capabilities of PHREEQC-2. Newer versions have expanded capabilities.

MT3DMS and RT3D do not calculate chemical speciation and therefore do not consider activity. PHREEQC-2 corrects for nonideality at high ionic strength using ion-association (Debye Hückel), specific ion-interaction (SIT) or the Pitzer model.

## Functionalities

MODFLOW/MT3DMS has been coupled with a number of different geochemical modules leading to a range of functionalities. This review focuses on 2 of these couplings: RT3D (Clement et al., 2011) and PHT3D (Prommer et al., 2003). Tables 15 and 16 lists the relevant chemical functionalities for the waste IPSC challenge milestones and indicates which functionalities are included in RT3D and PHT3D respectively.

## Code structures

MT3DMS, RTD3 and PHT3D are Fortran-based codes and run successfully with Lahey FORTRAN 95 and FORTRAN 90 compilers, depending on the version.

MT3DMS routines include:

- Main program – MAIN350
- Basic Transport Package – BTN350
- Advection Package – ADV350
- Dispersion Package– DSP350
- Sink & Source Mixing Package – SSM350
- Chemical Reaction Package – RCT350
- Generalized Conjugate Gradient Solver Package – GCG350
- Flow Model Interface Package – FMI350
- Utility Package – UTL35094

RT3D Files include:

- RT3DSUP (Super file): File type identifier: defines all input data file names, specie names, and reaction constant names.
- BTN "filenarne.btn" - The basic transport package file: specifies initial and boundary conditions of various mobile and immobile species
- ADV "filenarne.adv" - Advection package file
- DSP "filename.dsp" - Dispersion package file
- SSM "filename.ssm" - Source/sink mixing package file: specifies multi-species concentration information at point-sources/sinks, such as wells, rivers, and drains.

- RCT “filename.ret” - Chemical reaction package file: defines spatially variable reaction kinetic parameters and sorption parameters for isotherms.
- FLO “filename.hff” - MODFLOW head and flow file
- OUT “filename.out” - Standard output file
- CON “filename.con” - Binary concentration output files for Groundwater Modeling System (GMS) post processing
- DSS “filename.dss” - Concentration data set super file for GMS
- MAS “filename.mm” - Standard mass balance file

RT3D requires that geochemical interactions be defined via reaction modules. The original release of RT3D (Clements, 1997) included several preprogrammed reaction modules:

- Module 1: Instantaneous aerobic decay of BTEX
- Module 2: Instantaneous degradation of BTEX using multiple electron acceptors
- Module 3: Kinetic-1imited degradation of BTEX using multiple electron acceptor
- Module 4: Rate-limited sorption reactions
- Module 5: Double Monod model
- Module 6: Sequential decay reactions
- Module 7: Aerobic/anaerobic model for PCEITCE degradation
- Module 10: User-defined reaction module

*Calculation sequence:* MODFLOW simulations consists of one or more stress periods or blocks of time that represent a particular set of flow and/or concentration conditions (e.g., the on/off status of an extraction well). The stress period are subdivided into flow time steps and transport time steps. A head solution is calculated for each flow time step within a stress period. RT3D uses subdivisions of the flow time steps, termed transport time steps, in the solution of the contaminant transport problem. The differential equation solver uses subdivisions of each transport time step when solving the kinetic reaction equations.

The operator splitting (OS) strategy helps solve the complex coupled reactive transport system in a modular fashion. The solution algorithm initially solves the advection, dispersion and source-sink mixing steps for all mobile components for a transport time step. The length of the transport step is restricted by the constraints posed by the advection, dispersion, and source-sink mixing solvers. After solving the transport for a single time step, the coupled reaction equations are solved implicitly by using a differential equation solver. The solver automatically computes the time-step sizes required to precisely integrate the reaction equations.

*Code Output:* The codes can provide several types of output. The primary output from RT3D is a set of whole-grid data sets (one for each chemical species) describing solute concentrations for all grid cells in the model at times specified by the user. Whole-grid data sets may be used to examine the spatial distribution of time-varying solute concentrations in the form of concentration contours or isosurfaces (in third-party visualization software). RT3D can also generate concentration data at specified points over time, which can be used to generate time series plots for fixed points in space. Commercial third-party graphical user interface software is typically used to define simulation model systems and to visualize isosurfaces of results. Several commercial GUI software products that support interfaces to RT3D and MT3DMS are available, including the Groundwater Modeling System (GMS; www.aquaveo.com), Visual Modflow (www. swstechnology.com/groundwater- software), Processing Modflow for Windows (PMWIN; www.pmwin.net), and Groundwater Vistas (www.groundwatermodels. - com).

## Numerical algorithms

MT3DMS uses a standard operator-split (OS) numerical strategy (sequential non-iterative approach) to develop a general numerical solution scheme for solving the coupled partial/ ordinary differential equations. The advection equations are solved by:

- the method of characteristics,
- a modified method of characteristics,
- a hybrid method of characteristics,
- the upstream finite-difference solution scheme

MT3DMS includes three major classes of transport solution techniques:

- the standard finite-difference method,
- the particle-tracking-based Eulerian-Lagrangian methods, and the
- higher-order finite-volume TVD method.

The dispersion and source-sink mixing packages use explicit finite-difference approximations.

Table 17 summarizes the solutions options available in the original MT3DMS code (Zheng et al. 1999). The newest version (v5.3) incorporates:

- third-order total-variation-diminishing (TVD) scheme that is mass conservative for solving the advection term This does not introduce excessive numerical dispersion and artificial oscillation;
- an iterative solver based on generalized conjugate gradient (GCG) methods with three preconditioning options and the Lanczos/ORTHOMIN acceleration scheme for nonsymmetrical matrices to remove stability constraints on the transport time stepsize.

In RT3D, the kinetic reaction terms are assembled as a set of ordinary differential equations (ODEs) that are always solved implicitly, using one of two types of solvers:

- Runge-Kutta methods for “well behaved” reaction kinetics.
- the implicit ordinary differential equation (ODE) solver LSODA to solve arbitrary kinetic problems

When there are widely varying time scales in the rate of change in concentrations, the automatically switching stiff/non-stiff “Gear” solver (i.e., LSODA) is the better choice.

PHT3D uses a modified version of the standard sequential split-operator technique. The user-defined time step length consists of two steps. In the first step, MT3MDS is used to solve the advection and diffusion equations. In the second step, PHREEQC-2 is used to solve the geochemical calculations in a batch system to obtain the changes in concentrations in components before and after the reaction step. For concentrations of kinetic reactions, PHREEC-2 uses a fifth-order Runge-Kutta integration scheme. To improve computational efficiency, the reaction step is temporarily omitted in cells where no reactive changes are expected (e.g. uncontaminated regions downstream of a slowly-spreading plume).

## Databases

The key parameters such as reaction rates for the standard reaction modules are built-into RT3D and have default values based on data reported in the literature. However, the user can adjust these parameters to better fit with data from a specific site. PHT3D uses PHREEQC-2 database files to define equilibrium and kinetic reactions (see review of PHREEQC code in this report).

## Demonstrated applications

The MT3DMS code has been applied in a number of studies including comparison to analytical solutions, comparison to results from other numerical codes, and laboratory and field applications. The code verification efforts for RT3D generally apply to MT3DMS, since RT3D is a sister code sharing the same basic transport routines. Additional applications are described for PHT3D below.

RT3D code performance has been validated by comparing RT3D results for several test problems with existing analytical solutions as well as results from other numerical codes as reported by Clement et al. (1998, 2001; 2011). These include:

- one-dimensional transport, adsorption, and sequential first order degradation
- hydrocarbon and oxygen plumes in a uniform, two-dimensional aerobic aquifer with instantaneous reactions
- one-dimensional transport of non-adsorbing species undergoing serial, parallel, and reversible reactions with first-order reaction kinetics
- one-dimensional transport of species (distinct retardation factors) with reversible reactions under zero and non-zero initial conditions
- fate and transport of a chlorinated solvent plume at a complex Superfund site location
- DNAPL dissolution, rate-limited sorption, and biological reaction kinetics.

The PHT3D code has been evaluated for the following by Prommer et al. (2003):

- single species transport with Monod kinetics
- multiple species transport with kinetic, sequential/parallel degradation
- equilibrium and kinetic-based mineral dissolution/precipitation
- ion exchange during artificial recharge
- two-dimensional biodegradation including sequential first-order degradation of PCE and Monod-type BTEX degradation

## Accessibility of source codes

Executable versions of all these code are internet accessible and can be obtained for no fee, no registration and for unlimited use. Source codes are available for MT3DMS and RT3D but not for PHT3D.

MT3DMS is available from the url: http://hydro.geo.ua.edu/mt3d/. Executables, source codes, user's guides, utilities, and benchmark test problems are available from this site.

RT3D is available from http://bioprocess.pnl.gov/rt3d.htm. Documentation, executables, source code, examples, utilities for version 2.5 are available from that site.

PHT3D is available from http://pht3d.org/. The PHT3D installation file contains the PHT3Dv2.10 executable for Windows, the PHT3Dv2.10 manual and the 13 benchmark/application examples described in the manual. The PHREEQC-2 code can be obtained at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html. Source codes are not downloadable for either of these codes from the websites.

### Other unique features

The codes built on the MODFLOW/MT3DMS framework are designed to allow easy coupling with user-defined modules or stand-alone geochemical codes. In addition to the coupling with PHREEQC-2 used for PHT3D, other codes such as HARPHRQ and SEAWAT have been coupled with MT3DMS. For scenarios with contaminants or reaction kinetics other than those available in the preprogrammed reaction modules, the RT3D software provides a "user-defined" reaction module. The RT3D user can define their own reaction kinetics and plug those modules into RT3D.

In addition to the current features, a number of other capabilities can be achieved with varying amounts of effort: virus transport, heat transport and risk analysis. With a moderate effort, the capabilities of RT3D can be extended to include features such as time varying porosity, interaction with the vadose zone or surface waters, and full geochemistry. Addition of these types of extended capabilities requires coupling an external code to RT3D.

### Limitations

- Neither RT3D nor PHT3D solves groundwater flow equations and relies on an externally supplied head/velocity solution from U.S. Geological Survey's MODFLOW code.

- MT3DMS is based on the assumption that changes in the concentration field will not affect the flow.

- The following are considered unachievable by the RT3D code developers (Clement and Johnson, 2011):
    - variable density flow
    - dual permeability (mobile/mobile)
    - surface water flow and transport
    - multiphase transport
    - unsaturated transport
    - equilibrium constants are not corrected by the code for changes in pressure.

**Table 15.** Chemical Functionality Needs versus RT3D Capabilities

| Functionality | High-Fidelity Model | PA Model | Code Capability | Comments |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | No | |
| Mineral equilibration | Yes | Yes | No | |
| Solid solutions | Yes | Yes | No | |
| Gas species equilibration | Yes | Yes | No | |
| Gas phase modeling | Yes | Yes | No | |
| Temperature corrections | Yes | Yes | No | |
| Pressure corrections | Yes | Yes | No | |
| Pitzer equations | Yes | Yes | No | |
| Ion exchange | Yes | Yes | limited | Expressed as sorption isotherm |
| Surface complexation | Yes | Yes | limited | Expressed as sorption isotherm |
| Uncertainty propagation | No | Yes | No | |
| Uncertainty evaluation | No | Yes | No | |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

| | | | | |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Yes | |
| Flow-through | Yes | Yes | No | Requires MODFLOW to calculate flow. |
| 3-D mesh | Yes | No | Yes | |
| Stress corrosion cracking | Yes | Yes | No | |
| Radiolysis | Yes | Yes | Yes | Can be defined by user. |
| Reactive transport | Yes | Yes | Yes | |
| THC reactive transport | Yes | Yes | Limited | Thermal transport is handled through same subroutines as solute transport. Thermally-related changes in density and thermally-driven convection are not handled. |
| Uncertainty propagation | Yes | Yes | No | |
| *Other Potentially Important Chemical Functionalities* | | | | |
| Colloids | Yes | Yes | Yes | Code can transport colloids via user-defined reactions. |
| Solution density calculation | Yes? | No? | No | |
| Decay and ingrowth | Yes | Yes | Yes | |

**1.**

**Table 16.** Chemical Functionality Needs versus PHT3D Capabilities

| **Functionality** | **High-Fidelity Model** | **PA Model** | **Code Capability** | **Comments** |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | Yes | |
| Mineral equilibration | Yes | Yes | Yes | |
| Solid solutions | Yes | Yes | Yes | |
| Gas species equilibration | Yes | Yes | Yes | |
| Gas phase modeling | Yes | Yes | Yes | |
| Temperature corrections | Yes | Yes | Yes | |
| Pressure corrections | Yes | Yes | No | Equilibrium constants are not corrected by the code for changes in pressure. |
| Pitzer equations | Yes | Yes | Yes | With additional interface with PHREEQC-2 |
| Ion exchange | Yes | Yes | Yes | |
| Surface complexation | Yes | Yes | Yes | |
| Uncertainty propagation | No | Yes | No | |
| Uncertainty evaluation | No | Yes | No | |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

| | | | | |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Yes | |
| Flow-through | Yes | Yes | Yes | |
| 3-D mesh | Yes | No | Yes | |
| Stress corrosion cracking | Yes | Yes | No | |
| Radiolysis | Yes | Yes | Yes | |
| Reactive transport | Yes | Yes | Yes | |
| THC reactive transport | Yes | Yes | Limited | Thermal transport is handled through same subroutines as solute transport. Thermally-related changes in density and thermally-driven convection are not handled. |
| Uncertainty propagation | Yes | Yes | No | |
| *Other Potentially Important Chemical Functionalities* | | | | |
| Colloids | Yes | Yes | Yes | . |
| Solution density calculation | Yes? | No? | Yes | |
| Decay and ingrowth | Yes | Yes | Yes | |

**Table 17.** Solution Options Available in the MT3DMS Code

| Group | Solution Options for Advection | Solution Options for Dispersion, Sink/Source, and Reaction1 |
|---|---|---|
| A | Particle-tracking-based Eulerian-Lagrangian methods<br>• MOC<br>• MMOC<br>• HMOC | Explicit finite-difference method |
| B | Particle Tracking Based Eulerian-Lagrangian Methods<br>• MOC<br>• MMOC<br>• HMOC | Implicit finite-difference method |
| C | Explicit Finite-Difference Method<br>• Upstream weighting | Explicit finite-difference method |
| D | Implicit Finite-Difference Method<br>• Upstream weighting<br>• Central-in-space weighting | Implicit finite-difference method |
| E | Explicit 3rd-order TVD (ULTIMATE) | Explicit finite-difference method |
| F | Explicit 3rd-order TVD (ULTIMATE | Implicit finite-difference method |

MOC = Method of Characteristics; MMOC = Modified Method of Characteristics; HMOC = Hybrid Method of Characteristics; TVD = Total-Variation-Diminishing scheme.

### 4.2.7 CORE$^{2D}$ V4

CORE$^{2D}$ V4 (Samper et al, 2003) is the most recent version in a family of computer programs in the CORE series: a COde for modeling partly or fully saturated water flow, heat transport and multicomponent REactive solute transport. The codes were developed by the University of La Coruña (UDC) and improved within several research projects funded by ENRESA and European Union. The code family comprises CORE-LE$^{2D}$; CORE$^{2D}$ V2; INVERSE-CORE$^{2D}$; BIOCORE$^{2D}$ and is based on an earlier code TRANQUI. CORE$^{2D}$ V4 (Samper, 2003) was developed from CORE$^{2D}$ V2 and shares the capabilities of BIOCORE$^{2D}$ and INVERSE-CORE$^{2D}$ such as automatic time stepping, kinetic aqueous complexation reactions, microbial processes, and inverse subroutines of INVERSE-CORE$^{2D}$. It can model abiotic reactions including acid-base, aqueous complexation, redox, mineral dissolution/precipitation, gas dissolution/exsolution, ion exchange and sorption reactions (linear $K_d$, Freundlich and Langmuir isotherms, and surface complexation using constant capacitance, diffuse layer and triple layer models) and microbial processes. Hydraulic parameters may change in time due to mineral precipitation/dissolution reactions. A sequential iterative approach is used for the numerical solution of coupled reactive transport equations.

**Physical basis/mathematical model**

CORE solves simultaneously for groundwater flow, heat transport and multi-component reactive solute transport under the following conditions:

- 2-D confined or unconfined,
- saturated or unsaturated,
- steady-state or transient groundwater flow with general boundary conditions;

The code can handle heterogeneous and anisotropic media having irregular internal and external boundaries.

Biogeochemical reactions are divided into three classes:

- Homogeneous reactions which occur in the liquid phase:
  - acid-base
  - redox
  - aqueous complexation
  - radioactive decay
- Heterogeneous reactions which involve mass transfer from the liquid to the solid/ gas phases
  - cation exchange
  - sorption isotherms (linear Kd, Freundlich and Langmuir isotherms)
  - surface complexation (constant capacitance, diffuse layer and triple layer models)
  - gas dissolution/exsolution
  - mineral dissolution/precipitation: dissolution/precipitation reactions can be described by the mass action law that includes terms for the molar fraction and the thermodynamic activity coefficient of the solid phase.
- Biological reactions

- Microbial growth is described by Monod kinetics; consumption and yield rates of chemical species involved in microbiological processes are related to microbial growth rates by means of yield coefficients.
- Other microbial processes can also be modeled such as:
    i. metabolic competition
    ii. decay
    iii. metabiosis
    iv. endogeneous respiration and
    v. attachment/detachment of micro-organisms on biofilms.

Heat transport accounts for:

- conduction,
- heat dispersion
- convection

Conductive transport of heat is related to the temperature gradient in the fluid and solid while the convective transport of heat is related to the groundwater flow.

Changes in the porosity are computed from dissolution/precipitation rates and can change flow and transport properties (e.g., diffusion coefficient and permeability).

- A Kozeny-Carman equation accounts for the relationship between hydraulic conductivity and porosity.
- Different expressions of effective diffusion coefficient in terms of porosity are available.

Temperature-dependent chemical parameters such as chemical equilibrium constants and activity coefficients are corrected. Several options for activity corrections are available in different versions of the code:

- Extended Debye Hückel – standard in CORE$^{2D}$ and later versions
- Pitzer model – implemented in a version of BIO-CORE$^{2D}$ (Zhang et al, 2004)

## Functionalities

Table 18 lists the relevant chemical functionalities for the waste IPSC challenge milestones and indicates which functionalities are included in the code.

## Code structures

The general code structure is shown by the flow diagram for the MAIN Program in Figure 9.

The calculation sequence is:

- *Solution of the groundwater flow equation*
    - Solved in terms of hydraulic heads for flow in saturated media (confined or unconfined aquifers).
    - Solved iteratively using a predictor-corrector scheme for unconfined aquifer flow
    - Solved in terms of pressure heads by a Newton-Raphson iterative method for flow in variably saturated media

- *Computation of the groundwater velocity*.
    - Water velocities, needed to evaluate the advective and dispersive solute and heat fluxes, are computed from nodal head values by direct application of Darcy's law to the finite element solution

- *Solution of the heat transport by thermal conduction and advection*
    - Solution of the heat transport equation shares the subroutines used for solving the solute transport equation.
    - Nodal temperatures are used to update temperature-dependent chemical parameters.

- *Solution of the solute transport equations*.
    - Each chemical component has a transport equation in terms of its total dissolved concentration.

- *Solution of the biogeochemical equations*.
    - Biogeochemical reactions are solved in a node-wise manner.
    - Geochemical equations are solved by Newton-Raphson method.
    - Temperature-dependent chemical constants are updated in non-isothermal conditions.
    - Time step can be specified in advance by the user or derived from an automatic time stepping algorithm.

## Numerical algorithms

- Galerkin finite element method is used to solve the groundwater flow, solute and heat transport equations.
- Solution of coupled biogeochemical and transport equations is carried out using a sequential partly iterative approach (SPIA), which improves the accuracy of the traditional sequential non-iterative approach (SNIA) and is more efficient than the general sequential iterative approach (SIA)
- Two types of stabilization are adopted to reduce the numerical oscillations produced by classical finite element methods when solving advection- dominated problems:

- stream upwinding Petrov-Galerkin (SUPG) method
- subgrid scale stabilized method.

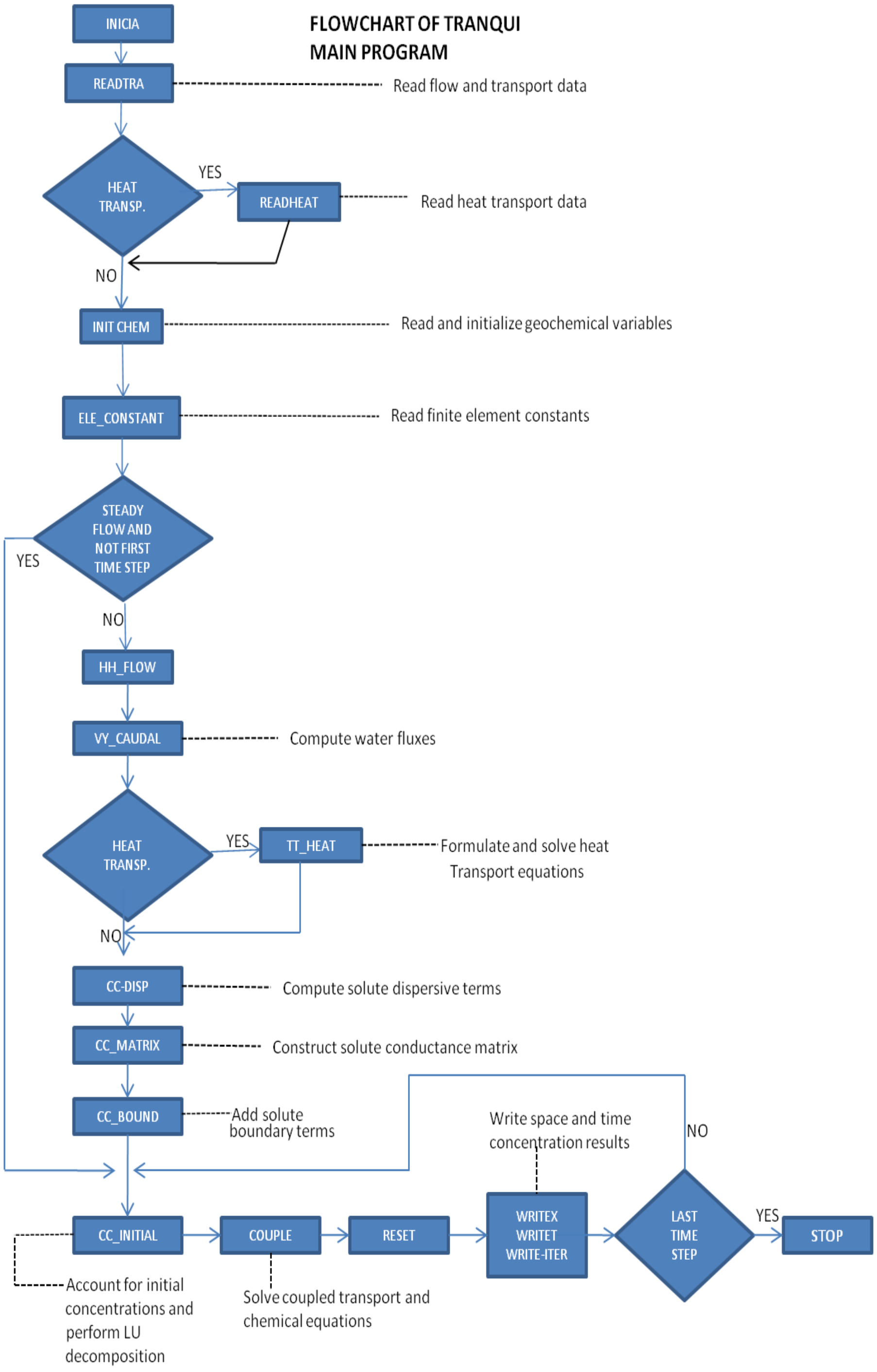


**Figure 9.** Flow chart of CORE2D MAIN Program based on earlier code TRANQUI

**Database**

Thermodynamic data and stoichiometric coefficients of chemical equilibrium reactions are read directly from databases modified from the EQ3NR database. (EQ3/6 releases 6.0 and 7.0a)

- *Master25* - valid for calculations at a constant temperature of 25 ºC and 1 bar
- *Masterte* – an extension from 0 to 300ºC and pressure along the steam saturation curve above 100 ºC is automatically activated when an input temperature is different from 25 ºC.
- A pre-processor converts the contents of other thermodynamic databases into the format of CORE databases: PHREEQE, MINTEQ, NEA, CHEMVAL and HATCHES

**Demonstrated applications**

- Verification against analytical solutions:
  - 1-D conservative solute and heat transport subroutines
  - 1-D semi-infinite confined aquifer under steady-state uniform flow
  - 1-D reactive transport with kinetic dissolution precipitation reactions and kinetic aqueous in saturated media
  - multi-component reactive transport coupled with cation exchange reactions
  - microbial processes

- Verification against other computer codes
  - 1DREACT: reactive transport with kinetic rate laws for calcite and smectite dissolution
  - DYNAMIX: redox processes with uranium migration through a column
  - PHREEQM: reactive transport with cation exchange
  - BIOCLOG$^{3D}$ and FEREACT: subroutines for solving microbial processes
- Real-world applications:
  - CORE$^{2D}$ V4 and its predecessors has been used to interpret the results of a number of field experiments including in situ experiments performed at Underground Rock Laboratories (URL), the DI B, DR and VE experiments at Mont Terri (Switzerland) the CERBERUS experiment at Mol (Belgium), DIR experiments at Bure (France), Redox Zone II and REX experiments at Äspö (Sweden), and the FEBEX (Full-scale Engineered Barrier EXperiment ) experiment at Grimsel (Switzerland). CORE$^{2D}$ V4 has been also used to simulate the long-term geochemical evolution of HLW repositories in clay and in integrated performance assessment projects such as BENIPA, NFPRO and PAMINA. References to all these applications can be found in Samper et al. (2011).
  - The code has been used to model solute transport in aquifers including uranium transport in the Andújar aquifer (Spain), the geochemistry of the Aquia aquifer (USA) and salt water flushing in the Llobregat Delta aquitard.

  - The code has also been used for **s**imulation of the long-term geochemical evolution of the near field of a high level radioactive waste (HLW) repository in clay (Yang 2008),
  - Samper et al (2011) demonstrates the current capabilities of CORE$^{2D}$ V4 with applications involving:
    - laboratory concrete degradation experiment,
    - reactive transport in a physically and geochemically heterogeneous medium,
    - experiment of $CO_2$ injection in the vadose zone,
    - prediction of the water quality of a pit lake, and
    - coupled thermohydrochemical processes of compacted bentonite after the FEBEX in situ test.

**Accessibility of source codes**

Undetermined at this time

**Other unique features**

- Anisotropic diffusion to deal with diffusion anisotropy in clay media
- Isotopic transport coupled with chemical reactions for the purpose of simulating radionuclide release from a HLW repository
- Automatic estimation of flow, solute transport, chemical and biological parameters
- Calculation of solution density from aqueous concentrations
- CORE codes have been coupled with a variety of codes such as the INVERS-FADES-CORE code to simulate other coupled processes in deformable porous media in both forward and inverse model applications.

**Limitations**

- Diffusion and dispersion coefficients are the same for all aqueous species
- Amount of dissolved/precipitated mineral cannot be computed explicitly
- No massively parallel version exists for use in Monte Carlo simulations
- Code is limited to 2D simulations except for axially symmetric systems
- Limited mechanical processes demonstrated except for soil properties
- Colloid transport not demonstrated.

**Table 18.** Chemical Functionality Needs versus CORE$^{2D}$ V4 Capabilities

| **Functionality** | **High-Fidelity Model** | **PA Model** | **Code Capability** | **Comments** |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | Yes | |
| Mineral equilibration | Yes | Yes | Yes | |
| Solid solutions | Yes | Yes | Yes | |
| Gas species equilibration | Yes | Yes | Yes | |
| Gas phase modeling | Yes | Yes | Yes | |
| Temperature corrections | Yes | Yes | Yes | |
| Pressure corrections | Yes | Yes | No | Equilibrium constants are not corrected by the code for changes in pressure. |
| Pitzer equations | Yes | Yes | Yes | BIOCORE-2D only |
| Ion exchange | Yes | Yes | Yes | |
| Surface complexation | Yes | Yes | Yes | |
| Uncertainty propagation | No | Yes | No | |
| Uncertainty evaluation | No | Yes | No | |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

| | | | | |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Yes | |
| Flow-through | Yes | Yes | Yes | |
| 3-D mesh | Yes | No | limited | Axially-symmetric systems only |
| Stress corrosion cracking | Yes | Yes | No | |
| Radiolysis | Yes | Yes | no | |
| Reactive transport | Yes | Yes | Yes | |
| THC reactive transport | Yes | Yes | Yes | |
| Uncertainty propagation | Yes | Yes | No | |
| *Other Potentially Important Chemical Functionalities* | | | | |
| Colloids | Yes | Yes | No | . |
| Solution density calculation | Yes? | No? | Yes | Coupled to DYRESM code |
| Decay and ingrowth | Yes | Yes | Yes | |

## 4.3 Thermal-Hydrologic-Mechanical (THM) Codes

### 4.3.1 SIERRA/Aria

Aria is a Galerkin finite element based program for solving coupled-physics problems described by systems of PDEs and is capable of solving nonlinear, implicit, transient and direct-to-steady state problems in two and three dimensions on parallel architectures. The suite of physics currently supported by Aria includes: the incompressible Navier-Stokes equations, energy transport equation, species transport equations, nonlinear elastic solid mechanics, and electrostatics as well as generalized scalar, vector and tensor transport equations. Additionally, Aria includes support for arbitrary Lagrangian-Eulerian (ALE) and level set based free and moving boundary tracking (Notz et al. 2007).

Different regions of the physical domain (i.e., the input mesh) may have either different materials and/or different collections of physics (viz., PDEs) defined on them. These systems of equations may be solved alone, in a segregated but coupled algorithm (“loosely coupled”) or as a single, fully-coupled system. Currently, Aria’s loose coupling capabilities are handled by the Arpeggio application which also allows Aria to couple (loosely) to the quasi-static structural mechanics code, Adagio (SIERRA Solid Mechanics TEAM 2010c). The reference version for this analysis is 4.18. Aria is based on the Sierra Framework (Edwards and Stewart 2001).

**Physical basis/mathematical model**

The mathematical model of SIERRA/Aria is described by:

- Conservation of Mass
- Conservation of Energy
- Conservation of Chemical Species
- Conservation of Fluid Momentum
- Conservation of Solid Momentum
- Voltage Equation
- Current Equation
- Suspension Equation
- Porous Flow
- Brinkman Momentum
- Stress Tensor Projection Equation

**Functionalities**

Basic physics capabilities include:

- Navier-Stokes - incompressible, variable density
- Elasticity - including large deformation, large rotation constitutive models
- Energy transport (temperature)
- Multi-species transport with reactions
- Electrostatics

Free and moving boundaries are tracked:

- ALE moving mesh
- Level set interface tracking

Ability for coupling nonlinear problems is provided:

- Fully-coupled Newton's method with analytic Jacobian (single matrix)
- Fully-coupled Picard's method (single matrix)
- Colored finite-difference Jacobian formulation via NOX
- Loosely-coupled: Aria couples to itself so subsets of the physics can be coupled in a segregated way, i.e., Gauss-Seidel or Jacobi iterations
- Aria can also couple loosely to the quasistatic structural mechanics code Adagio and the boundary element code BEM (that's done in the Arpeggio code)
- All coupling techniques are defined through the input file

Other features are added:

- Transient analysis
- Steady-state analysis
- Continuation, stability and turning point tracking via LOCA
- 2D and 3D analysis
- Parallel or serial
- Error estimation - classical ZZ and adjoint-based (steady state)
- Uniform and adaptive mesh (h-) refinement
- Dynamic load balancing
- Restart
- Initial conditions from existing ExodusII file with interpolation in space and time
- Input fields from and output solutions to different meshes ("Input/Output Regions")

Aria supports the following elements, including any combinations:

- 3-node triangles - tri3 (2D, "Q1")
- 6-node triangles - tri6 (2D, "Q2")
- 4-node quads - quad4 (2D, "Q1")
- 9-node quads - quad9 (2D, "Q2")
- 4-node tets - tet4 (3D, "Q1")
- 10-node tets - tet10 (3D, "Q2")
- 8-node hexes - hex8 (3D, "Q1")
- 27-node hexes - hex27 (3D, "Q2")
- P0 and P1 element variables (2D/3D, "P0" and "P1")

## Code Structures

Code written in ANSI C++, but can interface with C and FORTRAN90.

### Numerical algorithms

Coupled physics problems are solved in several ways including fully-coupled Newton's method with analytic or numerical sensitivities, fully-coupled Newton-Krylov methods and a loosely-coupled nonlinear iteration about subsets of the system that are solved using combinations of the aforementioned methods.

### Database

The code uses the Exodus II (Schoof and Yarberry 1994) database.

### Demonstrated applications

Test problems available with software:

- A regression test that provides examples of how to setup problems for Aria simulations within the Sierra environment. The Aria regression test suite is comprised of more than 270 problems that exercise the functionality of the code. The test suite problems are designed to ascertain that the code interaction with Sierra Framework remains intact throughout the development process. Beginning with variants of scalar problems, the test suite then moves to vector problems and problems with both scalars and vectors before moving on to different physics. Although the problems are often simple, they provide code coverage for various physics models and for extensible features within the Aria code.

Repository-like problems:

- A thermal-mechanical generic HLW salt repository problem (Stone et al. 2010) that included: Utilization of two different analysis domains and mesh discretizations; one for the thermal analysis and a different discretization for the geomechanics analysis. Field transfer operators in the SIERRA toolkit were used to pass interpolated nodal temperature and displacement data between the different domains. Some of the discriminating features of this highly nonlinear, thermal-mechanical analysis include the use of large strain, large deformation mechanics, the use of both thermal and mechanical contact surfaces and the use of continuously updated radiation view factor calculations for the deforming storage rooms.
- A thermal-hydrologic-mechanical-chemical generic HLW clay/shale repository problem (Stone et al., 2011) that included: A multi-phase porous flow capability that has been recently added to Aria. Aria also has some basic geochemistry functionality available through embedded chemistry packages that was used in this analysis. The mechanics portion of the THMC coupling is handled by Adagio. It solves for the quasi-static, large deformation, large strain behavior of nonlinear solids in three dimensions. Adagio has some discriminating Sandia-developed technology for solving solid mechanics problems, that involves matrix-free iterative solution algorithms for efficient solution of extremely large and highly nonlinear problems. The THMC coupling is done through a solution controller within SIERRA Mechanics called Arpeggio.

### Accessibility of source codes

At present, only internally accessible at Sandia National Laboratories

### Other unique features

Error estimation, uniform and dynamic h-adaptivity and dynamic load balancing are some of Aria's more advanced capabilities.

### Limitations

Table 19 indicates functional limitations with regard to Challenge Milestones 1, 2 and 3. The "reactive transport" capability available in Aria is relatively new and limited. The main driver to date for this development has been the "$CO_2$ capture and sequestration" problem. Further development is needed to advance it to a state that is compatible with the needs of NEAMS Waste IPSC.

**Table 19.** Chemical Functionality Needs versus ARIA Capabilities

| Functionality | High-Fidelity Model | PA Model | Code Capability | Comments |
|---|---|---|---|---|
| *Challenge Milestone 1* | | | | |
| Aqueous speciation | Yes | Yes | Limited | Improvement ongoing |
| Mineral equilibration | Yes | Yes | Limited | Improvement ongoing |
| Solid solutions | Yes | Yes | No | Can be added |
| Gas species equilibration | Yes | Yes | Limited | Can be added |
| Gas phase modeling | Yes | Yes | Yes | |
| Temperature corrections | Yes | Yes | Yes | |
| Pressure corrections | Yes | Yes | Yes | |
| Pitzer equations | Yes | Yes | No | Ready to be added |
| Ion exchange | Yes | Yes | Limited | Simple equilibrium partitioning already included |
| Surface complexation | Yes | Yes | No | |
| Uncertainty propagation | No | Yes | No | |
| Uncertainty evaluation | No | Yes | No | |
| *Challenge Milestone 2 (additional functionalities)* | | | | |

| | | | | |
|---|---|---|---|---|
| Kinetic reactions | Yes | Yes | Limited | Improvement ongoing |
| Solid-centered flow-through mode | Yes | Yes | No | N/A |
| 3-D mesh | Yes | No | Yes | |
| Stress corrosion cracking | Yes | Yes | Yes | Adaption needed |
| Radiolysis | Yes | Yes | No | |
| Reactive transport | Yes | Yes | Limited | Improvement ongoing |
| THC reactive transport | Yes | Yes | Limited | Improvement ongoing |
| Uncertainty propagation | Yes | Yes | No | |
| *Challenge Milestone 3: Tunnel Closure (Salt Creep)* | | | | |
| Fluid Movement in Deforming Media | Yes | N/A | Yes | |
| Simulation of fluid phase changes and binary diffusion in the gas phase | Yes | N/A | Limited | |
| Simulation of heat transport in non-isothermal systems by convection, conduction, and radiation heat transfer | Yes | N/a | Yes | |
| *Other Potentially Important Chemical Functionalities* | | | | |
| Colloids | Yes | Yes | No | |
| Solution density calculation | Yes? | No? | Yes? | |
| Decay and ingrowth | Yes | Yes | No | |

### 4.3.2 SIERRA/Adagio

Adagio is a Lagrangian, three-dimensional, implicit finite element code for the analysis of solids and structures. It has some discriminating technology that has been developed at Sandia National Laboratories involving the use of matrix-free iterative solution algorithms. Its use of a multi-level iterative solver enables it to solve problems with large deformations, nonlinear material behavior, and contact quite efficiently. It also has a versatile library of continuum and structural elements, and an extensive library of material models. Adagio is written for parallel computing environments, and its solvers allow for efficient and scalable solutions of very large problems on massively parallel (MP) computers. Adagio uses the SIERRA Framework (Edwards and Stewart, 2001), which allows for coupling with other-physics SIERRA codes. The multi-physics coupling to other SIERRA codes is done through a flexible solution controller within SIERRA Mechanics called Arpeggio. The reference version for Adagio used in this analysis is 4.18.

**Physical basis/mathematical model**

The mathematical model is described by:

- Conservation of Mass
- Conservation of Energy
- Conservation of Linear Momentum
- Conservation of Angular Momentum

**Funcationalities**

Basic Capabilities:

- 3D Analysis
- Quasi-static
- Large strain; large deformation
- Arbitrary Contacts (with numerous advanced controls)
- Nonlinear Material Behavior
- Implicit Dynamics

Boundary and Initial Conditions:

- Initial Variable Assignment
- Kinematic Boundary Conditions (fixed displacement, prescribed displacement, prescribed velocity, etc.)
- Initial Velocity Conditions
- Force Boundary Conditions (pressure, traction, prescribed force, prescribed moment)
- Gravity
- Prescribed Temperature
- Pore Pressure
- Fluid Pressure
- Specialized Boundary Conditions

Material Models:

- Elastic Model
- Thermoelastic Model
- Elastic-Plastic Model
- Elastic-Plastic Power-Law Hardening Model
- Orthotropic Crush Model
- Karagozian and Case Concrete Model
- Multi-Mechanism Deformation (MD) Creep Model
- Power Law Creep Model
- Soil and Crushable Foam Model
- Kayenta (formerly, Sandia Geomodel)
- More than 30 different material models available

Other Features:

- Predictor (used to generate an initial trial solution for a load step or for a multilevel solver model problem)
- Parallel or serial
- Numerous output options (including history variables)
- Restart
- Initial conditions from existing ExodusII file with interpolation in space and time
- Input fields from and output solutions to different meshes ("Input/Output Regions")
- Transfers (for interfacing with other SIERRA physics)

Adagio Supports the Following Elements:

- Eight-node, uniform-gradient hexahedron
- Eight-node, selective-deviatoric hexahedron
- Four-node tetrahedron
- Eight-node tetrahedron
- Ten-node tetrahedron
- Four-node, quadrilateral, uniform-gradient membrane
- Four-node, quadrilateral shell
- Four-node, quadrilateral, selective-deviatoric membrane
- Linear elastic shell element
- Two-node beam
- Two-node truss
- Two-node spring
- Point mass
- Rigid body

### Code Structures

Code written in ANSI C++, but can interface with C and FORTRAN90.

## Numerical algorithms

- Conjugate Gradient Solver
    - Full Tangent Pre-conditioner
- FETI Equation Solver
- Multi-level Solver
    - Control Contact
    - Control Stiffness
    - Control Failure
- Control Modes

## Database

The code primarily uses the Exodus II (Schoof and Yarberry, 1994) database. Code can also use the XDMF database (http://www.xdmf.org).

## Demonstrated applications

Test problems available with software:

- A regression tests that provides examples of how to set up problems for Adagio simulations within the Sierra environment. The Adagio regression test suite is comprised of more than 240 problems that exercise the functionality of the code. The test suite problems are designed to ascertain that the code interaction with Sierra Framework remains intact throughout the development process. Although the problems are often simple, they provide code coverage for various physics models and for extensible features within the Adagio code.

Repository-like problems:

- A thermal-mechanical generic HLW salt repository problem (Stone et al., 2010) that included: Utilization of two different analysis domains and mesh discretizations; one for the thermal analysis and a different discretization for the geomechanics analysis. Field transfer operators in the SIERRA toolkit were used to pass interpolated nodal temperature and displacement data between the different domains. Some of the discriminating features of this highly nonlinear, thermal-mechanical analysis include the use of large strain, large deformation mechanics, the use of both thermal and mechanical contact surfaces and the use of continuously updated radiation view factor calculations for the deforming storage rooms.
- A thermal-hydrologic-mechanical-chemical generic HLW clay/shale repository problem (Stone et al., 2011) that included: A multi-phase porous flow capability that has been recently added to Aria. Aria also has some basic geochemistry functionality available through embedded chemistry packages that was used in this analysis. The mechanics portion of the THMC coupling is handled by Adagio. It solves for the quasi-static, large deformation, large strain behavior of nonlinear solids in three dimensions. Adagio has some discriminating Sandia-developed technology for solving solid mechanics problems, that involves matrix-free iterative solution algorithms for efficient solution of extremely

large and highly nonlinear problems. The THMC coupling is done through a solution controller within SIERRA Mechanics called Arpeggio.

### Accessibility of source codes

At present, only internally accessible at Sandia National Laboratories

### Other unique features

Arpeggio includes Control Modes (a multi-grid solution method), Cohesive Zones (useful for modeling stratigraphic discontinuities, faults, etc.), Adaptive Time Stepping (useful for modeling creep of rock salt), Generalized Robust Contact (useful for modeling large deformations of tunnel closure, thin clay layers at stratigraphic boundaries, faults, etc.).

### Limitations

Table 20 indicates functional limitations with regard to Challenge Milestones. In NEAMS Waste IPSC application space, there will be a need to model creep of rock salt, clay/shale, hard rock, etc. The main current limitation of Adagio lies in the relatively limited number of material models available for advanced modeling of some geologic materials. A detailed gap analysis for the constitutive models for rock salt is provided in Appendix B of this report.

There are only two material models incorporated into the code that permit the simulation of geologic creeping media, a standard Norton power law (secondary) creep model and the so-called Multi-mechanism Deformation (MD) Creep model (Munson, 1993). While the MD model is relatively advanced in comparison to some creep models, it lacks other features that are important for more-advanced modeling of salt response. A descendant of the MD model that incorporates a few more advanced features is the Multi-mechanism Deformation Creep Fracture (MDCF) Model (Chan et al., 1992). At a minimum, this model needs to be incorporated into the code.

However, even this model (MDCF) is somewhat dated in that its development was arrested in the mid-90’s and lacks some additional features that other recognized leaders in the field of rock salt constitutive modeling are currently including in their state-of-the-art (SOA) rock salt creep models (Hampel et al., 2010). The MDCF model needs to be further developed so that it incorporates all of the advanced features found in other SOA models. In addition, if available, incorporation of a couple of these SOA models (Hampel, 2007; Gunter and Salzer, 2007) from some of the other recognized leaders in the field should be incorporated into the code to allow flexibility in modeling rock salt creeping behavior and permit cross-comparisons with those models.

In addition, for other repository settings, specifically Clay/Shale, there are currently no constitutive models in the code to capture its appropriate behavior. As a start, something like the “Barcelona Basic Model (Alonso et al., 1990)” should be incorporated into the code, and it would also be desirable to incorporate the more advanced "double-structure" Extended Barcelona Model (Sanchez et al., 2005) into the code.

**Table 20.** Hydrological Functionality Needs versus ADAGIO Capabilities

| **Functionality** | **High-Fidelity Model** | **PA Model** | **Code Capability** | **Comments** |
|---|---|---|---|---|
| *Challenge Milestone 1: Chemical Equilibrium Calculation* | | | | |
| None | | | | |
| *Challenge Milestone 2: Waste Form and Waste Package Degradation* | | | | |
| None | | | | |
| *Challenge Milestone 3: Tunnel Closure (Salt Creep)* | | | | |
| Elastic/plastic deformation | Yes | Yes | Yes | |
| Large strain; large deformation | Yes | Yes | Yes | |
| Fluid Movement in Deforming Media | Yes | N/A | Yes | |
| Simulation of fluid phase changes and binary diffusion in the gas phase | Yes | N/A | No | |
| Simulation of heat transport in non-isothermal systems by convection, conduction, and radiation heat transfer | Yes | N/a | Yes | |

## 4.4 Other Codes

## 4.4.1 WAPDEG

The WAPDEG Version 4.07 (WAste Package DEGradation) was developed to support the License Application of the then-proposed Yucca Mountain repository, and the code is the most comprehensive integrated waste package degradation simulation software to date.

### Physical Basis and Mathematical Model

The WAPDEG code simulates corrosion degradation of waste packages by three penetration modes: 1) patch penetration (due to general corrosion), 2) crack penetration (due to crack tip growth or stress corrosion cracking (SCC)), and 3) pit penetration (due to pitting corrosion or crevice corrosion). Other degradation modes considered include microbiologically induced corrosion (MIC), aging and phase instability, and hydrogen induced cracking (HIC).

The localized corrosion modes that WAPDEG can treat include stress corrosion cracking (SCC), crack tip growth, and pitting. In the WAPDEG code cracking can be initiated at incipient flaws and/or defect flaws. The incipient flaws result from the presence of crack nucleation sites, such as grain boundary junctions and surface roughness. The defect flaws result from manufacturing defects, primarily weld flaws, and as a result of rocks falling on the waste package.

### Functionalities

Every corrosion model functional form available in WAPDEG is linked to a unique set of numbers corresponding to the corrosion mode, the barrier type, and the water condition. The seven functional forms available are:

- Multiplier functional form
- Covariance functional form
- Rate vs. temperature functional form
- Arrhenious functional form
- General linear functional form
- Power law functional form
- Log time functional form

The corrosion-affecting events are intended to trigger specific degradation processes. Eleven event models are available in WAPDEG:

- Barrier Separation
- Manufacturing Defects
- Crevice Corrosion
- Rockfall
- SCC Slip Dissolution
- Critical Relative Humidity

- SCC Stress Intensity Factor
- Aging and Phase Instability
- Hydrogen Induced Cracking (HIC)
- Microbiologically Influenced Corrosion (MIC)
- General Corrosion Initiation

WAPDEG has been designed to simulate waste package degradation utilizing a stochastic approach. Many WAPDEG variables can be described by probability distributions. WAPDEG implements eighteen different probability distributions including uniform, log uniform, etc.

### Code Structures

The WAPDEG code and other supporting codes are written in Fortran 90. The WAPDEG engine which calculates the waste package degradation is provided as a Dynamic Link Library (DLL), callable by other applications. The user must provide a calling program, which provides a means of passing input to the WAPDEG DLL.

Two additional codes are called to provide required input to the WAPDEG DLL. The CWD DLL (Version 2.0) is called to calculate the probability of occurrence and size of manufacturing defects in the closure lid welds of a waste disposal container. The SCCD DLL (Version 2.01) is called to calculate the stress and stress-intensity factor profiles in the closure-lid welds of a waste disposal container.

### Numerical algorithms

WAPDEG accepts input from a calling program and simulates events and corrosion on waste packages. The user specifies all input through the driver program. WAPDEG itself has no input editing capabilities. Some of the input parameters are fixed values, whereas others are defined stochastically.

WAPDEG transforms inputs into outputs in the following steps. After processing the contents of the array passed to it, WAPDEG enters a loop over waste packages. The parameters for a waste package that were defined stochastically are sampled to account for variability, and the sampled values are then treated as fixed for the current waste package. Each waste package is then simulated from time zero to the end of simulation before proceeding to the next waste package.

WAPDEG translates the entries in the input vector it receives from the calling program into its own data structures. The code performs general input preparation that is not specific to individual waste packages, rather to the overall simulation. This includes efforts such as assigning random seeds for the waste packages, apportioning waste packages to exposure conditions, and decomposing correlation matrices. It also performs some input consistency checking.

The next core efforts are inside the looping for waste packages. WAPDEG treats the set of waste packages one waste package at a time. A waste package is simulated from initial time to the simulation time before proceeding to the next. To simulate a waste package, WAPDEG first sets the properties of the waste package, which can include a significant amount of statistical sampling, such as sampling package-level properties for patch sizes, corrosion models, events, thresholds, water drip sequences, etc.

WAPDEG simulates the waste container from initial time to simulation time. This includes the treatment of any events that affect the waste container and the corrosion processes that affect the waste container, both of which can be subject to variability and hence require statistical sampling at the patch level. The step also includes routines for the implementation of corrosion model, event sampling, threshold comparison, pit and crack growth simulation, and eventually a barrier penetration.

Results from a waste package are written to optionally selected output files after simulation. The detailed files for patch and event properties (the DET and EVN files) are written throughout WAPDEG as they are generated. Selected results are accumulated across all waste packages. The results for the current waste package are accumulated into variables designed for all waste package results. After all the waste packages are simulated, WAPDEG places the accumulated results into the output vector.

### Database

There are no default data values contained in the WAPDEG code. No database is maintained in the code. The WAPDEG code has built-in corrosion models, associated corrosion event models, applicable functional forms and probability distribution functions. The user supplies necessary corrosion model parameter values, including associated probability distributions if needed, and exposure condition parameters for its specific applications.

### Demonstrated Applications

The WAPDEG code was developed under the quality assurance (QA) programs of the Yucca Mountain Project. A series of QA documentations for the code is available (BSC 2002a to 2002f), including the verification and validation test problems and user’s manual.

Most demonstrated applications of the code have been for the Yucca Mountain Project to support the License Application of the then-proposed Yucca Mountain Repository, and the code applications and its scientific basis are described in a number of the project documents (BSC 2004; SNL 2008). The code applications have been reported in numerous external publications.

### Accessibility of source code

The WAPDEG code is not readily available to general public, pending the on-going legal proceedings on the status of the Yucca Mountain Repository License Application. For those who have legitimate business needs, the source code and executable are available through U.S. DOE.

### Other unique features

The user interface to prepare the input vector for WAPDEG.DLL is not well designed and requires substantial training. The current practice is to use a spreadsheet to prepare the input vector, and copy and paste it into a file to be read by the calling program. This manual preparation practice is prone to input errors. A graphical user interface for the input vector preparation is needed for enhanced application of the code.

Because it was developed for application to the Yucca Mountain Repository, the WAPDEG code has provision to simulate degradation of a drip shield placed above waste package, but the modeling capability can be opted out in the input vector.

The WAPDEG code provides an extensive provision for the error handling and error messages. The input data is subject to extensive checking, both at the time it is initially read and as the distributions and tables required for the simulation are constructed. The input data is also subject to internal checking for consistency. In addition, checks are placed throughout WAPDEG to avoid potential arithmetic computation errors.

### Limitations

WAPDEG is to a large extent based on empirical relationships. It is expected that waste package degradation will be modeled in a more mechanistic way using the THCMBR capabilities developed the waste IPSC project.

## 4.4.2 DAKOTA

DAKOTA (Design Analysis Kit for Optimization and Terascale Applications) (Eldred et al. 2002) is a software toolkit that provides a flexible and extensible interface between simulation codes and iterative analysis methods used in large-scale systems engineering optimization, uncertainty quantification, and sensitivity analysis. It is an open source code developed at Sandia National Laboratories (http://endo.sandia.gov/DAKOTA). One example of such applications is shown in Figure 10.

### Physical Basis and Mathematical Model

DAKOTA is a physical/chemical process code. It is generally used to wrap a physical/chemical model to facilitate:

- Parameter studies
- Sensitivity analysis
- Optimization
- Uncertainty quantification (UQ)
- Reliability analysis

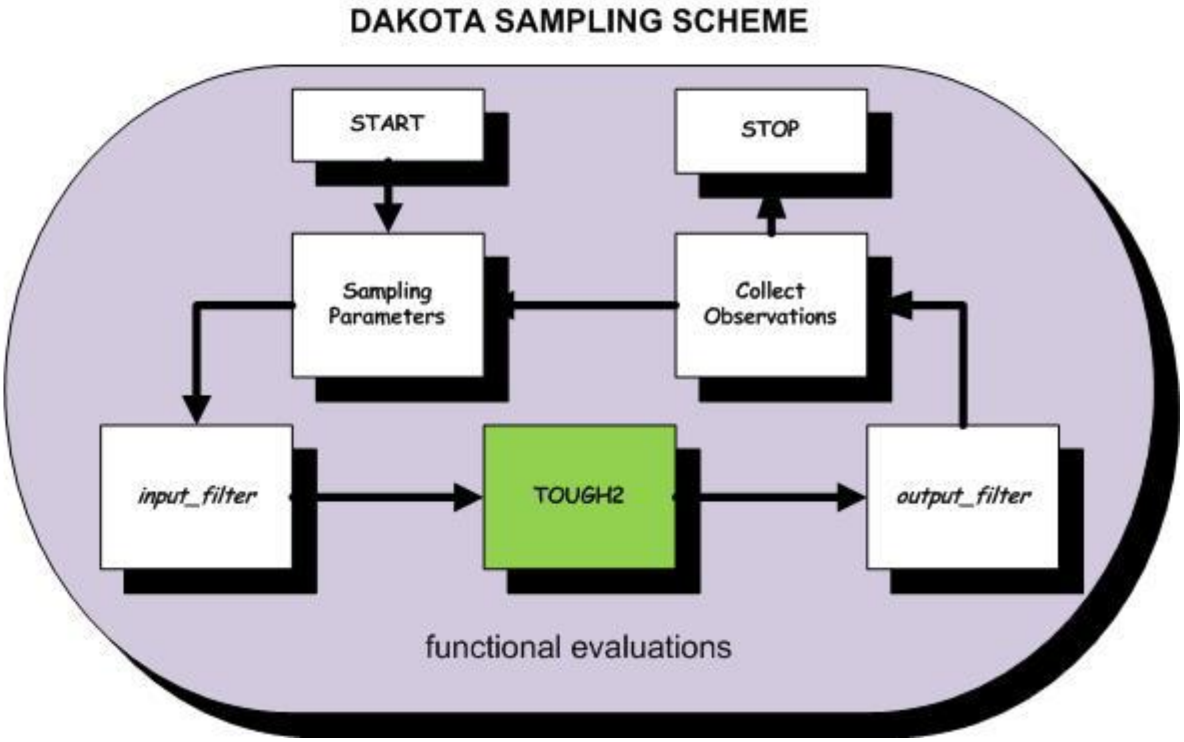


**Figure 10.** Using DAKOTA as a driver for a performance assessment of a carbon sequestration and storage system. In this case, TOUGH2 was used as a reservoir simulator (Wang et al., 2010)

**Functionalities**

- Optimization methods and strategies
    - OPT++: library of optimization methods
    - SGOPT: stochastic global optimization
    - PICO: parallel integer combination optimization
    - Pattern search methods
    - CONMIN: freeware gradient-based optimization
    - Interface to DOT & NPSOL commercial optimization codes
- Sampling methods (sensitivity analysis and uncertainty quantification
    - Monte Carlo
    - Latin hypercube
    - Orthogonal arrays
    - Central composite design
    - Box-Behnken
    - k-level full factorial
- Reliability methods
    - AMV/AMV+, FORM, SORM, SFE

    - Surrogate modeling and optimization
    - Multidimension surface fitting

- Parallel computing capabilities
    - Desktop single or multiprocessor workstation
    - Network of workstations
    - Enterprise computing server
    - Massively parallel computers

**Code Structures**

By employing object oriented design to implement abstractions of the key components required for iterative systems analyses, the DAKOTA toolkit provides a flexible and extensible problem-solving environment for design and performance analysis of computational models on high performance computers.

**Numerical Algorithms**

See the section of functionalities.

**Database**

N/A

**Demonstrated Applications**

Directly relevant to the waste IPSC application, DAKOTA has been used as a driver for a performance assessment of a carbon sequestration and storage system (Wang et al. 2010).

**Accessibility of source code**

The code is fully accessible. It is an open source code developed at Sandia National Laboratories.

**Other unique features**

Full code service support is available within Sandia National Laboratories.

**Limitations**

Certain code adaptation and enhancement may be needed for waste IPSC applications. For example, an immediate enhancement may include adding new capabilities for multiple process code optimization and uncertainty quantification.

# 5.0 SUMMARY AND RECOMMENDATIONS

The codes described in Section 4.0 all have the potential to simulate coupled THC processes, with capabilities for representing reactive transport ranging from fledgling (SIERRA) to advanced (TOUGHREACT, HYDROGEOCHEM, PFLOTRAN). However, there is an apparent lack of complete coupling of mechanical (M) capability in all but one of them (SIERRA). Large gaps exist in modeling chemical processes and their couplings with other processes. First of all, there is no single code able to fully account for all THCMBR processes involved in a waste disposal system. For example, EQ3/6, which is widely used in nuclear waste management, is not able to simulate surface complexation, microbial reactions, radiolysis, and the partitioning of a chemical speciation between aqueous and gaseous phases (because it does not explicitly calculate the volume of gaseous phase). Second, the coupling of chemical processes with flow, transport and mechanical deformation remains challenging. The resulting mathematical equations are generally nonlinear, involve sharp moving reaction fronts, and need to be solved over a large span of time scales, thus posing a serious issue for numerical solutions. Third, the data for extreme environments (e.g., for elevated temperature) that are needed for repository modeling are lacking. Fourth, most of existing reactive transport codes were developed for non-radioactive contaminants, and they need to be adapted to account for radionuclide decay and in-growth. Finally, the accessibility to the source codes is generally limited.

Because the problems of interest for the Waste IPSC are likely to result in relatively large computational models, a compact memory-usage footprint and a fast/robust solution procedure will be needed. In addition, a robust massively parallel processing (MPP) capability will also be required to provide reasonable turnaround times on the analyses that will be performed with the code. Finally, because the Waste IPSC applications will entail multi-physics, an effective and robust framework that will allow the efficient coupling of THCMBR processes to occur seamlessly is needed. Such a framework will need to provide an assortment of time-stepping and physics-coupling algorithms or strategies that permit physics of disparate time-scales and length-scales to be solved efficiently. Some of the THC codes evaluated in this gap analysis may have certain capabilities to perform simulations in a MPP environment (e.g., PFLOTRAN and TOUGH2-MP). However, the MPP capability is not built-in to most of the existing THC codes.

A PA calculation for a radioactive waste disposal system generally requires a large number (hundreds to thousands) of model simulations to quantify the effect of model parameter uncertainties on the estimated repository performance. For this purpose, a code included in a PA calculation must be sufficiently robust and fast in terms of code execution while still capturing the essential behavior of a disposal system. A PA system model as a whole must be able to provide multiple alternative submodels for a specific set of physical/chemical processes, so that the users can choose various levels of modeling complexity based on their modeling needs. This requires PA codes to preferably be high modular. Most of the existing codes have difficulties meeting these requirements.

Based on the gap analysis results, we make the following recommendations for the code selection and code development for the NEAMS waste IPSC:

**Recommendation 1 - Build fully coupled high-fidelity THCMBR codes on SIERRA platform:** Predictive simulation of geologic repositories to enable engineering decision-making and system performance assessments can benefit from orders of magnitude increases in fidelity of the underlying multi-scale physics. Tightly coupled THCMBR simulation capabilities spanning the vast time and length scales characteristic of geologic repository applications are required to assess their long-term integrity. The development of the SIERRA Mechanics code suite (Edwards and Stewart, 2001) has been funded by the DOE ASC program for over ten years. The goal has been the development of massively parallel multi-physics capabilities to support the Sandia engineering sciences mission. SIERRA Mechanics was designed and developed to run on the latest and most sophisticated massively parallel computing hardware; spanning the hardware computing space from a single workstation to computer systems with 1000's of processors. The foundation of SIERRA Mechanics is the SIERRA toolkit which provides finite element application code services such as: (1) mesh and field data management, both parallel and distributed, (2) transfer operators for mapping field variables from one mechanics application to another, (3) a solution controller for code coupling, and (4) included third party libraries (e.g. solver libraries, MPI communications package, etc.).

Recent additional investments in the SIERRA Mechanics code suite have supplied the basic building blocks for realizing this multi-physics capability for repository systems engineering. These pieces have been assembled for the past 2 ½ years under an existing Laboratory-Directed Research & Development (LDRD) project to demonstrate an adaptive framework for addressing the disparate time and length scales associated with geomechanics problems such as storage and resource extraction. The SIERRA Mechanics code suite is comprised of application codes that address specific physics regimes. The two SIERRA Mechanics codes which are used in the THMC coupling for repository systems engineering are Aria (Notz et al., 2007) and Adagio (SIERRA Solid Mechanics TEAM, 2010c). The suite of physics currently supported by Aria includes: the incompressible Navier-Stokes equations, the energy transport equation, and species transport equations; as well as generalized scalar, vector and tensor transport equations. Both a saturated porous flow capability and a multiphase porous flow capability are recent additions to Aria (Martinez and Stone, 2008). In addition, Aria also has some basic geochemistry functionality available through existing chemistry packages such as Chemeq and Cantera. Although in its infancy, this reactive transport capability in Aria should be extendable to the Waste IPSC solution space with additional but relatively incremental effort, as compared to a new development effort starting from zero.

The mechanics portion of the THCMBR coupling is handled by Adagio which solves for the quasi-static, large deformation, large strain behavior of nonlinear solids in three-dimensions. Adagio has some discriminating technology that has been developed at Sandia for solving solid-mechanics problems. This technology involves the use of matrix-free iterative solution algorithms that allow extremely large and highly nonlinear problems to be solved efficiently. This technology also lends itself to effective and scalable implementation on MP computers. The THMC coupling is done through a solution controller within SIERRA Mechanics called Arpeggio.

Thus, based on the codes which have been evaluated in this gap analysis, the justification for moving forward with SIERRA as the THCM capability (Aria/Adagio) for the waste IPSC is:

- It offers an existing proven framework for coupled multi-physics (solution domains may be different for different physics);
- The capability is finite-element based ( which makes for more natural coupling);
- The capability is already massively parallel (scalability from 1 to 1000s of processors on a variety of platforms);
- It allows for various levels of coupling within the thermal-hydrologic-chemical code (Aria) and loose coupling to Sierra's solid mechanics capability (Adagio); and
- It can be used as the launching point for fully integrated THCMBR with adaptive solution control.

The SIERRA THM capabilities have successfully applied to geologic repository systems (see Figure 11).

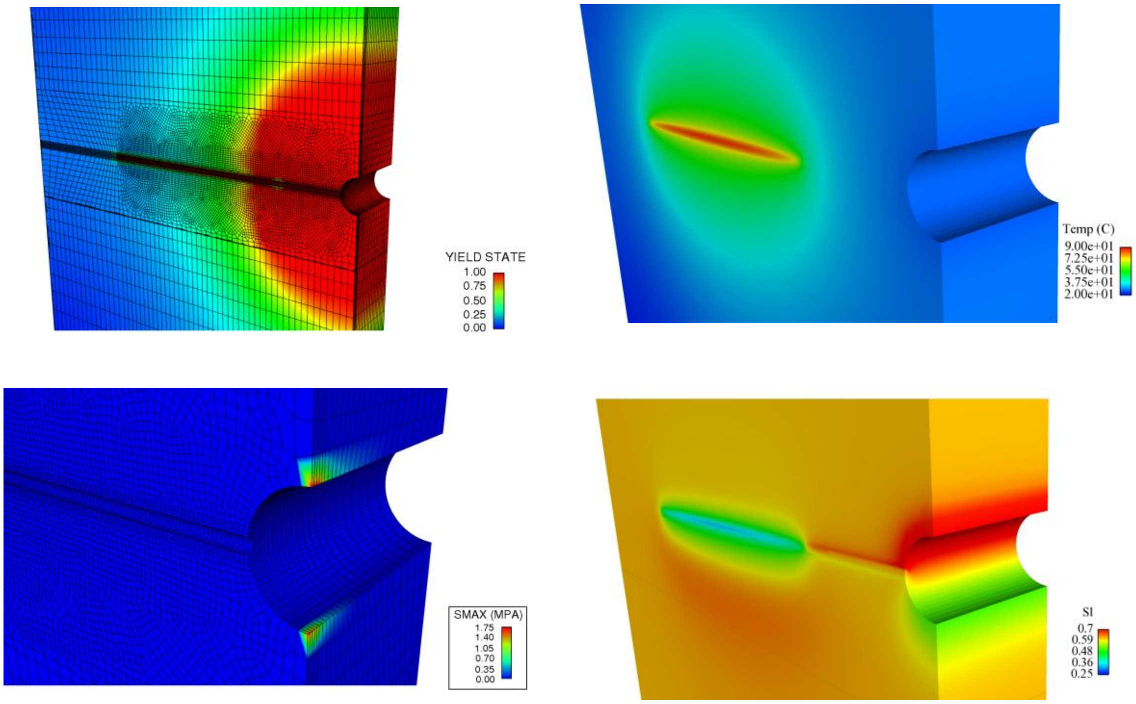


**Figure 11.** Yield state, maximum principal stress (SMAX), temperature, and liquid saturation (Sl) calculated with SIERRA THM capabilities for a shale/clay repository.

It should be noted that other potential THM codes that might be applicable to the NEAMS Waste IPSC solution space were not readily available for hands-on evaluation for several reasons. For example, there is a TOUGH2-to-FLAC coupled capability (Pruess, 1991; Itasca Consulting Group Inc., 1997; Rutqvist et al., 2002) found documented in the open literature that upon further investigation did not appear to be readily accessible. Furthermore, it required the purchase of a relatively expensive commercial license for the accompanying Itasca code FLAC. Such an expense, at this stage in the gap analysis, was not deemed justifiable. It may be that in subsequent gap assessments, we may wish to revisit this decision.

**Recommendation 2 - Use DAKOTA to build an enhanced performance assessment system (EPAS):** The concept of an EPAS for a radioactive waste disposal system is shown in Figure 12 (Wang et al., 2010). The forward model components represent the typical steps of the existing PA methodology. According to the existing methodology, a PA starts with Feature, Event, and Process (FEP) evaluation, through which potentially important FEPs are identified for inclusion for further PA analysis. FEP evaluation also helps define the performance scenarios of interest a disposal system by identifying major radionuclide release pathways. The next step of a PA analysis is to develop appropriate computational models for the selected FEPs and the defined performance scenarios and then to constrain model input parameters. The model input parameter values and their uncertainty distributions are constrained from field observations and laboratory experimental data. The whole cycle of a PA analysis is then completed by uncertainty quantification and sensitivity analysis, typically performed using multiple Monte-Carlo simulations. The whole PA process is generally iterative. EPAS extends the existing PA methodology by adding the inverse model components, as shown in Figure 12. These inverse components provide necessary tools for parameter calibration, engineered barrier design, and data fusion from field monitoring. These new functionalities require the EPAS to have a built-in optimization capability. As described in Section 4.4.2, DAKOTA is able to provide a flexible and extensible interface between simulation codes and iterative analysis methods used in large-scale systems engineering optimization, uncertainty quantification, and sensitivity analysis. In addition, DAKOTA has a capability to assign multiple simulation tasks to multiple processors in parallel. We therefore recommend using DAKOTA as a PA driver for the waste IPSC. For this purpose, certain code adaptation and enhancement for DAKOTA may be needed. The EPAS will consist of the enhanced PA driver DAKOTA and various process modules that simulate the coupled THCMBR processes of disposal systems.

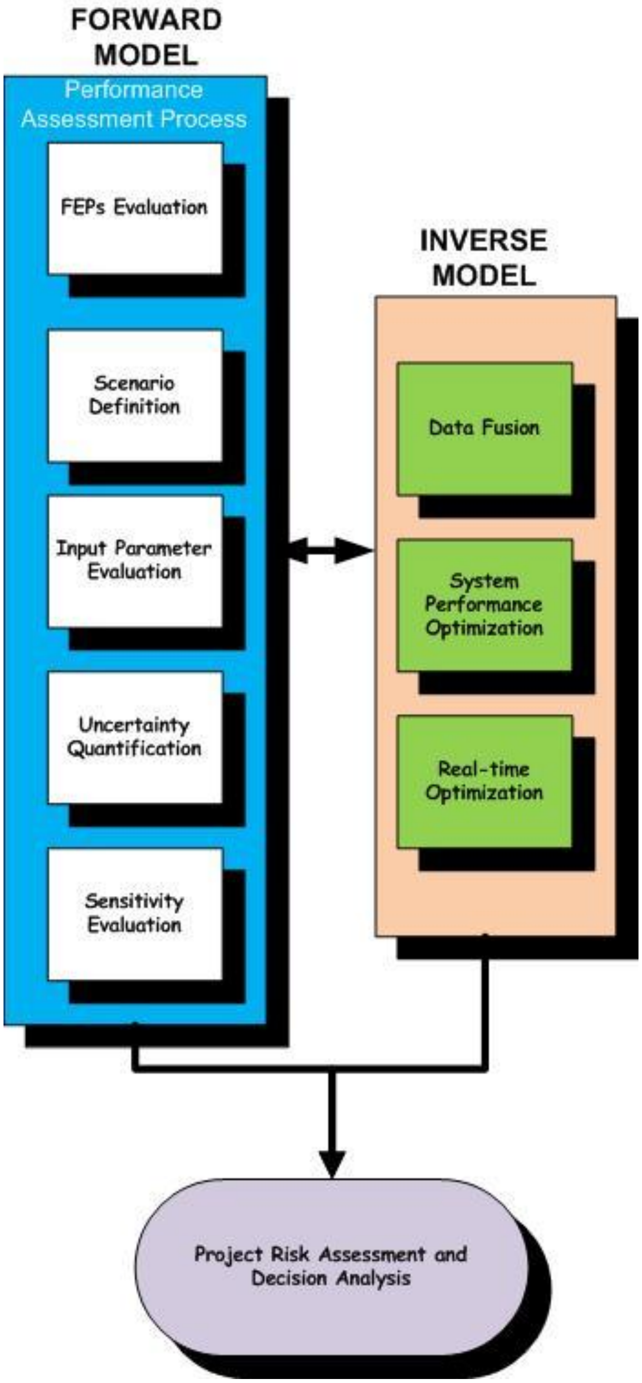


**Figure 12.** Enhanced Approach to Performance Assessment of a Waste Disposal System (Wang et al., 2010)

**Recommendation 3 - Build a modular code architecture and key code modules for performance assessments:** As discussed in Section 2, a preferable PA system should be able to accommodate multiple levels of model complexity for different uses, ranging from a simple calculation for FEP screening to a full assessment of total disposal system performance. To do so, a PA system must be highly modularized such that the needed modules can be readily assembled and linked to form a specific PA model to solve a specific problem. Unlike a traditional monolithic code, the modular architecture has an advantage in terms of software quality assurance (QA) (i.e., code verification and validation). In this modular architecture, software QA can be implemented at two hierarchy levels: the component level and the PA model level (i.e. a set of linked modules). Since a major portion of software QA work is devoted to the verification and validation of individual code modules, the proposed modular architecture is expected to expedite the QA process and reduce the associated cost while still maintaining high quality for code development.

We recommend using the object oriented programming approach from the very beginning of NEAMS waste code development. As noted in Section 4.1.2, code CANTERA provides an excellent example for this new code design paradigm, in which each of calculation functionalities is implemented and encapsulated in a class and each class is able to inherit some common features from its parent classes. The inheritance capability greatly improves the reusability of legacy codes.

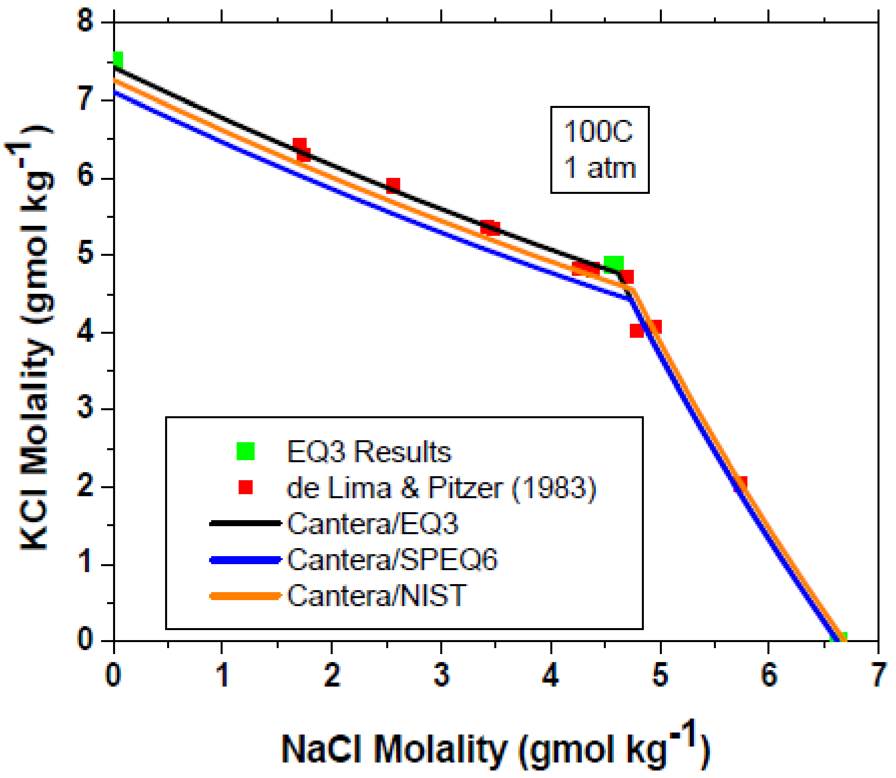


**Figure 13.** Solubility of KCl and NaCl calculated with CANTERA

The current Waste IPSC strategy is to acquire and integrate the necessary Waste IPSC capabilities wherever feasible, and develop only those capabilities that cannot be acquired or suitably integrated, verified, or validated. Our gap analysis shows that there exist significant capabilities in existing THCM codes even though no single existing code can meet all the requirements for the NEAMS waste IPSC. Effective integration of those capabilities into the IPSC is crucial for the success of the NEAMS code development. Based on the suggested modular code architecture, such integration should be carried out at a module component level. Ideally, the NEAMS waste IPSC will extract the best components from existing codes and integrate them into a new system. However, difficulties may exist in such integration because the source code accessibility to the existing codes is limited and also because many existing codes are coded in FORTRAN. It is anticipated that the NEAMS waste IPSC modules will be coded in C++.

To develop key modules for the NEAMS waste IPSC, we suggest starting with chemical calculation modules, since chemical calculations are the weakest, but the key, part of the existing THCMBR codes. This can be done by expanding the CANTERA capabilities. The existing CANTERA code has already included basic chemical equilibrium calculation capabilities (see Figure 13). These capabilities can be expanded to include full sets of calculations for multiphase equilibrium, chemical reaction kinetics, radionuclide decay and ingrowth, surface sorption, ion exchanges, etc. Associated with code development, the supporting chemical database must also be enhanced, given the large gaps existing in thermodynamic data for elevated temperatures and ionic strength media. There is an ongoing activity to integrate CANTERA into ARIA. The expansion of CANTERA capabilities will be an integral part of this effort. CANTERA is an open source code (BSD open source license) and currently under heavy development within Sandia National Laboratories.

Robust chemical equilibrium calculation modules are the key components of NEAMS waste IPSC. The existing CANTERA code performs such calculations by minimizing the total Gibbs free energy of a chemical system using the VCS algorithm. This approach is expected to be inherently more robust than a mass action law approach generally used in many existing THC codes (e.g., EQ3/6, PHREEQC). Further testing is needed for CANTERA's implementation. To improve the CANTERA performance in chemical equilibrium calculations, we suggest examination of other Gibbs free energy minimization algorithms, in particular, the so-called primal-dual interior point method implemented in GEM-Selektor (Karpov et al., 1997). An international collaboration may be necessary for this exploration because GEM-Selektor is developed at the Paul Scherrer Institute in Villigen, Switzerland.

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# APPENDIX A:  REACTIVE TRANSPORT CODES

Table A-1 lists reactive transport codes with certain THC capabilities that are potentially relevant to the Waste IPSC.

## Table A-1. Reactive Transport Codes with THC Capabilities Potentially Relevant to the Waste IPSC

| Model Name | | Dim. | Processes and Approaches | | | | | | | Activity models | Sorption models | Solver Appr. | Num. Meth. | Notes |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Reactions | | | | | | | | |
| | | | Flow | Thermal | Chem. Transport | Aq. Complex | Sorp | P/D | Bio | | | | | |
| FLOTRAN family | FLOTRAN (LANL) | 1D/ 2D/ 3D | MF | Yes | MC | EK | EK | EK | No | Davies, extended Debye-Huckel (B-dot) | SCM? + IE | DSA/ GIA | FD | Includes colloid transport. |
| | PFLOTRAN (SciDAC) | 1D/ 2D/ 3D | MF | Yes | MC | EK? | EK | EK | No? | Debye-Huckel (B-dot) | LI, SCM | DSA/ GIA, SNIA | FV | Massively parallel. Based on earlier FLOTRAN. |
| CORE family | CORE$^{2D}$ V.2 | 2D/ 3D[a] | VF | Yes | MC | EQ | EQ | EK | No | extended Debye-Huckel (B-dot) | DLM, LI, IE | SIA | FE | Based in part on the earlier code TRANQUI. |
| | FADES-CORE, INVERSE-FADES-CORE | 2D/ 3D[a] | VF | Yes | MC | EQ | EQ | EK | No | extended Debye-Huckel (B-dot) | DLM, LI, IE | SIA | FE | THMC code, created by coupling CORE$^{2D}$ version 2 with FADES, a soil THM code. An inverse-modeling version (INVERSE-FADES-CORE) is available. |
| | Bio-CORE$^{2D}$ (LBNL) (Zhang 2001) | 2D/ 3D[a] | VF | Yes | MC | EQ | EQ | EK | Yes | extended Debye-Huckel (B-dot), Pitzer | DLM, LI, IE | SIA | FE | Based on CORE$^{2D}$ V. 2. Implements a large suite of biological processes. One version of Bio-CORE$^{2D}$ has implemented the Pitzer model. |
| | CORE$^{2D}$ V.4 (LBNL) (Sampler et al. 2003; Yang et al. 2007) | 2D/ 3D[a] | VF | Yes | MC | EK | EQ | EK | Yes | extended Debye-Huckel (B-dot) | DLM, LI, NLI, IE | SIA/ SNIA/ SPIA | FE | This version incorporates the biological reactions from Bio-CORE$^{2D}$ and the inverse modeling capabilities of INVERSE-CORE and other changes; it does not include mechanical deformation. |

# Table A-1. Reactive Transport Codes with THC Capabilities Potentially Relevant to the Waste IPSC

| | | | Processes and Approaches | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Reactions | | | | | | | | |
| Model Name | | Dim. | Flow | Thermal | Chem. Transport | Aq. Complex | Sorp | P/D | Bio | Activity models | Sorption models | Solver Appr. | Num. Meth. | Notes |
| MT3DMS family | MT3DMS | 3D | No | Yes[b] | MC | No | Emp | No | No | N/A | LI | SNIA | FD* | Transport code that is designed to couple readily with MODFLOW. *Also does particle tracking and total-variation-diminishing. |
| | RT3D (PNNL) | 3D | No | Yes[b] | MC | No | Emp | No | Yes | N/A | LI, NLI, implement sorption kinetics | SNIA | FD | Based on MT3DMS, requires coupling with MODFLOW for flow. Used to perform calculations of subsurface transport and biodegradation of organic contaminants, primarily in support of natural attenuation studies. |
| | SEAM3D (US Army Engineer R&D Center) | 3D | No | Yes[b] | MC | No | Emp | No | Yes | N/A | LI | SNIA | FD | Based on MT3DMS, requires coupling with MODFLOW for flow. Used to perform calculations of subsurface transport and biodegradation of organic contaminants. |
| | SEAWAT (USGS) | 3D | SF | Yes | MC | No | No | No | No | N/A | N/A | SNIA | FD | A code SEAWAT combines MT3DMS and MODFLOW under conditions of changing density. Designed to model salt-water intrusion into freshwater aquifers. This code *does* consider effects of thermally-driven differences in density or thermally-driven flow (convection). |
| | PH3TD | 3D | SF | Yes[b] | MC | EK[c] | EK | EK | No | Davies, extended Debye-Huckel[e] | DM, NEM | SNIA | FD | Based on PHREEQC V.2 and MT3DMS. |
| | PHWAT | 3D | SF | Yes | MC | EK[c] | EK | EK | No | Davies, extended Debye-Huckel[e] | DM, NEM | SNIA | FD | Based on coupling SEAWAT and PHREEQC V.2, this code does consider thermal effects on flow (e.g., convection). |

## Table A-1. Reactive Transport Codes with THC Capabilities Potentially Relevant to the Waste IPSC

| | | | **Processes and Approaches** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **Reactions** | | | | | | | | |
| **Model Name** | | **Dim.** | **Flow** | **Thermal** | **Chem. Transport** | **Aq. Complex** | **Sorp** | **P/D** | **Bio** | **Activity models** | **Sorption models** | **Solver Appr.** | **Num. Meth.** | **Notes** |
| Other codes utilizing PHREEQC for chemistry | PHREEQC (Parkhurst and Appelo 1999) | 1D | SF | Yes* | MC | EK[c] | EK | EK | Yes (KI?) | Davies, extended Debye-Huckel, WATEQ Debye-Huckel, Pitzer, SIT | DM, NEM, CDM | SIA | FD | * Incorporates the effects of heat on transport (reaction kinetics, diffusion and dispersion), but not on flow (e.g., no convection). |
| | PHAST (Parkhurst et al. 2004) | 3D | Yes | No | MC | EK[c] | EK | EK | Yes (KI?) | Davies, extended Debye-Huckel, WATEQ Debye-Huckel, Pitzer, SIT | DM, NEM, CDM | SNIA | FD | Based on PHREEQC V.2 and HST3D. Updated regularly. Parallel version available. |
| | HP1 (SCK-CEN) | 1D | VF | Yes* | MC | EK[c] | EK | EK | No | Davies, extended Debye-Huckel, WATEQ Debye-Huckel[e] | DM, NEM | SNIA | FE | Couples HYDRUS-1D and PHREEQC V.2.<br>* Incorporates the effects of heat on transport (reactions, diffision and dispersion), but not on flow (e.g., no convection). |
| Codes utilizing CHESS for chemistry | ALLIANCE (CAST3M; CASTEM) (CEA) | 1D/ 2D/ 3D | ? | Yes | MC | EQ | EK | EK | No | Debye Huckel, extended Debye Huckel (B-dot), Davies | CCM, DLM, NEM | SIA | MFE, FV | Developed by the CEA, combines CAST3M (hydromechanical code), with CHESS (chemistry). |
| | CHEMTRAP (Lucille et al. 2000) | 2D/ 3D | VF | No | MC | EQ | EK | EK | No | Debye Huckel, extended Debye Huckel (B-dot), Davies | CCM, DLM, NEM | SIA | FE | Based on coupling of SUBIEF (transport) and CHESS (chemistry). |
| | HYTEC (van der Lee et al. 2003) | 1D/ 2D/ 3D | VF | Yes | MC | EQ | EK (EQ?) | EK | No | Debye Huckel, extended Debye Huckel (B-dot), Davies | CCM, DLM, NEM, IC | SIA | FD, FE, FV | Modular code, based on the chemical speciation code CHESS, coupled with one of three flow and transport codes: RT1D (1D, FD), METIS (2D/3D, FE), and R2D2 (2D, FV). Includes colloidal transport. Parallel version available. |

## Table A-1. Reactive Transport Codes with THC Capabilities Potentially Relevant to the Waste IPSC

| | | Processes and Approaches | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Reactions | | | | | | | | |
| **Model Name** | **Dim.** | **Flow** | **Thermal** | **Chem. Transport** | **Aq. Complex** | **Sorp** | **P/D** | **Bio** | **Activity models** | **Sorption models** | **Solver Appr.** | **Num. Meth.** | **Notes** |
| CRUNCH<br>(Steefel 2001) | 2D/ 3D | VF | Yes | MC | EQ | EQ | KI | Yes | extended Debye-Huckel | DLM, NEM, IE | DSA, SIA | IFV | Based on codes OS3D and GIMRT. Implements radioactive decay chains. OS3D simulations are up to 3D and implement SIA; GIMRT simulations are up to 2D, and implement DSA (global implicit). Restricted to orthogonal grids. |
| FEHM<br>(LANL)<br>(Dash 2006; Zyvoloski 2007; FEHM 2010) | 1D/ 2D/ 3D | MF, VF | Yes | MC* | EK* | Emp. | KI | Yes[d] | All activities assumed to be unity? | LI and NLI, with kinetics | ? | CVFE | Uses particle tracking to model transport. *Up to 10 solutes with chemical reactions between each. Reactions can be kinetic (e.g., biodegradation). |
| FEMWATER<br>(WES) | 3D | VF | No | SC | No | Emp | No | KI | N/A | LI, NLI | SIA | FE/ FE-LE | |
| FRACHEM<br>(CGR) | 3D | SF | Yes | MC | EQ | No | EK | No | Pitzer | N/A | SNIA | FE | Based on CHEMTOUGH2 (chemistry) and FRACTure (flow in fractured, porous rock) |
| GeoSysBRNS<br>(Centler et al. 2010) | 1D/ 2D/ 3D | MF, VF | Yes | MC | EK? | EK? | EK | EK | ? | ? | SNIA | FE | Couples Biogeochemical Reaction Network Simulator (BRNS) with GeoSys, a THM flow and transport simulator. Current version does not account for changes in porosity due to mineral prrecipitation. Parallel version available. |
| GWB professional | 1D/ 2D | No* | Yes | MC | EK | ? | EK | ? | Debye Huckel, Pitzer | ? | ? | ? | *Flow fields imported as a table or from MODFLOW |
| HYDROGEOCHEM 4.1/5.1<br>(Yeh and Tripathi 1990;<br>Yeh et al. 2004) | 2D/ 3D | VF | Yes | MC | EK | EK | EK | EK | Davies equation, and ? | CCM, DLM, TLM | DSA, SIA | FE, FE-LE | Version 4.1 is 2D; version 5.1 is 3D. These versions of HYDROGEOCHEM appear to incorporate all capabilities of earlier versions, as well as of of the codes developed in parallel (LEHGC, HYDROBIOGEOCHEM and HGBC123). Note that (1) applications are limited to single fluid phase flows and (2) dual-porosity media cannot be effectively dealt with. |
| HYDRUS (2D/3D) | 2D/ 3D | VF | Yes | MC | No* | Emp-KI | No | Yes[d] | N/A | EI; LI and NLI; uses two-site sorption (fast-slow) for sorption kinetics | SNIA | FE | Includes colloidal transport. |

## Table A-1. Reactive Transport Codes with THC Capabilities Potentially Relevant to the Waste IPSC

| | | Processes and Approaches | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Reactions | | | | | | | | |
| Model Name | Dim. | Flow | Ther-mal | Chem. Tran-sport | Aq. Com-plex | Sorp | P/D | Bio | Activity models | Sorption models | Solver Appr. | Num. Meth. | Notes |
| MCOTAC<br>(PSI) | 1D/<br>2D | ? | ? | MC | EQ | Emp. + ? | EK | No | ? | LI,<br>SCM(?) | SNIA | FD | Does not include matrix diffusion. |
| MIN3P<br>(UBC) | 1D/<br>2D/<br>3D | VF | No | MC | EK | EQ | KI | Yes[d] | extended Debye Huckel, Davies, Pitzer | NEM, IE | DSA | FV | |
| MULTIFLO<br>(SWRI-CNWRA) | 1D/<br>2D/<br>3D | MF | Yes | MC | EK | Yes? | KI | No? | ? | ? | ? | IFD? | |
| NUFT-C<br>( LLNL) | 1D/<br>2D/<br>3D | MF,<br>VF | Yes | MC | EQ | ? | KI | No | extended Debye-Huckel (B-dot) | ? | SIA | IFD | Massively parallel. |
| POLLUTRANS<br>(Kuechler and Noack 2002) | 1D | VF | No | MC | EQ | No | KI | No | Davies equation | N/A | SIA | IFD<br>(FV) | Calculates transport of water and pollutants downward through the unsaturated zone. |
| RETRASO-CODEBRIGHT<br>(Saaltink et al. 2005) | 1D/<br>2D/<br>3D | MF | Yes | MC | EQ | EQ | EK | No | extended Debye-Huckel (B-dot) | CCM, DM, TM, IE | DSA | FE | Formed by combining of RETRASO (reactive transport) with CODEBRIGHT (multiphase THM--but the mechanical part was not implemented in RETRASO-CODEBRIGHT)--these codes were not coupled, but combined (hence the DSA solver). |
| SMART | 1D/<br>2D/<br>3D | VF | No | SC | No? | Emp | No | Yes[d] | N/A? | LI, NLI, and uses intraparticle diffusion to capture kinetics. | ? | ? | Streamtube Model for Advective and Reactive Transport. Commonly used for organic transport through soils. Not truly multidimensional, as it converts everything to 1D streamtubes. |
| STORM<br>(PNNL) | 3D | MF | Yes | MC | EK | Emp. | KI | Yes[d] | extended Debye Huckel (B-dot) | LI | SIA | FD | Parallel version available. Implements radioactive decay. |
| TOUGHREACT<br>(LBNL)<br>(Xu et al. 2004) | 1D/<br>2D/<br>3D | MF | Yes | MC | EQ<br>(EK*) | No<br>(Emp-K*) | EK | No<br>(Yes*) | extended Debye-Huckel (Pitzer in unreleased version) | N/A | SIA/<br>SNIA | IFDM<br>(FV) | Xu (2004) created a version of TOUGHREACT with reaction kinetics for aqueous species, and kinetic biodegradation and sorption ($K_d$-based). |
| STOMP<br>(PNNL)<br>(White and Oostrom 2006) | 3D | VF* | No* | MC | EK | Emp. | KI | KI | Davies, extended Debye Huckel (B-dot), Pitzer | LI with kinetics | SNIA | FD | STOMP represents a series of modules that can be coupled together. Some modules are available in parallel versions. Biological reactions are incorporated through use of a preprocessor (BIOGEOCHEM). *Some versions of STOMP do multiphase, non-isothermal flow, but the version coupled with the chemical module does not. |

## Table A-1. Reactive Transport Codes with THC Capabilities Potentially Relevant to the Waste IPSC

| | | Processes and Approaches | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Reactions | | | | | | | | |
| Model Name | Dim. | Flow | Thermal | Chem. Transport | Aq. Complex | Sorp | P/D | Bio | Activity models | Sorption models | Solver Appr. | Num. Meth. | Notes |
| UTCHEM | 3D | MF | No | MC | EQ | Emp. | EQ/KI * | Yes[d] | All activities assumed to be unity | LI, NLI | ? | FD | Chemical flooding simulator for oilfield reservoirs and for bioremediation of organics in aquifers. Chemical database is limited to reactions important to these processes.<br>* Precipitation/dissolution of minerals is handled as an equilibrium process, but gels are treated as a kinetic process. Organics dissolve kinetically. |
| 3FLO (Itasca) | 3D | VF | No? | MC | Yes? | Yes? | KI? | No? | ? | ? | ? | FE, MFE | Simulates flow in fracture networks as a 3D network of 1D pipes or channels. Simulates transport by the random walk (particle tracking) method. |

a. Members of the CORE family can only do 3-D for axially symmetric cases.

b. These members of the MT3DMS family of codes do not explicitly model heat transport, but include it by reformulating it into solute transport expressions. These codes do not consider the effects of thermally-related changes in density or thermally-driven flow (convection).

c. Codes implementing PHREEQC as the chemistry solver can apply kinetics to aqueous species reactions, but only if the species are redefined in the database as solution master species.

d. These codes implement biodegradation only, through kinetic reactions

e. PHREEQC V.2 now includes Pitzer and SIT activity models--it is not clear if several of the models that use PHREEQC for chemistry can use the newer version. Presumably, if coupling is done externally, they can.

## Legend/Acronyms for Table A-1

SF - Saturated flow
VF - Variably saturated flow
MF - Multiphase flow
SC - Single component
MC - Multicomponent
EQ - Equilibrium reactions
KI - Kinetic reactions
EK - Mixed equilibrium-kinetic reactions
Emp. - Empirical
LI - linear isotherm
NLI - non-linear isotherm (e.g., Freundlich, Langmuir)
SCM - surface complexation model
SDM - diffuse layer model
DLM - double-layer model
TLM - triple-layer model
CCM - constant capacitance model
CDM - CD-MUSIC model
NEM - non-electrostatic model
IE - ion exchange

SIA - Sequential iterative approach
SNIA - Sequential noniterative approach
SPIA - Sequential partly interative approach
DSA - Direct substitution approach (same as Global implicit method, GIM)
FE - Finite element
FV - Finite volume
FD - Finite difference
IFD - Integrated finite difference (equivalent to finite volume)
MFE - Mixed-hybrid finite elements
CVFE - Control volume finite element
LE - Lagrangian-Eulerian

# APPENDIX B

# A COMPARISON OF CONSTITUTIVE FEATURES OF THREE ADVANCED MODELS FOR THE MODELING OF CREEP DEFORMATION IN ROCK SALT

## B1.0 Introduction

Rock salt, whose long-term deformation under constant load is dominated by thermally activated and time-dependent creep, is an attractive host for high level waste repositories, because the dominant mode of deformation results in the encasement of waste over time. Certifying long-term reliability and safety of waste repositories demands constitutive models for the deformation behavior of salt that are accurate over very large timescales and a variety of boundary and initial conditions. During the 1970s, 1980s, and early 1990s, due in large part to the Waste Isolation Pilot Plant (WIPP) program, Sandia National Labs (SNL) invested significant resources in advancing the state of technology in the modeling of the creep deformation behavior of rock salt. From the mid-1990s on, the constitutive models developed in previous decades matured and their applicability was extended to a variety of salt types. However, during this time, the advancement of the state of technology in the modeling of salt deformation slowed.

In recent years, the need for long term high level waste storage in the United States has placed new emphasis on the importance of advancing the state of the art in the rock salt models currently used. In particular, more strict regulations for the storage of high level waste has placed a greater emphasis on accurately modeling the nucleation and growth of microcracks, and the interaction of the solid rock salt with any fluid that may permeate the resultant void space. Such a calculation allows more accurate determination of the extent of the damage in the rock salt away from the encapsulated waste and an ascertainment of the threat level that waste may impose on its surroundings. Due to an expanding need for long term storage of their own chemical and high level waste, several European nations have increased their engagement in the study of creep deformation in rock salt and have begun implementing many of these important features in their models. Meanwhile, further model development has been relatively stagnant at SNL since the mid 1990s.

Clearly, improving the creep deformation constitutive models is an important part of the NEAMS waste IPSC development. In this appendix, a comparison of constitutive features in two models from recent literature will be made with the most commonly used model at SNL, for the purpose of bringing to light features in the newer models that would be important to implement in SNL models. The appendix is divided as follows: Section B2 is brief outline of creep deformation behavior, Section B3 outlines the salient features of three different constitutive models, comparison of the features is made in Section B4, and recommendations and conclusions for future development are made in Section B5.

## B2.0 Overview of Creep Deformation

As shown in Figure B1, creep deformation is typically described by three primary phases of deformation: transient, steady-state, and tertiary.

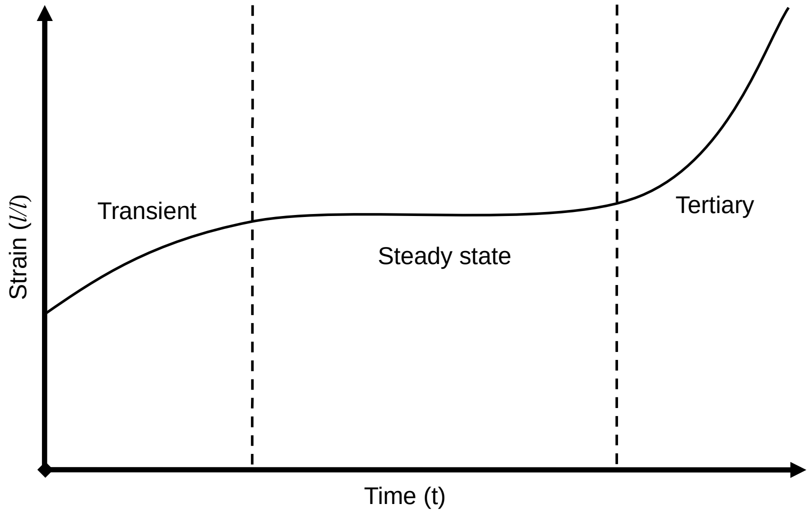

**Figure B1.** Three stages of creep.

Dislocation motion is the dominant deformation mechanism in the first and second phases of creep. In the transient phase, dislocation production and pile-up dominate and material hardening occurs. Further deformation and thermal loads result in dislocation healing until the hardening and recovery mechanism become equilibrated in the steady-state phase. In the final tertiary phase, the deformation is accelerated as micro-cracks nucleate and coalesce into larger networks of cracks, resulting in a weakening of the material and reduction in load carrying capability.

Because the dominant mechanism in creep deformation is dislocation generation, movement, and recovery, it is a thermally activated process, most often modeled by a modified Arrhenius equation of the form

$$\dot{\varepsilon}^{cr} = \frac{C\sigma^n}{d^m} e^{-\frac{Q}{k\theta}} \tag{B1}$$

where $\dot{\varepsilon}^{cr}$, is the one dimensional rate of creep strain, $C$, $m$, and $n$ are model parameters, $d$ represents the grain size of the material, $\sigma$ is the stress, $Q$ is the activation energy, $k$ is the Boltzmann constant, and $\theta$ is the absolute temperature. In the following section, these and other quantities will be further described in the context of their roles in each particular constitutive model.

In addition to the standard creep diagram of Figure B1, another useful tool for visualizing the individual dislocation mechanism involved in creep deformation are so-called deformation maps, like the one in Figure B2 for rock salt from the WIPP repository (Munson and Wawersik, 1992) In the deformation map, dominant dislocation mechanisms in the σ/μ versus homologous temperature space, where σ is the effective shear stress and μ is the shear modulus, are identified.

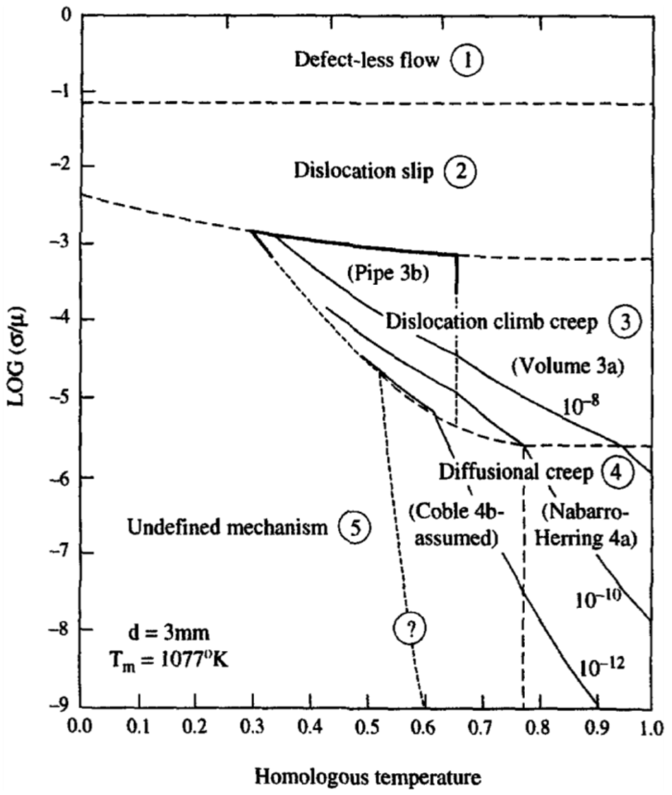

**Figure B2.** Deformation map for the WIPP repository salt (Munson and Wawersik, 1992).

## B2.1 Creep Softening

In the tertiary phase of creep, as shown on the right hand side of Figure B1, the rate of deformation accelerates due to the nucleation and coalescence of microcracks in the deforming material. The opening of microcracks is manifest in dilation and a decrease in the load carrying capability in the deforming material. Dilation and reduction in strength occur when the material is loaded beyond the dilatancy boundary, a boundary in stress space similar to the boundary between elastic and inelastic deformation defined by isosurfaces of the yield function in plasticity theory. Constitutively, softening is achieved by modeling the inelastic volume strain and strength reduction as functions of a damage parameter ω that evolves as the material is loaded beyond the dilatancy boundary.

## B2.2 Numerical Implementation of Creep

The solution to the creep problem is obtained by computing the rate of stress $\dot{\sigma}$ during a time step as

$$\dot{\boldsymbol{\sigma}} = \boldsymbol{C}:\dot{\boldsymbol{\varepsilon}}^{e} \tag{B2}$$

where ***C*** is the fourth-order elastic stiffness tensor and $\dot{\varepsilon}^{e}$ is the second order rate of elastic strain tensor. In Equation (2), it is presumed that the total rate of strain $\dot{\varepsilon}$ over the time step can be split additively into elastic and inelastic parts

$$\dot{\boldsymbol{\varepsilon}} = \dot{\boldsymbol{\varepsilon}}^{e} + \dot{\boldsymbol{\varepsilon}}^{i} \tag{B3}$$

where $\dot{\boldsymbol{\varepsilon}}^{i}$ is the rate of inelastic strain, which is expressible in terms of its magnitude and direction

$$\dot{\boldsymbol{\varepsilon}}^{i} = \dot{\lambda}\widehat{\boldsymbol{\varphi}} \tag{B4}$$

where $\dot{\lambda}$ is the magnitude of the rate of inelastic strain and $\widehat{\boldsymbol{\varphi}}$ a unit tensor in the direction of inelastic material flow. Often, $\dot{\boldsymbol{\varepsilon}}^{i}$ is taken to represent inelastic flow due to creep deformation though, generally, it may contain contributions from other inelastic deformation mechanisms, such as plasticity or softening. Unlike plasticity theory, the magnitude of the rate of inelastic strain $\dot{\lambda}$ is not constrained to certain values based on a consistency condition, and the direction of creep flow need not derive from a stress gradient of a flow potential, though often it does.

For isotropic materials, combining Equations (B2) – (B4), the rate of stress is given by

$$\dot{\boldsymbol{\sigma}} = 3\kappa \,\mathbf{iso}\left(\dot{\boldsymbol{\varepsilon}} - \dot{\lambda}\widehat{\boldsymbol{\varphi}}\right) + 2\mu \,\mathbf{dev}\left(\dot{\boldsymbol{\varepsilon}} - \dot{\lambda}\widehat{\boldsymbol{\varphi}}\right) \tag{B5}$$

where $\kappa$ and $\mu$ are the bulk and shear modulus, respectively, and iso(*arg*) and dev(*arg*) are the isotropic and deviatoric parts of *arg*, respectively.

Equations (B4) and (B5) represent the most general forms for the inelastic rate of strain and rate of stress, respectively. It is more common in the creep deformation literature for the rate of inelastic strain to be represented as

$$\dot{\boldsymbol{\varepsilon}}^i = \dot{\varepsilon}^i \boldsymbol{\varphi} \qquad \text{(B6)}$$

where $\dot{\varepsilon}^i$ is a scalar measure of the rate of inelastic strain (not necessarily the magnitude of the rate of inelastic strain) and $\boldsymbol{\varphi}$ is a tensor in the direction of creep flow with . This convention will be used throughout this report.

## B3.0 Constitutive Models

Constitutive models for the creep behavior of rock salt are distinguished from one another by their formulations for $\dot{\varepsilon}^i$ and the direction of creep flow $\boldsymbol{\varphi}$ . With that in mind, the formulations for three constitutive models for the creep behavior of rock salt are reviewed. Rather than provide an exhaustive development of each constitutive model, only salient features of how $\dot{\varepsilon}^i$ and $\boldsymbol{\varphi}$ are formulated are provided. See references for more detailed descriptions of each model. The three constitutive models reviewed are the multimechanism deformation coupled fracture model (Chan et al., 1992; Chan et al., 1994; Munson, 1993), representing the state of the art creep model developed through the mid-90s and used at SNL, the composite dilatancy model (Hampsel, 2007), and a rock salt model that describes transient, stationary, and accelerated creep and dilatancy (Salzer et al., 2006; Gunter and Salzer, 2007). The latter two models represent state of the art constitutive models developed in the last decade.

## B3.1 Multimechanism Deformation Coupled Fracture Model

The multimechanism deformation coupled fracture constitutive (MDCF) model (Chan et al., 1992; Chan et al., 1994; Munson, 1993), represents the most advanced salt creep model developed and used at SNL. In the MDCF, the second order inelastic strain rate tensor is given by

$$\dot{\boldsymbol{\varepsilon}}^i = \left(\dot{\varepsilon}^{cr}_{eq} + \dot{\varepsilon}^{\omega}_{eq}\right)(b_1 \boldsymbol{s} + b_2 \boldsymbol{t}) - \dot{\varepsilon}^{\omega}_{eq}\,(b_4(\boldsymbol{\delta} - \boldsymbol{m}) + b_5 \boldsymbol{m} \qquad \text{(B7)}$$

where $\dot{\varepsilon}^{cr}_{eq}$ is the equivalent creep strain rate induced by dislocation flow, $\dot{\varepsilon}^{\omega}_{eq}$ is the inelastic strain rate induced by damage mechanisms, $\boldsymbol{s}$ is the deviatoric part of the stress $\boldsymbol{\sigma}$ , $\boldsymbol{t}$ is the deviatoric part of $\boldsymbol{s}^2$, $\boldsymbol{\delta}$ is the second order identity tensor, $\boldsymbol{m}$ is a second order tensor dependent on the stress state, and the $b_i$ are stress state dependent coefficients. From equation (A7), $\dot{\boldsymbol{\varepsilon}}^i = f\left(\dot{\varepsilon}^{cr}_{eq}, \dot{\varepsilon}^{\omega}_{eq}, \boldsymbol{\sigma}\right)$, and the direction of of inelastic strain $\boldsymbol{\varphi}$ is a combination of $\boldsymbol{s}, \boldsymbol{t}, \boldsymbol{\delta}$ , and $\boldsymbol{m}$ . For $b_4 \neq 0$ , the presence of $\boldsymbol{\delta}$ allows for inelastic volume strain to develop with deformation.

The equivalent creep strain rate is given by

$$\dot{\varepsilon}_{eq}^{cr} = F\,\dot{\varepsilon}_{ss}^{cr} \tag{B8}$$

where *F* is a transient function relating the steady state creep strain rate $\dot{\varepsilon}_{ss}^{cr}$ with transient behavior. The steady state creep strain rate is the sum of individual mechanism dependent steady state creep rates

$$\dot{\varepsilon}_{ss}^{cr} = \sum_{n=1}^{3} \dot{\varepsilon}_{ss_n}^{cr} \tag{B9}$$

with the individual mechanism dependent components given by

$$\dot{\varepsilon}_{ss_1}^{cr} = A_1 e^{-\frac{Q_1}{R\theta}} \left(\frac{\sigma}{\mu}\right)^{n_1} \tag{B10}$$

$$\dot{\varepsilon}_{ss_2}^{cr} = A_2 e^{-\frac{Q_2}{R\theta}} \left(\frac{\sigma}{\mu}\right)^{n_2} \tag{B11}$$

$$\dot{\varepsilon}_{ss_3}^{cr} = H[\sigma - \sigma_0]\left(B_1 e^{-Q_1/R\theta} + B_2 e^{-Q_2/R\theta}\right) \sinh \frac{q(\sigma-\sigma_0}{\mu} \tag{B12}$$

representing dislocation movement by dislocation climb, an undefined mechanism, and dislocation glide, respectively, as shown in the deformation map in Figure B2. The transient function *F* is given by

$$F = \begin{cases} e^{\Delta\left(1-\frac{\varsigma}{\varepsilon_t^{*}}\right)^2} & ;\ \varsigma \le \varepsilon_t^{*} \\ 1 & \\ e^{-\delta\left(1-\frac{\varsigma}{\varepsilon_t^{*}}\right)^2} & ;\ \varsigma \ge \varepsilon_t^{*} \end{cases} \tag{B13}$$

where $\Delta$ and $\delta$ are the workhardening and recovery parameters, respectively, $\varepsilon_t^{*}$ is the transient strain limit, and $\varsigma$ is an internal state variable that evolves with deformation.

Beyond the dilatancy boundary, the inelastic strain rate is modified to include damage mechanisms, which is given by

$$\dot{\varepsilon}_{eq}^{\omega} = c_1 \omega H[\sigma_{eq}^{\omega}] \left(\sinh \frac{c_2 H[\sigma_{eq}^{\omega}]}{\mu} \frac{\sigma_{eq}^{\omega}}{1-\omega}\right)^{n_3} \tag{B14}$$

where $\omega$ is the damage parameter, *H*[*arg*] is the Heaviside function with argument *arg*, $c_1$, $c_2$, and $n_3$ are model constants and $\mu$ is the shear modulus. The damage parameter $\omega$ is taken as a function of stress and temperature.

## B3.2 Composite Dilatancy Model

In the Composite Dilatancy Model (CDM) (Hampsel, 2007), the total rate of inelastic strain is given by

$$\dot{\varepsilon}^{i} = \dot{\varepsilon}^{cr} F_{h} \delta_{dam} P_{F} \tag{B15}$$

where $\dot{\varepsilon}^{cr}$, $F_h$, $\delta_{dam}$, and $P_F$ represent contributions to the total inelastic strain rate from non-dilatant creep, humidity effects, damage, and post failure deformation.

The contribution to the total inelastic strain rate from non-dilatant creep is given by an Arrhenius equation of the form

$$\dot{\varepsilon}^{cr} = \frac{b}{M}\frac{1}{r^{2}}\upsilon_{0} e^{-\frac{Q}{R\theta}} \sinh\frac{b\Delta a\sigma^{*}}{Mk\theta} \tag{B16}$$

where *b* is the Burgers vector, *r* is the average dislocation spacing, $\upsilon_0$ is a model parameter, *Q* is the constant activation energy, $\theta$ is the absolute temperature, *R* is the universal gas constant, *k* is Boltzmann’s constant, $\Delta a$ is the activation area, $\sigma^*$ is the effective internal stress, and *M* is the Taylor factor that takes into account that natural rock salt is a polycrystalline material. The hyperbolic sine function represents the fact that creep is salt type-dependent.

In deformation processes beyond the dilatancy boundary, the effects of humidity, damage, and the increase in the strain rate post failure are accounted for by the factors $F_h$, $\delta_{dam}$, and $P_F$, respectively. The humidity factor is given by

$$F_{h} = f(\Phi, \sigma_{3}, \tau_{oct}) \tag{B17}$$

where $\Phi$ is the relative humidity within pore space of the rock salt, $\sigma_3$ is the minimum principal stress, and $\tau_{oct}$ is the octahedral shear stress. The factor representing damage is given by

$$\delta_{dam} = e^{\delta_{1}\left(\frac{\omega}{\sigma_{u}}\right)^{\delta_{2}\sigma_{3}}} \tag{B18}$$

where $\delta_1$ and $\delta_2$ are model parameters, and the evolution of the damage variable ω given by

$$\dot{\omega} = \sigma_{oct}\dot{\varepsilon}_v^i \tag{B19}$$

and the evolution of inelastic volume strain (dilatancy) is a function of $F_h$ and the stress state. Finally, the evolution of $P_F$ is given by:

$$\dot{P}_F = c_{PF}\frac{\tau_D}{1 + |\Delta\tau_D|}\Delta\varepsilon_F^{n_{PF}} \text{ for} \varepsilon_F > 0 \tag{B20}$$

$$P_F = 1 \text{ otherwise} \tag{B21}$$

A three dimensional formulation of the CDM is obtained by applying the Levy-Mises theory:

$$d\varepsilon^i = \frac{3}{2}\frac{d\varepsilon_{eff}^{cr}}{d\sigma_{eff}}\boldsymbol{s} \tag{B22}$$

## B3.3 Transient, Stationary, and Accelerated Creep and Dilatancy

In their new rock salt model that describes transient, stationary, and accelerated creep and dilatancy (TSACD), Günther and Salzer (Salzer et al., 2006; Gunter and Salzer, 2007) give the inelastic rate of strain as:

$$\dot{\varepsilon}^i = \frac{3}{2}\dot{\varepsilon}_{eff}^{cr}\frac{\boldsymbol{s}}{\sigma_{eff}} \tag{B23}$$

where $\dot{\varepsilon}_{eff}^{cr}$ is the effective rate of creep strain, given by:

$$\dot{\varepsilon}_{eff}^{cr} = A_P\frac{\sigma_{eff}^{n_p}}{\left(\varepsilon_{eff}^{v,0} + \varepsilon_{eff}^{cr}\right)^{\lambda}} \tag{B24}$$

where $A_P$, $n_P$, and $\lambda$ are model parameters, $\varepsilon_{eff}^{v,0}$ is the initial hardening, and $\varepsilon_{eff}^{cr}$ is the effective creep strain.

Below the dilatancy region, the competing effects of creep hardening due to an increase in dislocation density with deformation and thermally activated recovery are modeled by assuming that the effective rate of creep strain is the sum of hardening and recovery components:

$$\dot{\varepsilon}_{eff}^{cr} = \dot{\varepsilon}_{eff}^{\mathbf{h}} + \dot{\varepsilon}_{eff}^{r} \tag{B25}$$

where $\dot{\varepsilon}_{eff}^{\mathbf{h}}$ is the strain hardening component and $\dot{\varepsilon}_{eff}^{r}$ the thermally activated recovery component, given by

$$\dot{\varepsilon}_{eff}^{r} = \frac{\varepsilon_{eff}^{cr,\mathbf{h}}}{t_c e^{\frac{Q}{R\theta}}} \tag{B26}$$

where $Q$ is the activation energy for recovery processes and $t_c$ is a model parameter.

With the initial hardening assumed negligible ($\varepsilon_{eff}^{v,0} \approx \mathbf{0}$), the creep strain rate of Equation (B24) decreases with increasing $\varepsilon_{eff}^{cr}$, in response to an increase in dislocation density, as observed experimentally.

When loaded beyond the dilatancy boundary, the effective rate of creep strain is given by:

$$\dot{\varepsilon}_{eff}^{cr} = \dot{\varepsilon}_{eff}^{\mathbf{h}} + \dot{\varepsilon}_{eff}^{r} + \dot{\varepsilon}_{eff}^{\omega} \tag{B27}$$

where $\dot{\varepsilon}_{eff}^{\omega}$ is the contribution due to damage and dilatancy. Numerically, $\dot{\varepsilon}_{eff}^{\omega}$ is taken as the rate of inelastic volumetric strain, $\dot{\varepsilon}_{v}^{i}$ and is modeled as a function of the minimum principal stress and the work done beyond the boundary of the dilatancy region $U^{\omega}$. The inelastic volumetric strain, as a function of the dilatant work and minimum principal stress, is taken to be:

$$\varepsilon_{v}^{i} = A_1 U^{\omega} + \frac{A_2}{A_3} e^{A_3 U^{\omega}} \tag{B28}$$

where the $A_i$ are functions of the minimum principal stress

$$A_i = a_{3i-2} + a_{3i-1} e^{a_{3i}\sigma_3} \tag{B29}$$

and the nine $a_i$ are model parameters. Finally, the rate of inelastic volume strain is

$$\dot{\varepsilon}_{v}^{i} = A_1 \dot{U}^{\omega} + \frac{A_2}{A_3} e^{A_3 U^{\omega}} \dot{U}^{\omega} \tag{B30}$$

## B4.0 Comparison of Constitutive Model Features

In the previous section, three very different constitutive creep models were described. In this section, a comparison of constitutive features in each model will be provided. At this time, only the MDCF model is available at SNL, thus, only a comparison of model features published in the open literature will be provided. Efforts are currently underway to secure access rights to the CDM and the TSACD models. At such time that access to these models is granted, numerical comparisons of model predictions and trends in model behavior can be made based on simulations run at SNL.

## B4.1 Rate of Creep Strain

As previously outlined, in each of the constitutive models reviewed, the second order inelastic strain tensor is reducible to

$$\dot{\boldsymbol{\varepsilon}}^i = \dot{\varepsilon}^i \boldsymbol{\varphi} \tag{B31}$$

The difference in each model is in how is calculated and in the direction of inelastic flow $\boldsymbol{\varphi}$ . In the MDCF model, $\dot{\varepsilon}^i$ is taken as the scaled sum of individual contributions due to creep and damage mechanisms, relating each term to a region of the deformation map in Figure A2. The CDM treats $\dot{\varepsilon}^i$ very differently, taking it as the scalar rate of creep strain $\dot{\varepsilon}^{cr}$, scaled by the effects of moisture, damage, and post damage mechanisms. The CDM formulation allows transient creep to develop gradually towards steady-state creep and eventually tertiary creep. The TSACD model treats the magnitude of the inelastic strain rate tensor differently still, taking it as the sum of hardening, recovery, and softening components.

In the MDCF model, the direction of inelastic flow $\varphi$ is derived from a pressure dependent dilatancy boundary condition, allowing for an isotropic component in the inelastic strain tensor. Interestingly, though both the CDM and TSACD are formulated with dilatancy contributions to the magnitude of $\dot{\varepsilon}^i$, the direction of inelastic flow $\varphi$ is deviatoric. Thus, as published (Note: clarifications from the authors of these as-published models has been requested), inelastic volume strain cannot develop in each finite element during a simulation for materials using these two constitutive models.

## B4.2 Benchmarking and Numerical Comparisons by the German BMBF

The German Federal Ministry for Education and Research (BMBF) has been involved in a multi-year study comparing model calculations for the mechanical behavior of underground rock salt mines (Schulze et al., 2007a; Schulze at al., 2007b; Gunter et al., 2010; Hampel et al., 2010). The study included the CDM and the TSACD models, among others, and is quite extensive. Rather than repeat their findings, which can be found in the cited references, it is noted that the study found that all of the models investigated gave satisfactory-to-good results depending on the problem domain of interest. For example, the CDM model, which emphasizes the hardening and recovery responses of the material under stress, matches sections of a standard triaxial creep test almost perfectly. On the other hand, the TSACD model gave exemplary results for the modeling of the evolution of volumetric strain (softening) in rate-controlled short-term triaxial strength tests. See the referenced materials for more comparisons and analysis.

## B4.3 Model Parameterization

A major complication in the actual implementation and use of deformation creep models is the difficulty in fitting the large number of parameters in each model. For perspective, each of the creep models reviewed requires two to three dozen parameters. In contrast, the number of parameters needed for a basic nonlinear Drucker-Prager linear elastic-plastic model can be as few as six. Clearly, given that experimental data is usually limited to uniaxial and triaxial data sets, fitting any one of the reviewed creep models to experimental data is a difficult task. Even in models where parameters can be derived from theoretical microphysical considerations, it is often necessary to adjust the theoretical values to better fit experimental data, resulting in hybrid microphysical/empirical models.

As an example of the difficulty of fitting model parameters to experimental, consider a recent effort by RESPEC to fit the MDCF model to Sondershausen salt and Asse salt for SNL. SNL provided a total of 13 experimental data sets for each material. However, the data was insufficient to determine temperature dependent parameters for the Sonderhausen salt, and a lack of data in the stress-drop domain of creep tests resulted in unsuccessful attempts to fit the MDCF recovery parameters to the data. Additionally, the data did not allow the fitting of the softening and damage parameters, and previously calculated parameters (Chan et al., 1996) for rock salt from WIPP site gave unfavorable model predictions. Furthermore, when a model is fit to experimental data in one loading domain, it may not give results in other loading domains using those same parameters, as discussed in Section B4.2. These examples are only mentioned to illustrate the extreme difficulty in assigning values to model parameters in creep deformation models. In addition to a solid theoretical foundation, it is necessary to have an extensive collection of experimental data in multiple loading domains and have the expertise to fit the model to that data for model predictions to be considered reliable.

## B4.4 Dilatation, Softening, and Hydro-Chemical-Mechanical Coupling

Modeling the evolution of dilatancy and creep failure remain active focuses of research. All of the models reviewed require further investigation in their formulations in loading domains beyond the dilatancy boundary. In addition, the connection of dilatation and crack nucleation/coalescence predicted by each model to the permeability and porosity of the material must be better understood to make reliable predictions concerning the ability of the rock salt repositories to seal in contaminants as deformation and compaction evolve. This remains an important and active area of research in the constitutive modeling of rock salt.

On a curious note, all of the models reviewed include some effect of dilatancy on the effective creep strain rate, but only the MDCF model includes an isotropic component to the second order inelastic strain tensor. The inelastic strain tensor in both the CDM and TSACD models is deviatoric and, thus, neither model should predict inelastic volume strain in model calculations, if they are implemented as published in the open literature (see note in B4.1).

Due to the process of microcracking and growing void spaces during a creep deformation event, moisture from the surrounding environment is allowed to flow through the host rock salt. Though the mechanical behavior of salt is thought to be influenced by the presence of fluid in the microcracks that nucleate and coalesce during creep deformation processes, only the CDM includes terms accounting for this coupling. The effect of humidity on model predictions from the CDM model is to accelerate deformation in the presence of humidity. Models that do not include humidity effects on the magnitude of the rate of creep strain must compensate in other ways to match experimental data displaying an increase in deformation rate in humid environments. It is unlikely that a model fit to data in this manner would fit data from dry environments equally well.

None of the models reviewed include effects of chemical reactions of rock salt with the fluid in void spaces. Modeling the coupling of the hydrological and the associated chemical processes with the mechanical response requires further investigation for all of the models reviewed.

## B4.5 Thermo-Mechanical Coupling

On the micro-scale, creep deformation models the generation, movement, and healing of dislocations in the crystal lattice. As such, each of the models reviewed includes coupling of the thermal and mechanical responses of the candidate material through an Arrhenius equation, symbolizing the temperature dependence of dislocation motion. The thermo-mechanical coupling of creep deformation has been widely studied and each model has been shown to model its effects satisfactorily.

## B5.0 Conclusions

The modeling of creep deformation of rock salt for the purpose of assessing the reliability of waste isolation storage repositories through numerical simulations, has been an active area of research for several decades. Improved understanding of the response of rock salt to repository conditions, improved computing resources, and just as importantly, improved sets of experimental data, have led to the development of more accurate and reliable constitutive models. However, the state of the art in constitutive modeling can still be improved.

For more accurate predictions of waste repository reliability, it is in the interest of SNL to further the development of the MDCF model to include the effects of moisture and humidity on the overall rate of inelastic strain. These effects should be related to the inelastic volume strain and associated change in permeability of the host rock salt. Doing so will likely require re-evaluating model parameters describing material behavior beyond the dilatancy boundary which heretofore have been calculated without considering moisture effects. Such an effort would likely require two – three years of model development and verification/validation. The payoff would be a capability at SNL to more accurately predict the long term ability of salt repositories to contain and seal in high level wastes from the surrounding environment.

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