PNL-10830
UC-510

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Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

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SUMMARY

Planned performance assessments for the proposed disposal of low-level waste (LLW) glass produced from remediation of wastes stored in underground tanks at Hanford, Washington will require calculations of radionuclide release rates from the subsurface disposal facility. These calculations will be done with the aid of computer codes. Currently available computer codes were ranked in terms of the feature sets implemented in the code that match a set of physical, chemical, numerical, and functional capabilities needed to assess release rates from the engineered system. The needed capabilities were identified from an analysis of the important physical and chemical process expected to affect LLW glass corrosion and the mobility of radionuclides. The highest ranked computer code was found to be the AREST-CT code developed at PNL for the U.S. Department of Energy for evaluation of arid land disposal sites.

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1.0 INTRODUCTION

Recently, the Tri-Party agreement (TPA) between the State of Washington Department of Ecology, the U.S. Department of Energy (DOE), and the U.S. Environmental Protection Agency (EPA) was revised. The agreement specifies vitrification as the encapsulation technology for low-level wastes (LLW). By DOE Order 5820.2A, before any LLW can be disposed, a performance assessment covering the disposal facility must be approved by DOE headquarters. The performance assessment is to provide "reasonable assurance" that the disposal activities will not adversely impact long-term human health and safety.

The Hanford Low-Level Waste Performance Assessment Group currently plans to publish an interim performance assessment for the disposal facility in December 1996, followed by a preliminary performance assessment due in June 1998, and a final performance assessment in July 1999. The interim performance assessment will be based on as much site and materials-specific data as possible to demonstrate a high likelihood that the final performance assessment will be approved, and therefore, support a decision to begin construction of vitrification facilities.

Performance assessments for the disposal of Hanford LLW will require calculating radiation dose to a future population as result of any release and transport of radionuclides to the unconfined aquifer located approximately 70 m below the disposal facility. The processes controlling release and transport of radionuclides to the unconfined aquifer are expected to be simulated by using computer models. However, the specific processes to be simulated by computer codes are not well defined because facility design, waste form selection, and data collection needs are currently undecided. However, three major functions will be modeled by computer codes:

1. release of contaminants from the vitrified waste form,
2. transport of those contaminants through the engineered system, and
3. transport through the vadose zone and groundwater.

This document describes the rationale and approach used to select a computer code suitable for simulating major functions 1 and 2. For reasons which are discussed in detail in the following sections, functions 1 and 2 cannot be readily decoupled. As a result, functions 1 and 2 are discussed in this report in combination as an engineered-system release model.

1.1 CODE SELECTION CRITERIA

The following general criteria (Mann 1994) were used to identify codes suitable for modeling engineered-system release:

1. The theoretical framework of the selected computer code shall be based on appropriate scientific principles (for example, conservation of mass, momentum, and energy) and well established engineering equations (for example, Darcy's law and Fick's law).

2. The selected code shall be documented in a technical report and contain descriptions of
   a) model theory, governing equations, and assumptions
   b) computational techniques and algorithms
   c) example applications.

3. The selected code shall be maintained under a software quality management program that assures that modifications and updates are traceable, auditable, and documented. Audits by Westinghouse Hanford Company (WHC) and other organizations may occur.

4. The selected code shall allow the use of site- and facility-specific data/standards/guidelines as appropriate. For example, the ability to use site-specific vadose zone parameters is required rather than parameters for a generic soil type.

5. Because some simulations are expected to be conducted for long-time periods (e.g., a million years), diagnostic monitoring capability of the simulation during actual run-time or else a restart option as a minimum is required.

The following desirable features were also considered:

1. The selected code should be certified (that is, simulation results compared with field and/or laboratory data) for a system similar to that being modeled.

2. The degree of complexity of the selected code shall be consistent with the quantity and quality of data and the objectives of the computation. Screening calculations and sensitivity analyses should be used to simplify conceptual models and ultimately direct code selection.

3. Computer hardware requirements for the selected code should be consistent with available platforms and be affordable. Compatibility among computing platforms is highly desirable.

4. Proprietary codes should be used only if they provide a distinct advantage over public domain codes; and only if the author(s)/custodian(s) allow inspection and verification of the source code. If a proprietary code is used,

   a) the source code must be made available by lease or purchase to WHC and
   b) the executable version must be made available by lease or purchase to interested parties.

5. Consideration must be given to the ease of interfacing code input/output with other codes. The availability of pre- and post-processors should be given adequate consideration in selecting a code.

6. Familiarity with the selected code is also a consideration in light of time and resource constraints.

7. To enhance technical acceptability, the selected code should be generally known and accepted by the user community.

8. To reduce the presence of known bugs, the selected code should be a recent version, preferably the last one that has been fully tested, of a family of codes.

These code selection criteria are based on information from the LLW programs of the DOE (Case 1988) and U.S. Nuclear Regulatory Commission (Kozak 1989), as well as experience gained from submitted DOE radiological performance assessments (WSRC 1992; Kincaid 1993). A summary description of risk-assessment codes at Hanford (DOE/RL 1991) was also used.

1.2 CODE IDENTIFICATION METHODOLOGY

Although the above code selection criteria provide useful guidance for code selection, a methodology is needed to identify suitable codes for engineered-system release calculations. The methodology used in this report consists of 1) identifying model requirements, and 2) critically reviewing the capabilities of existing codes against the model requirements. In identifying model requirements, the best current information on the system geometry and materials under consideration was used to identify those physical and chemical processes that must be simulated in the selected engineered-system release model. Any computer model that met at least 50% of the requirements was included in the set of codes from which the final selection was made. Each computer code was then ranked in accordance with a point ranking system described in the Code Selection section. The intent was to make the code selection process as unbiased as possible, although the authors' opinion as to the importance of a particular process certainly influenced the final ranking.

2.0 MODEL REQUIREMENTS

In this section, the model requirements are described, given the best current information on the design and materials that are under consideration for use in the engineered system.

2.1 SYSTEM DESCRIPTION

Figure 1 gives a schematic illustration of a multi-barrier, engineered-system concept for Hanford LLW. The engineered system is assumed to begin with the water chemistry conditioner and end at the chemical retardation barrier. No specific materials have been selected for any of the engineered components depicted in Figure 1, and some of these components may not be included in the final design of the disposal facility. However, Table 1 gives a list of general types of materials that have been considered. By evaluating the important physical and chemical properties of these materials, the important physical and chemical processes that must be modeled in the engineered system can be derived. The important physical processes are discussed in the next section followed by a discussion of the important chemical processes.

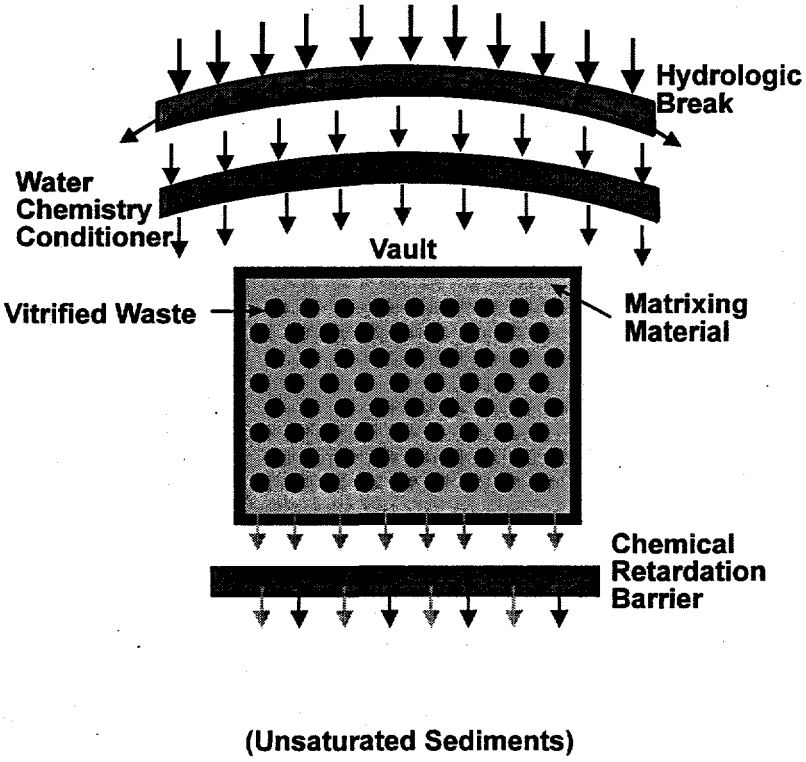

Figure 1. Engineered-System Concept for Hanford LLW

Table 1. List of Materials Under Consideration for Engineered-System Components

System Component	Materials
Water chemistry conditioner	Diatomaceous earth Amorphous silica Cristobalite Crushed glass
Vault	Portland concrete Reinforced portland concrete Sulfur polymer concrete
Matrix	Hanford soil Sulfur polymer concrete Bitumen Asphalt Clay and clay-soil mixtures
Container	Carbon steel Stainless steel
Glass	Aluminosilicate Soda-lime silicate Borosilicate Phosphate
Retardation pad	Iron metal-soil mixture Zeolites

2.2 PHYSICAL PROCESSES

Neglecting physical intrusion or a catastrophic event such as volcanism or meteor impact, radionuclide release from the engineered system can only occur by mass transport processes. Solid-state diffusion can be neglected because it is extremely slow at expected soil temperature (<25°C), and therefore, would contribute vanishingly small mass flux from the engineered system. The principal processes to be considered are therefore aqueous- and gas-phase mass transport.

2.2.1 Aqueous Phase Mass Transport

With the exception of the glass waste form, possibly a sulfur polymer concrete (SPC) matrix, and a steel container, the materials being considered for the LLW engineered system are porous

materials. Aqueous transport through porous materials has, traditionally, been treated with concepts derived from continuum mechanics. By averaging microscopic variations in the properties of the porous material over a representative elementary volume (REV), macroscopic properties for the REV are derived. Using the macroscopic properties of the REV and the fundamental principle of conservation of mass, the following equation can be derived:

$$\frac{\partial \theta_l c_l^i}{\partial t} = -\nabla \cdot \mathbf{q}_l^i + \theta_l \rho_l R_l^i + \dot{m}_l^i, \quad i = 1,2,...N_l \tag{1}$$

where c_l^i = aqueous concentration of component i, g/m^3

$\dot{m}_l^i$ = total mass source or sink rate of component i, g/m^3·s

N_l = number of aqueous components

$\mathbf{q}_l^i$ = total flux of component i, g/m^2·s

R_l^i = rate of production or consumption of i due to chemical reactions, g/g$_l$·s

θ_l = volumetric water content

ρ_l = fluid density, g/m^3.

If it is assumed that the phenomena of hydrodynamic dispersion in the REV can be represented by a Fickian type law, then the total flux due to advection, dispersion, and diffusion is given by

$$\mathbf{q}_l^i = \theta_l (c_l^i \mathbf{V} - \mathbf{D}_l(\theta_l) \cdot \nabla c_l^i). \tag{2}$$

where $\mathbf{D}_l$ = hydrodynamic dispersion tensor, m^2/s

$\mathbf{V}$ = fluid velocity vector, m/s.

Substituting Equation (2) into Equation (1), ones arrives at

$$\frac{\partial \theta_l c_l^i}{\partial t} = \nabla \cdot \theta_l \mathbf{D}_l(\theta_l) \cdot \nabla c_l^i - \nabla \cdot \theta_l c_l^i \mathbf{V} + \theta_l \rho_l R_l^i + \dot{m}_l^i, \quad i = 1,2,...N_l \tag{3}$$

which is commonly known as the advection-dispersion equation. The solution to Equation (3), in various forms, is the basis for almost every subsurface transport code that has been developed to date.

In principle, Equation (3) should be applicable for analyzing radionuclide release from the engineered system. However, Equation (3) may not be an adequate model for the SPC matrix.

In this case, the concept of an REV may break down because the SPC will be produced with an unknown number of fractures. If the degree of fracturing is sufficiently dense, the matrix may be treated as an equivalent nonfractured continuum (Berkowitz, Bear, and Braester 1988) or by a dual porosity model (Rowe and Booker 1990), and Equation (3) may be applicable. However, if the fracturing is discrete, then an alternative mathematical treatment of transport along the fractures must be developed. For the code selection, it will be assumed that the SPC can be treated with an equivalent continuum model so that codes with the capability of solving a form of Equation (3) are all that is required.

2.2.2 Gas Phase Mass Transport

The radionuclides incorporated in a silicate-based glass product have a low vapor pressure under disposal system conditions; therefore, gas-phase transport can be neglected for these species. However, gas-phase transport will be an important consideration when modeling chemical processes in the engineered system and must be considered in the engineered-system code. For example, dissolved O_2 may be consumed/produced from oxidation/reduction reactions that occur with an engineered-system material like SPC. These oxidation/reduction reactions can have a very large effect on the solubility (and hence release) of radionuclides like ^{99}Tc.

Gas phase mass transport is treated in much the same way as the development of the aqueous phase transport Equation (3). Gas phase transport can occur through the gas phase and as a dissolved component in the aqueous phase. Assuming Darcy's law applies for the advective transport, and a Fickian type law for the dispersive transport, the gas phase conservation equation is

$$\frac{\partial \theta_g c_g^i}{\partial t} = \nabla \cdot \theta_g \mathbf{D}_g(\theta_g) \cdot \nabla c_g^i + \nabla \left[\frac{\tilde{k} k_g c_g^i}{\mu_g} (\nabla P_g + \rho_g \mathbf{g} \nabla z) \right] + \theta_g \rho_g^i R_g^i + \dot{m}_g^i, \quad i = 1,2,\ldots N_g \qquad (4)$$

where c_g^i = concentration of gas phase component *i*, g/m^3

$\mathbf{D}_g$ = gas dispersion tensor, m^2/s

$\mathbf{g}$ = gravitational constant, m/s^2

$\tilde{k}$ = intrinsic permeability tensor, m^2

k_g = relative gas phase permeability

$\dot{m}_g^i$ = total mass source or sink rate of gas component *i*, $g/m^3 \cdot s$

N_g = number of gas components

P_g = total gas phase pressure, Pa

R_g^i = rate of production or consumption of *i* due to chemical reactions, $g/g_g \cdot s$

z = elevation, m

μ_g = gas phase dynamic viscosity, Pa·s

θ_g = volumetric gas content

ρ_g = gas phase density, g/m^3.

The same caveats regarding the applicability of the REV concept discussed in Section 2.2.1 apply to the solution of Equation (4). Equation (3) for aqueous component transport and Equation (4) for gas component transport are coupled through the terms R_l^i and R_g^i, which account for interphase (gas-water) chemical reactions.

2.2.3 Fluid Flow

Water flow in the near-surface unsaturated zone is transient because of intermittent precipitation events. Transient water flow begins with the entry of water at the ground surface and subsequent infiltration downward into the disposal facility. The rate of infiltration into the facility is controlled by the rate and duration of water application at the surface, the hydraulic conductivity of engineered barriers, the vault, and surrounding soil, and the matric and gravity potential gradients. At some distance from the ground surface, transient effects will dampen out and the downward flowing water will reach a steady infiltration rate. The distance at which steady infiltration occurs is sometimes referred to as the penetration depth (Eagleson 1978; Salvucci 1993). Thus, the unsaturated zone essentially comprises two regions: an unsteady-flow region between the ground surface and penetration depth, and a steady-flow region between the penetration depth and the saturated zone water table. The steady flux in the lower unsaturated region is equal to the annual rate of ground-water recharge, and therefore comprises contributions not only from the most recent pulse, but from previous precipitation events as well. Given expected recharge rates

for the Hanford Site, the disposal facility will be situated below the penetration depth in the region of steady flow.

Assuming, once again, that the concept of a REV applies and that Darcy's law is valid for modeling fluid flow through the engineered system, a water mass conservation equation can be derived

$$\frac{\partial \rho_l \theta_l}{\partial t} = \nabla \left[\frac{\tilde{k} k_l(\theta_l) \rho_l}{\mu_l} (\nabla P_l + \rho_l \mathbf{g} \nabla z) \right] + \theta_l \rho_l R_l + \dot{m}_l \qquad (5)$$

where k_l = relative water permeability

P_l = liquid phase pressure, Pa

R_l = rate of water consumption due to all chemical reactions, $g_w/g_l \cdot s$

$\dot{m}_l$ = total mass source or sink rate of fluid, $g/m^3 \cdot s$

μ_l = liquid phase dynamic viscosity, Pa·s.

The need to solve the fluid mass conservation Equation (5) in the engineered-system simulator is dependent on

1. assumptions regarding the effects of mass transport and chemical reactions on the properties of the engineered components, such as porosity and permeability
2. assumptions regarding the influence of chemical reactions on the water mass balance, i.e., moisture content.

If it is assumed that mass transport and chemical reactions have a negligible impact on the properties and moisture content of the engineered system, then there is no need to solve Equation (5) in the engineered-system simulator. The flow field can be calculated from any number of codes capable of simulating unsaturated flow. However, because chemical reactions are likely to play a significant role in altering the properties of the engineered-system components and in consuming/releasing water, the preferred engineered-system code would include the capability for solving the water mass conservation equation (5). An accurate evaluation of Equation (5) would require a means to estimate the change in the water permeability function (k_l) as the distribution of solids changed as a function of time. This could be done with an empirical function or weighted sum for the major mineral phases affecting k_l.

2.2.4 Heat Transport

The process of radioactive decay generates heat in a solid due to the energy loss associated with the interactions of the emitted charged particles or photons with the atoms in the solid and the energy loss associated with collisions from the recoiling nucleus. Because of the long half-life and small concentration of radionuclides in LLW, the increase in temperature of the engineered system over ambient conditions is expected to be small. This conjecture was checked with a simple heat transfer calculation.

The dimensions of the vault can be estimated by assuming that the total volume of glass is 210,000 m^3, which is packed at a uniform volume fraction of 0.6 and the interstitial volume filled with SPC. If the vault is assumed to be 10 m thick, and assumed square in its other two dimensions, then the block must be 187.08 m wide by long. This configuration can readily be treated as an infinite slab with constant uniform temperature on its surfaces, for which the temperature rise owing to constant, uniform volumetric heat generation is given by

$$\Delta T_c = Qa^2 / 8\kappa \qquad (6)$$

where a = slab thickness, m

ΔT_c = steady-state temperature rise at slab centerline, K

Q = heat generation rate, W/m^3

κ = thermal conductivity, W/m·K.

With the thickness a stated, κ and Q remain to be found for the waste glass/SPC composite.

Treat the composite as a volume-weighted mixture of glass and elemental sulfur representing the SPC. The CRC Handbook (56th Ed., pp E-6 - E-9, E-15) gives thermal conductivity data pertinent to these materials. The thermal conductivities of glasses range from 0.0013 to 0.0035 cal/cm·s·°C, depending on the type of glass. Use a value of 0.0027 cal/cm·s·°C, or 1.13 W/m·K, for glass; this is based on values for Pyrex-type chemically resistant borosilicate glass at about 20°C. For the elemental sulfur, the same reference gives thermal conductivity ranging from 0.0020 to 0.0027 W/cm·K, depending on the temperature and whether the sulfur is amorphous or polycrystalline. We assume a value of 0.22 W/m·K for the SPC.

Tsotsas and Martin (1987) give Zehner and Bauer's equations for calculating the bulk thermal conductivity of a composite

$$B = 1.25\left(\frac{1-\varphi}{\varphi}\right)^{1.111} = 1.96 \tag{7}$$

where φ is the volume fraction of the less conductive material,

$$\kappa_p = (\text{higher } \kappa)/(\text{lower } \kappa) = 5.13 \tag{8}$$

$$N = 1 - \frac{B}{k_p} = 0.618 \tag{9}$$

$$k_c = \frac{2}{N}\left(\frac{B}{N^2}\frac{k_p - 1}{k_p}\ln\frac{k_p}{B} - \frac{B+1}{2} - \frac{B-1}{N}\right) = 3.05 \tag{10}$$

$$\kappa_b = (\text{lower } \kappa)\left(1-(1-k_c)\sqrt{1-\varphi}\right) = 0.570\ \frac{\text{W}}{\text{m}\cdot\text{K}}. \tag{11}$$

The Zehner and Bauer equations have been validated for particle sizes and shapes that include the 1-cm diameter rough spheres assumed for the glass.

The volumetric heat generation rate, Q, can be determined from the available information (Rawlins et al. 1994) on the total radioactive inventory for the glass slab. Assuming the total decay energy from each radionuclide is deposited in the solid, a decay heat generation rate of 0.321 W/m^3 was estimated. The maximum (center) temperature difference between the slab and its immediately surrounding soil is, therefore,

$$\Delta T_c = Qa^2 / 8\kappa_b = 7.04 \text{ K}. \tag{12}$$

This temperature rise is unlikely to have any significant effect on the performance of the engineered system. Also, because 99.6% of the internal heat generation is due to the ^{90}Sr and ^{137}Cs inventory, which have 28.1 and 30.3 y half-life, respectively, the 7-degree temperature rise calculated here will persist for a relatively short time compared with the time span of a performance assessment calculation. Consequently, the engineered-system model need not consider temporal or spatial variations in temperature, which obviates the need for solving a heat transport equation.

2.2.5 Radioactive Decay

Although the process of radioactive decay is not an important process when considering heat transfer for a LLW site, the process is very important when modeling radionuclide release from the engineered system. Radioactive decay is a straightfoward physical process that is usually included in subsurface transport codes. Much less common, however, is the capability for simulating radioactive decay chains and decay chain ingrowth. For reasons which will be discussed in Section 2.3.7, modeling radioactive decay and decay chain ingrowth in multicomponent chemical-transport codes requires careful consideration.

2.3 CHEMICAL PROCESSES

The selected engineered-system code must consider several important chemical processes coupled with the physical processes described in Section 2.2. Chemical processes control such important factors as radionuclide solubility and retardation, and corrosion rate of the LLW glass. The chemical processes to be modeled include

- aqueous complexation
- acid-base reactions
- oxidation/reduction
- dissolution/precipitation
- ion-exchange
- adsorption.

Each of these chemical processes is discussed in more detail below.

2.3.1 Aqueous Complexation

In complexation reactions, a central cation such as a radionuclide or metal ion reacts with an anion, commonly called a ligand, to form a new soluble species called a complex. In turn, these complexes can react with other ligands to form additional complexes. Complexation reactions are especially important because these reactions significantly modify the stability, and hence, mobility of actinide and transition metals. Inorganic ligands include common anions in natural waters, e.g., OH^-, Cl^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, etc. These ligands may also be contributed to the aque-

ous phase as a result of glass-water reactions. Inorganic ligands are typically present in solution in excess compared to radionuclides and metals. Important organic ligands include molecules associated with natural humic substances and synthetic organic complexing agents.

2.3.2 Acid-Base Reactions

Acid-base reactions involve the transfer of the proton (H^+) between two species. Chemical species which lose a proton are called acids and species which gain a proton are called bases. The pH of a solution is a measure of the activity of H^+ (more precisely, H_3O^+ ion) in solution; it is defined as the net negative logarithm of the H^+ activity ($pH = -\log a_{H^+}$). Acid-base reactions are involved in many aqueous complexation, precipitation, or sorption reactions. Solution pH controls aqueous speciation, solubility of compounds, sorption behavior of elements (e.g., K_d values), complex formation, and oxidation-reduction processes. For example, under oxidizing conditions in carbonate free aqueous media, the Pu^{+6} species is in the form of PuO_2^{2+} for $pH < 5$. At pH between 5 and 7, it is in the form of $PuO_2(OH)^-$, and at pH above 7 it is in the form of $PuO_2(OH)_3^-$. Corresponding measured values for the K_d of Pu range from less than 10 ml/g at low pH, to between 10 and 100 ml/g for the neutral pH range, to over 1000 ml/g at high pH. Solution pH also impacts the corrosion rate of many materials including silicate-based glass waste forms where higher pH is more corrosive to the glass.

2.3.3 Oxidation-Reduction Reactions

Oxidation-reduction (redox) reactions involve the transfer of electrons from one species to another resulting in changes in oxidation states. Redox reactions can be classified as either aqueous complexation, precipitation, or adsorption reactions; these reactions can significantly alter the mobility of multiple-oxidation state radionuclides. For example, the effectiveness of adsorption mechanisms often depends on the oxidation state of the radionuclide. Important radionuclides such as ^{99}Tc, the transition metals, and the actinides uranium and plutonium have much lower solubilities in natural waters in their lower oxidation states.

The transfer of electrons in oxidation-reduction reactions is often treated in a mathematically analogous manner as the transfer of protons in acid-base reactions. For example, the activity of

the hypothetical electron in solution is defined by the parameter *pe*, which equals the negative logarithm of the hypothetical electron activity. The *pe* can also be expressed in terms of the redox potential (Eh), which is related to *pe* by

$$pe = \left(\frac{\mathrm{F}}{2.303\mathrm{R}T}\right) Eh \tag{13}$$

where F is the Faraday constant, R is the gas constant, and T is the absolute temperature. However, the overall redox state of real aqueous systems usually cannot be characterized by a single parameter such as Eh. The concept of a "system" *Eh* or a "system" *pe* is based on the assumption that all redox reactions in a system are in a state of thermodynamic equilibrium. This assumption is a poor one for most real systems (Jenne 1981; Hostetler 1984; Lindberg and Runnells 1984). Redox disequilibrium in natural aqueous systems is created by solar irradiation, radioactive decay, fluid mixing, slow reaction kinetics, and transfer of redox components from one phase to another. It should also be clear that *pe* is not a perfect analog to pH, because pH is defined with respect to H^+, a real aqueous species, whereas *pe* is defined with respect to a hypothetical species.

Oxidation-reduction in aqueous systems is commonly treated in terms of redox couples and their associated half-reactions. Common couples in aqueous solution include $O_{2(aq)}/H_2O_{(l)}$, $H_{2(aq)}/H_2O_{(l)}$, Fe^{2+}/Fe^{3+}, HS^-/SO_4^{2-}, SO_3^{2-}/SO_4^{2-}, $S_2O_3^{2-}/SO_4^{2-}$, NH_4^+/NO_3^-, $N_{2(aq)}/NO_3^-$, and a host of organic/HCO_3^- couples. Each couple can be treated as having its own redox state. This can be expressed in a variety of ways, including a couple-specific *Eh* or *pe*.

Another way of expressing redox state that has become increasingly popular in geochemical models is the concept of a hypothetical oxygen fugacity in aqueous solution. Oxygen fugacity in an aqueous solution is hypothetical because fugacity is a property of gas species and gas species do not exist in aqueous solution. However, $O_{2(g)}$ makes a good hypothetical aqueous species, much like the hypothetical aqueous electron is used to calculate *pe*.

The concept of a hypothetical $O_{2(g)}$ aqueous species is important because it allows the modeler to express the redox state of a system in terms of a variable that does not necessarily imply redox equilibrium as does a *pe* or *Eh*. Consequently, the preferred method for treating redox reactions in the engineered-system model is with the hypothetical $O_{2(g)}$ aqueous species.

2.3.4. Dissolution-Precipitation Reactions

Dissolution-precipitation reactions are heterogeneous chemical reactions that directly remove or release radionuclides and other elements from solution. Therefore, these types of reactions play a very important role in the overall performance of the engineered system. Extensive amounts of precipitation or dissolution can also alter the pore or fracture structure of an engineered-system component and thereby indirectly alter the mass transport properties of the component.

Dissolution-precipitation of a solid phase in an aqueous solution is a dissociation-association process in which two or more soluble species are released into or removed from solution. It is subject to the common ion effect, which occurs when a solution already contains the same ions that would be released or removed when the solid dissolves or precipitates. The presence of common ions from other sources reduces the solubility of the solid relative to its solubility in pure water.

Glass corrosion is a special type of dissolution-precipitation reaction in that it is an irreversible process. Glass corrosion is the primary mechanism of releasing radionuclides from the LLW form into the adjacent environment and must be accurately described in the engineered-system model. Fortunately, there is an extensive body of work on borosilicate glass waste forms from which a widely accepted mathematical model has been developed. Using this model, the flux of any element i released from the glass into the aqueous phase, J_i^a, is given by

$$J_i^a = \nu_i k_0 (1 - e^{\frac{A}{RT}}) \prod_j \gamma_j c_j^{-\eta_j}, \quad i = 1, 2, \ldots N \tag{14}$$

where

ν_i = stoichiometric coefficient of element i in the glass
k_0 = forward rate constant, g/(m^2·s)
A = chemical affinity of the reaction, J/mol
N = number of elements
R = gas constant, J/mol/K
T = temperature, K
c_j = concentration of jth aqueous reactant species, g/m^3

γ_j = activity coefficient of jth reactant species

η_j = stoichiometric coefficient for the jth reactant species.

Equation (14) represents a constitutive relationship that relates temperature and the composition of water contacting the glass to the corrosion rate. Because these quantities are known or calculated at each node in a chemical-transport model [Equation (3)], incorporation of a glass corrosion model [Equation (14)] can be done naturally.

Mathematically, dissolution-precipitation reactions assumed to be at equilibrium can be treated via mass-action expressions or in terms of chemical potentials. A mass-action formulation results in a system of non-linear algebraic equations that must be solved, whereas a formulation in chemical potentials requires a solution to a global free energy minimization problem. Either formulation should yield equivalent results.

Because the temperature of the LLW disposal site is expected to be <25°C, an assumption of chemical equilibrium for all reactions may not be appropriate, particularly for some dissolution-precipitation reactions. At 20°C, metastable phases may persist for indefinite periods of time and many of these phases may be amorphous. This is a consequence of the Ostwald Step Rule (Ostwald 1897), which states that the reaction products initially obtained are the least stable ones lying nearest to the original state in free energy and also the "simplexity principle" (Goldsmith 1953), which states that the most disordered phase should form from a random system of components. Consequently, the selected engineered-system code should have the capability for specifying kinetically constrained reaction sets. This capability is particularly critical for modeling the long-term behavior of a material like SPC that is not thermodynamically stable in waters percolating through unsaturated Hanford soils (Pourbaix 1974).

2.3.5 Ion-Exchange

Ion-exchange reactions are a class of adsorption reactions that may be an important control on the mobility of radionuclides and other species, especially through clays and zeolites. Ion-exchange occurs when there is a free energy reduction from the substitution of an ion in the aqueous phase with an atom in the exchangeable solid. The ability of a solid to exchange ions is usually expressed by the cation exchange capacity (CEC), which is defined as the number of

milliequivalents (meq) of monovalent cations per unit mass of dry solid. The equivalent of an ion is its molecular weight divided by the absolute value of its charge. Typical CEC values for soils containing organic materials range from 30 to 100 meq/100g, depending on the mineral type, pH, and composition of the contacting solution.

As was the case for the dissolution precipitation reactions, ion-exchange reactions may be treated mathematically via mass-action expressions or chemical potentials. Mass action formulations for ion-exchange reactions are similar to those for dissolution-precipitation reactions with the exception that the equilibrium constant of the latter is replaced by a selectivity coefficient. The chemical potential formulation requires a state equation that relates the change in electrostatic potential that occurs from the ion-exchange reaction.

2.3.6 Adsorption

Adsorption is the phenomenon of increase in the mass of a substance on the solid at a fluid-solid interface. The component's affinity for adsorption to the solid surface is due to 1) electrical attraction such as van der Waals attraction, or 2) chemisorption, which is a surface complexation reaction that binds the adsorbed species to the solid surface.

The main factors affecting the adsorption and desorption of species to or from the solid are the physical and chemical characteristics of the adsorbent and of the solid surface. Interactions between mineral surfaces and dissolved ions can depend strongly on solution pH and the mineral's zero point of charge (ZPC). If the pH of the contacting solution is above the ZPC, the mineral surface will have a net negative charge and an affinity for cations; the reverse occurs if the pH is less than the ZPC. This phenomena is particularly important in systems containing clays and particles coated with common hydrous oxides such as those of aluminum, manganese, and iron. These materials are often dominant sorbents in geochemical systems. Clay minerals tend to have overall negative charges for all but very acidic conditions (i.e., pH<4). Metal oxides, however, may have reactive sites capable of removing anionic radionuclide species from solution for the near-neutral to slightly basic pH range.

Numerous adsorption models exist that may be used in an engineered-system code. Empirical models are the most popular type of adsorption model, usually expressed as an isotherm, that

relates the quantity of an adsorbed species to its quantity in the aqueous phase at constant temperature. Equilibrium isotherms are based on the assumption that the quantities of the component on the solid and in the adjacent solution are in equilibrium. Any change in the concentration of one of the species produces an instantaneous change in the other. Common isotherms include the linear equilibrium isotherm or K_d model given by

$$F_s^i = K_d^i c_l^i, \quad i = 1,2,...N_l \tag{15}$$

where F_s^i = mass of component i per unit mass of solid
K_d^i = distribution coefficient of component i, m^3/g,

and the Langmuir isotherm

$$F_s^i = \frac{k_3 c_l^i}{1 + k_4 c_l^i}, \quad i = 1,2,...N_l \tag{16}$$

where k_3 and k_4 are constants. There are also a variety of non-equilibrium isotherms, although these have been almost never applied in transport codes.

A semi-empirical type of adsorption model that is used in several chemical-transport codes is a surface complexation model. As was the case for the chemical reactions discussed previously, the surface complexation model may be formulated in terms of mass-action expressions or by chemical potentials. Mass-action formulations require equilibrium constants for the surface complexation reactions being considered and the chemical potential formulation requires information on the change in electrostatic potential that occurs from the adsorption reaction. This is usually done with the aid of a double or triple-layer site binding model. For the selected engineered-system code, both empirical and surface complexation adsorption model options should be available. The latter model is expected to be used in cases where particular adsorption reactions play a crucial role in the mobility and release of a radionuclide.

2.3.7 Radioactive Decay

As discussed in section 2.2.5, the process of radioactive decay is a simple physical process to include in a transport code. However, the process of decay-chain ingrowth is not so easily implemented. Decay-chain ingrowth refers to a series of parent and daughter decay reactions that

can result in the accumulation of daughter radionuclide(s) because of the differences in half-life between the members of the chain. For example, consider the decay chain

$$^{243}_{95}\mathrm{Am} \xrightarrow{7.37 \times 10^{3}\ \mathrm{y}} {}^{239}_{93}\mathrm{Np} \xrightarrow{2.35\ \mathrm{d}} {}^{239}_{94}\mathrm{Pu} \xrightarrow{2.44 \times 10^{4}\ \mathrm{y}} {}^{235}_{92}\mathrm{U}. \tag{17}$$

Because the half-life of ^{235}U is 7.1 x 10^8 y, the decay of this radionuclide is usually insignificant over the time scales of performance assessment calculations. However, the ^{243}Am parent is usually completely decayed over typical performance assessment time scales of 10^6 y. Consequently the decay of the parent results in the accumulation of ^{239}Pu and ^{235}U.

The difficulty in describing decay-chain ingrowth in coupled chemical transport codes is the fact that each radionuclide is partitioned into multiple chemical species. These species may be aqueous, precipitated, adsorbed, etc. To maintain proper mass balance, it is, therefore, necessary to explicitly write "chemical reactions" that describe the decay of each parent species. For example, the decay of the aqueous species $AmOHCO_3$ can be written as

$$^{243}_{95}\mathrm{AmOHCO_3}(aq) \rightarrow {}^{239}_{94}\mathrm{Pu}^{3+} + \mathrm{OH}^- + \mathrm{CO_3^{2-}}. \tag{18}$$

The decay reaction (18) is written as an irreversible, kinetically constrained reaction with the rate constant given simply by the decay constant for the ^{243}Am parent. Equation (18) is only valid when the time step being taken is much larger than the 2.35d half-life of the $^{239}_{93}$Np intermediate. Similar reactions can be written for all the radioactive species to be considered in a simulation. Obviously, for a kinetically constrained reaction like Equation (18) to be implemented, the selected engineered-system code must be capable of treating kinetically constrained reaction sets in addition to the usual equilibrium reaction sets.

3.0 COMPARISON OF EXISTING CODES

Having described in the previous section the important physical and chemical processes that are expected to significantly impact the performance of the engineered system, we now need to evaluate the capabilities of existing computer codes in meeting these requirements and develop a means to rank the computer codes. The mechanism chosen to do this is to 1) develop a list of needed capabilities and 2) assign a figure of merit score from 1 to 10 to each capability. The figure of merit score is broken into two parts:

a) importance to modeling the performance of the engineered system

b) degree of difficulty in adding the capability to an existing code.

The figure of merit score is intended as an unbiased scheme to rank computer codes with similar capabilities. For Part *a*, a score of 1 indicates that the process has little or no importance for modeling radionuclide release from the engineered system, whereas a score of 10 means that the process is critical to the model and must be included in the selected code. Part *b* of the figure of merit score is needed because it is expected that no existing code meets all of the capabilities identified in Sections 1.0 and 2.0. Consequently, the degree of difficulty in modifying or adding a particular capability to an existing code is an important consideration in the code selection process. A Part *b* score of 1 indicates that a person familiar with the process and the code could add the capability in less than a man-week, whereas a score of 10 indicates that at least a man-year of effort would be required to add the capability to the code.

To be selected for detailed ranking, the computer code must have the capability for simulating coupled chemical reactions and transport. This requirement excluded a large number of subsurface solute transport codes (such as PORFLOW) and batch equilibrium chemistry codes such as EQ3/6.

3.1 COMPUTER CODE RANKING

The needed (or desired) code capabilities were divided into four categories. These are

- Physical Processes
- Numerical Methods
- Chemical Processes
- Functionality

Each category was then broken down into specific capabilities that were assigned the two part figure of merit score discussed in the previous section. A detailed description of the important physical and chemical capabilities was provided in Section 2.0; these are reproduced in Table 2. The total possible composite score for the first two categories is 265 out of a possible 400 points, which is 66% of the score. This fact reflects an emphasis in selecting the code with the most complete physical and chemical models.

The capabilities shown in Table 2 under the Numerical Methods category reflect general issues associated with the numerical solution of the governing partial differential equations. An emphasis was placed on codes with capabilities for 2-D simulations. Wave front sharpening is an important consideration in the solution of advection-dominated transport problems and to minimize numerical dispersion. Preference was given to codes with an option to solve the reaction transport equation implicitly versus the more typical operator splitting scheme. Operator splitting schemes are conceptually easier to implement since the reaction and transport equations are solved separately. However, the method is often slow to converge and may have mass balance problems when taking large time steps with radioactive decay (Valocchi and Malmstead 1992). Finally, parallel processing features are considered important when attempting to run problems with a large number of chemical species.

The capabilities listed under the Functionality category were given only a composite figure of merit score since these capabilities do not directly impact the use of the code for performance assessment calculations. The functionality categories considered important were the availability of a graphical user interface, a separate version of the code compiled for parallel computing, familiarity in the waste management community with code (name recognition), public availability of the code, and finally whether the code is under active software quality assurance configuration management.

Each part *a* and *b* figure of merit score was added together to arrive at a composite figure of merit score. Codes having a specific capability were assigned the composite figure of merit score for that capability. Codes not having the capability were assigned a composite figure of merit score of zero for that capability. Figure of merit scores for each code were then tabulated to arrive at a total figure of merit score for the computer code. Table 2 gives a detailed listing of the figure of merit score for each computer code considered. The references used to compile the information on the capabilities of each code are given in Section 5.1 following the formal reference list.

Table 2. List of Engineered-System Code Capabilities and Figure of Merit Scores.[a] References for each code are given at the end of the References section.

Capability List	Merit(a)	Merit(b)	Composite		HYDROGEOCHEM	UT-CHEM	UNSATCHEM-2D	CHMTRNS	CIRF.A	BLT-EC	THCC	DYNAMIX	CHEQMATE	CAT	AREST-CT
Physical Processes															
Solute advection	10	5	15		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Solute diffusion	5	.2	7		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Solute dispersion	8	5	13		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Gas advection	7	5	12			✓	✓								✓
Gas diffusion	7	2	9			✓	✓								✓
Gas dispersion	7	5	12			✓	✓								✓
Water mass conservation	9	10	19			✓	✓								☑
Energy conservation	1	3	4				✓	✓	✓		✓				
Permeability texture relationsh	3	1	4			✓			✓						✓
Fluid density equation of state	1	1	2			✓	✓	✓	✓		✓				✓
					35	93	93	41	45	35	41	35	35	35	74
Chemical Processes															
aqueous complexation	10	8	18		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
acid-base reactions	10	8	18		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
oxidation/reduction	10	10	20		✓			✓	✓	✓	✓	✓	✓	✓	✓
dissolution/precipitation	10	10	20		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
ion-exchange	4	7	11		✓	✓	✓	✓	✓	✓	✓		✓		✓
adsorption(empirical)	8	1	9		✓				✓	✓	✓		✓		✓
adsorption(surface complexati	4	7	11		✓			✓	✓	✓					☑
reaction kinetics	8	9	17					✓	✓					✓	✓
radioactive decay	10	1	11		✓			✓	✓	✓	✓		✓		✓
decay-chain ingrowth	7	10	17							✓					✓
user-defined reactions	10	6	16		✓			✓	✓	✓	✓	✓	✓	✓	✓
					134	67	67	142	151	151	123	92	123	109	157
Numerical Methods															
1-D geometry	10	2	12		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
2-D geometry	10	8	18		✓	✓	✓		✓	✓		✓			✓
3-D geometry	3	10	13			✓						✓			
wave front sharpening	8	5	13			✓									✓
operator splitting	2	3	5		✓		✓			✓		✓	✓	✓	
global implicit	6	8	14			✓		✓	✓		✓				✓
parallellized algorithms	5	8	13											✓	
					35	70	35	26	44	35	26	48	17	30	57
Functionality															
graphical user interface			10						✓	✓				✓	✓
workstation version			2		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
supercomputer version			3												
MPP version			9											✓	
code name familiarity			5		✓			✓				✓	✓		✓
publicly available			8		✓	✓	✓	✓	✓		✓	✓	✓		✓
software quality management			10												✓
					15	10	10	15	20	12	10	15	15	21	35
OVERALL FIGURE OF MERIT			400		219	240	205	224	260	233	200	190	190	195	323

[a]The symbol ☑ denotes a code capability that is under development and was not included in the figure of merit score.

4.0 CONCLUSIONS AND RECOMMENDATIONS

The results from the composite figure of merit scores for the computer codes listed in Table 2 clearly show that the AREST-CT code is the most suitable model for the purposes of conducting performance assessment calculations for the Hanford LLW engineered system. The second highest ranked code is the CIRF.A. This code has been developed by Dr. Peter Ortoleva and his students at the University of Indiana.[a] CIRF.A has been primarily used for the analysis of matrix acidizing process for the U.S. oil and gas industry. Consequently, the code has not been designed for waste disposal applications. In particular, the code lacks capabilities for simulations in unsaturated media and radioactive decay-chain ingrowth processes. On the other hand, the code does have capabilities for simulating nearly all of the required chemical processes, including reaction kinetics. The third highest ranked code is UT-CHEM, which has been developed by Dr. Gary Pope and his students at the University of Texas-Austin. This code met most of the physical process modeling requirements and is also one of the few codes with 3-D modeling capabilities and a wave front sharpening. The principal weakness of this code is that relatively few of the required chemical process models are included, and the code has been designed around a fixed set of components and chemical reactions important to modeling subsurface oil recovery processes.

The AREST-CT code meets all of the general code selection criteria specified in Section 1.1 and nearly all of the desirable features. Desirable feature #1, "The selected code should be certified (that is, simulation results compared with field and/or laboratory data) for a system similar to that being modeled," has not been performed. However, experiments are underway that will be used to confirm the AREST-CT code. Confirmation efforts to date only include verification of the numerical algorithms in AREST-CT. Desirable feature #2, "The degree of complexity of the selected code shall be consistent with the quantity and quality of data and the objectives of the computation," is only partially met. The complexity of the AREST-CT code is consistent with the objectives of the computation to calculate radionuclide release from the engineered system but specific thermodynamic and kinetic data required to run the code have not been meas-

[a]A principal developer of the CIRF.A code is now employed at PNL, which is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

ured for the proposed LLW engineered-system components. However, experimental programs are in progress so that these data will be available for use in AREST-CT calculations.

The AREST-CT code has been developed for the DOE specifically for the analysis of radionuclide releases from waste packages being designed for high-level waste disposal at the proposed Yucca Mountain repository in the state of Nevada. The characteristics of this site, i.e., unsaturated zone, glass waste forms, etc., has led to the incorporation of process models that are directly applicable to assessing the performance of currently anticipated engineered-system designs for the LLW site at Hanford. Hence, the relatively high ranking of this code is to be expected. The fact that this code is also supported for use on a separate DOE program is an additional benefit in lowering the overall cost of code development and maintenance to the DOE.

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