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FERROCYANIDE SAFETY PROGRAM

COMPUTATIONAL ANALYSIS OF FLUID
FLOW AND ZONAL DEPOSITION IN
FERROCYANIDE SINGLE-SHELL TANKS

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October 1993

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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SUMMARY

Safety of single-shell tanks containing ferrocyanide wastes is currently of concern because ferrocyanide, in the presence of an oxidizer like NaNO_3 or NaNO_2 , is explosively combustible when sufficiently concentrated and exposed to elevated temperature. Consequently, evaluating processes that could affect the fuel content of the waste and distribution of the tank heat load is important. Highly alkaline liquid wastes were transferred in and out of the single-shell tanks over several years in the past when the tanks were in active use. Laboratory experiments have shown that $\text{Na}_2\text{NiFe}(\text{CN})_6$ is much more soluble in alkaline media. If convective mixing of alkaline fluids with ferrocyanide wastes occurs, the ferrocyanide could be solubilized and subsequently dispersed or removed from the tank. This process could account for the lower cyanide content measured in some recent core samples than expected from historical records of tank transfers. If $\text{Cs}_2\text{NiFe}(\text{CN})_6$ or $\text{CsNaNiFe}(\text{CN})_6$ is also soluble in alkaline media, solubilization and transport of ^{137}Cs could also occur. Transporting this heat generating radionuclide to a localized area in the tanks is a potential mechanism for generating a "hot spot." Fluid convection could potentially speed the transport process considerably over aqueous diffusion alone.

A stability analysis was performed for a dense fluid layer overlying a porous medium saturated by a less dense fluid. Given several assumptions, it was found that the configuration is unconditionally unstable and independent of the properties of the porous medium or the magnitude (non-zero) of the fluid density difference. Therefore, finger-like convection will always occur in the system under consideration. If this configuration occurred in the tanks, the fluid contents would tend to mix. Maximum velocity estimates for fingering convection in this system are approximately 3 m/yr.

A parametric modeling study of buoyancy-driven flow due to a thermal gradient was also conducted to establish the relationship between the waste physical and thermal properties and natural convection heat transfer. The maximum convection velocities were found to be directly proportional to the hydraulic conductivity of the waste but varied little as a function of tank heat load or thermal conductivity of the waste. Predicted convection velocities assuming typical properties for ferrocyanide wastes were found to be about 0.1 to 0.001 m/yr.

The effects of diffusion and fluid convection on redistribution of the ^{137}Cs in a idealized waste tank were evaluated with a 2-D coupled heat and mass transport model. Redistribution of the ^{137}Cs was predicted to occur in geometrically complex deposition zone assuming a retrograde temperature dependence for the solubility of $\text{Cs}_2\text{NiFe}(\text{CN})_6$. Concentration factors of 10 were found assuming upper bound values for convection velocities. However, the maximum predicted temperature rise associated with the formation of the zones was only 5°C (peak temperature of 65°C) and thus is of no concern in terms of generating a localized area or "hot spot" that could lead to a propagating exothermic reaction.

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1.0 INTRODUCTION

Beginning in the early 1940s, radioactive wastes were generated on the Hanford Site in Washington state from processing irradiated uranium fuels to extract plutonium for the U.S. nuclear weapons program. The wastes are primarily stored underground, as alkaline slurries in 500,000 to 1,000,000 gallon capacity steel tanks. Through 1964, 149 of the tanks were built with a single-shell design (SST) consisting of a concrete shell and steel liner. Beginning in 1971, the design was changed to a double-shell (DST) configuration consisting of a primary and secondary steel tank surrounded by a concrete shell. To date, the total volume of waste in storage is over 40,000,000 gal (Anderson 1990).

During the 1950s, Hanford Site scientists developed a carrier precipitation process to remove radioactive cesium from tank waste liquids. By removing this heat-generating radionuclide from the waste stream, it was possible to discharge the treated liquids to the ground, and thus, obtain additional tank storage space without constructing more tanks. The process utilized salts of either sodium $[\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}]$ or potassium $[\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}]$ ferrocyanide to precipitate the cesium, ideally as $\text{Cs}_2\text{NiFe}(\text{CN})_6$ or $\text{CsNaNiFe}(\text{CN})_6$. In practice, the compound(s) precipitated in the process are not completely known. Overall, 140 metric tons of ferrocyanides were added to the SSTs.

In 1990, safety concerns about the SSTs containing ferrocyanides were raised (Deaton 1990). The safety of these tanks is at issue because ferrocyanide, in the presence of an oxidizer like NaNO_3 or NaNO_2 , is explosively combustible when sufficiently concentrated and exposed to elevated temperatures (Burger and Scheele 1988; Burger and Scheele 1991). The SSTs contain abundant amounts of nitrate and nitrite with molar ratios ranging from 30:1 to 50:1 mol NO_3 : mol $\text{Fe}(\text{CN})_6$ (Grigsby et al. 1992). Consequently, SSTs containing ferrocyanide wastes currently exist in a stable but theoretically combustible state.

Westinghouse Hanford Company instituted a program to resolve safety concerns about the ferrocyanide wastes in SSTs. The fundamental goal of this program is to determine whether existing or future conditions in the SSTs are consistent with the conditions needed to support explosive combustion of ferrocyanide wastes and if so, to recommend corrective action. To conduct this analysis, it is necessary to know 1) the quantities of ferrocyanide and oxidant that are needed to support a runaway exothermic reaction, 2) the temperature required for the onset of combustion, and 3) the concentrations of heat-generating radionuclides needed to achieve combustion temperatures.

Item 1 can be easily determined from thermodynamic principles. Using historical records of tank waste transfer operations to estimate ferrocyanide concentrations, studies show that peak ferrocyanide concentrations ($\sim 0.35 \text{ M}$) in some SSTs are sufficient to support a propagating reaction, provided the water content of the sludge is below 12 to 15 wt%. For item 2, laboratory investigations of the energetics of ferrocyanide reactions with nitrate and nitrite salts show that runaway exotherms do not occur below temperatures of at least 220 to

250°C. Although temperatures are measured at only one location in the SSTs, maximum temperatures are less than 55°C, far below the required ignition temperature. Barring development of a thermally isolated zone or "hot spot" that is not being monitored, the ferrocyanide wastes are safe from a propagating exothermic reaction under these conditions.

Studies concerning item 3 have used heat conduction models assuming various geometries and boundary conditions for a "hot spot" to determine the radionuclide concentrations needed to achieve combustion temperatures of 220°C+. The most significant finding from these studies is that both lateral and axial concentration of the heat load must occur to generate temperatures of 170°C+ with corresponding radionuclide concentrations 20 to 500 times larger than average values. Relatively large spheres or cubes (2 to 3 m radius or cube edge) require the smallest concentration factors of ~20 to 75 (Dickinson et al. 1993).

The heat conduction models used to analyze "hot spots" in the SSTs are incapable of modeling the effects of fluid flow or mass transport. These processes have potentially significant effects on the availability of ferrocyanide fuel to support a propagating reaction and development of a "hot spot." Highly alkaline liquid wastes were transferred in and out of the SSTs over several years in the past when the tanks were in active use. Laboratory experiments have shown that $\text{Na}_2\text{NiFe}(\text{CN})_6$ is much more soluble in alkaline media (Lilga et al. 1992). The transfer of alkaline waste streams into the SSTs may have allowed dissolution of the ferrocyanide that could then diffuse and possibly be convected away from the original precipitate, and finally, removed from the tank during a subsequent liquid transfer operation. Solubilization and transport of the ferrocyanide have two effects. First, the fuel concentration is lower, and thus, the possibility of generating a propagating exothermic reaction is reduced. Second, in the event of an exotherm, less energy is released, and thus, the amount of radioactive material dispersed would be smaller. If $\text{Cs}_2\text{NiFe}(\text{CN})_6$ or $\text{CsNaNiFe}(\text{CN})_6$ is also soluble in alkaline media, solubilization and transport of ^{137}Cs could also occur. Transport of this heat generating radionuclide to a localized area in the tanks is a potential mechanism for generating a "hot spot." Fluid convection could speed the transport process considerably over aqueous diffusion alone.

The purpose of this report is to address issues associated with fluid motion and mass transport in SSTs. However, these processes will be treated separately in this report. Analysis using a highly complex coupled fluid-heat-chemical-transport model is not currently justified given the current sparsity of available physical and chemical data on ferrocyanide wastes. Also, we selected simpler models that could be run many times to get a better understanding of parameters that significantly affect either fluid motion or the redistribution of ^{137}Cs .

2.0 FINGERING CONVECTION IN FERROCYANIDE TANKS

A linear stability analysis was performed for a case where a semi-infinite, dense, fluid layer overlies a semi-infinite porous medium saturated with a less dense fluid. Several assumptions were necessary to obtain a closed form solution to the problem. The assumptions considered in the analysis include

- inviscid overlying fluid
- neglect species transport between the fluid layers
- neglect the inertia, Forchheimer, and Brinkman terms in the porous flow equations
- neglect thermal effects
- neglect surface tension effects
- homogeneous isotropic porous matrix
- layers are semi-infinite.

The effect of the overlying fluid viscosity is to decrease the magnitude of the disturbance amplification rate at high wavenumbers. That is, disturbances with very small spatial wavelengths (on the order of 1 mm) grow more slowly than those with larger wavelengths. Since the viscosity of the overlying fluid does not determine the global system stability (the sign of the amplification rate), it can be neglected (Chen and Lu 1991). Since we are interested in the onset of convection from a stationary state, the inertia and Forchheimer drag terms can be neglected. The Brinkman term is only important in porous flows near impermeable walls, hence it is neglected.

Surface tension forces can be a powerful stabilizing force within a porous medium if the two fluids are immiscible. The surface tension force, in that case, is inversely proportional to the pore size in the porous matrix. However, if the two fluids are miscible, no surface tension exists and can be neglected. While it is unlikely that the actual salt cake is homogeneous or isotropic, deviations from this assumption would likely destabilize the system through channeling phenomena. The assumption of a semi-infinite medium allows for closed form solutions and does not influence the sign of the amplification rate because the underlying physical mechanisms are independent of the boundary conditions. For these reasons, the above assumptions will yield a conservative solution for the convective stability of the system in question. The assumptions are realistic if, in fact, the contents and conditions of some of the ferrocyanide tanks correspond to a denser fluid overlying a fluid-saturated porous matrix.

2.1 THEORY

After using the assumptions discussed above, linear stability theory can be used to determine whether the system, composed of a fluid layer of density ρ_2 overlying a layer of porous medium saturated with a fluid of density ρ_1 , is stable or not (Chandrasekhar 1961). The analysis can be simplified by assuming that the fluid layer and the fluid-saturated porous

layer extend to infinity in the horizontal direction and are semi-infinite in the vertical direction as depicted in Figure 2.1.

The linearized perturbation continuity and momentum equations for the fluid layer are

$$\frac{\partial \rho'}{\partial t} = 0 \quad (2.1)$$

$$\rho_2 \frac{\partial U}{\partial t} = -\nabla P + \mu \nabla^2 U - g \rho' \quad (2.2)$$

The same equations for the porous layer are

$$\frac{\partial \rho'_m}{\partial t} = 0 \quad (2.3)$$

$$\frac{\rho_1}{\phi} \frac{\partial U_m}{\partial t} = -\nabla P_m - \frac{\mu}{K} \nabla^2 U_m - g \rho'_m \quad (2.4)$$

where

- ρ' = perturbation density in the fluid layer
- ρ'_m = perturbation density in the porous layer
- ρ_1 = density of the fluid in the porous layer

Figure 2.1. Schematic of Fluid Layers for Stability Analysis

ρ_2 = density of the fluid layer
 $\mathbf{U}$ = perturbation velocity vector in the fluid layer
 $\mathbf{U}_m$ = perturbation velocity vector in the porous layer
 P = perturbation pressure in the fluid layer
 P_m = perturbation pressure in the porous layer
 μ = viscosity of the fluid in both layers
 $\mathbf{g}$ = gravitational acceleration vector
 K = permeability of the porous medium
 ϕ = porosity of the porous medium

A normal mode analysis is performed by considering that the perturbation quantities for both layers have a horizontal periodic structure in space of the form

$$\begin{bmatrix} \mathbf{U} \\ \mathbf{U}_m \\ P \\ \rho' \end{bmatrix} = \begin{bmatrix} \mathbf{u}(z) \\ \mathbf{u}_m(z) \\ p(z) \\ \rho(z) \end{bmatrix} e^{\sigma t + i(a_1 x + a_2 y)} \quad (2.5)$$

where the horizontal wavenumber a is given by

$$a^2 = a_1^2 + a_2^2. \quad (2.6)$$

Then after some algebra and neglecting viscosity it can be obtained that for the fluid layer the perturbation equation for the vertical component of the velocity w is

$$\frac{d^2 w}{dz^2} - a^2 w = 0. \quad (2.7)$$

For the porous layer the corresponding equation is

$$(K\rho_1\sigma^2 + \phi\mu\sigma) \left(\frac{d^2 w_m}{dz^2} - a^2 w_m \right) = 0. \quad (2.8)$$

This implies that the solution for w in the upper layer is

$$w = w(0)e^{-az} \quad (2.9)$$

and that for w_m in the lower layer is

$$w_m = w_m(0)e^{az}. \quad (2.10)$$

Note that both solutions are bounded at $z = +\infty$ and $z = -\infty$, respectively.

Figure 2.2. Schematic of Interface Perturbation

The question to be answered in this stability analysis is whether or not disturbances will grow or decay at the interface between the two layers. Focusing attention in an interface between miscible fluids, surface tension effects need not be considered. At the interface, the velocities and shear stresses are continuous. Thus, a dispersion relation can be obtained by matching the perturbation pressures that arise as a result of a disturbance, δ' , at the interface (Figure 2.2)

$$\delta' = \delta(z)e^{\sigma t + i(a_1 x + a_2 y)}. \quad (2.11)$$

The following velocity condition must be satisfied:

$$w(0)e^{\sigma t + i(a_1 x + a_2 y)} = w_m(0)e^{\sigma t + i(a_1 x + a_2 y)} = \left. \frac{\partial \delta'}{\partial z} \right|_{z=0} \quad (2.12)$$

where the mean surface approximation has been invoked. The time-dependent, linearized perturbation Bernoulli equation for the fluid layer is

$$\frac{\partial \varphi'}{\partial t} + \frac{P}{\rho_2} + gz = 0 \quad (2.13)$$

where φ' is the perturbation velocity potential. Enforcing the kinematic condition at $z=0^+$ yields

$$p^+ = -\rho_2 \left[g - \frac{\sigma^2}{a} \right] \delta(0). \quad (2.14)$$

For the porous layer the analog of Equation (2.13) is

$$\frac{1}{\phi} \frac{\partial \varphi'}{\partial t} + \frac{P}{\rho_1} + \frac{\mu}{\rho_1 K} + gz = 0. \quad (2.15)$$

By similar reasoning at $z=0^-$

$$p^- = - \left[\rho_1 g + \rho_1 \frac{\sigma^2}{\phi a} + \sigma \frac{\mu}{Ka} \right] \delta(0). \quad (2.16)$$

At the interface, both expressions for the pressure must match. Solving for the most unstable value of the growth rate

$$\sigma = \frac{\mu}{2 \left(\frac{\rho_1}{\phi} + \rho_2 \right) K} \left[-1 + \sqrt{1 + \frac{8\pi(\rho_2 - \rho_1) \left(\frac{\rho_1}{\phi} + \rho_2 \right) g K^2}{\mu^2 \lambda}} \right]. \quad (2.17)$$

Note that if $\rho_2 > \rho_1$, then the growth rate will always be positive and the system will always be unstable to all wavelengths.

2.2 DISCUSSION

The most important result of the above analysis is that a dense fluid layer overlying a porous medium that is saturated by a less dense fluid is unconditionally unstable, given that the fluids are miscible. *Finger-like convection always occurs for this configuration.* Simple checks of Equation (2.17) can be made by considering certain limiting cases. If the porosity is zero, the stability is neutral (in this limit $\sigma \rightarrow \phi^{1/2}$). If the densities are equal, the stability is neutral. If the overlying fluid is less dense, the system is unconditionally stable. These limiting cases are all consistent with logical expectations. This result is consistent with the experimental observations of Kerr and Tait (1985) who reported that "Immediately after introduction of the upper layer, small fingers of heavy fluid developed at the top of the porous medium." Similar experimental observations were observed by Wooding (1959).

Figure 2.4 shows the growth rate as a function of the wavelength of the disturbance for the following parameters:

$$\begin{aligned} \rho_1 &= 1000 \text{ kg/m}^3 \\ \rho_2 &= 1100 \text{ kg/m}^3 \\ \mu &= 1.12 \times 10^{-3} \text{ Pa}\cdot\text{s} \\ K &= 1.97 \times 10^{-12} \text{ m}^2 \\ \Phi &= 0.3. \end{aligned}$$

Note that short wavelengths are the most unstable. The simplifying assumptions in our analysis cannot yield the most critical wavelength which depends on the particular

Figure 2.4. Growth Rate of Interface Perturbation as a Function of the Wavelength of the Disturbance

structure of the porous matrix (which is not known experimentally). In addition, length scales associated with inhomogeneities in the porous matrix may affect the wavelength of disturbances and thus, the size of the convecting fingers. Even so, the order of magnitude of the growth rate can be estimated using Equation (2.17).

2.2.1 Propagation Velocity of Fingers

From the previous analysis, it can be shown that the functional dependence of the perturbation velocity is

$$w \propto \frac{(\rho_2 - \rho_1)gK}{\mu}. \quad (2.18)$$

However, a proportionality constant, that must be determined experimentally, is needed for the above expression. The velocity at which fingers propagate downward (V_F) in the porous matrix can be written as

$$V_F = C \frac{(\rho_2 - \rho_1)gK}{\phi\mu}. \quad (2.19)$$

where C is a constant. Kerr and Tait (1985) estimated this constant to be 0.55 where fingers move downward from the interface into a porous matrix comprised of glass beads. Measurements for the ferrocyanide simulants show that the porosity value lies between 0.6 and 0.7, and that 97% of the particle size in the porous matrix is between 2 and 3 μm (Jeppson and

Wong 1993). Based on the particle diameter, d , the permeability K can be estimated using the Rumpf and Gupta correlation (Kerr and Tait 1985)

$$K = \frac{d^2 \phi^{5.5}}{5.6}. \quad (2.20)$$

For a porosity of 0.65 and particle diameter of $2.5 \mu\text{m}$, the permeability is approximately 10^{-13} m^2 . Tables 2.1 and 2.2 show the effects of varying the porosity and permeability on the finger velocity and the time it takes for a finger to penetrate 1 m below the fluid-porous layer interface.

Table 2.1. Effect of Sludge Porosity and Permeability on Finger Velocity for Values of $\rho_1=1000 \text{ kg/m}^3$, $\rho_2=1100 \text{ kg/m}^3$, and $\mu=1.12 \times 10^{-3} \text{ Pa}\cdot\text{s}$

Porosity	Permeability [m^2]	Finger Velocity [m/sec]	Time to penetrate 1 m [months]
0.50	2.47×10^{-14}	2.38×10^{-8}	16.2
0.55	4.17×10^{-14}	3.65×10^{-8}	10.6
0.60	6.72×10^{-14}	5.40×10^{-8}	7.1
0.65	1.04×10^{-13}	7.74×10^{-8}	5.0
0.70	1.57×10^{-13}	1.08×10^{-7}	3.6

Table 2.2. Effect of Sludge Porosity and Permeability on Finger Velocity for Values of $\rho_1=1000 \text{ kg/m}^3$, $\rho_2=1500 \text{ kg/m}^3$, and $\mu=2.0 \times 10^{-3} \text{ Pa}\cdot\text{s}$

Porosity	Permeability [m^2]	Finger Velocity [m/sec]	Time to penetrate 1 m [months]
0.50	3.55×10^{-14}	9.58×10^{-8}	4.0
0.55	6.00×10^{-14}	1.47×10^{-7}	2.6
0.60	9.68×10^{-14}	2.17×10^{-7}	1.8
0.65	1.50×10^{-13}	3.12×10^{-7}	1.2
0.70	2.26×10^{-13}	4.35×10^{-7}	0.9

In the analysis presented here, fingering convection was analyzed assuming the waste behaves as an isotropic porous solid. However, because of sedimentation processes that have occurred in the tanks, this model may be an unrealistic representation of the waste. The

actual convection process is likely to be dependent on the precise morphology of the porous matrix. Anisotropic permeability of the waste may suppress or enhance convection patterns because of the anisotropic resistance to motion in the porous medium. This in turn could affect the temperature distribution and transport within the tank. The distribution of solutes throughout the tank could also be enhanced by thermally-induced convection in the porous layer. Internal heat generation within the porous layer could lead to a hydrostatically unstable stratification, and hence, convection. This will be discussed in Section 3.0.

Further experiments in a model isothermal tank using the ferrocyanide waste simulants could be carried out to obtain more precise correlations between mixing times and the porous matrix parameters. Mixing can be assessed by using conductivity probes at various locations within the porous matrix. By identifying the relevant dimensionless numbers, the experimental data could be extrapolated to give good estimates of mixing times in a real system.

3.0 NATURAL CONVECTION IN HEAT GENERATING POROUS BEDS

A numerical modeling study, of limited scope, was conducted to explore the role of natural convection in transporting chemical constituents and cooling ferrocyanide waste tanks. Density driven flows in porous materials are typically very slow, but might play a significant role in reducing maximum temperatures, and in distributing certain chemical species in porous waste beds.

Density driven flow of incompressible fluids in saturated porous media results from temperature differences caused by internal heat generation or by differences in system boundary temperatures. Flow resistance is caused by viscous and form drag forces as the fluid is forced through the interstitial space of the porous media. Under certain conditions, turbulent effects will contribute to the flow resistance. Material physical properties such as density, specific heat, and thermal conductivity also play an important role in the thermal hydraulic behavior of the porous system.

Exploratory simulations were conducted using the TEMPEST computational fluid dynamics and heat transfer computer code (Trent and Eyler, 1993). TEMPEST has the capability to model three-dimensional, transient or steady-state, thermal hydraulics in porous beds and coupled open flow regions. Flow resistance in porous media can be modeled with the TEMPEST code using any of the following options: 1) Darcy models, 2) Ergun particle bed correlations, or 3) form and friction drag correlations (Bird, Stewart, and Lightfoot, 1960). Both the Ergun correlation and friction drag correlations were used in the current study.

This work includes

- parametric analyses to explore the relative influence of natural convection heat transfer in one-dimensional heat-generating porous beds
- parametric simulations of two-dimensional heat generating porous beds with constant boundary temperatures
- simulation of systems more representative of SSTs where the dome space and surrounding earth are included in the analysis.

In the first two cases, modeling studies were conducted to establish the relationship between the bed hydraulic conductivity and natural convection heat transfer for a given set of bed parameters. In the third case, conditions more typical of a SST were modeled to establish the role of natural convection for several different physical parameters.

This work deals only with exploratory calculations that were conducted to obtain order-of-magnitude temperature and velocity information. Therefore, the values used for physical properties, geometry, and heat generation rates were only roughly approximated, or else parametric values were used. Simulations involving the more complete tank systems were not directed to any specific tank, but toward generic tanks having porous-bed wastes. Accurate simulation of a specific tank (which was not the intention of this study) would require detailed and specific input data for that system. Therefore, results obtained in this study are useful only for understanding thermally-driven convection processes in saturated porous media having SST geometry, and for order-of-magnitude estimates of temperature and convection velocities given different heat generation rates and hydraulic conductivities.

3.1 THERMAL CONVECTION AND DIFFUSION IN POROUS BEDS

A quantitative understanding of the relationship between bed hydraulic conductivity and convective/diffusive heat transfer mechanisms can be developed by considering one-dimensional flow in a heat generating porous bed as shown in Figure 3.1. As illustrated by this figure, fluid at temperature T_0 is induced vertically through the porous bed as a result of the heat generation, $\dot{q}$, and exits at temperature T_L . Heat generation causes the bed and fluid temperature to rise. As the bed temperature increases, the fluid density decreases (fluid expands). The fluid is then more bouyant than the surroundings and rises through the column with a flow rate that depends on the bed flow resistance and temperature rise, ΔT . It is assumed that the convecting fluid remains single-phased even though the computed temperature may be greater than the boiling point.

An order-of-magnitude relationship between convective and diffusive heat transport mechanisms can be obtained using the definition of the Peclet Number

Figure 3.1. Heat Generating Porous Bed

$$Pe = \frac{\rho c_p UL}{\kappa} \quad (3.1)$$

where U = fluid velocity, m/s
 L = characteristic length, m
 κ = thermal conductivity, J/m-s-K
 ρ = density, kg/m³
 c_p = specific heat, J/kg-s

In this approximation, the thermal conductivity, κ , is associated with the aggregate saturated porous material, whereas the density, ρ , and specific heat, c_p , have values of the fluid.

The superficial fluid velocity, U , is given by

$$U = -\frac{K_H}{\rho g} \frac{\Delta P}{L} \quad (3.2)$$

where ΔP = pressure drop, Pa
 g = gravity, m/s²
 K_H = Hydraulic conductivity, m/s.

The pressure difference, ΔP , available for driving convection caused by the fluid density difference is

$$\Delta P = \Delta \rho g L \quad (3.3)$$

Thus,

$$U = -K_H \frac{\Delta \rho}{\rho} = K_H \beta \Delta T \quad (3.4)$$

where

$$\Delta \rho = -\left(\frac{\partial \rho}{\partial T}\right) \Delta T \quad (3.5)$$

and for an incompressible fluid, the coefficient of expansion, β , is defined as

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T}\right) \quad (3.6)$$

Inserting Equation (3.4) into the Pe number definition, Equation (3.1), yields

$$Pe = \frac{K_H L}{\left(\frac{\kappa}{\rho c_p} \right)} \beta \Delta T. \quad (3.7)$$

For non-flowing systems, the maximum temperature increase over the length, L , is

$$\Delta T_{\max} = \frac{\dot{q} L^2}{2\kappa}. \quad (3.8)$$

Inserting this expression into Equation (3.7) gives

$$Pe = \frac{K_H L}{\left(\frac{\kappa}{\rho c_p} \right)} \left(\frac{\beta \dot{q} L^2}{2\kappa} \right) \quad (3.9)$$

which is an order-of-magnitude measure of the thermal convection/diffusion ratio. Equation (3.9) infers that for small values of Pe , natural convection can be eliminated from the thermal hydraulic analysis because temperature distributions will be dominated by conduction. The maximum convection velocity for this situation is

$$U_{\max} = K_H \left(\frac{\beta \dot{q} L^2}{2\kappa} \right). \quad (3.10)$$

3.2 PHYSICAL PROPERTIES

Material properties used in this study are summarized in Table 3.1. Property values listed in this table might not be the best values to use in analyzing a particular tank, but are thought to be representative of Hanford SST waste storage systems. Because this study is concerned with relative effects of convection and conduction, highly accurate values for the physical properties are not needed.

3.3 ONE-DIMENSIONAL PARAMETRIC STUDIES

Inserting values listed in Table 3.1 in Equation (3.7) yields $Pe = 1.51 \times 10^6 K_H L \beta \Delta T$. The maximum temperature change, $\Delta T_{\max}$, that would occur for pure conduction where the heat generation rate, $\dot{q} = 5 \text{ W/m}^3$, $L = 10 \text{ m}$, and thermal conductivity, $\kappa = 2.3 \text{ J/m-s-K}$ is

Table 3.1. Property Values Used in Thermal Modeling

Material	Thermal conductivity	Density	Specific Heat	Dynamic Viscosity	Emissivity
	W/m-K	kg/m ³	J/kg-K	kg/m-s	
Waste	2.3	1580	2200	0.024	0.9
Concrete	0.93	2240	837		0.9
Earth	0.88 & 1.76	1680	2200	N/A	N/A

The surrounding earth was assumed to be sand with 20% saturation and 0.4 void fraction with property values given by Hillel (1980). The thermal conductivity and density values for the ferrocyanide waste were taken from the simulant data of Jeppson and Wong (1993). Because no literature values of specific heat and liquid viscosity were found, the waste specific heat was estimated as that of earth and the liquid viscosity was taken as 0.024 Pa-s (kg/m-s). The emissivities for radiative thermal transfer are similar to those given by Welty et al. (1976). Properties of the dome air were obtained from the TEMPEST computer code properties library.

$$\Delta T_{\max} = \frac{qL^2}{2\kappa} = 108.7^\circ\text{C}. \quad (3.11)$$

The coefficient of thermal expansion, β , will vary by a factor of about 10 over the temperature range of interest. Therefore, an approximate mean value is assumed to be $\beta = 1.5 \times 10^{-4}/^\circ\text{C}$. The Peclet number for these parameters is $Pe = 2.46 \times 10^5 K_{II}$. Simulant data from Jeppson and Wong (1993) indicates that hydraulic conductivity of the ferrocyanide may be on the order of 5×10^{-8} m/s which is on the same order as hard rock conductivity (de Marsily, 1986). Thus, $Pe_{\max} = 0.0123$, indicating that natural convection would play a very small role in transferring heat within the heat generating waste material. Using the Peclet number to estimate the relative influence of natural convection is, at best, a very rough approximation.

The estimated maximum convection velocity, $U_{\max}$, for these data is

$$U_{\max} = K_{II}\beta\Delta T = (1.5 \times 10^{-4})(108.7) K_{II} = 1.63 \times 10^{-2} (5 \times 10^{-8}) = 8.15 \times 10^{-10} \text{ m/s}.$$

Numerical results for this one-dimensional porous bed problem were also obtained using the TEMPEST computer code. Temperature distributions for various values of hydraulic conductivity, K_{II} , are illustrated in Figure 3.2 for a uniform heat generation rate of 5 W/m^3 . For high values of hydraulic conductivity, the temperature profile varies nearly linearly with increasing elevation which indicates that heat transfer is dominated by convection. For small

Figure 3.2. Vertical Temperature Profiles as a Function of Hydraulic Conductivity. One-dimensional particle bed with heat generation rate of 5 W/m^3 .

Figure 3.3. Convection Velocity as a Function of Hydraulic Conductivity. One-dimensional particle bed with heat generation rate of 5 W/m^3 .

values of hydraulic conductivity, ($<10^{-7}$ m/s), the temperature profile has a parabolic shape, typical of pure conduction heat transfer. Thus, in this range of hydraulic conductivity values, heat transfer occurs almost entirely by conduction. Mixed natural convection/conduction occurs in the mid-range of hydraulic conductivity values, i.e., 10^{-3} to 10^{-7} for the data used.

Figure 3.3 shows convection velocity as a function of hydraulic conductivity. As expected, the convection velocities for very low values of hydraulic conductivity are also very low. For the case of $K_H=5 \times 10^{-8}$, liquid would move about 1 cm/year as result of natural convection. However, if K_H were 5×10^{-5} (1000 time greater), the liquid might move as much as 3 meters during a year, which might be significant.

3.4 TWO-DIMENSIONAL PARAMETRIC STUDIES

The one-dimensional analysis presented in the previous section assumed open boundary conditions, and thus, predicts convection velocities larger than those expected for a closed, recirculating system. Parametric analysis were, therefore, done for an idealized two-dimensional tank as described below.

3.4.1 Idealized Tank Model

Figure 3.4 illustrates the cylindrical coordinate computational grid system used for the two-dimensional computer simulations. The porous media model used for this analysis

Figure 3.4. TEMPEST Computer Model Grid System

of 24 computational cells in the radial direction, and 22 in vertical direction. The cell thickness is constant at 0.5 m in both the radial and vertical directions. Properties are assumed to be spatially uniform for the porous media, with values given in Table 3.1. Lateral and vertical dimensions are similar to those of the waste layer in SSTs. The heat generation rate for this model is 2.0 W/m^3 which is typical of current heat generation rates for certain SSTs (Burger et al. 1991). The boundary temperatures were assumed to be constant at 20°C .

Steady-state simulations were conducted using a range of hydraulic conductivities. Vertical temperature profiles for these simulations are illustrated in Figure 3.5. The maximum temperature increase for this case is about 11°C , which provides very little potential for natural convection. For the exponent, n , greater than about 4, there is no noticeable effect of convection velocity on the temperature distributions. For $2 < n < 4$, the flow is in a mixed convection/diffusion heat transfer regime. For very large values of hydraulic conductivity ($n \approx 1$ or less), the heat transfer is dominated by convection and the flow field becomes marginally stable. That is, small changes in the top boundary temperature distribution will cause major readjustment of the flow field in the porous bed.

Isotherms and convection velocity vectors are illustrated in Figures 3.6 and 3.7, respectively, for a porous bed having hydraulic conductivity, $K_H = 5 \times 10^{-8} \text{ m/s}$. In this case, the convection velocities are very small, being in the range of 1×10^{-12} to $4 \times 10^{-11} \text{ m/s}$. Thus, the temperature distribution within the porous bed develops from pure conduction. Results shown in Figure 3.5 indicate that the hydraulic conductivity must increase to about 10^{-3} m/s before convection begins to influence the bed temperature distribution.

Figure 3.5. Vertical Temperature Profiles as a Function of Hydraulic Conductivity at the Bed Centerline

Figure 3.6. Isotherms for $K_H = 5 \times 10^{-8}$, $\dot{q} = 2.0 \text{ W/m}^3$

Figure 3.7. Velocity Vectors for $K_H = 5 \times 10^{-8}$, $\dot{q} = 2.0 \text{ W/m}^3$.
 $U_{\max} \approx 4.4 \times 10^{-11} \text{ m/s}$.

Figure 3.8. Isotherms for $K_H = 5 \times 10^{-2}$, $\dot{q} = 2.0 \text{ W/m}^3$

Figure 3.9. Velocity Vectors for $K_H = 5 \times 10^{-2}$, $\dot{q} = 2.0 \text{ W/m}^3$.
 $U_{\max} \approx 3.0 \times 10^{-6} \text{ m/s}$.

Figures 3.8 and 3.9 show isotherms and velocity vectors, respectively, for a bed having hydraulic conductivity, $K_H = 5 \times 10^{-2}$ m/s. In this case, flow resistance of the porous bed is significantly diminished and the small, thermally induced pressure difference causes substantial fluid circulation. This circulation causes the maximum temperature of the bed to be reduced to about 50% of that for pure conduction case. Maximum velocities are approximately 3×10^{-6} m/s. In both cases the maximum velocity occurs near the vertical, constant temperature boundary where the fluid is the coldest. Typical velocities, which are remote from this boundary, are reduced by about 50% of the maximum velocity.

Figure 3.10 illustrates centerline temperature profiles for various values of hydraulic conductivity where the bed heat generation rate is assumed to be much higher (26.8 W/m^3). This heat load is based on an assumed upper bound for Hanford tank waste heat generation (Burger, et al. 1991) but is much higher than in any of the ferrocyanide tanks. The maximum temperature change in this case is 157.6°C (for the purpose this analysis, we assume that boiling does not occur).

As was found in the preceding analysis, conduction dominates the heat transfer for beds having a low hydraulic conductivity (because convection velocities are very small). This is also true in the present case, where the thermal driving potential for convection is much higher. In the previous case, convection became significant when the hydraulic conductivity was increased to about 5×10^{-3} . In this case, convection begins to affect the temperature profile when the hydraulic conductivity is larger than about 5×10^{-5} . Increasing the heat generation rate by a factor of about 15 increases the convection effect by a factor of about

Figure 3.10. Vertical Temperature Profiles as a Function of Hydraulic Conductivity

100. This factor can also be established by forming a Peclet number ratio for the two situations using Equation (3.9).

Temperature contours and velocity vectors are illustrated in Figures 3.11 and 3.12, respectively, for the case $K_H = 5 \times 10^{-4}$. Isotherms (Figure 3.11) show a somewhat stratified temperature field. The maximum temperature has diminished considerably ($T_{\max} = 121.4^\circ\text{C}$) from the previous case and has shifted the location upward from the center of the bed because of convection (Figure 3.12). The convection velocities are considerably stronger than for the heat generation rate of 2 W/m^3 case because the thermal driving force is much larger.

The two-dimensional analysis presented in this section indicates that convection heat transfer is insignificant if the bed heat generation rate is about 2 W/m^3 and hydraulic conductivity is less than about 10^{-3} m/s . For low heat generation rates, the thermal driving potential for natural convection is very weak. This results in very weak convection currents for beds where the hydraulic conductivity is less than about 10^{-3} m/s . However, for higher heat loads the circulating convection currents, can be substantial and might be important in mobilizing certain chemical species.

3.4.2 Tank System Model

In the third step of this analysis, a simplified tank system model is constructed to incorporate actual boundary conditions more realistically. This model, illustrated in Figure 3.13, includes the surrounding earth, concrete shell, and dome space in addition to the heat-generating waste. The modeled tank consists of a concrete shell 15.25 cm (6 in) thick with a radius 11.6 m (38 ft) and a height of 16.5 m (54 ft). Within this shell, the bottom 11.6 m was filled with a homogeneous waste mixture where heat is generated; the remaining 4.88 m (16 ft) above the waste was modeled as an air space through which convective and radiative thermal transfer occur. The shell is buried beneath 3.0 m (10 ft) of earth and the computational domain includes earth within 9.8 m (32 ft) radially from the tank and 8.5 m (28 ft) beneath the tank.

Figure 3.13 also illustrates the heat transfer mechanisms modeled in each region. The TEMPEST code has the capability to model combined conduction, convection, and radiation. Heat transfer in the concrete shell and the earth surrounding the tank was modeled as pure conduction. The dome air space was modeled as a convecting region with radiation heat transfer from the surface of the waste material to top of the dome. The TEMPEST k- ϵ turbulence model was employed for computing the turbulent fluid dynamics and heat transfer in the dome space.

Simulations were conducted using transient methods as well as "false" transient and steady-state options to obtain steady-state temperature distributions. The computer time used for each simulation was minimal, requiring no more than a few minutes on a Hewlett-Packard Model 730 workstation or about 20 minutes on an Apple MacIntosh Quadra 950.

Figure 3.11. Isotherms for $K_{II} = 5 \times 10^{-4}$, $\dot{q} = 26.8 \text{ W/m}^3$

Figure 3.12. Velocity Vectors for $K_{II} = 5 \times 10^{-4}$, $\dot{q} = 26.8 \text{ W/m}^3$.
 $U_{\max} \approx 1.5 \times 10^{-6} \text{ m/s}$

Figure 3.13. Schematic Diagram of Tank System

Table 3.2. Summary of Test Cases

Case	Hydraulic Conductivity	Heat Generation		Soil Thermal Conductivity	
	(m/s)	(kW)	(W/m ³)	(W/m-K)	(Btu/hr-ft-°F)
1	5x10 ⁻⁸	30	6.2	1.76	1.0
2	5x10 ⁻⁸	10	2.0	1.76	1.0
3	5x10 ⁻⁸	30	6.2	0.88	0.50
4	5x10 ⁻⁸	10	2.0	0.88	0.50
5	5x10 ⁻⁶	30	6.2	1.76	1.0
6	5x10 ⁻⁴	30	6.2	1.76	1.0
7	5x10 ⁻¹¹ (Pure conduction)	30	6.2	1.76	1.0

Seven cases were considered, as summarized in the Table 3.2. These were chosen to demonstrate the effects of hydraulic conductivity, heat generation, and thermal conductivity on the role of thermal convection in the tank waste. Case 1 is considered to be the "base case" with the other cases having one to three quantities varied from this base case.

The base hydraulic conductivity value of 5x10⁻⁸ was taken from the simulant data of Jeppson and Wong (1993). This was varied by several orders of magnitude (from 5x10⁻¹¹ to 5x10⁻⁴). The variety of heat generation values was inferred from Burger et al. (1991) who reported that hot spots were observed in tanks with heat generation > 30 kW although none of the Hanford waste tanks currently generate more than 33 kW. The thermal conductivities were also taken from the data of Jeppson and Wong (1993), who reported that conductivities in the simulants varied from 2.0 to 2.6 W/m-K.

3.4.2.1 Results

Calculations were performed using the model for the cases as described in Table 3.2. Comparisons were made based on the maximum temperatures, maximum velocities, and the temperature distributions that were observed for each case. Figure 3.14 gives contours of the temperature distribution for Case 1 along with the velocity vectors indicating the convection velocities within the air space above the waste. Figure 3.15 gives these contours within the tank region only. The vectors shown in Figure 3.15 indicate the convection velocities within the waste.

Figure 3.14. Temperature Contours and Velocity Vectors for Case 1.
 $K_H = 5 \times 10^{-8} \text{ m/s}$; $\dot{q} = 6.2 \text{ W/m}^3$; $\kappa = 1.76 \text{ W/m-K}$.

Figure 3.15. Temperature Contours and Velocity Vectors Inside Tank for Case 1. $K_H = 5 \times 10^{-8} \text{ m/s}$; $\dot{q} = 6.2 \text{ W/m}^3$; $\kappa = 1.76 \text{ W/m-K}$.

3.4.2.1.1 Hydraulic conductivity

Hydraulic conductivity of the waste material was varied from 5×10^{-11} to 5×10^{-4} in Cases 7, 1, 5, and 6. The results are presented in Table 3.3. The results indicate that, for these values of material properties and heat generation, thermal convection mechanisms do not significantly affect the steady-state temperature distributions within the waste. In these cases, only when the hydraulic conductivity is much higher than 5×10^{-6} m/s is there any significant change in the temperature profiles. Large thermal convection cells like those shown in Figure 3.15 develop even with the lower values of hydraulic conductivity, but have little effect on the temperature distribution when the convection velocities are less than 10^{-7} m/s.

Increasing the hydraulic conductivity to 5×10^{-4} m/s results in slight changes in the temperature and velocity distributions. These are evident in the temperature contours of Figure 3.16 (Case 6). The maximum temperature for this case is more than 9°C lower ($\approx 8\%$ decrease) than the case where the hydraulic conductivity is 5×10^{-8} m/s. The region of maximum temperature is lifted and more diffuse, particularly in the horizontal direction because of the increase in the peak convection velocity from 10^{-10} to 10^{-7} m/s. The shape of the convection roll also shifts slightly upward and toward the tank wall.

Table 3.3. Temperature and Velocity Variations as a Function of Hydraulic Conductivity

Case	Hydraulic Conductivity	Maximum Temperature	Maximum Velocity
	(m/s)	($^\circ\text{C}$)	(m/s)
7	5×10^{-11}	114	10^{-13}
1	5×10^{-8}	114	10^{-10}
5	5×10^{-6}	114	10^{-9}
6	5×10^{-4}	105	10^{-7}

3.4.2.1.2 Heat Generation

Waste heat generation was varied from 10 kW (2.0 W/m^3) to 30 kW (6.2 W/m^3) in Cases 1 and 2. Results are presented in the Table 3.4. As expected, there is a large increase in the maximum temperature of the waste with the increased heat load. Convection velocities, and thus, the convective heat transfer, remain small even at the highest heat generation rates

Figure 3.16. Temperature Contours and Velocity Vectors Inside Tank for Case 6. $K_H=5 \times 10^{-4}$ m/s; $\dot{q}=6.2$ W/m³; $\kappa=1.76$ W/m-K.

Table 3.4. Temperature and Velocity Variations as a Function of Heat Generation

Case	Heat Generation	Maximum Temperature	Maximum Velocity
	(kW)	(°C)	(m/s)
1	30	114	10^{-10}
2	10	47	10^{-11}

3.4.2.1.3 Thermal Conductivity

The thermal conductivity of the soil was varied from 1.76 to 0.88 W/m-K in Cases 1 and 3 for high heat generation (6.2 W/m³) and Cases 2 and 4 for low heat generation (2.0 W/m³). These results are given in the Table 3.5. As expected, a decrease in the value of thermal conductivity causes an increase in the maximum temperature. The convection velocities increase slightly with the increase in temperature, but remain too small to have any impact on the temperature distribution in the waste.

Table 3.5. Temperature and Velocity Variations as a Function of Thermal Conductivity

Case	Heat Generation	Thermal Conductivity	Maximum Temperature	Maximum Velocity
	(kW)	(W/m·°K)	(°C)	(m/s)
1	30	1.76	114	10^{-11}
3	30	0.88	165	10^{-11}
2	10	1.76	47	10^{-11}
4	10	0.88	63	10^{-11}

4.0 HEAT AND MASS TRANSPORT

In this section, we develop the governing equations and solution techniques for a two-dimensional analysis of heat and mass transport in a porous medium that is assumed to represent the ferrocyanide waste sludge.

4.1 BACKGROUND

There have been two reported heat conduction studies of "hot spots" in the ferrocyanide tanks. Grigsby et al. (1992) used the HEATING7 code (Childs 1991) to analyze slabs of varying thickness with various volumetric heating rates. They found, for a slab with an edge length equal in diameter to the tank, that the available heat generation rate could only raise the slab temperature to 90°C, far below temperatures needed to sustain a propagating exothermic reaction. However, using spherical geometry with a radius for the hot spot of 1.2 m, a center temperature of 200°C could be reached by concentrating the decay heat by factors of 75 to 500 over the average. Similar results were found by Dickinson et al. (1993) although lower concentration factors were shown to be needed (~20) for a zone in the shape of a square cylinder of 5 m height and diameter. Although no supporting results were given, the authors conclude that no credible mechanism exists for concentrating the tank heat load by these large factors.

Unfortunately, the heat conduction models used in the simulations described above are not capable of modeling radionuclide mass transport as a process for redistribution of the tank heat load. Mass transport processes could potentially concentrate the heat generating radionuclides in local zones because of thermal or chemical potential gradients. For example, mineral deposition reactions play a key role in the development of geothermal ore deposits (Sharp and Kyle 1988; Ellis and Mahon 1977). The purpose of the modeling studies described in this section is to determine under what conditions mass redistribution may occur and whether or not the process has any significance to the development of "hot spots" in ferrocyanide waste tanks.

4.2 THEORY

A solution is sought to the following set of coupled equations:

1) *Energy*

$$\overline{\rho C_v} \frac{\partial T}{\partial t} = \nabla \cdot (\bar{\kappa} \nabla T) - \epsilon(\rho C_v)_l \mathbf{V} \cdot \nabla T + \dot{q} \quad (4.1)$$

where ρ = density, g/m³
 C_v = heat capacity, J/(g·°C)
 T = temperature, °C
 t = time, s

κ = thermal conductivity, J/(m·s·°C)
 ϵ = porosity
 V = Darcy fluid velocity, m/s
 $\dot{q}$ = heat generation rate, J/(m³·s),

and

$$\overline{\rho C_v} = \epsilon(\rho C_v)_l + (1 - \epsilon)(\rho C_v)_s \quad (4.2)$$

$$\overline{\kappa} = \epsilon \kappa_l + (1 - \epsilon) \kappa_s \quad (4.3)$$

where the subscript *l* refers to the liquid phase and *s* to the solid phase.

2) Diffusion-Advection

$$\frac{\partial c_l}{\partial t} = \nabla \cdot (D \nabla c_l) - V \cdot \nabla c_l - \lambda c_l \quad (4.4)$$

where c_l = concentration of heat generating radionuclide in the liquid, mol/kg
 D = diffusion coefficient, m²/s
 λ = decay constant, s⁻¹.

3) Mass-Action

$$c_l = \left\{ \begin{array}{ll} \left(\frac{K_s}{\prod_{j=1}^N c_j^{v_j}} \right)^{-1/v_s}, & c_s > 0 \\ c_l, & c_s = 0 \end{array} \right\} \quad (4.5)$$

where K_s = solubility product
 c_j = concentration of *j*th species in aqueous phase
 v = stoichiometric coefficient
 c_s = concentration of heat generating radionuclide in the solid, mol/kg.

4) Mass-Balance

$$\frac{\partial c_s}{\partial t} = - \left(\frac{\rho_l}{\rho_s} \frac{\partial c_l}{\partial t} + \lambda c_s \right) \quad (4.6)$$

Equation (4.1) is coupled to Equations (4.4) through (4.6) through the heat generation rate $\dot{q}$ which is given by

$$\dot{q} = \frac{\bar{\rho}(c_s + c_l)G}{1000} \quad (4.7)$$

where G = heat generation rate, J/mol.

In a 2-D cartesian coordinate system, Equations (4.1) and (4.4) become

$$\frac{\partial T}{\partial t} = \bar{\alpha}(T) \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) - \beta(T) \left(v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} \right) + Q(x, y, t) \quad (4.8)$$

$$\frac{\partial c_l}{\partial t} = D \left(\frac{\partial^2 c_l}{\partial x^2} + \frac{\partial^2 c_l}{\partial y^2} \right) - v_x \frac{\partial c_l}{\partial x} - v_y \frac{\partial c_l}{\partial y} - \lambda c_l \quad (4.9)$$

where

$$\bar{\alpha} = \text{mean thermal diffusivity, } \frac{\bar{k}}{\rho C_v}, \text{ m}^2/\text{s}$$

$$\beta = \frac{\varepsilon(\rho C_v)_l}{\rho C_v}$$

$$v_x, v_y = \text{fluid velocity vector components, m/s}$$

$$Q(x, y, t) = \frac{\dot{q}(x, y, t)}{\rho C_v}$$

In Equation (4.9), it is assumed that the species diffusion coefficient is constant and independent of both temperature and c_l . Equations (4.5), (4.6), (4.8), and (4.9) represent the basic equation system to be solved subject to the following initial and boundary conditions:

$$T(x, y, 0) = T_0(x, y) \quad (4.10)$$

$$\left\{ \begin{array}{l} T(0, y, t) = T_1 \\ \bar{\alpha} \frac{\partial T}{\partial x} \Big|_{x=0} = F_1 \end{array} \right\} \quad \left\{ \begin{array}{l} T(w, y, t) = T_3 \\ \bar{\alpha} \frac{\partial T}{\partial x} \Big|_{x=w} = F_3 \end{array} \right\} \quad 0 \leq y \leq h, \quad t > 0 \quad (4.11)$$

$$\left\{ \begin{array}{l} T(x, 0, t) = T_2 \\ \bar{\alpha} \frac{\partial T}{\partial y} \Big|_{y=0} = F_2 \end{array} \right\} \quad \left\{ \begin{array}{l} T(x, h, t) = T_4 \\ \bar{\alpha} \frac{\partial T}{\partial y} \Big|_{y=h} = F_4 \end{array} \right\} \quad 0 < x < w, \quad t > 0 \quad (4.12)$$

where T_1, T_2, T_3, T_4 are specified wall temperatures (Dirichlet boundary)
 F_1, F_2, F_3, F_4 are specified heat fluxes at each wall (Neumann boundary).

Equation (4.10) specifies that the initial temperature is a known function of x and y . Equation (4.11) specifies that the vertical walls are held at either a constant temperature or constant thermal flux. Of course, an adiabatic wall is simply a special case where $F=0$.

For the diffusion-advection equation (4.9), the initial and boundary conditions are

$$c_i(x, y, 0) = c_{i0}(x, y) \quad (4.13)$$

$$\frac{\partial c_i}{\partial x} \Big|_{x=0} = 0 \quad \frac{\partial c_i}{\partial x} \Big|_{x=w} = 0 \quad 0 \leq y \leq h, \quad t > 0 \quad (4.14)$$

$$\frac{\partial c_i}{\partial y} \Big|_{y=0} = 0 \quad \frac{\partial c_i}{\partial y} \Big|_{y=h} = 0 \quad 0 < x < h, \quad t > 0 \quad (4.15)$$

Equation (4.13) specifies that the initial concentration is a known function of x and y . Equations (4.14) and (4.15) specify that the tank walls are impermeable.

Before turning to solution techniques for this equation system, it is useful to review computer codes that may be suitable to solving this type of problem. Surprisingly, there are very few. CHMTRNS (Noorishad, Carnahan, and Benson 1987) is a reactive chemical transport code that is capable of simulating the simultaneous flow of heat and solute transport. Unfortunately, CHMTRNS is a 1-D model. As we are interested in evaluating the effects of fluid flow and mass transport in a 2-D geometry, this model was not suitable. HYDROGEO-CHEM is a complex, finite-element, multicomponent reactive transport code (Yeh and Tripathi 1990). Unfortunately, this code requires excessive computational resources

and was designed for isothermal transport simulations in a subsurface environment. The CFEST-SC, Coupled-Fluid-Energy-Solute Transport Supercomputer Version (Cole, Yabusaki and Kincaid 1988), is a single solute, finite-element transport simulator. Although this code is capable of modeling heat and solute transport in 2- and 3-D, it requires extensive computational resources and would need modification to enforce chemical equilibrium constraints throughout the spatial domain. Consequently, a simple, computationally efficient, finite-difference computer code was developed to solve the equation system described above. The difference equation formulation is given in the Appendix.

4.2.1 Solution Method

The finite-difference equations and associated boundary difference equations (see Appendix) result in two tridiagonal systems of algebraic equations for both the heat and diffusion-advection equation that must be solved at each time step. A standard forward and back substitution algorithm is the core routine used to solve the equation systems (Press et al. 1988). A computer code Tank Waste Simulator was developed to implement the solution method. Tank Waste Simulator runs under the Microsoft Windows™ operating environment. A graphical user interface provides access to all file I/O and data input needed to run the code and to view computed results on-screen in either a tabular format or graphically in a 2-D, high-resolution color plot. Figure 4.1 is a full screen view of the user interface and typical color map display. Tank Waste Simulator can be obtained from the authors.

Figure 4.1. Example Screen From Tank Waste Simulator Code

4.3 RESULTS

In this section, results from selected computations done with the Tank Waste Simulator code are presented. First, because Tank Waste Simulator is a new computer code, we present two benchmark calculations against standard analytical solutions to the heat equation to verify that the code correctly solves the governing equations.

4.3.1 Verification Tests

The first verification test is against a solution to the Laplace heat equation on a rectangle of width w and height h with the surface at $y=0$ kept at a constant temperature, T_2 , and the other surfaces at zero. The solution is (Carslaw and Jaeger 1959)

$$T(x,y) = \frac{4T_2}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \frac{(2n+1)\pi x}{w} \sinh \frac{(h-y)(2n+1)\pi}{w} \operatorname{cosech} \frac{(2n+1)\pi h}{w}. \quad (4.16)$$

We evaluated this function using *Mathematica*® on a 10x10 grid with $h=w=10$ m and $T_2=2$. Calculations with the numerical code were also done on a 10x10 grid using the same dimensions and boundary conditions and with all coefficients set to 1. Approximately 25 iterations were required for convergence to the steady-state solution. The results are shown in Figure 4.2 and the agreement is excellent with a maximum standard error of 2.5%.

Figure 4.2. Comparison of Tank Waste Simulator Output with Analytical Solution. Lines are computed from Equation (4.16) and numbers indicate the y -position and data points from the code.

The second verification test performed was again for steady-state heat conduction in a rectangle, but with a constant internal heat generation rate, $\dot{q}$, and walls maintained at 0°C. The analytical solution is

$$T(x,y) = \frac{\dot{q}(w^2 - x^2)}{2\kappa} - \frac{16\dot{q}w^2}{\kappa\pi^3} \sum_{n=0}^{\infty} \frac{\cos \frac{(2n+1)\pi x}{2w} \cosh \frac{(2n+1)\pi y}{2w} \operatorname{sech} \frac{(2n+1)\pi h}{2w}}{(2n+1)^3} \quad (4.17)$$

Equation (4.17) was solved with *Mathematica*[®] using a heat generation rate of 0.5586 W/m³ corresponding to a uniform concentration of ¹³⁷Cs of 10⁻⁵ mol/kg, thermal conductivity(κ) for H₂O of 0.6 W/m·°C, and $w=10$ m and $h=10$ m. The results are plotted in Figure 4.3 along with the results from the Tank Waste Simulator using the same parameters. The agreement is again excellent.

4.3.2 Base Case (Uniform Heat Load-No Flow-No Transport)

As a basis for comparison with the other simulations reported in this section, the calculated temperature profiles for a hypothetical waste tank of diameter 23m and height of waste in the tank of 10m are shown first. It is assumed that the fluid density and thermal conductivity are temperature dependent in accordance with published values for distilled water and the heat capacity of the Na₂NiFe(CN)₆ waste is given by 0.245+0.000273T J/g·°C. All

Figure 4.3. Comparison of TWS Output with Analytical Solution to the Heat Equation with Constant Internal Heat Generation. Data points indicate y-position and are data points from TWS.

Table 4.1. Constant Parameters Used in Tank Heat and Mass Transport Simulations

<u>Parameter</u>	<u>Value</u>
<u>Waste</u>	
Porosity	0.4
Diffusion coefficient	$1.5 \times 10^{-5} \text{ cm}^2/\text{s}$
Tortuosity	1.0
Density	1.6 g/cm^3
Thermal conductivity	$1.7 \text{ W/m}\cdot^\circ\text{C}$
<u>Fluid</u>	
Heat capacity	$4.19 \text{ J/g}\cdot^\circ\text{C}$

other parameters are held constant and are listed in Table 4.1. Heat load is assumed to derive exclusively from radioactive decay of ^{137}Cs with a half-life of 30.23 yr and generating 0.00472 W/Ci. The ^{137}Cs is assumed, initially, to be uniformly distributed at a concentration of $2 \times 10^{-5} \text{ mol/kg}$ which corresponds to a volumetric heating rate of 1.78 W/m^3 . Initial temperature in the tank is assumed to be a uniform 25°C and the tank headspace is assumed to be held at a constant 30°C with the other tank walls taken as adiabatic surfaces. The predicted time-dependent vertical temperature profile at the tank centerline using these conditions is given in Figure 4.4. Because of the assumed adiabatic surfaces for the tank walls, the temperature profile varies little in the radial direction.

4.3.3 Case 1: Heat and Mass Transport By Diffusion Only

This case differs from the base case described in Section 4.3.2 only in that both heat and mass transport are allowed to take place by diffusion. In all of the following simulations, we have calculated a temperature-dependent solubility product, K_{sp} , for $\text{Cs}_2\text{NiFe}(\text{CN})_6$ using a van't Hoff relationship

$$K_{\text{sp}}(T) = K_{\text{sp}}^0 - \frac{\Delta H}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \quad (4.18)$$

where K_{sp}^0 = solubility product at the temperature T_0
 ΔH = enthalpy of reaction, J/mol
 R = gas constant, $8.314 \text{ J/mol}\cdot\text{K}$.

Figure 4.4. Base Case Centerline Temperature Profiles for a Hypothetical Waste Tank. Initial ^{137}Cs concentration = 2×10^{-5} mol/kg. No fluid flow or mass transport.

Inspection of Equation (4.18) shows that for $T > T_0$, if $\Delta H < 0$, then the solubility of $\text{Cs}_2\text{NiFe}(\text{CN})_6$ increases with increasing temperature and, if $\Delta H > 0$, then the solubility decreases with increasing temperature. The phenomenon of decreasing solubility with increasing temperature is known as retrograde solubility. Examples of solids that exhibit this behavior in aqueous solution include CaCO_3 , LiF , and NaSO_4 . Because the temperature dependence for the solubility of $\text{Cs}_2\text{NiFe}(\text{CN})_6$ is not known, simulations were run using a range of positive and negative values for ΔH .

Figure 4.5 illustrates a predicted centerline temperature and ^{137}Cs profile after 30 yr using the parameters given in Table 4.1 and assuming a value for ΔH of -20 kJ/mol. Because of the lower solubility for Cs at the lower temperature near the top of the tank, mass redistribution occurs, resulting in higher concentrations of Cs in a thin layer at the top of the tank. Because Cs concentrations are lower throughout the rest of the tank compared with the simulations for the base case, the predicted centerline temperatures are lower by about 10°C.

Considerably more complex behavior is predicted when retrograde solubility ($\Delta H > 0$) is assumed for $\text{Cs}_2\text{NiFe}(\text{CN})_6$. As Figure 4.6 shows, the Cs concentrates by different amounts and at different vertical positions depending on the assumed solubility product for $\text{Cs}_2\text{NiFe}(\text{CN})_6$. The vertical position of the peak Cs concentration also varies as a function of time as shown in Figure 4.7. However, the maximum concentration factor achieved in any Case 1 simulation is only about two. The effect of these small concentration factors spread nearly uniformly across the tank diameter is minimal on the predicted temperature profile as illustrated in Figure 4.8.

Figure 4.5. Predicted Tank Centerline Temperature and ^{137}Cs Concentration Profile for Case 1 - Diffusion Only and $\Delta H < 0$.

Figure 4.6. Variation in Centerline Concentration Profile for ^{137}Cs at 30 yr for Case 1 - Diffusion Only and $\Delta H > 0$.

Figure 4.7. Movement of Peak ^{137}Cs Concentration at Tank Centerline as Function of Time for Case 1 - Diffusion Only and $\Delta H > 0$.

Figure 4.8. Comparison of Base Case Centerline Temperature Profiles (Solid Lines) with Case 1 Model (Dashed Lines) Assuming Diffusion Only and Retrograde Solubility for $\text{Cs}_2\text{NiFe}(\text{CN})_6$.

4.3.4 Case 2: Fingering Convective Flow

As discussed in Section 2.0, highly alkaline liquid wastes that were transferred to the ferrocyanide tanks may have induced convective flows in the shape of fingers in the waste sludge. We have attempted a simulation of these flows using Tank Waste Simulator. Because TWS does not solve the Navier-Stokes equations, fluid velocity vectors must be input to the code. Moreover, the current implementation assumes a constant flow rate. With these limitations, we set up a velocity field with all the x-components set to zero and the y-components as illustrated in Figure 4.9. The magnitude of the y-component was set to 1.6×10^{-7} m/s at the tank centerline and $\pm 8 \times 10^{-8}$ m/s as shown in Figure 4.9 to ensure that the continuity equation was satisfied, or $\nabla \cdot \mathbf{V} = 0$. These velocities are roughly the same order of magnitude as calculated from the fluid stability analysis (see Section 2.0).

Again assuming retrograde solubility for $\text{Cs}_2\text{NiFe}(\text{CN})_6$, the simulated convective finger establishes a complex precipitation pattern in the tank as illustrated in Figure 4.10. The pattern is characterized by a precipitation front that forms within the first 2 m of the waste surface. At the center of the front, Cs is concentrated by a factor of 10 over the main portion of the tank. However, as shown in Figure 4.10b, this concentration factor results in almost no change in the temperature contours over the base case simulation with a uniform Cs distribution. This is because the convecting finger descends from the cooler top of the tank, transferring cool fluid to the precipitation front and mitigating the increased heat generation rate in this zone.

Figure 4.9. Velocity Vectors Used to Simulate Fingering Convection in Ferrocyanide Sludge Caused by a Fluid Density Gradient. Flow magnitude at the tank centerline is 1.6×10^{-7} m/s.

Figure 4.10. Contour Map of ^{137}Cs Concentration and Temperature at 30 y For Fingering Convection at the Tank Centerline. $\text{Log } K_{sp}^0 = -19$; $\Delta H = 20 \text{ kJ/mol}$.

Reducing the steepness of the temperature dependence for the solubility of $\text{Cs}_2\text{NiFe}(\text{CN})_6$ moves the location of the precipitation front toward the bottom of the tank, as illustrated in Figure 4.11. Peak Cs concentrations are about a factor of three larger than in the majority of the tank and, again, there is very little change in the predicted temperature profiles versus the base case. We varied the K_{sp}^0 over a wide range of values and plot the effect on the tank centerline temperature profile in Figure 4.12. As shown in the figure, an over 3-order-of-magnitude shift in the solubility for $\text{Cs}_2\text{NiFe}(\text{CN})_6$ had very little effect on the predicted temperature profile. As a test on the effect of fluid flow in influencing the temperature profiles, the simulation shown in Figure 4.11 was repeated except that for $t > 20$ yr, the flow rate vectors were set to zero everywhere in the spatial domain. The resulting effect on the centerline temperature profile is labeled as "No Flow" in Figure 4.12. Although the Cs remained concentrated in a pattern nearly identical to that shown in Figure 4.11, the effect on the temperature profile was again minimal with an increase of only 5°C over the case with constant flow.

4.3.5 Case 3: Thermal Buoyancy-Driven Flow

Simulations with the TEMPEST code were described in Section 3.0 where internal heat generation from radioactive decay established thermal gradients in a hypothetical waste tank. Because the density of water is temperature-dependent, buoyancy forces establish a recirculating flow pattern in the tank (see Figure 3.16). To determine whether this slow, recirculating convection pattern could give rise to a hot spot over long periods of time, simulations were conducted with Tank Waste Simulator. The steady-state flow velocity vectors output from the TEMPEST code were used to establish the flow field. The tank dimensions were adjusted in this case to correspond with the 11.6 m high by 11.6 m diameter tank used in the TEMPEST simulations.

Simulations conducted with $\Delta H = -20$ kJ/mol showed essentially the same pattern as was found for Case 1 (Figure 4.5) where the ^{137}Cs concentrated by about 4 times over tank average in a thin layer near the cooler top of tank. The mass redistribution again resulted in a slight overall cooling of the tank centerline temperature after 30 yr by about 7°C maximum.

As was found for the previous cases, assuming a retrograde solubility for $\text{Cs}_2\text{NiFe}(\text{CN})_6$ ($\Delta H = +20$ kJ/mol) resulted in a complex precipitation pattern as shown in Figure 4.13. The pattern is again characterized by a precipitation front that forms near the right wall of the tank where the maximum downward flow velocity was predicted by the TEMPEST code. However, the peak ^{137}Cs concentration near the precipitation front is only about a factor of 1.6 more concentrated than near the top of the tank where the minimum concentrations are found. The small degree of mass redistribution results in a minimal change in the predicted temperature profile for the hypothetical tank over the case of no flow and uniform distribution of the Cs.

Figure 4.11. Contour Map of ^{137}Cs Concentration and Temperature at 30 y for Case 2 - Fingering Convection. $\text{Log } K_{sp}^0 = -19$; $\Delta H = 10$ kJ/mol.

Figure 4.12. Effect of K_{sp}^0 on Predicted Centerline Temperature Profile after 30 y for Case 2 - Fingering Convection

Figure 4.13 Color Contour Map of ^{235}U Concentrations and Temperatures for Case 3: Thermal Buoyancy-Driven Convection
 $\Delta H = 20 \text{ kJ/mol}$, $\text{Log } K_d = 19$

5.0 CONCLUSIONS

Computer simulations of fluid, heat, and mass transport were conducted on idealized SSTs which contained ferrocyanide wastes that were assumed to behave as an isotropic porous medium. The models predict that fluid convection will occur in these wastes because of density-gradients induced from chemical composition differences and/or thermal gradients. The predicted velocities were approximately 3 m/yr for a sludge with 50% porosity, and permeability of 0.002 Pa-s, and assuming a 50% density difference between a fluid overlying the waste and the interstitial fluid. Convective velocities were much smaller for the case of thermal buoyancy-driven flow, approximately 10^{-5} to 10^{-2} m/yr depending on the assumed heat generation rate and hydraulic conductivity of the waste. Thus, at least two mechanisms exist for inducing convective mixing in the SSTs. Radiolytic generation of gas bubbles in the waste may be another mechanism for inducing convection but this process has not yet been analyzed.

A coupled fluid, heat, and mass transport computer model was developed to determine the extent of redistribution of ^{137}Cs as a result of diffusion and convection in the wastes over a period of 30 yr. Assuming an increasing solubility for $\text{Cs}_2\text{NiFe}(\text{CN})_6$ as a function of increasing temperature, the results show that ^{137}Cs partially redistributes in a thin layer at the colder top of the tank. The effect of the mass redistribution is to lower the predicted centerline tank temperature by about 10°C over the case where the ^{137}Cs is assumed to be uniformly distributed. Assuming a retrograde temperature dependence for the solubility of $\text{Cs}_2\text{NiFe}(\text{CN})_6$ results in complex precipitation patterns in the tank. Simulations of fingering and thermal buoyancy-driven convective flows with retrograde solubility were characterized by the formation of sharp precipitation fronts. Because of the larger flow velocity associated with fingering convection, these simulations showed the largest increase in ^{137}Cs concentrations near the front which was about a factor of 10 over the tank average. However, the mass redistribution had a minimal effect on the tank temperature profile with peak temperatures increasing by only about 5°C . Consequently, redistribution of the ^{137}Cs as a result of aqueous diffusion and natural convection is of no concern in terms of generating a localized area or "hot spot" that could lead to a propagating exothermic reaction.

Quantitative predictions of the amount of ferrocyanide that could have been removed from the SSTs during liquid transfer operations were not possible with the current model. This would require implementing a complete aqueous speciation model and data on the kinetics of $\text{Na}_2\text{NiFe}(\text{CN})_6$ dissolution as a function of temperature and pH. Modifications to the computer codes presented in this report could be done and would allow a solution to this problem.

6.0 REFERENCES

- Anderson, J. D. 1990. A History of the 200 Area Tank Farms. WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington.
- Bird, R. B., W. E. Stewart, and E. N. Lightfoot. 1960. Transport Phenomena. John Wiley and Sons, Inc. New York.
- Burger, L. L., and R. D. Scheele. 1988. Interim Report: Cyanide Safety Issues. PNL-7175, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L., and R. D. Scheele. 1991. The Reactivity of Cesium Nickel Ferrocyanide Towards Nitrate and Nitrite Salts. PNL-7550, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L., D. A. Reynolds, W. W. Schultz, and D. M. Strachan. 1991. A Summary of Available Information on Ferrocyanide Tank Wastes. PNL-7822, Pacific Northwest Laboratory, Richland, Washington.
- Carslaw, H. S., and J. C. Jaeger. 1959. Conduction of Heat in Solids. Oxford University Press, New York.
- Chandrasekhar, S. 1961. Hydrodynamic and Hydromagnetic Stability. Oxford University Press, London, United Kingdom.
- Chen, F. J., and W. Lu. 1991. "Influence of Viscosity Variation on Salt-Finger Instability in a Fluid Layer, a Porous Layer, and Their Superposition." *Journal of Applied Physics* 70(8):4121-4131.
- Cole, C. R., S. B. Yabusaki, and C. T. Kincaid. 1988. CFEST-SC Coupled Fluid, Energy, and Solute Transport Code SuperComputer Version. Documentation and User's Manual, Battelle, Pacific Northwest Laboratories, Richland, Washington.
- Deaton, D. E. 1990. Unreviewed Safety Question Regarding Tanks Containing Ferrocyanide. Occurance Report, WHC-90-B003-R1, Update, 10-22-90, Westinghouse Hanford Company, Richland, Washington.
- Dickinson, D. R., J. M. McLaren, G. L. Borsheim, and M. D. Crippen. 1993. Credibility of Dryout in Ferrocyanide Sludge Due to Local Hot Spots. WHC-EP-0648, Westinghouse Hanford Company, Richland, Washington.
- Ellis, A. J. and W. A. J. Mahon. 1977. Chemistry and Geothermal Systems. Academic Press, New York, New York.

Grigsby, J. M. et. al. 1992. Ferrocyanide Waste Tank Hazard Assessment - Interim Report. WHC-SD-WM-RPT-032, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Hillel, D. 1980. Fundamentals of Soil Physics. p. 296. Academic Press, New York.

Jeppson, D.W., and J.J. Wong. 1993. Ferrocyanide Waste Simulant Characterization, WHC-EP-0631, Westinghouse Hanford Company, Richland, Washington.

Lilga, M. A., M. R. Lumetta, W. F. Riemath, R. A. Romine, and G. F. Schiefelbein. 1992. Ferrocyanide Safety Project, Subtask 3.4 Aging Studies, FY 1992 Annual Report. PNL-8387, Pacific Northwest Laboratory, Richland, Washington.

Kerr, R. C., and S. R. Tait. 1985. "Convective Exchange Between Pore Fluid and an Overlying Reservoir of Denser Fluid: a Post-Cumulus Process in Layered Intrusions." *Earth and Planetary Science Letters* 75:147-156.

Noorishad, J., C. L. Carnahan, and L. V. Benson. 1987. Development of the Non-Equilibrium Reactive Chemical Transport Code CHMTRNS. LBL-22361, Lawrence Berkeley Laboratory, Berkeley, California.

Peaceman, D. W., and H. H. Rachford. 1955. *J. Soc. Indus. Appl. Math.* 3:28-41.

Press, W. H., B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling. 1986. Numerical Recipes. Cambridge University Press, United Kingdom.

Sharp, J. M., and J. R. Kyle. 1988. Hydrogeology. Geologic Society of North America.

Trent, D. S., and L. L. Eyler. 1993. TEMPEST- A Computer Program for Three-Dimensional, Time-Dependent Computational Fluid Dynamics: Theory Manual. Version T, Mod 3. PNL-8857, Pacific Northwest Laboratory, Richland, Washington.

Welty, J. R., R. E. Wilson, and C. E. Wicks. 1976. Fundamentals of Momentum, Heat, and Mass Transfer. John Wiley and Sons, Inc. New York.

Wooding, R. A. 1959. "The Stability of a Viscous Liquid in a Vertical Tube Containing Porous Material." *Proceedings of the Royal Society of London A* 256:120-134.

Yeh, G. T., and V. S. Tripathi. 1990. HYDROGEOCHEM: A Coupled Model of Hydrologic Transport and Geochemical Equilibria in Reactive Multicomponent System. DE91-007825, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

APPENDIX

FINITE-DIFFERENCE EQUATIONS

APPENDIX

FINITE-DIFFERENCE EQUATIONS

Derived here are the finite-difference equations for solution of the coupled heat and mass transport equations as described in Section 4.0. The basic solution method is the alternating-direction implicit method originally developed by Peaceman and Rachford (1955). Explicitly developed here are the finite-difference equations for the energy equation (4.8). The difference equations for the diffusion-advection equation are essentially the same with the exception of handling the mass action and mass balance constraints of Equations (4.5-4.6). Figure A.1 illustrates a typical domain of width w and height h with a finite-difference grid of m nodes in the x -direction and l nodes in the y -direction.

A.1 DERIVATION

First, the following notation is introduced for the spatial discretization variables obtained from second-order central difference formula

$$\begin{aligned}\delta_x^2 &= \Delta x^{-2}(T_{i-1,j} - 2T_{i,j} + T_{i+1,j}) \\ \delta_y^2 &= \Delta y^{-2}(T_{i,j-1} - 2T_{i,j} + T_{i,j+1})\end{aligned}\tag{A1}$$

Figure A.1. Example Finite-Difference Grid for Solution of Coupled Equation System

where Δx and Δy are the spatial step sizes. Using first-order upwind differencing

$$\delta_x = \begin{cases} \frac{(T_{i,j} - T_{i-1,j})}{\Delta x} , & v_x > 0 \\ \frac{(T_{i+1,j} - T_{i,j})}{\Delta x} , & v_x < 0 \end{cases} \quad (\text{A2})$$

$$\delta_y = \begin{cases} \frac{(T_{i,j} - T_{i,j-1})}{\Delta y} , & v_y > 0 \\ \frac{(T_{i,j+1} - T_{i,j})}{\Delta y} , & v_y < 0 \end{cases} \quad (\text{A3})$$

The semidiscretized form of the energy Equation (4.8) then becomes

$$\frac{\partial T}{\partial t} = \bar{\alpha}(T)(\delta_x^2 + \delta_y^2)T - \beta(T)(v_x \delta_x + v_y \delta_y)T + Q(x, y, t). \quad (\text{A4})$$

For the time discretization, we choose the Crank-Nicolson method. After some manipulation, Equation (A4) becomes

$$\left[1 - \frac{\bar{\alpha}^{n+1} \Delta t}{2} (\delta_x^2 + \delta_y^2) \right] T^{n+1} = \left[1 + \frac{\bar{\alpha}^n \Delta t}{2} (\delta_x^2 + \delta_y^2) - \beta^n \Delta t (v_x \delta_x + v_y \delta_y) \right] T^n + \Delta t Q(x, y, t). \quad (\text{A5})$$

Applying operator splitting, $\frac{1}{2}$ time step is taken and the x -direction is treated implicitly and y -direction is treated explicitly, followed by another $\frac{1}{2}$ time step where the y -direction is treated implicitly and the x -direction is treated explicitly. The finite-difference equations are

$$\left[1 - \frac{\bar{\alpha}^{n+\frac{1}{2}} \Delta t}{2} \delta_x^2 \right] T^{n+\frac{1}{2}} = \left[1 + \frac{\bar{\alpha}^n \Delta t}{2} \delta_y^2 - \beta^n \Delta t (v_y \delta_y) \right] T^n + \frac{\Delta t}{2} q^n \quad (\text{A6})$$

$$\left[1 - \frac{\bar{\alpha}^{n+1} \Delta t}{2} \delta_y^2 \right] T^{n+1} = \left[1 + \frac{\bar{\alpha}^n \Delta t}{2} \delta_x^2 - \beta^n \Delta t (v_x \delta_x) \right] T^{n+\frac{1}{2}} + \frac{\Delta t}{2} q^n. \quad (\text{A7})$$

The nonlinear term $\bar{\alpha}^{n+1}$ results in a coupled set of nonlinear algebraic equations to solve at each time step. Instead, the problem was linearized by introducing

$$\bar{\alpha}(T^{n+1}) = \bar{\alpha}(T^n) + (T^n - T^{n-1}) \frac{\partial \bar{\alpha}}{\partial T}. \quad (\text{A8})$$

Expanding Equations (A6) and (A7) with the help of Equations (A1) through (A3) gives the final form of the difference equations to be solved

$$a_x T_{i-1,j}^{n+1/2} + b_x T_{i,j}^{n+1/2} + c_x T_{i+1,j}^{n+1/2} = d_y T_{i,j-1}^n + e_y T_{i,j}^n + f_y T_{i,j+1}^n + \frac{\Delta t}{2} q_{i,j}^n \quad (\text{A9})$$

$$a_y T_{i,j-1}^{n+1} + b_y T_{i,j}^{n+1} + c_y T_{i,j+1}^{n+1} = d_x T_{i-1,j}^{n+1/2} + e_x T_{i,j}^{n+1/2} + f_x T_{i+1,j}^{n+1/2} + \frac{\Delta t}{2} q_{i,j}^n \quad (\text{A10})$$

where

$$a_x = -\frac{\bar{\alpha}^{n+1} \Delta t}{2 \Delta x^2} \quad b_x = \left(1 + \frac{\bar{\alpha}^{n+1} \Delta t}{\Delta x^2}\right) \quad c_x = -\frac{\bar{\alpha}^{n+1} \Delta t}{2 \Delta x^2} \quad (\text{A11})$$

$$a_y = -\frac{\bar{\alpha}^{n+1} \Delta t}{2 \Delta y^2} \quad b_y = \left(1 + \frac{\bar{\alpha}^{n+1} \Delta t}{\Delta y^2}\right) \quad c_y = -\frac{\bar{\alpha}^{n+1} \Delta t}{2 \Delta y^2} \quad (\text{A12})$$

$$d_x = \begin{cases} \frac{\bar{\alpha}^n \Delta t}{2 \Delta x^2} + \frac{\beta^n \Delta t}{\Delta x} v_x, & v_x > 0 \\ \frac{\bar{\alpha}^n \Delta t}{2 \Delta x^2}, & v_x < 0 \end{cases} \quad d_y = \begin{cases} \frac{\bar{\alpha}^n \Delta t}{2 \Delta y^2} + \frac{\beta^n \Delta t}{\Delta y} v_y, & v_y > 0 \\ \frac{\bar{\alpha}^n \Delta t}{2 \Delta y^2}, & v_y < 0 \end{cases} \quad (\text{A13})$$

$$e_x = \begin{cases} 1 - \frac{\bar{\alpha}^n \Delta t}{2 \Delta x^2} - \frac{\beta^n \Delta t}{\Delta x} v_x, & v_x > 0 \\ 1 - \frac{\bar{\alpha}^n \Delta t}{2 \Delta x^2} + \frac{\beta^n \Delta t}{\Delta x} v_x, & v_x < 0 \end{cases} \quad e_y = \begin{cases} 1 - \frac{\bar{\alpha}^n \Delta t}{2 \Delta y^2} - \frac{\beta^n \Delta t}{\Delta y} v_y, & v_y > 0 \\ 1 - \frac{\bar{\alpha}^n \Delta t}{2 \Delta y^2} + \frac{\beta^n \Delta t}{\Delta y} v_y, & v_y < 0 \end{cases} \quad (\text{A14})$$

$$f_x = \begin{cases} \frac{\bar{\alpha}^n \Delta t}{2 \Delta x^2}, & v_x > 0 \\ \frac{\bar{\alpha}^n \Delta t}{2 \Delta x^2} - \frac{\beta^n \Delta t}{\Delta x} v_x, & v_x < 0 \end{cases} \quad f_y = \begin{cases} \frac{\bar{\alpha}^n \Delta t}{2 \Delta y^2}, & v_y > 0 \\ \frac{\bar{\alpha}^n \Delta t}{2 \Delta y^2} - \frac{\beta^n \Delta t}{\Delta y} v_y, & v_y < 0 \end{cases} \quad (A15)$$

A.2 BOUNDARY CONDITIONS

Difference equations for both Dirichlet and Neumann type boundary conditions will be derived here since both types of boundaries need to be simulated.

A.2.1 Dirichlet

Because wall temperatures on the boundary are specified, difference equations are derived from Equations (A9) and (A10) for one node in from the wall boundary

Left Wall

$$0 + b_x T_{2,j}^{n+1/2} + c_x T_{3,j}^{n+1/2} = d_y T_{2,j-1}^n + e_y T_{2,j}^n + f_y T_{2,j+1}^n + \frac{\Delta t}{2} q_{2,j}^n + a_x T_1 \quad (A16)$$

Right Wall

$$a_x T_{m-2,j}^{n+1/2} + b_x T_{m-1,j}^{n+1/2} + 0 = d_y T_{m-1,j-1}^n + e_y T_{m-1,j}^n + f_y T_{m-1,j+1}^n + \frac{\Delta t}{2} q_{m-1,j}^n + c_x T_3 \quad (A17)$$

Bottom

$$0 + b_y T_{i,2}^{n+1} + c_y T_{i,3}^{n+1} = d_x T_{i-1,2}^{n+1/2} + e_x T_{i,2}^{n+1/2} + f_x T_{i+1,2}^{n+1/2} + \frac{\Delta t}{2} q_{i,2}^n + a_y T_2 \quad (A18)$$

Top

$$a_y T_{i,l-2}^{n+1} + b_y T_{i,l-1}^{n+1} + 0 = d_x T_{i-1,l-1}^{n+1/2} + e_x T_{i,l-1}^{n+1/2} + f_x T_{i+1,l-1}^{n+1/2} + \frac{\Delta t}{2} q_{i,l-1}^n + c_y T_4 \quad (A19)$$

A.2.2 Neumann

Difference equations for the flux boundary condition are derived by introducing a fictitious grid one node beyond the boundary of each wall. The finite-difference equations for Equations (4.11) and (4.12) then are

$$\bar{\kappa}_{1,j} \frac{T_{2,j} - T_{0,j}}{2\Delta x} = F_1 \quad \bar{\kappa}_{m,j} \frac{T_{m-1,j} - T_{m+1,j}}{2\Delta x} = F_3 \quad (\text{A20})$$

$$\bar{\kappa}_{i,1} \frac{T_{i,2} - T_{i,0}}{2\Delta y} = F_2 \quad \bar{\kappa}_{i,l} \frac{T_{i,l-1} - T_{i,l+1}}{2\Delta y} = F_4 \quad (\text{A21})$$

Solving Equations (A20) and (A21) for the temperature at the fictitious grid point and substituting into Equations (A9) and (A10) the following equations are derived:

Left Wall

$$0 + b_x T_{1,j}^{n+1/2} + (a_x + c_x) T_{2,j}^{n+1/2} = d_y T_{1,j-1}^n + e_y T_{1,j}^n + f_y T_{1,j+1}^n + \frac{\Delta t}{2} q_{1,j}^n - \frac{\Delta t F_1}{\Delta x \rho C_{v,1,j}^{n+1}} \quad (\text{A22})$$

Right Wall

$$(a_x + c_x) T_{m-1,j}^{n+1/2} + b_x T_{m,j}^{n+1/2} + 0 = d_y T_{m,j-1}^n + e_y T_{1,j}^n + f_y T_{m,j+1}^n + \frac{\Delta t}{2} q_{m,j}^n - \frac{\Delta t F_3}{\Delta x \rho C_{v,m,j}^{n+1}} \quad (\text{A23})$$

Bottom

$$0 + b_y T_{i,1}^{n+1/2} + (a_y + c_y) T_{i,2}^{n+1/2} = d_x T_{i-1,1}^n + e_x T_{i,1}^n + f_x T_{i+1,1}^n + \frac{\Delta t}{2} q_{i,1}^n - \frac{\Delta t F_2}{\Delta y \rho C_{v,i,1}^{n+1}} \quad (\text{A24})$$

Top

$$(a_y + c_y) T_{i,l-1}^{n+1/2} + b_y T_{i,l}^{n+1/2} + 0 = d_x T_{i-1,l}^n + e_x T_{i,l}^n + f_x T_{i+1,l}^n + \frac{\Delta t}{2} q_{i,l}^n - \frac{\Delta t F_4}{\Delta y \rho C_{v,i,l}^{n+1}} \quad (\text{A25})$$

A.3 DIFFUSION-ADVECTION EQUATION

Similar sets of difference equations (A9 and A10) and associated boundary conditions can be derived for the diffusion-advection equation (4.4). The major difference occurs in dealing with the additional mass-action (4.5), and mass-balance equations (4.6). After completing a transport step, Equation (4.6) is solved to obtain new values for the concentration c_s . This is accomplished with

$$(c_s)_{i,j}^{n+1} = [1 - \lambda \Delta t](c_s)_{i,j}^n - \frac{\rho_l}{\rho_s}[(c_l)_{i,j}^{n+1} - (c_l)_{i,j}^n]. \quad (\text{A26})$$

Once the new values for the solid phase concentration are obtained, Equation (4.4) is solved to maintain equilibrium with the solid phase throughout the spatial domain provided $c_s > 0$.

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