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Sludge Treatment Evaluation:
1992 Technical Progress

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Summary

This report documents Fiscal Year 1992 technical progress on the Sludge Treatment Evaluation Task(a), which is being conducted by Pacific Northwest Laboratory(b). The objective of this task is to develop a capability to predict the performance of pretreatment processes for mixed radioactive and hazardous waste stored at Hanford and other U.S. Department of Energy (DOE) sites. Significant cost savings can be achieved if radionuclides and other undesirable constituents can be effectively separated from the bulk waste prior to final treatment and disposal. The predictive capability being developed as part of this task will facilitate tank waste pretreatment technology development, as well as design and operation of pretreatment processes.

This work is initially focused on chemical equilibrium prediction of water washing and acid or base dissolution of Hanford single-shell tank (SST) sludges, but may also be applied to other steps in pretreatment processes or to other wastes. Since many key streams in the pretreatment process will be concentrated, highly non-ideal electrolyte solutions, high ionic strength electrolyte thermodynamic theories (Pitzer or NRTL) need to be used to predict process chemistry. These electrolyte models require species-specific data, much of which can be obtained from the literature. Additional needed data can be developed from experiments (i.e., solubility, isopiestic). This work does not address kinetics of pretreatment processes, but focuses on chemical reactions that would be expected to be at or near equilibrium.

Although SST wastes contain many chemical species, there are relatively few constituents--Na, Al, NO_3, NO_2, PO_4, SO_4, and F--contained in the majority of the waste. These constituents comprise 86% and 74% of samples from B-110 and U-110 SSTs, respectively. The major radionuclides of interest (Cs, Sr, Tc, U) are present in the sludge in small molal quantities. For these constituents, and other important components that are present in small molal quantities, the specific ion-interaction terms used in the Pitzer or NRTL equations may be assumed to be zero for a first approximation. Of course, the model can be refined to include these additional parameters when available. Model development can also be accelerated by considering only the acid or base conditions that apply for the key pretreatment steps. This significantly reduces the number of chemical species and chemical reactions that need to be considered. Therefore, significant progress can be made by developing all the specific ion interactions for a base model [for the chemical system $Na^+\text{-}NO_3^-\text{-}NO_2^-\text{-}SO_4^{2-}\text{-}CO_3^{2-}\text{-}F^-\text{-}PO_4^{3-}\text{-}OH^-\text{-}Al(OH)_4^-\text{-}H_2O$] and an acid dissolution model [for the chemical system $Na^+\text{-}H^+\text{-}Al^{3+}\text{-}NO_3^-\text{-}NO_2^-\text{-}SO_4^{2-}\text{-}HSO_4^-\text{-}HF\text{-}F^-\text{-}H_3PO_4\text{-}H_2O$]. A large amount of information was collected from a literature search that can be used to predict the chemical behavior of these systems. This information needs to be analyzed and thermodynamic parameters determined. An experimental program has been planned to fill important gaps in needed data. Some of the experiments needed to obtain the missing information have been initiated in FY 1992.

(a) This work was funded by the U.S. Department of Energy Office of Technology Development under the Efficient Separations and Processing Integrated Program (IP-3).

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ASPEN-PLUS™[(a)] -- an existing, commercial software package -- is a convenient tool for performing electrolyte thermodynamic and flowsheet calculations. ASPEN-PLUS™ can also be used to fit model parameters from experimental data.

Some of the information gathered during the literature review has been analyzed and included in a template ASPEN PLUS™ input file, which will be continuously expanded and updated as additional model parameters are determined. This template can be used as a starting point for flowsheet simulation calculations. Binary ion-interaction parameters for electrolyte thermodynamic calculations have been obtained for interactions between Na^+ and the following anions: Cl^-, F^-, NO_3^-, NO_2^-, OH^-, SO_4^{2-}, PO_4^{3-}, HPO_4^{2-}, and $Al(OH)_4^-$. Ternary ion-interaction parameters have been obtained for interactions between Na^+ and the following anion pairs: OH^- and NO_3^-, OH^- and NO_2^-, OH^- and F^-, NO_3^- and NO_2^-, NO_3^- and F^-, and OH^- and $Al(OH)_4^-$. Correlations of salt dissolution equilibrium constants have been obtained for $NaNO_3$, $NaNO_2$, NaF, Na_2SO_4, and $Al(OH)_3$. These parameters have been obtained by a combination of regressing published experimental data, refitting published correlations for these parameters, or using published parameters directly with no additional adjustment. When fitting the data to model parameters, some judgment needs to be made on the required accuracy and quality of these parameters. Certainly, trade-offs can be made between model accuracy and the time and cost associated with improving model predictions.

To illustrate use of the model parameters determined in FY 1992, a simple solid dissolution flowsheet was developed. Calculations were conducted for water dissolution and dilute caustic dissolution of a solid feed assuming perfect solid-liquid separations. The feed was assumed to be a mixture of $NaNO_3$, $NaNO_2$, and NaF in the same proportions that were calculated from a B-110 sludge material balance. A three-stage, cross-current dissolution flowsheet was designed to dissolve all of the $NaNO_2$ in the first stage; dissolve the remaining $NaNO_3$ in the second stage; and dissolve the remaining NaF in the third stage. The simulation was then optimized to calculate the minimum amount of water that would have to be added to each stage to accomplish these objectives. These calculations illustrate that the advantages of this predictive capability include 1) identifying opportunities for more efficient separations and processing, 2) waste minimization, and 3) prediction of feed composition to downstream processes to facilitate separations technology development.

Results are also given from amorphous SiO_2 solubility experiments that were conducted this year. Obtaining experimental data on the solubility of amorphous SiO_2 in various acid and base solutions was identified early as a priority for predicting chemical behavior during sludge pretreatment, principally as a result of the potential for scale formation. Hence, accurate experimental and thermodynamic data are required to predict the solubilities of silicate phases for changing pretreatment process conditions. Data collected for SiO_2 solubility in HNO_3 and HCl will be combined with other existing literature data to determine the model parameters that describe the interactions of H_4SiO_4, the principal aqueous silica species below pH 9, with other bulk chemical species.

(a) ASPEN PLUS™ is licensed by Aspen Technology, Inc., Cambridge, Massachusetts.

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1.0 Introduction

This report documents Fiscal Year 1992 technical progress on the Sludge Treatment Evaluation Task[(a)], which is being conducted by Pacific Northwest Laboratory[(b)] (PNL). The objective of this task is to develop a capability to predict the performance of pretreatment processes for mixed radioactive and hazardous waste stored at Hanford and other U.S. Department of Energy (DOE) sites. Previous estimates of remediating DOE high-level waste tanks exceed $50 billion for a case of minimal pretreatment. There are significant opportunities for cost savings if radionuclides and other undesirable constituents can be efficiently separated from the bulk waste prior to final treatment and disposal.

The predictive capability being developed as part of this task will facilitate tank waste pretreatment technology development. This is being accomplished by collecting data needed to use existing, commercial software for process design and modeling. The software selected, ASPEN PLUS™[(c)], contains equations that can be used to accurately and rigorously model equilibrium of highly concentrated solutions and reactions of these solutions with solids, such as sludges. These calculations are then integrated with ASPEN PLUS™ flowsheet and equipment sizing and costing calculations to evaluate pretreatment processes. The resulting process chemistry/process design tool will help streamline pretreatment design, reduce the probability of costly mistakes in process or equipment design, identify opportunities for efficient separations, and assist in pretreatment operations.

This work is initially focused on prediction of water washing and acid or base dissolution of Hanford single-shell tank (SST) sludges, which contain small amounts of organic constituents. Processes for removing high-level constituents from SST waste depend on the extent to which SST sludge will dissolve and the composition of the resulting solution. The database is being developed such that the data for the major constituents of the SST sludge are included first and are consequently available for ASPEN PLUS™ simulations. It is essential to include these major constituents first, since their chemical behavior will greatly affect the chemical behavior of the minor components. In general, the effects of minor components on other minor components are not as large, unless extremely large complexation effects are present. Also, in this way, the modeling technology will be available for early application to important constituents, even though all chemical components may not be included in early versions of the database. This work will later expand to include organic constituents and other waste types.

This report describes progress on the ongoing effort to incorporate literature data and experimental results into process flowsheet calculations. This model is then verified for accuracy. Model parameters for several sodium salts, which are among the major constituents in tank waste have been obtained and incorporated into a simple flowsheet calculation.

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A literature search was conducted to obtain the following information:

- the status of the current model database. The ASPEN PLUS™ model contains some of the parameters needed. However, few of these parameters are applicable to Hanford tank waste. Also, the concentration and temperature range for which these parameters are valid need to be determined or tested.

- the literature data that are available and can be analyzed to obtain the necessary model parameters. Necessary model parameters can be calculated from published equilibrium data. Vapor-liquid equilibrium (VLE), osmotic coefficients, solubility, solvent extraction, and electromotive force (emf) data are examples of information that can be used for this purpose.

- the exact experimental studies that need to be conducted to determine additional model parameters. There are gaps in the literature which can only be filled through experimentation. Also, some of the chemical components of interest, such as Bi and U, are not commonly encountered in typical industrial processes or geochemical systems. There may also be cases where needed model parameters will have to be estimated using data from chemically analogous systems. This will be done where the data are unavailable and the cost of the experimental studies probably does not justify the additional accuracy of the model. Examples of where the parameters may be estimated rather than experimentally determined are for minor sludge constituents (i.e., Zn, Mn, etc.), which do not have a major impact on subsequent processes (such as solvent extraction or vitrification).

Results are also given from amorphous SiO_2 solubility experiments that were conducted this year. Obtaining experimental data on the solubility of amorphous SiO_2 in various acid and base solutions was identified early as a priority for predicting the chemical behavior during sludge pretreatment.

A brief description of the SST sludge and pretreatment processes and an overview of the ASPEN PLUS™ code and thermodynamic equations are given for background information. The appendices contain a template ASPEN PLUS™ input file, as well as input files and results from flowsheet simulations for a simple sodium salt dissolution process.

2.0 Background

Underground storage tanks at Hanford and other DOE sites contain mixed high-level radioactive and hazardous wastes. These tanks typically contain a heterogeneous sludge that may or may not be in contact with a concentrated liquid supernate phase. There may also be a "salt cake" waste present that was precipitated due to evaporation of the liquid supernate phase. The relative volumes and composition of the sludge, salt cake, and sludge wastes depend on the types of processing wastes that were added to the tanks, as well as the aging processes that have occurred in the tanks. The tank wastes contain a complex mixture of inorganic and organic compounds.

Current Hanford cleanup plans call for tank waste retrieval, partitioning the waste into high- and low-level waste streams. The low-level waste will subsequently be incorporated into grout; the high-level waste will be converted into a borosilicate glass waste form in the Hanford Waste Vitrification Plant (HWVP) and then stored in a high-level waste repository. Cost estimates for producing and storing each glass canister range from $700K to $1 million. Technology development for efficient separations is needed to minimize the quantity of high-level glass canisters that will be produced by the HWVP by maximizing removal of less hazardous, nonradioactive constituents. Several pretreatment steps will be necessary prior to final processing of these wastes.

Of the 177 underground storage tanks at the Hanford Site, 149 are single-shell tanks (SSTs). The work for this task is currently centered on SST sludge pretreatment, although other waste types may be considered in the future. Section 2.1 summarizes a proposed pretreatment strategy for SST sludge.

2.1 SST Pretreatment

One proposed SST pretreatment scheme is shown in Figure 2.1. This process includes water washing, acid dissolution of the sludge, neutralization of undissolved solids, ion exchange for Cs and Tc removal, and solvent extraction for removal of transuranic elements and strontium (i.e., TRUEX, SREX). The processes that will eventually be selected for pretreatment must be developed for a wide variety of complex waste compositions. In addition, options such as recycling water or acid leaching solutions must be considered to minimize the overall amount of waste sent to vitrification or grout. Hence, the capability to adjust the amount of solutions added or recycled and the solution concentrations used for solid dissolution or neutralization are critical to optimizing pretreatment.

The value of the predictive capability being developed using the ASPEN PLUS™ code is that it is likely to prevent unnecessary costs in the design and operation of pretreatment processes. The equilibrium and flowsheet calculations in this model are being used to account for the chemical reactions that would occur during a proposed process and predict what will occur at each step. The principal alternative would be to conduct solely empirical pretreatment studies using numerous possible processes over a range of temperatures and for many different waste types. Although some of these studies will provide useful information and should be conducted, empirical studies alone offer only very limited information on why certain pretreatment processes were effective or ineffective, and

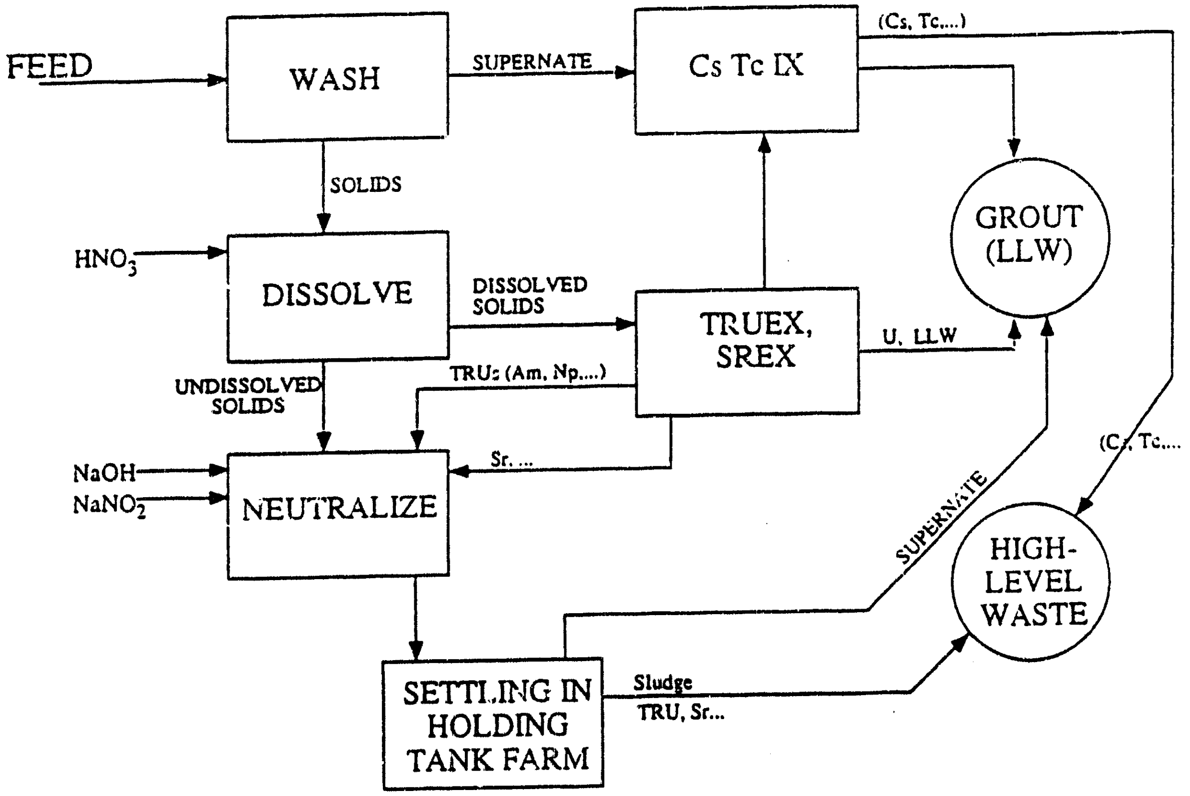


Figure 2.1. Proposed Block Flow Diagram: Single-Shell Tank Pretreatment

this limits the usefulness of this information for different waste compositions or different pretreatment processes. Consequently, empirical studies need to be repeated and repeated with little information from one study applying to another study. Such an approach makes process optimization and design very difficult. In contrast, a predictive capability would require only a limited number of empirical studies on actual or simulated waste as a check to ensure that all important chemical reactions have been included.

2.2 Overview of ASPEN PLUS™

ASPEN, which stands for Advanced System for Process Engineering, is a software system for computer-aided process design. The original ASPEN code was developed at the Massachusetts Institute of Technology during the period of 1976-1981, through work sponsored by DOE and industrial participants. Expanded and updated versions of ASPEN are available for purchase or lease from Aspen Technology, Inc., Cambridge, Massachusetts, which leases ASPEN PLUS™, and from Simulation Sciences of Fullerton, California, which leases ASPEN/SP.

ASPEN PLUS™ is used by chemical and petrochemical, petroleum refining, oil and gas processing, pulp and paper, metal, food processing, pharmaceutical, and biotechnology industries. It is used for process design, process troubleshooting and evaluation, and process and product development. For example, ASPEN PLUS™ may be used during process development to evaluate alternative process configurations and determine their technical and economic advantages and disadvantages. Pilot-plant data can be used to model a new or changed process to obtain preliminary economic information. Plant design and process evaluation can also be facilitated with ASPEN PLUS™, using detailed material and energy balances to analyze the effects of process and equipment changes on the operational and economic performance of the plant.

The ASPEN PLUS™ code was designed for performing rigorous steady-state material and energy balances for plants in the process industries. Input files contain keywords that are the "building blocks" necessary for defining the processes to be modeled. These keywords define chemical components; methods for calculating thermodynamic properties (i.e., equations of state); and unit operation information such as type of equipment, operation sequence, and performance specifications. The code will perform the necessary calculations, including equilibrium calculations, to produce a material and energy balance that describes the flowsheet. The output includes flowrates and compositions of feed, product, internal, and recycle streams. Key equipment specifications and energy consumption are also determined. Capital and operating costs of the modeled process can be estimated. ASPEN PLUS™ also includes capabilities for running sensitivity analysis case studies, optimizing the process for a specified parameter (i.e., cost), and data regression for estimating various equilibrium and physical property parameters.

Material balances are rigorously calculated using the internal physical and thermodynamic property models selected by the user. ASPEN PLUS™ contains several of these property models for this purpose, including models for equations of state, enthalpy, activity coefficients, transport properties, and others. The user selects either the Pitzer model or the Electrolyte NRTL model (see Section 2.3) for electrolyte solid/liquid equilibrium. Some of the physical property parameters required to use these property models are contained in ASPEN PLUS™ databanks for common chemical components. However, binary and ternary ion-interaction parameters and chemical equilibrium data for solid dissolution and precipitation for most of the tank waste species are not available in the databanks. Also, databank values are, in some cases, valid for only limited ranges of concentration and temperature.

ASPEN PLUS™ can be run on several types of computing platforms, including IBM-compatible 386 or 486 personal computers. Graphical user interfaces have been developed for each of the ASPEN PLUS™ models to facilitate input file generation. The user interface is called ModelManager. ModelManager can be used as an expert system to build a flowsheet model and prevent problem overspecification or underspecification. ModelManager can also be used to organize ASPEN PLUS™ run results graphically by generating plots and drawings. ModelManager also enables users to work interactively with ASPEN PLUS™; provides users with on-line help; and can interface to databases and other engineering software. Section 2.3 summarizes the equations used in this study for modeling the Hanford SST waste.

2.3 Electrolyte Thermodynamics

The chemical systems that are present in the tank waste and that will be present in the pretreatment processes are highly concentrated, non-ideal electrolyte chemical systems. The chemical equilibrium between various aqueous and solid species is governed by the activities of the reactants and products of a particular chemical reaction. These reactions can include dissolution and precipitation of salts or ionic association reactions in solution. Therefore, calculations to determine the equilibrium concentrations for the species in liquid/solid equilibrium must take into account the activity coefficient of each species.

Thermodynamic chemical models have routinely been used to model geochemical systems. Several of these models are based on the approximation that activity coefficients of aqueous species are a universal function of ionic strength. However, these models, which are typically based on the Davies equation or extended Debye-Huckel equation, are applicable only in the dilute solution region. The definition of this dilute solution region depends on the specific ions in solution. For example, calculations using the Davies equation for 1:1 electrolytes (Figure 2.2) show reasonable agreement with the measured mean ionic activity coefficients to molalities of approximately 0.4 for 1:1 electrolytes. However, similar calculations for 2:1 or 1:2 electrolytes (Figure 2.3) show reasonable agreement to molalities of only about 0.05. Therefore, the range of applicability of a model that

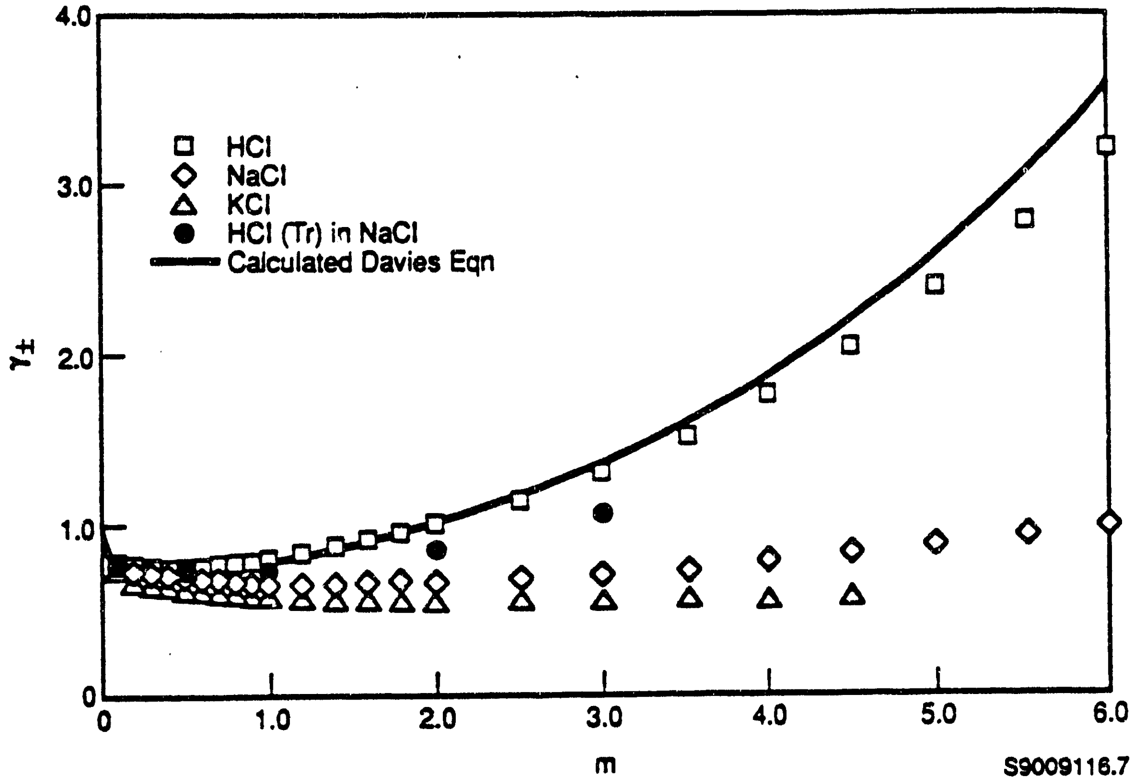


Figure 2.2. Experimental and Calculated Activity Coefficients for 1:1 Electrolytes

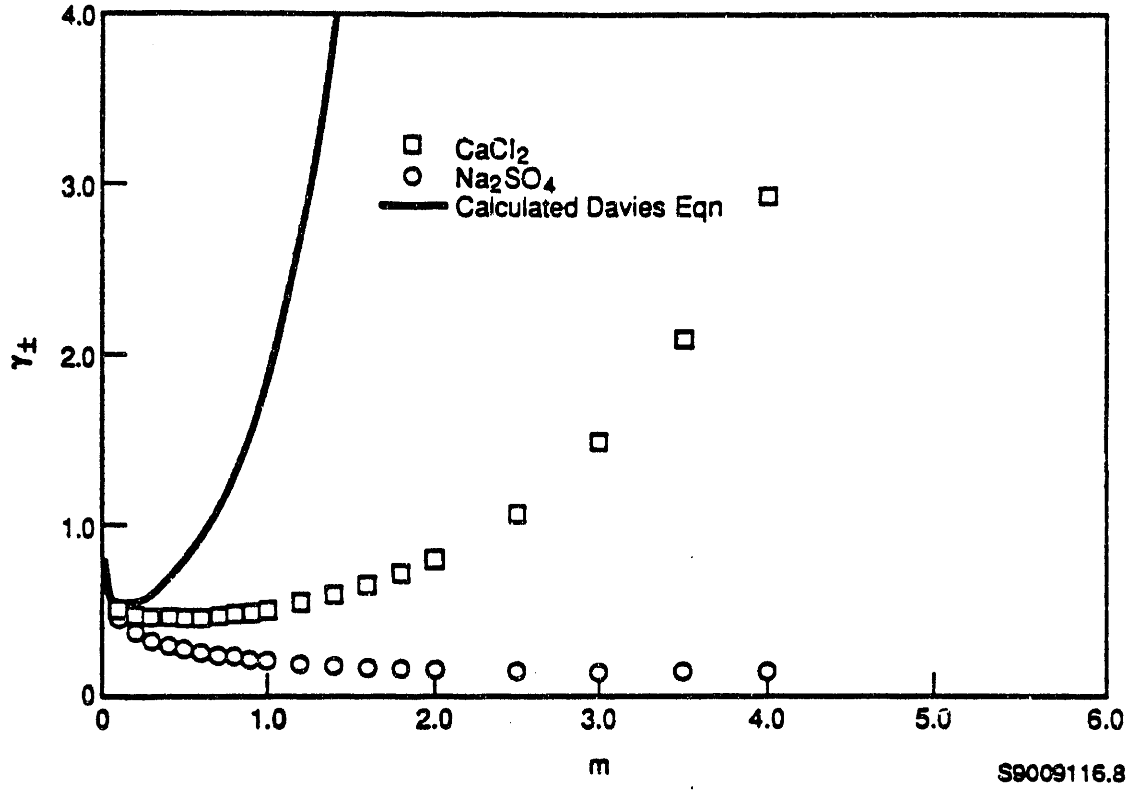


Figure 2.3. Experimental and Calculated Activity Coefficients for 2:1 and 1:2 Electrolytes

treats activity coefficients as universal functions of ionic strength is dependent both on the specific ions present in solution and on their specific concentrations. This fact makes it difficult or even impossible to determine precisely the range or applicability of such models as the Davies equation or the extended Debye-Huckel equation for complex multicomponent solutions.

Various thermodynamic equations exist to predict the activity coefficients of species in high ionic strength solutions. Two approaches in particular can be used to accurately predict activity coefficients of the strong electrolyte behavior exhibited by tank waste: the Pitzer approach (Pitzer 1973; 1979) or the Electrolyte Nonrandom Two-Liquid (NRTL) approach (Chen 1986; Chen and Evans 1986; Chen et al. 1982). These approaches have been shown to accurately predict mineral solubilities in very concentrated solutions, even as high as 20 molal. ASPEN PLUS™ includes the necessary equations to use either approach to model liquid/solid equilibrium, although the necessary model parameters are currently available for only a limited number of systems.

2.3.1 Pitzer Approach

The Pitzer method for calculating activity coefficients for electrolytes in solution has been developed by Kenneth Pitzer and coworkers (Pitzer 1979; Harvie, Mφller, and Weare 1984; Felmy and Weare 1986). The model is based on parameterizing the specific ion interactions in solutions.

These specific interactions must be considered for solution concentrations greater than about 0.1 molal, because the activity coefficients are not universal functions of ionic strength. The activity coefficients of weakly associating ionic species in solution are given by a virial expansion:

$$\ln \gamma_i = \ln \gamma_i^{DH} + {}_j\Sigma B_{ij} m_j + \Sigma_j \Sigma_k C_{ijk} m_j m_k + \ldots.., \tag{1}$$

where γ_i = activity coefficient of species i
γ_i^{DH} = modified Debye-Huckel activity coefficient, which is a function of solution ionic strength
m_j, m_k = molality of species j,k in solution
B_{ij} = functions of specific ion interactions and ionic strength
C_{ijk} = functions of specific ion interactions.

The expressions for B_{ij} and C_{ijk} contain binary ion-interaction parameters and ternary common-ion-interaction parameters. There are four potential binary parameters for cation-anion interactions: $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^{(\phi)}$. The cation-cation and anion-anion interactions which occur in common-ion ternary solutions are described with a constant, Θ_{ij}, parameter. The ternary common-ion-interaction parameters, ψ_{ijk}, may also be used to describe ternary interactions for a specific common-ion. For example, a ternary common-ion-interaction parameter may describe the interactions of the Na^+ and K^+ ions with the common Cl^- anion. The Pitzer ion-interaction parameters are all functions of temperature. This approach can be extended to account for interactions between molecular solutes and ion species.

The parameters described above may be determined from data for binary (i.e., NaCl-H_2O) and common-ion ternary (i.e., NaCl-KCl-H_2O) systems. The necessary data can be collected from experiments that reflect the particular chemical equilibrium to be described. These experiments may include solubility, isopiestic, emf, solvent extraction, or ion exchange studies. The parameters obtained from simple systems can then be used to accurately describe more complex multicomponent systems.

2.3.2 Electrolyte NRTL Model

The Electrolyte NRTL method for calculating activity coefficients for electrolytes in solution has been developed by Chen and coworkers (Chen 1986; Chen and Evans 1986; Chen et al. 1982). The model is based on the specific interactions between ion-pairs and the solvent and with other ion-pairs in solutions. The activity coefficients of weakly associating ionic species in solution are a combination of long-range, ion-ion interactions (which are described by the Pitzer-Debye-Huckel model); the Born equation; and the local interactions (which are described by the nonrandom two-liquid theory). The activity coefficient expression is as follows:

$$\ln \gamma_i = \ln \gamma_i^{*PDH} + \ln \gamma_i^{*Born} + \ln \gamma_i^{lc} \tag{2}$$

where γ_i = activity coefficient of species i

γ_i^{*PDH} = Pitzer-Debye-Huckel activity coefficient, which is primarily a function of solution ionic strength

γ_i^{*Born} = Born activity coefficient, which accounts for the difference in infinite dilution in an aqueous phase and infinite dilution in a mixed-solvent

γ_i^{lc} = local interaction contribution.

The expression for γ_i^{*PDH} is a function of ionic strength and ionic charge of the species. The expression for γ_i^{*Born} is a function of non-aqueous solvent dielectric constant and Born radius of the species. The expression for γ_i^{lc} contains binary parameters describing three types of interactions: 1) electrolytes (ion-pairs) with molecules, 2) molecules with other molecules, and 3) electrolytes and other electrolytes. The electrolyte-electrolyte binary parameters are for two electrolytes which share either one common cation or one common anion. Each of these binary parameters contains a "nonrandomness factor" and "energy parameters." The energy parameters are temperature dependent.

As with the Pitzer method, the parameters described above may be determined from data for binary and common-ion ternary systems. The necessary data can be collected from experiments that reflect the particular chemical equilibrium to be described. These experiments may include solubility, isopiestic, emf, solvent extraction, or ion exchange studies. The parameters obtained from simple systems can then be used to accurately describe more complex multicomponent systems.

Both the Pitzer model and the NRTL model have been used successfully to accurately model solid/liquid equilibrium process to very high concentrations (20 molal), given the necessary model parameters. These electrolyte models are the key to the successful application of ASPEN PLUS™ to tank waste pretreatment processes.

3.0 Model Development

This section describes progress on the Model Verification subtask, which is an ongoing effort to obtain and incorporate thermodynamic parameters into an ASPEN model and test the accuracy of model predictions by comparison with experimental results.

The predictive capability of ASPEN PLUS™ will initially focus on washing and acid dissolution of SST sludge (process illustrated in Figure 2.1). A simulation of a sludge pretreatment process must include

- a description of feed streams to the process. The composition of the sludge can be determined from a combination of analytical techniques and material balance, as illustrated in Section 3.1.
- process conditions and design specifications for each process unit operation. The process requirements will be set by downstream pretreatment processes used for efficient separations of waste components (i.e., solvent extraction). A process design must ultimately satisfy requirements set by final treatment (i.e., vitrification) and disposal (i.e., repository) of the various high-level and low-level constituents.
- an accounting of the chemical reactions that are expected to take place in the process. These chemical reactions may include dissolution and precipitation of inorganic solids or aqueous reactions of dissolved species. The stoichiometry and the equilibrium constant for the temperatures of interest are needed for each reaction. The procedure for including this information is described in Section 3.2.
- the parameters that will result in accurate predictions of thermodynamic quantities using the selected thermodynamic models. For electrolyte modeling, it is important to have terms describing binary and ternary ion interactions that result in accurate predictions of activity coefficients for all aqueous species. The procedure for including this information is also described in Section 3.2.

3.1 SST Waste

Processes for removing high-level constituents from SST waste depend on the extent to which SST sludge will dissolve and the composition of the resulting solution. Current sludge dissolution studies are being conducted on actual sludge samples from Tanks B-110 and U-110. Sludge from these tanks has been fairly well-characterized in comparison with the other tanks. Results from inductively coupled plasma (ICP) and ion chromatography (IC) analyses, which were reported earlier (Jones, Colton, and Bloom 1991; WHC 1990), are shown in Table 3.1. Preliminary X-ray diffraction (XRD) results are shown in Table 3.2.

The major sludge constituents are Na, Si, Fe, NO_3, and PO_4. Aluminum is also a major constituent in most SST sludges. Bismuth is present in significant quantities in waste from the $BiPO_4$

Table 3.1. B-110 and U-110 Sludge Composition

	Dry Weight Percent(a)	
Element	B-110	U-110
Al	0.29	20.6
Ag	0.005	--
Ba	0.003	0.006
Bi	4.3	3.7
B	< DL(b)	0.02
Ca	0.21	0.10
Cr	0.20	0.10
Cu	< DL(b)	0.005
Fe	4.8	2.6
La	0.01	--
Pb	0.28	--
Mg	0.05	0.08
Mn	0.02	0.64
Ni	--	0.02
P	4.0	--
K	--	--
Si	2.3	9.1
Na	23.8	13.2
Sr	0.05	0.08
Zn	0.02	0.03
Zr	< DL(b)	0.01
NO_3^-	39.7	8.1
NO_2^-	2.4	0.007
TOC	0.10	0.17
PO_4^{3-}	6.2	6.7
SO_4^{2-}	2.6	2.0
U	0.06	1.1
F^-	0.40	1.5
Cl^-	0.13	0.16

(a) Results from inductively coupled plasma spectroscopy (ICP) and ion chromatography (IC). Data reported by Jones, Colton, and Bloom (1991); WHC (1990).

(b) Less than the detection limit.

Table 3.2. Preliminary B-110 and U-110 Sludge X-Ray Diffraction Results

B-110	U-110
$NaNO_3$[(a)]	$NaNO_3$[(a)]
$BiPO_4$[(a)]	AlOOH[(a)]
Sodium-aluminate-silicate-hydrate	$Al(OH)_3$[(a)]
	$Na_7F(PO_4)_2 \bullet 19H_2O$
	$Na_8(Al_6Si_6O_{24})SO_4 \bullet 3H_2O$
	Na_2SO_4
	$NaUO_2PO_4$
	Bi metal
	$Al_2Bi_{24}O_{39}$

(a) Indicates major species present.

process. It is essential to include these major constituents first in a predictive model, since it is expected that most of the bulk chemical behavior of the waste would be controlled by these constituents.

Analytical results were used to prepare a material balance for estimating the mineral composition of the sludge. However, it must be emphasized that knowing the mass of these initial phases is not crucial. ASPEN PLUS™ can be used to estimate mineral phases that could be present initially by dissolving or precipitating calculated equilibrium phases as appropriate. The results of this balance are shown in Tables 3.3 (B-110) and 3.4 (U-110). In each case, assumptions were made regarding the major crystalline and amorphous species that would be present. The relative amounts of each species were adjusted, within the constraints of element balances, in order to close the material balance. To date, SST sludge XRD analyses have not been conducted with the objective of obtaining quantitative results. Also, there may be several amorphous species present that would not be detected by an XRD analysis. Therefore, a complete sludge composition to be used as input for a predictive model may be estimated, but not completely described, by available information.

The material balance closed within 10% for the B-110 case. The error would be less if the oxide/hydroxide terms for all the minor constituents were added. Balances for aluminum, silicon, phosphate, sulfate, and fluoride were fixed to close to 100%. The 5% sodium balance error is acceptable considering the analytical uncertainties for nitrate, nitrite, phosphate, and sulfate, as well as for sodium.

The material balance for the U-110 sludge case closed within 6% if the oxides/hydroxides associated with all the minor constituents were neglected. The speciation of this sludge is much more complex. There are several potential species that contain multiple constituents. Additional characterization studies of these materials will assist in this area.

Table 3.3. B-110 Sludge Material Balance

Species	Formula	100 g Total Dry Sludge g mole	MW	grams	mol %
Sodium Nitrate	$NaNO_3$	0.6403	84.99	54.42	65.04
Sodium Nitrite	$NaNO_2$	0.0522	69.00	3.60	5.30
Sodium Fluoride	NaF	0.0211	41.99	0.88	2.14
Sodium Phosphate	Na_3PO_4	0.0447	163.94	7.33	4.54
Sodium Sulfate	Na_2SO_4	0.0271	142.04	3.84	2.75
Boehmite	AlO(OH)	0.0107	59.99	0.64	1.09
Silicon Dioxide	SiO_2	0.0819	60.09	4.92	8.32
Iron Hydroxide	FeO(OH)	0.0859	88.86	7.64	8.73
Bismuth Phosphate	$BiPO_4$	0.0206	303.95	6.25	2.09
Trace (elements only)				1.14	
Total		**0.9845**		**90.67**	**100.00**

Balances	g measured	g calc'd	% error
Na	23.8	20.73	12.89
Al	0.29	0.29	0.00
Si	2.3	2.30	0.00
PO_4	6.2	6.20	0.00
SO_4	2.6	2.60	0.00
F	0.4	0.40	0.00

Element Balance	g/100 g	MW	g mol/100 g
Al	0.29	26.98	0.0107
Bi	4.3	208.98	0.0206
Fe	4.8	55.85	0.0859
Si	2.3	28.09	0.0819
Na	23.8	22.99	1.0352
NO_3	39.7	62.00	0.6403
NO_2	2.4	46.01	0.0522
PO_4	6.2	94.97	0.0653
SO_4	2.6	96.06	0.0271
F	0.4	19.00	0.0211
Other	1.14	19.00	0.0599
Total	87.93		2.1002

Table 3.4. U-110 Sludge Material Balance

		100 g Total Dry Sludge			
Species	Formula	g mole	MW	grams	mol %
Sodium Nitrate	$NaNO_3$	0.1306	84.99	11.10	16.61
Sodium Nitrite	$NaNO_2$	0.0002	69.00	0.01	0.02
Sodium Fluoride	NaF	0.0790	41.99	3.32	10.04
Aluminum Silicate	$Al_2O_3SiO_2$	0.1991	162.04	32.26	25.32
Na-Phosphate	Na_3PO_4	0.0659	163.94	10.81	8.38
Na-Al-Si-Sulfate	$Na_8(Al_6Si_6O_{24})$ $SO_4{*}3H_2O$	0.0208	1048.42	21.83	2.65
Boehmite	AlO(OH)	0.2389	59.99	14.33	30.38
Iron Hydroxide	FeO(OH)	0.0466	88.86	4.14	5.92
Al-Bi-Oxide	$Al_2Bi_{24}O_{39}$	0.0007	5693.47	4.20	0.09
Na-U Phosphate	$NaUO_2PO_4$	0.0046	387.96	1.79	0.59
Trace (elements only)				1.42	
Total		**0.7864**		**105.21**	**100.00**

Balances	g measured	g calc'd	% error
Na	13.2	13.3	-0.79
Al	20.6	20.6	0.00
Si	9.1	9.1	0.00
PO_4	6.7	6.7	0.00
SO_4	2.0	2.0	0.00
F	1.5	1.5	0.00

Element Balance	g/100 g	MW	g mol/100 g
Al	20.6	26.98	0.7635
Bi	3.7	208.98	0.0177
Fe	2.6	55.85	0.0466
Si	9.1	28.09	0.3240
Na	13.2	22.99	0.5742
U	1.1	238.00	0.0046
NO_3	8.1	62.00	0.1306
NO_2	0.007	46.01	0.0002
PO_4	6.7	94.97	0.0705
SO_4	2.0	96.06	0.0208
F	1.5	19.00	0.0790
Other	1.42		
Total	70.03		2.0317

3.2 Data Regression

Thermodyanmic model parameters for the Pitzer method are obtained through data regression of equilibrium data. Several types of equilibrium data can be used, including vapor pressure, osmotic coefficient, solubility, solvent extraction, and emf. When regressing the data, some judgment needs to be made on the required accuracy and quality of these parameters. These parameters are intended to predict the data or similar data within some acceptable uncertainty. Certainly, trade-offs can be made between model accuracy and the time and cost associated with improving the model.

Pitzer parameters have been published by numerous investigators (see summaries in Pitzer 1979, 1986; Greenberg and Møller 1989; Felmy and Weare 1986) for several species. These published parameters were determined by regressing experimental data of certain concentration and temperature ranges. Extrapolation of these parameters far beyond the range of the experimental data may not result in accurate predictions. Therefore, it is important to understand the limitations of model parameters, and, if accurate results are required, to obtain any additional data necessary to extend the useful range of the parameters.

The source of the model parameters for each component studied thus far is described in the following sections. Model parameters for this project have been obtained by a combination of direct use of published parameters, refitting published parameters, or calculating parameters from published experimental data. As the work proceeds, parameters will also be determined from experimental data generated specifically for this project.

3.2.1 Binary Interactions

Binary interaction parameters for the electrolyte thermodynamic calculations have been obtained for interactions between Na^+ ions and the following anions: Cl^-, F^-, NO_3^-, NO_2^-, OH^-, SO_4^{2-}, PO_4^{3}, and $Al(OH)_4^-$. These parameters have been obtained by a combination of regressing published experimental data, refitting published correlations for these parameters, or using published parameters directly with no additional adjustment. Table 3.5 summarizes the values obtained for these parameters, as well as the applicable range and source for each binary pair. A more detailed description of the available literature on these interactions in given in Section 4.0.

Na^+-NO_3^- and Na^+-NO_2^- binary interaction parameters were regressed from published osmotic coefficient data as a function of composition at 25°C. Figure 3.1 compares the published data with the resulting correlation. The published $NaNO_3$ osmotic coefficients (Wu and Hamer 1980) were smoothed data from several investigators, ranging from 0.001 molal to saturation (10.83 molal). The published $NaNO_2$ osmotic coefficients (Staples 1981) were also smoothed data, ranging from 0.001 molal to saturation (12.34 molal).

There are significant gaps in $NaNO_3$ and $NaNO_2$ data at temperatures other than 25°C. First derivatives of Pitzer parameters as a function of temperature have been reported for $NaNO_3$, as well as for several other species (Silvester and Pitzer 1978). These derivatives were determined from heat of solution data for each of the electrolyte solutions reported. However, these derivatives were

Table 3.5. Values of Pitzer Binary Parameters in Model

Form of temperature-dependent equation:

$$f(t) = a + b(T-TR) + c(1/T-1/TR) + d*\ln(T/TR) + e(T^2-TR^2)$$
where TR=298.15 K

Cation	Anion	Term	B^0	B^1	C	Range	Source
Na^+	$Al(OH)_4^-$	a	0.045017	0.30455	-2.661E-04	0°C-100°C	Estimate by Wesolowski (1992)
		b	0	0	0		
		c	-448.3	-985.9	65.099		
		d	-1.3366	-2.9187	0.17457		
		e	0	0	0		
Na^+	Cl^-	a	0.07391	0.27386	0.001609	0°C-300°C	Greenberg and Mφller (1989)
		b	0	7.567E-4	0	0-6 m	
		c	-257.83	0	27.255		
		d	0.65385	0	0.0595435		
		e	0	6.339E8	0		
Na^+	F^-	a	0.0215	0.2107	0	25°C, 1 m	Pitzer (1979)
		b	5.36E-04	8.7E-04	0	0.7 m	Sylvester & Pitzer (1978)
Na^+	NO_2^-	a	0.0493	0.185	-2.452E-3	25°C, satn	Staples (1981)
Na^+	NO_3^-	a	0.003695	0.2049	-5.684E-5	25°C, satn	Wu and Hamer (1980)
Na^+	OH^-	a	0.1069	-0.8749	1.063E-3	0°C-100°C	Perry et al. (1984)
		b	-2.433E-3	0.0913	2.101E-4	0-10 m	
		c	0	0	0		
		d	0	0	0		
		e	3.15E-06	-1.342E-4	-3.526E-7		
Na^+	PO_4^{3-}	a	0.1781	-0.0583	-0.0533	25°C, 0.7 m	Pitzer (1979)
Na^+	SO_4^{2-}	a	0.0175	1.096	0.00614	25°C-300°C	Greenberg and Mφller (1989)
		b	0.2283	-0.1099	-0.00695	1.5 m	
		c	-11960	75.60	657.26		
		d	-90.313	22.860	3.784		
		e	-9.6E-6	6.75E-5	1.92E-6		

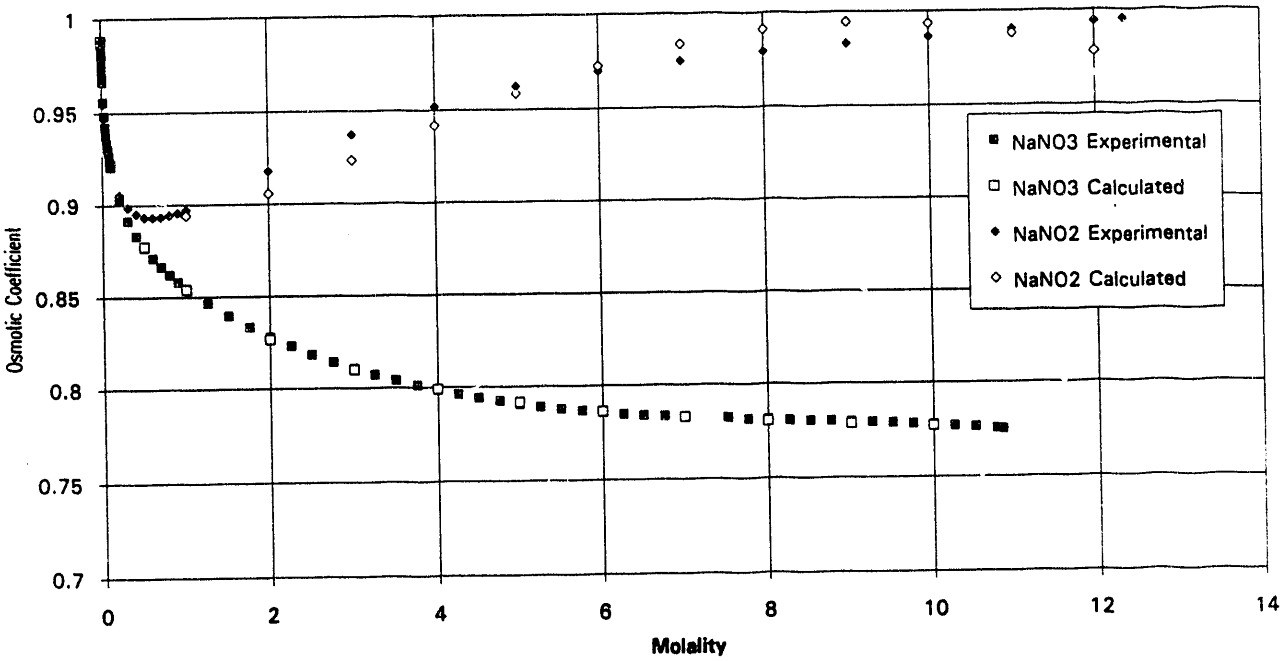


Figure 3.1. Experimental and Calculated Osmotic Coefficients for Sodium Nitrate and Sodium Nitrite at 25°C

determined for $NaNO_3$ solutions up to 2.2 molal, which does not cover the entire concentration range of interest for this project. When these temperature derivatives were used to extrapolate the Pitzer parameters to predict the solubility of sodium nitrate at higher temperatures, the resulting simulation had multiple solutions. Therefore, either additional data at higher temperatures (25°C to 100°C) or a different method of extrapolation is needed for this case. Since $NaNO_3$ and $NaNO_2$ are major components in tank waste, and proposed processes to treat these wastes would require operation at a variety of temperatures, osmotic studies of these constituents at higher temperatures have been started.

NaOH binary interaction parameters were regressed from published vapor pressure data (Perry 1984) for a composition range of 0 to 10 molal and temperature range of 0°C to 80°C. Figure 3.2 compares the published data with the resulting correlation. Extrapolation to higher concentration will probably not be necessary for this project, since the concentrations of NaOH during pretreatment will likely not exceed 2 molal. This also simplifies the model because NaOH can be assumed to be completely dissociated at concentrations less than 10 molal.

Na^+-F^- binary parameters at 25°C and up to 1 molal have been published by Pitzer (1979). First derivatives of these parameters with respect to temperature up to 0.7 molal have been published by Silvester and Pitzer (1978). These parameters are accurate enough to be used directly in the model at this time, since the solubility of NaF in water is about 1 molal at 25°C.

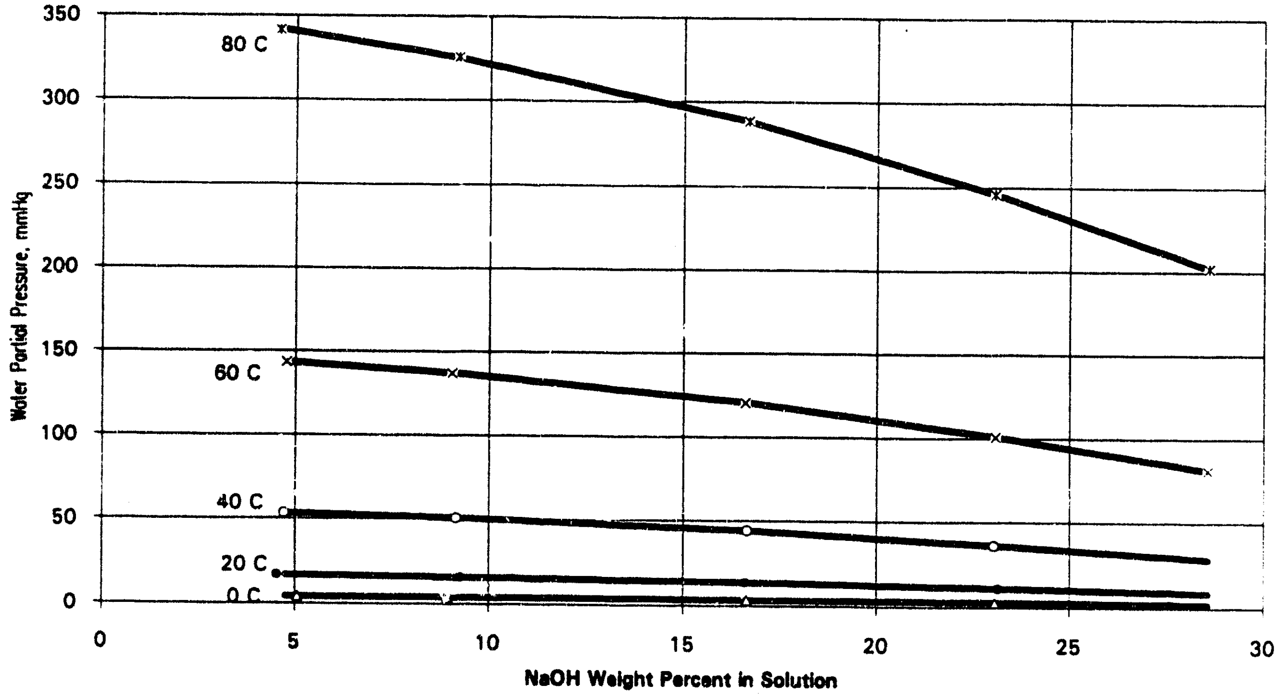


Figure 3.2. Experimental and Calculated Water Partial Pressure Over Caustic Solutions

Correlations for the Na_2SO_4 and NaCl binary parameters as functions of temperature have been published by Greenberg and Møller (1989) and Møller (1988). The Na_2SO_4 parameters apply to the temperature range of 25°C to 250°C at concentrations up to about 1.5 molal. The NaCl parameters apply to the temperature range of 0°C to 300°C at concentrations up to about 6 molal. These correlations have been refit for the functional form of the correlations used in ASPEN PLUS™.

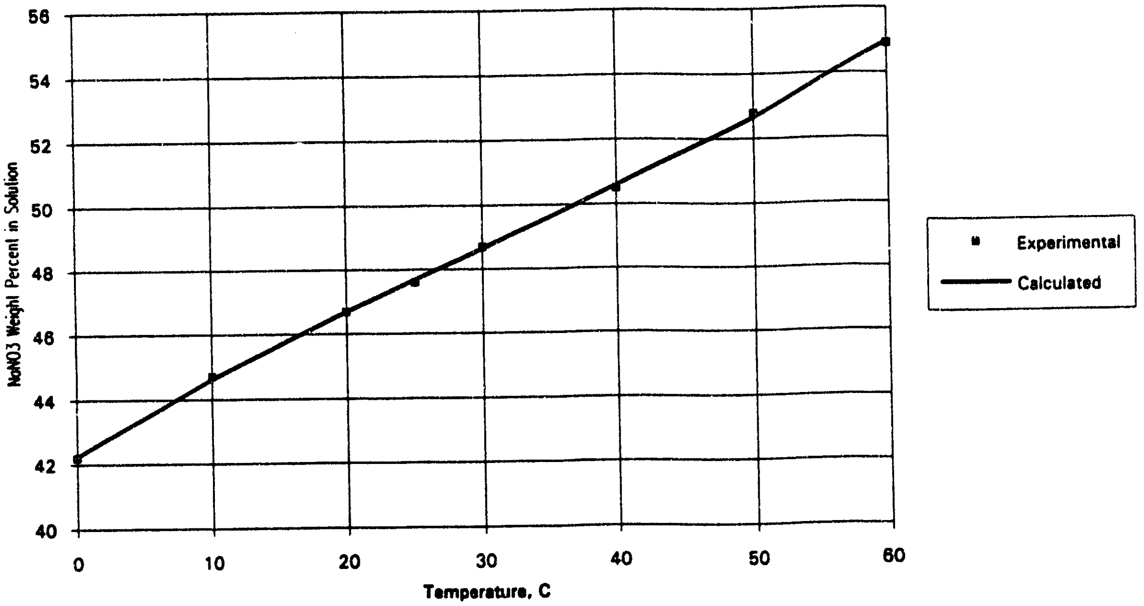
Binary parameters have been published (up to 0.7 molal) at 25°C (Pitzer 1979). These published parameters will be included in the model until additional information is available for other temperatures. Published binary parameters for Na^+-$Al(OH)_4^-$ (Wesolowski 1992) were calculated for the temperature range of 0°C to 100°C. These data have also been included in the model.

3.2.2 Chemical Reactions

Chemical equilibrium constants, as a function of temperature, are needed to predict dissolution and precipitation of solids and to predict important association and dissociation of aqueous species. Literature values are available for many important chemical equilibrium constants for aqueous association/dissociation reactions. For example, carbonic acid dissociation, sulfuric acid dissociation, and phosphoric acid dissociation are systems that have been well studied.

Accurate equilibrium constants for solids that dissociate to strong electrolytes are not as well known, since accurate activity coefficients are needed. These equilibrium constants are typically calculated using salt solubility data and accurate binary Pitzer parameters for the salt ion pair. Thus, the Pitzer ion-interaction parameters must be available for the appropriate binary solution as a function of temperature. Figures 3.3 to 3.6 show the solubility of important salts in water, $NaNO_3$, $NaNO_2$, NaF, and Na_2SO_4 as a function of temperature. The calculated curve in each figure represents a fitting of these data to the prescribed temperature-dependent equation (Table 3.6) for the salt dissolution constants. Such salt dissolution constants are reasonable for the NaF and Na_2SO_4 systems where the temperature dependence of the Pitzer ion-interaction parameters is known. However, for $NaNO_3$ and $NaNO_2$ as we have described, accurate values for the binary Pitzer ion-interaction parameters are available only at 25°C. These 25°C values were then used at all temperatures to calculate the salt dissolution equilibrium constants. More accurate salt dissolution constants will be calculated once accurate experimental data on $NaNO_3$ and $NaNO_2$ solutions are available with which to calculate the binary Pitzer ion-interaction over a range of temperatures.

An initial list of solids to be considered for sludge dissolution and precipitation reactions is shown in Table 3.7. There are many solid phases that could exist under a large range of system compositions and temperatures. However, in order to make this task more manageable, only those phases that are believed to exist, based principally on our analysis of experimental solubility data, under either strong acid or strong base conditions and under moderate temperatures will be included in this initial model. The quality of the assumptions and choices about which phases are present will be tested when model predictions are compared with experimental data generated from actual sludge pretreatment processes. Inaccuracies in the model are a symptom of failing to include an important chemical reaction in the calculations. Such calculations will also help guide our experimental efforts.



*used binary interaction terms valid only for 25 C

Figure 3.3. Experimental and Calculated Solubility of Sodium Nitrate in Water

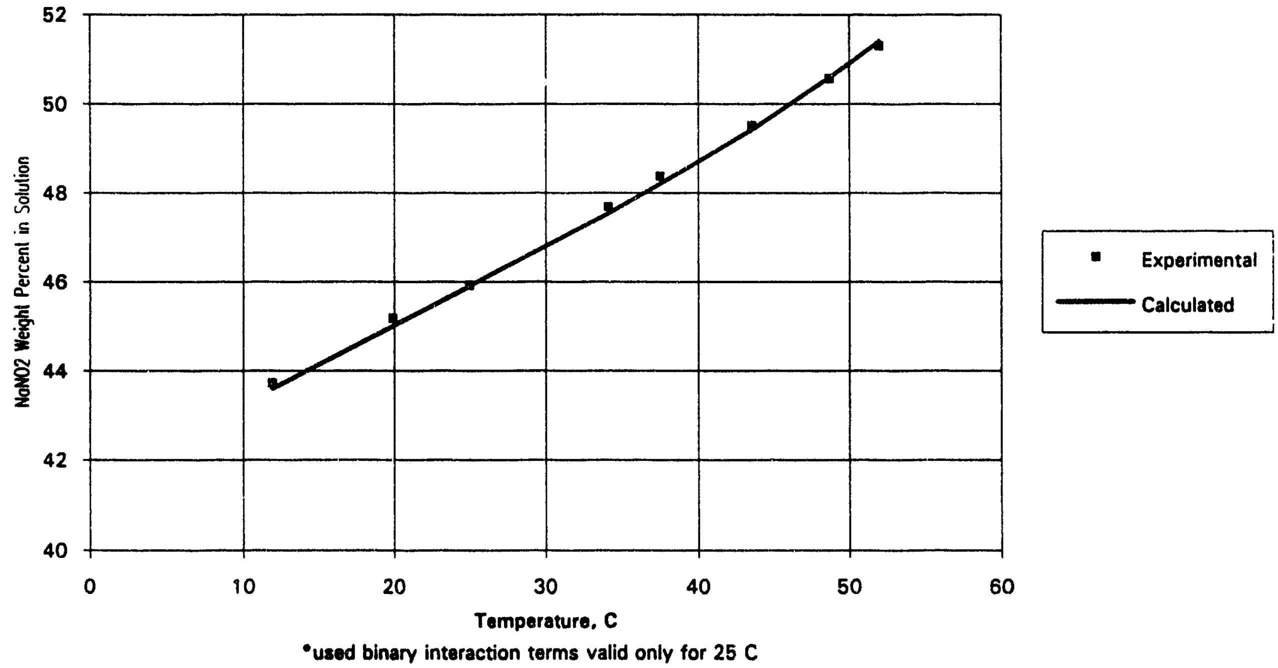


Figure 3.4. Experimental and Calculated Solubility of Sodium Nitrite in Water

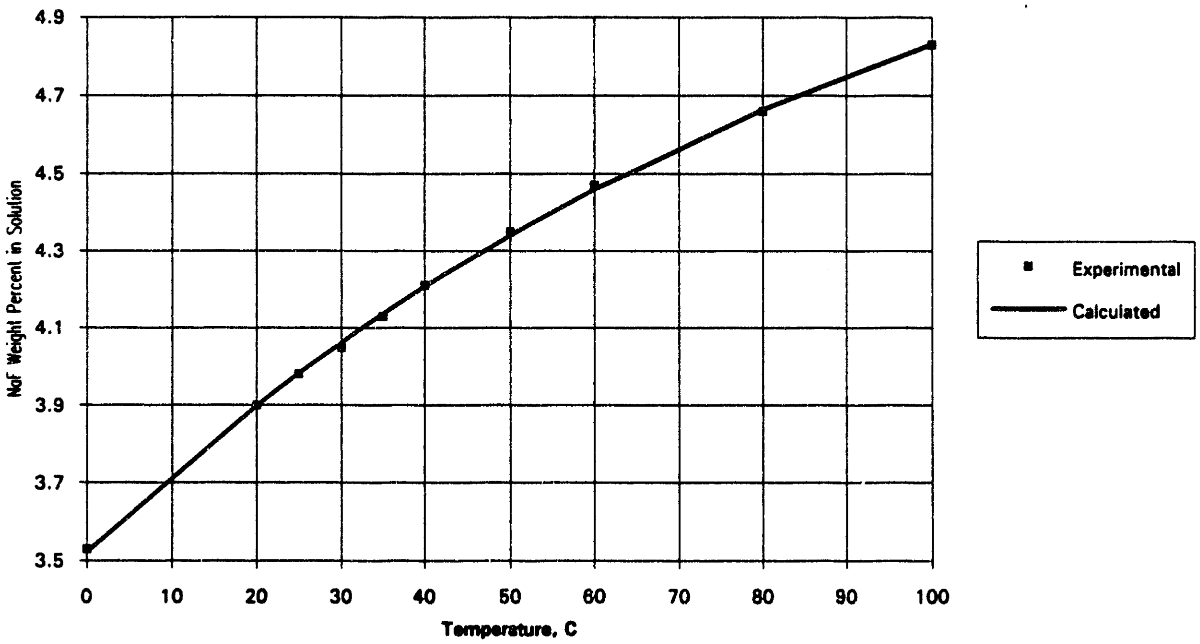


Figure 3.5. Experimental and Calculated Solubility of Sodium Fluoride in Water

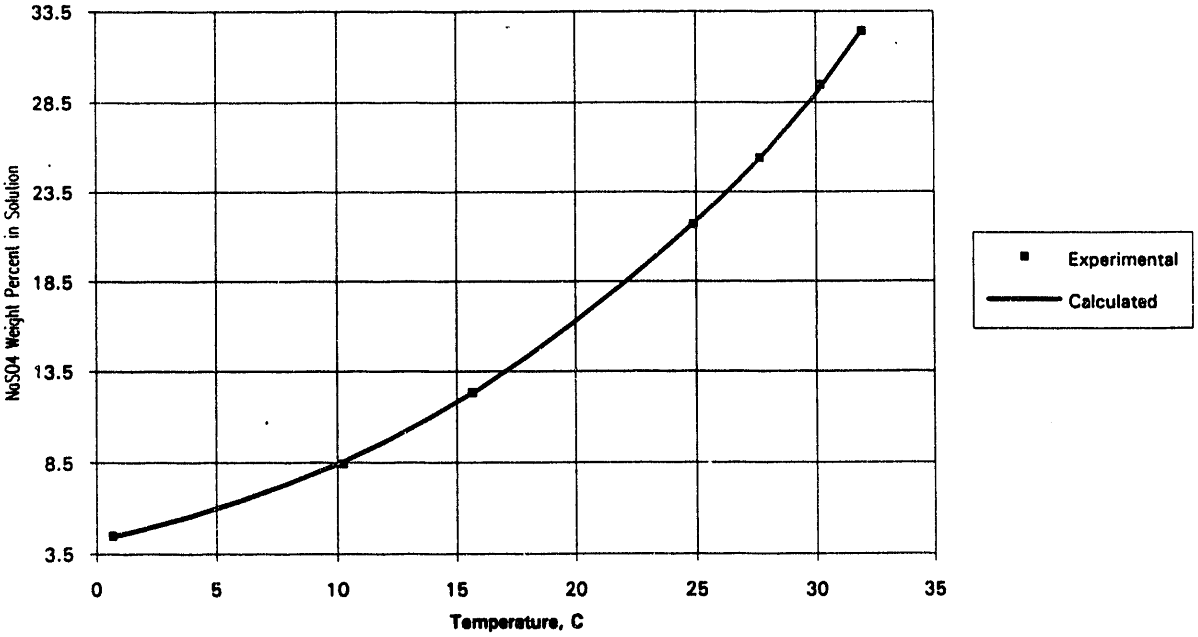


Figure 3.6. Experimental and Calculated Solubility of Sodium Sulfate ($Na_2SO_4 \cdot 10\ H_2O$) in Water

3.2.3 Ternary Interactions

Ternary interaction parameters have been obtained for interactions between sodium ions and the following anion pairs: OH^- and NO_3^-, OH^- and NO_2^-, OH^- and F^-, NO_3^- and NO_2^-, NO_3^- and F^-, and OH^- and $Al(OH)_4^-$. These parameters have been obtained by either regressing published experimental data or by using published parameters directly with no additional adjustment. Table 3.8 summarizes the values obtained for these parameters, as well as the applicable range and source for each ternary system. In each case, only the Θ parameters were obtained. So far, we have only considered a single cation, Na^+. In a single cation system, the Θ and the ψ parameters can be difficult to uniquely determine. When the model is expanded to include other cations, an improved value of Θ will be determined along with the appropriate values for ψ.

The Pitzer Θ parameter was determined for the $NaNO_3$-$NaNO_2$ system using solubility data for the mixed salt system at 21°C. Other inputs to the regression included binary Pitzer parameters (at 25°C) and correlations of the single salt dissolution equilibrium (lnK) as a function of temperature. The $NaNO_3$ lnK correlation was obtained from solubility data at 0°C to 60°C and binary Pitzer parameters at 25°C. The $NaNO_2$ lnK correlation was obtained from solubility data at 11°C to 52°C and binary Pitzer parameters at 25°C. Figure 3.7 shows the agreement of the resulting correlation with the experimental data.

Table 3.6. Values of lnK for Precipitation/Dissolution Reactions in Model

Form of temperature-dependent equation:
lnK = K-SALT = a + b/T + c*ln T + d*T (T in K)

K-SALT (mole fraction basis)(a)

Salt	a	b	c	d	Range	Source
NaF	30.788	-2370	-5.6177	0	0°C-100°C	Linke (1965), Vol. II, p. 1029.
$NaNO_3$	1245.5	-33988	-218.26	0.3573	0°C-60°C(b)	Linke (1965), Vol. II, p. 1069.
$NaNO_2$	49.340	-2920	-7.6764	0	0°C-52°C(b)	Linke (1965), Vol. II, p. 1066.
$Na_2SO_4*10H_2O$	18.191	-9850	0	0	0°C-32°C	Linke (1965) Vol II, p. 1122.
$Al(OH)_3$	-222.20	5469.45	36.9975	-0.032095	0°C-100°C	Wesolowski (1992)

(a) K-SALT is the ASPEN keyword for the natural logarithm of the equilibrium constant for the solid dissociation reaction.

(b) K-SALTs for sodium nitrate and nitrite were fitted using binary Pitzer parameters only for 25°C. Therefore, this K-SALT is accurate only for 25°C, and values at other temperatures are extrapolations.

Table 3.7. Initial List of Solids Included in Sludge Acid/Base Dissolution

$NaNO_3$
$NaNO_2$
Na_2SO_4
$Na_2SO_4 \bullet 10H_2O$
NaF
NaCl
Sodium Phosphate(a)
Sodium Carbonate(a)
Sodium Silicate(a)
$Na_2O \bullet Al_2O_3 \bullet 2.5H_2O$

$3Na_2O \bullet Al_2O_3 \bullet 6H_2O$
$Al_2O_3 \bullet 3H_2O$
Na_2SiF_6

$AlCl_3 \bullet 6H_2O$
$AlF_3 \bullet 3H_2O$
Aluminum Phosphate(a)
$Al(NO_3)_3 \bullet 9H_2O$
$Al_2(SO_4)_3 \bullet 16H_2O$
Aluminum Silicate(a)

$FeCl_3 \bullet 6H_2O$
$FeCl_3 \bullet 4H_2O$
$FeCl_3 \bullet 2H_2O$
$FeF_3 \bullet 3H_2O$
$Fe(NO_3)_3 \bullet 9H_2O$
$Fe(OH)_3$
Ferric Phosphate(a)
Ferric Sulfate(a)

(a) There are several possible solid phases for the sodium phosphate and the sodium silicate systems. However, phases that would expected under acid or base conditions will be considered first, neglecting phases that would precipitate from neutral solutions.

Table 3.8. Values of Pitzer Ternary Parameters in Model

Form of temperature-dependent equation:
$f(t) = a + b(T-TR) + c(1/T-1/TR) + d*\ln(T/TR) + e(T^2-TR^2)$
where TR=298.15 K

Ion 1	Ion 2	Term	Value	Range	Source
OH^-	$Al(OH)_4^-$	a	0.014	0°C-100°C	Estimate by Wesolowski (1992)
OH^-	NO_2^-	a	-0.055926	25°C	Plekhotkin & Bobrovskaya (1970)
OH^-	NO_3^-	a	-0.04590	25°C	Plekhotkin & Bobrovskaya (1970)
OH^-	F^-	a	0.1218	0°C-40°C	Linke (1965), Vol. II, p. 1032
		b	0.00318		
NO_3^-	F^-	a	0.03005	25°C	Zhikharev et al. (1978)
NO_3^-	NO_2^-	a	0.004526	21°C	Linke (1965), Vol. II, p. 1067$^{(a)}$

(a) Used binary ion-interaction terms for 25°C.

The Pitzer Θ parameters were determined for the $NaNO_2$-NaOH (Figure 3.8) and $NaNO_3$-NaOH systems at 25°C by using solubility (Plekhotkin and Bobrovskaya 1970) data of the salt in varying concentrations of caustic solution. Figures 3.8 and 3.9 show the ASPEN predictions and experimental data for the two systems.

The Pitzer Θ parameter for the NaOH-NaF system was obtained from regressing solubility data (Linke 1965) at 0°C, 20°C, and 40°C. Figure 3.10 compares the experimental data with ASPEN predictions at 20°C.

The Pitzer Θ parameter for the $NaNO_3$-NaF system was determined from salt solubility data at 25°C (Zhikharev et al. 1978). Figure 3.11 compares the experimental data with ASPEN predictions. The error in the prediction is much higher than the other systems studied so far. This system may benefit from the addition of a ψ term to fine-tune the model prediction.

The Pitzer Θ parameter for the NaOH-$NaAl(OH)_4$ system was estimated by Wesolowski (1992) for the temperature range of 0°C to 100°C. Clearly, the thermodynamic model being developed as part of this project is capable of accurately modeling a wide range of experimental solubility data.

3.3 Example Flowsheet

As the thermodynamic parameters are developed, they are included in a template ASPEN PLUS™ input file. A copy of the current template file is included in Appendix A. This template, which can be used as a starting point for building an input file for a complete process simulation, contains information on

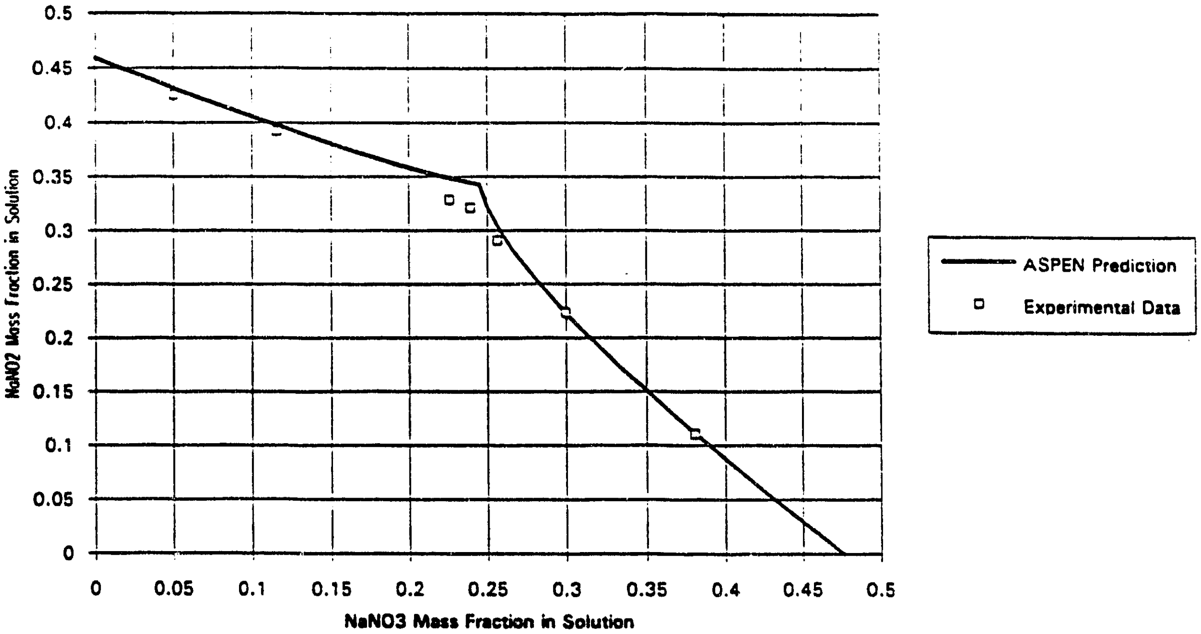


Figure 3.7. Solubility of $NaNO_3$-$NaNO_2$ in Water, 21°C

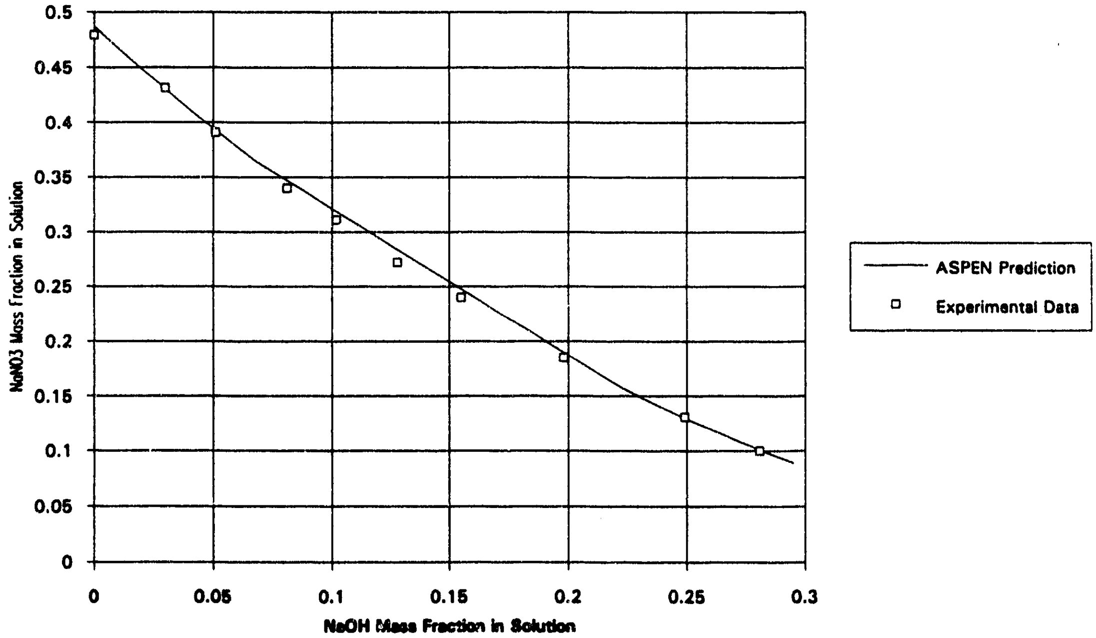


Figure 3.8. Solubility of $NaNO_3$ in Aqueous NaOH, 25°C

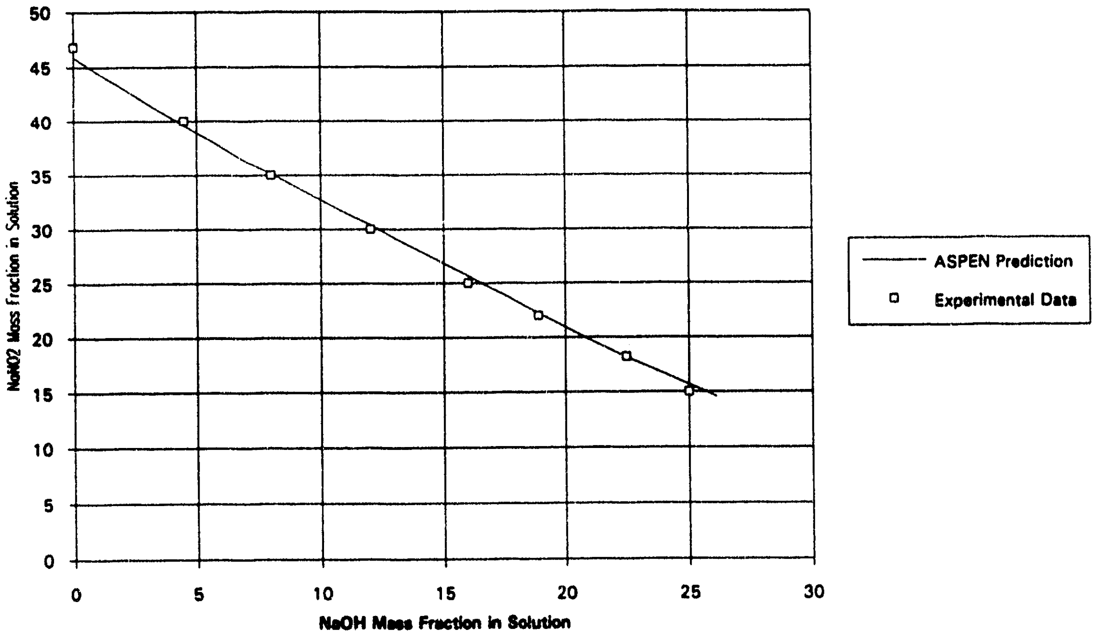


Figure 3.9. Solubility of $NaNO_2$ in Aqueous NaOH, 25°C

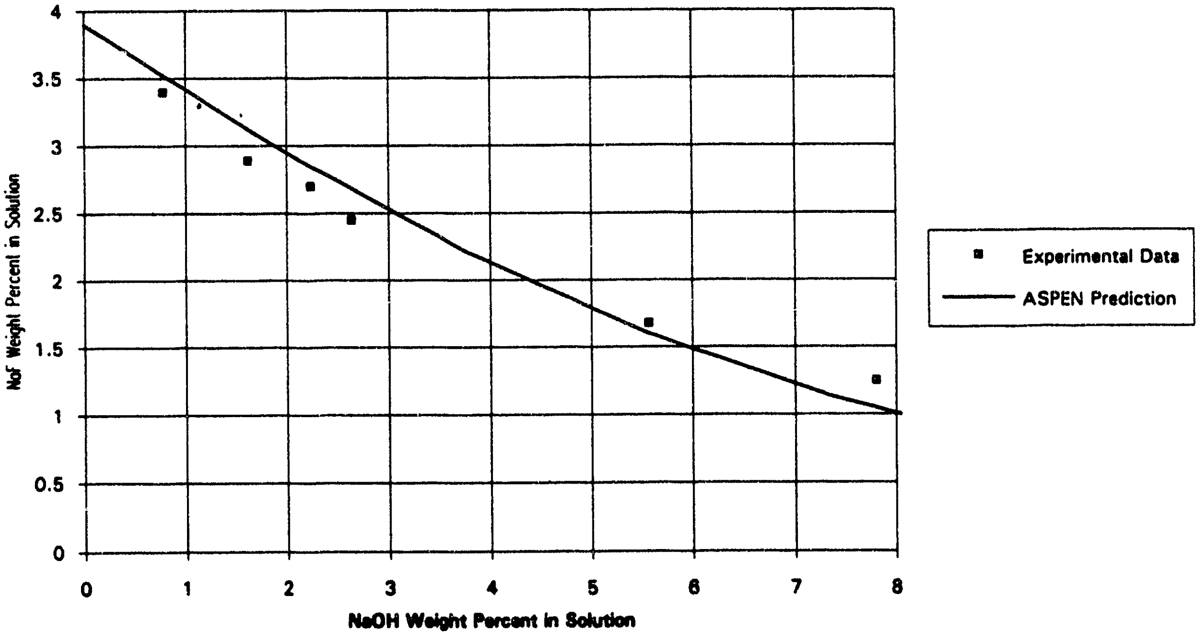


Figure 3.10. Solubility of NaF in Aqueous NaOH, 25°C

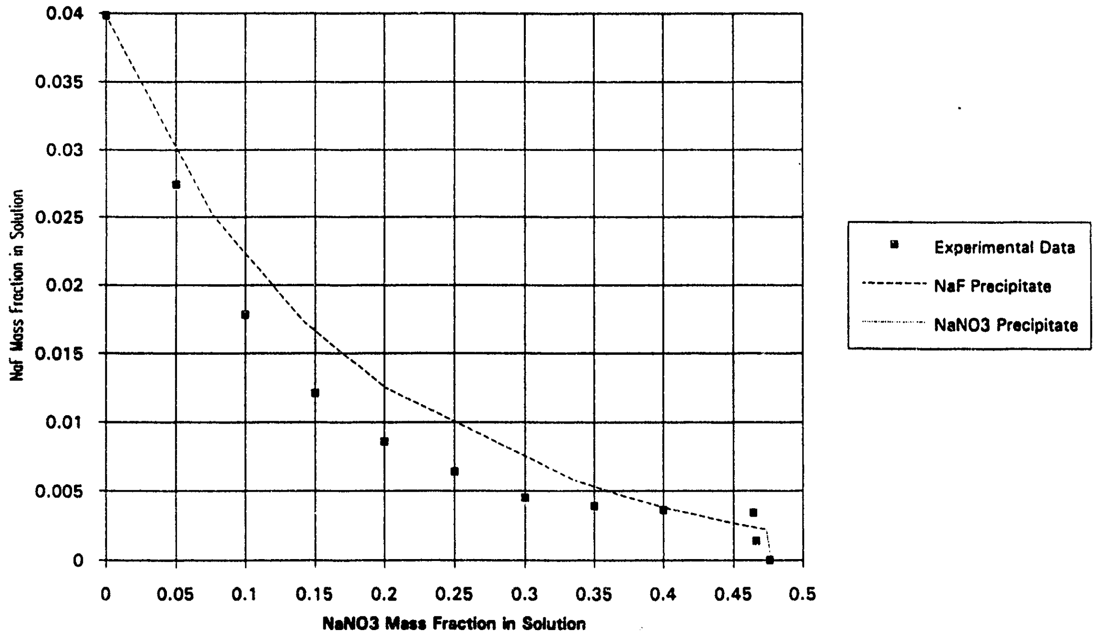


Figure 3.11. Solubility of $NaNO_3$-NaF in Water, 25°C

- chemical components to be used in the simulation and references to the ASPEN databanks containing component properties needed for the flowsheet calculations.

- the models to be used to calculate thermodynamic properties. In this case, the ASPEN physical property model SYSOP16 will be used, which uses the Pitzer equations to calculate activity coefficients.

- the physical properties that are needed for model calculations which are not included in the ASPEN databanks. Users may also input values for properties directly, which automatically override values that may be retrieved from ASPEN databanks. In this case, the Pitzer binary and ternary parameters are explicitly entered into the template input file.

- the chemical reactions that are expected to occur. This includes complete dissociation of strong electrolytes, dissolution and precipitation of salts, and aqueous association and dissociation reactions. Both the stoichiometry and the equilibrium constants are given. The equilibrium constants are typically entered as a function of temperature.

In addition, this template includes simple stream, flowsheet, and block paragraphs, which can be considered place-holders for information that will be required to model specific process flowsheets.

A simple water dissolution flowsheet was developed for the $NaNO_3$-$NaNO_2$-NaF-H_2O system using the binary and ternary parameters obtained as part of this project. Figure 3.12 is a simple block flow diagram of this flowsheet, which assumes perfect solid-liquid separations as a first approximation. Liquid and solid are contacted in the H1, H2, and H3 blocks, and the solid-liquid equilibrium calculations are performed in these blocks. The S1, S2, and S3 blocks are simple separation blocks, where the aqueous components and the solid components are separated into two product streams. A simulation could also be conducted with more detail, incorporating retention of some of the liquid with the solids, as would be the case in a real process. This three-stage cross-current wash process is designed to dissolve all of the $NaNO_2$ in the first stage, dissolve the remaining $NaNO_3$ in the second stage, and dissolve the remaining NaF in the third stage. The simulation was optimized to calculate the minimum amount of water that would have to be added to each stage to accomplish these objectives.

The feed consists of a mixture of $NaNO_3$, $NaNO_2$, and NaF in the same proportions that were calculated from the B-110 sludge material balance (Table 3.3). The input file and key pages of the output file are included in Appendix B. The only ion interactions that have not been characterized by the previous regression work is the Na-F-NO_2 ternary interaction. However, since the F^- and the NO_2^- are both present in small amounts, the interactions between these components would likely not be as great as the interactions between other ion pairs. The results show that the $NaNO_2$ is completely dissolved with the first 4.35 kg/hr of water added. The $NaNO_3$ is completely dissolved after another 51 kg/hr of water are added, and the NaF is completely dissolved after another 15.96 kg/hr of water are added. About 1.21 kg water is needed to completely dissolve each kg of this mixture.

For further illustration, a simple caustic dissolution flowsheet was also developed for this system, as shown in Figure 3.13. The solvent here is caustic solution (0.1 molal NaOH) instead of water. The input file and key pages of the output file are included in Appendix C. The results show that the $NaNO_2$ is completely dissolved with the first 4.34 kg/hr of caustic added. The $NaNO_3$ is completely dissolved after another 52.4 kg/hr of caustic are added, and the NaF is completely dissolved after another 17 kg/hr of caustic are added. About 1.25 kg caustic is needed to completely dissolve each kg of this solid. Therefore, dilute caustic washing would not have any advantages over water washing for dissolving this particular solid.

There are several advantages to this type of predictive capability, including

- identifying opportunities for more efficient separations and processing. For example, an electrochemical nitrite reduction process may be considered for supplying hydroxide ions for dissolution processes. Rather than apply a nitrite reduction process to the total liquid stream (LIQTOTAL), which is only 0.72 molal in $NaNO_2$, the process may be more efficiently applied to the liquid stream from the first wash stage (S1LIQ), which is 12 molal in $NaNO_2$.

- waste minimization. Flowsheet simulation can be used to identify targets for minimum amounts of solvents that need to be used to accomplish process objectives. Also, flowsheet simulation can be used to evaluate various solvent recycling schemes for complex processes.

- prediction of feed composition to downstream processes. Technology development of solvent extraction and other advanced separation processes will be facilitated by improved projections of expected feed compositions.

Process Conditions 25 C, 1 atm

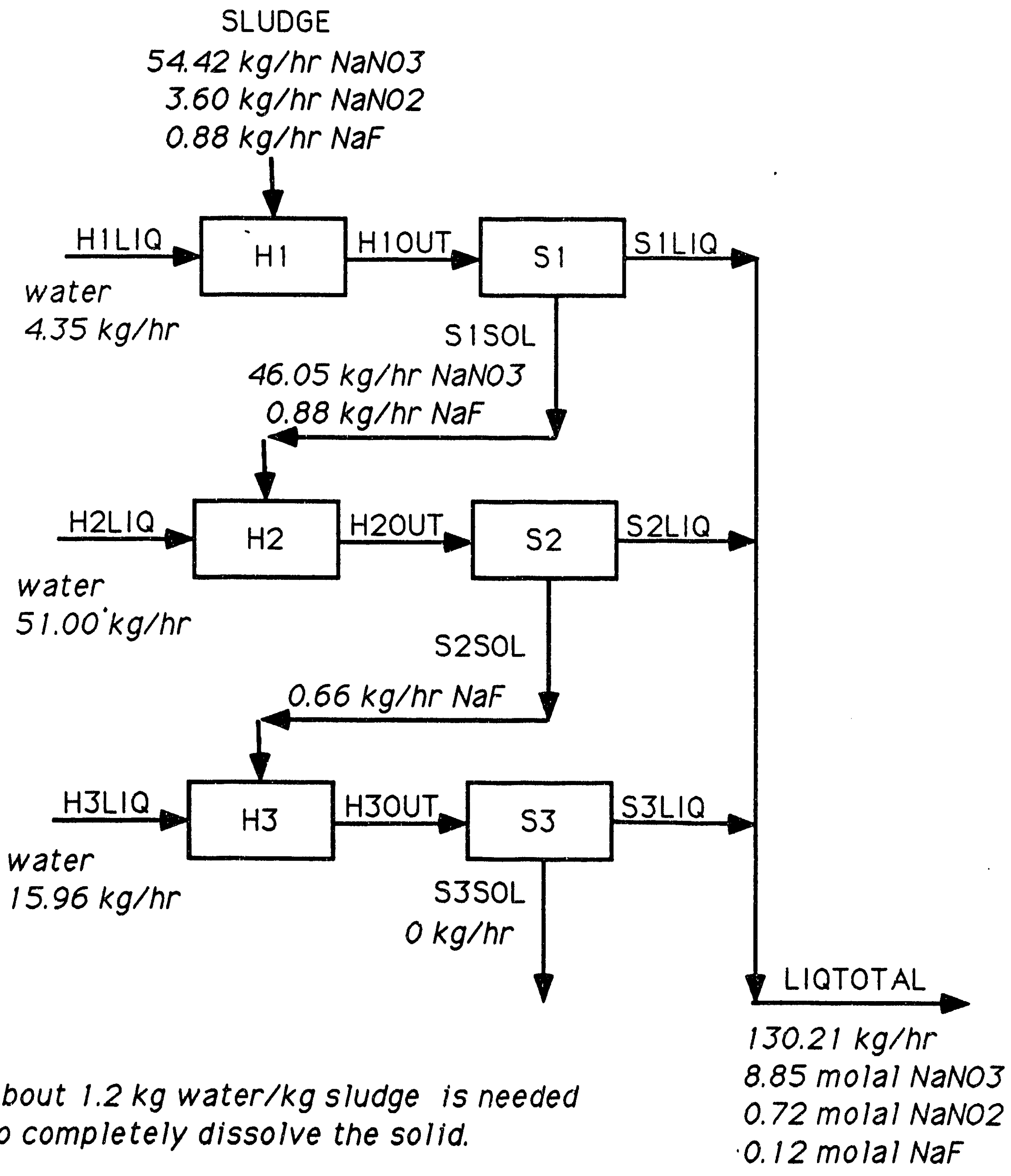
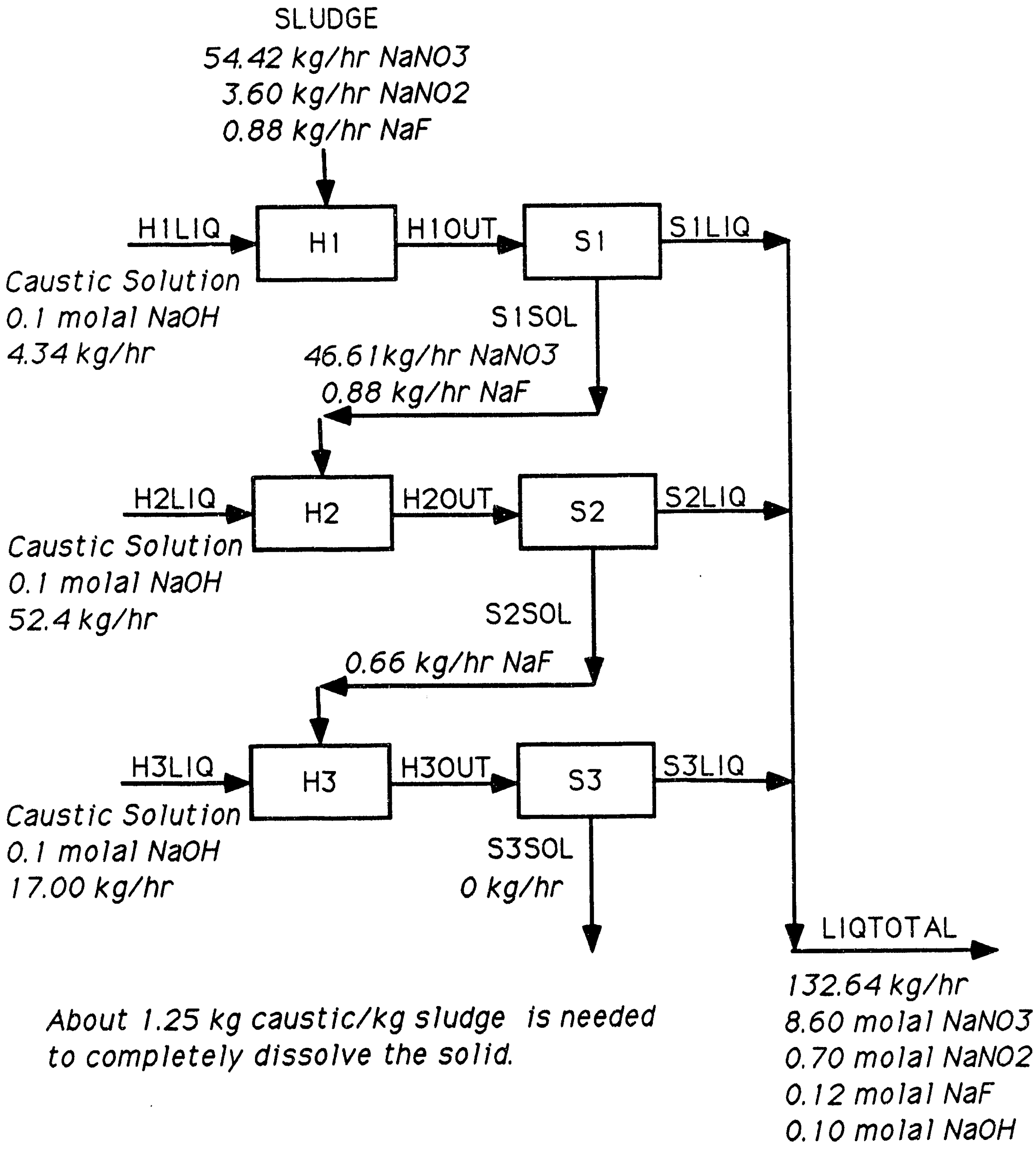


Figure 3.12. Block Flow Diagram: Water Dissolution of $NaNO_3$-$NaNO_2$-NaF Solid

Process Conditions 25 C, 1 atm



About 1.25 kg caustic/kg sludge is needed to completely dissolve the solid.

Figure 3.13. Block Flow Diagram: Caustic Dissolution of $NaNO_3$-$NaNO_2$-NaF Solid

Further steps needed to extend this dissolution model are

- incorporation of the other major constituents. This example flowsheet calculation included data for the Na-NO_3-NO_2-OH-H_2O system. As described in Section 4.0, model development will be simplified and accelerated by determining parameters for the basic chemical system [Na-NO_3-NO_2-SO_4-CO_3-F-PO_4-OH-$Al(OH)_4$] and the acidic system [Na-H-Al-NO_3-NO_2-SO_4-HF-F-Cl-H_3PO_4-H_2O]. Much existing data were collected as a result of the literature search conducted in FY 1992, as described in Section 4.0.

- extension of the model parameters to other temperatures. It is unlikely that sludge pretreatment processes will be conducted solely at 25°C.

- testing model accuracy by comparing model predictions with results of independent experiments. Since these solutions are highly non-ideal, errors in model parameters may result in large inaccuracies in the calculated results.

4.0 Literature Review

The purpose of the literature review was to obtain existing Pitzer ion-interaction parameters needed to model the tank waste chemical systems and existing data on emf, solubility, isopiestic, ion exchange, and solvent extraction measurements which can be analyzed (fit) to determine Pitzer ion-interaction parameters not found in the literature. This section summarizes the results of this review and recommends an experimental program to provide additional needed information.

4.1 Major Constituent Systems

As discussed in previous sections, this literature review centered on the chemical systems relevant to SST wastes. Because of the complexity of the tank waste chemical system, the review focused on the two specific problems relevant to waste pretreatment. Significant progress can be made by developing all the specific ion interactions for a chemical model of the current tank equilibrium reactions [the system Na^+-NO_3^--NO_2^--SO_4^{2-}-CO_3^{2-}-F^--PO_4^{3-}-OH^--$Al(OH)_4^-$-H_2O] and an acid dissolution model [the chemical system Na^+-H^+-Al^{3+}-NO_3^--NO_2^--SO_4^{2-}-HSO_4^--HF-F^--H_3PO_4-H_2O]. The first chemical model--the base model--will be designed to evaluate the chemical equilibrium currently occurring in the tanks and the implications of these chemical equilibria on waste removal and treatment options. The second model--the acid model--will be designed to evaluate pretreatment options arising from acid (HNO_3) dissolution of the tank wastes. Literature encompassing a range of temperatures (25°C to 100°C) was included in the review.

The major radionuclides of interest (Cs, Sr, Tc, U) are present in the sludge in small molal quantities. For these constituents, and other important components that are present in small molal quantities, the specific ion-interaction terms used in the Pitzer or NRTL equations may be assumed to be zero for a first approximation. The model can be refined to include these additional parameters when the necessary data are available. Literature data were obtained for important minor constituents, including Bi, Cs, Fe, Si, Sr, and U. Of these constituents, Bi and Si are of special importance, especially in the acid dissolution model, since most of the mass of these constituents appears to be tied up in solid phases, which are insoluble under acid conditions (i.e., $BiPO_4$ and SiO_2). Thus, these constituents may only partially dissolve under acid conditions and could precipitate during processing as a result of changing conditions.

Although the chemical systems involved in waste pretreatment optimization are quite complex (9 and 11 components), in terms of model parameter development, data are needed only for a limited number of binary (one salt + water) and common-ion ternary (two salts + water) systems. Of these simpler chemical systems, by far the most important are the binary chemical systems, since the model parameters for the dominant cation-anion interactions are determined from these data. The binary chemical systems of interest in this project (Table 4.1) can be divided into three categories: 1) those binary systems of importance only under base conditions, 2) those binary systems of importance only under acid conditions, and 3) those binary systems of importance under both acid and base conditions. Focusing on strong acid or base conditions considerably simplifies the model development task, since

Table 4.1. Binary Chemical Systems Relevant to Tank Waste Pretreatment Optimization

Needed for Both Acid and Base Conditions	Needed for Acid Conditions Only	Needed for Base Conditions Only
$NaNO_3$	HNO_3	$NaOH$
$NaNO_2$		Na_3PO_4
Na_2SO_4	H_2SO_4	Na_2CO_3
NaF	HF	$NaAl(OH)_4$
	H_3PO_4	
	$Al(NO_3)_3$	
	$Al(NO_2)_3$	
	$Al_2(SO_4)_3$	
	AlF_3	
	$NaHSO_4$(a)	

(a) Describes cation-anion interactions (Na^+-HSO_4^-) but evaluated from common-ion ternary data (Na_2SO_4-H_2SO_4-H_2O).

many chemical species, such as $Al(OH)_3(aq)$, $Al(OH)_2^+$, HPO_4^{2-}, and $H_2PO_4^-$ need not be considered; their concentrations would be extremely small under either strong acid (>0.1 m) or strong base (>0.1 m) conditions.

4.2 Binary Data

This section describes the information collected from the literature on binary ion-interaction parameters important to this project.

$NaNO_3$: Pitzer (1979) presents a tabulation of ion-interaction parameters for $NaNO_3$. However, these parameters are valid only to about 6 m and 25°C, and the solubility of $NaNO_3$ exceeds 10 m at 25°C (Andreeva 1985). Consequently, these data are inadequate for application to tank waste problems. Fortunately, accurate osmotic data on $NaNO_3$ solutions (Wu and Hamer 1980) are available at 25°C. These data extend to salt saturation (10.83 m); as previously described, these data were analyzed to obtain an accurate set of ion-interaction parameters at 25°C extending to salt saturation. In addition, Silvester and Pitzer (1978) present information on the temperature derivatives of the Na^+-NO_3^- ion-interaction parameters evaluated from heat of dilution and solution data. Unfortunately, the enthalpy data used in these calculations extend only to 2.2 m, and our attempts to use these data to predict the $NaNO_3$ solubility data as a function of temperature (Shenkin 1980; Linke 1965) were unsuccessful. Thus, experimental data on $NaNO_3$ osmotic coefficients will be required to model the higher temperature waste tanks. Such studies were initiated this year.

$NaNO_2$: Sufficient data to determine the ion-interaction parameters for $NaNO_2$ solutions are available only at 25°C (Staples 1981). These experimental osmotic coefficients extend to salt saturation (12.3 m). These data were analyzed to determine the $NaNO_2$ ion-interaction parameters at 25°C. The parameters published by Pitzer (1979) are only valid to about 6 m and 25°C. Hence, osmotic data on $NaNO_2$ solutions are also required at temperatures greater than 25°C. We have also initiated these studies. When these data become available, they can be combined with other existing data to determine the standard chemical potential of $NaNO_2$(c) as a function of temperature (Linke 1965).

Na_2SO_4: The necessary ion-interaction parameters for Na_2SO_4 solutions are known accurately as a function of temperature (Greenberg and Mϕller 1989). These data were recalculated and refit to the temperature-dependent expression used in ASPEN PLUS™. Greenberg and Mϕller (1989) also give the temperature-dependent expression for the standard chemical potential of several Na_2SO_4 containing phases including thenardite, Na_2SO_4(c).

NaF: Pitzer (1979) gives the Na^+-F^- ion-interaction parameters at 25°C. In addition, Sylvester and Pitzer (1978) present the necessary temperature derivatives evaluated from heat of dilution and solution data extending to 0.7 m which is near salt saturation ($\approx$ 1 m). In addition, Linke (1965) gives sufficient data to calculate the standard chemical potential of NaF(c) as a function of temperature.

Na_3PO_4: Pitzer (1979) gives the ion-interaction parameters for Na_3PO_4 solutions at 25°C. However, information is not available to calculate the temperature dependence of these parameters. Experimental studies will be required. Once these experimental data are obtained, the temperature dependence of the standard chemical potential of Na_3PO_4 solid phases can be determined from the solubility data given in Askertes (1988) and Linke (1965).

NaOH: The Pitzer ion-interaction parameters as a function of temperature have been thoroughly analyzed by Pabalan and Pitzer (1987). Their temperature-dependent expression differs from that in ASPEN PLUS™, so the parameters of Pabalan and Pitzer (1978) must be recalculated and refit to conform to the temperature-dependent expression in ASPEN PLUS™. This effort should improve the current values, which are based on data tabulated from Perry's Handbook.

$NaAl(OH)_4$: Recently, Wesolowski (1992) has calculated the Na^+-$Al(OH)_4^-$ ion-interaction parameters over the temperature range 0°C to 100°C. These data have been incorporated into ASPEN PLUS™.

Na_2CO_3: Peiper and Pitzer (1982) have published the Na^+-CO_3^{2-} ion-interaction parameters at 25°C. These values are in reasonable agreement with those of Harvie et al. (1984) in their thermodynamic model of the eight-component seawater system. In addition to the 25°C parameters, Peiper and Pitzer (1982) also evaluated the first and second temperature derivatives of these ion-interaction parameters.

HNO_3: Clegg and Brimblecombe (1990) have published a thorough review of the equilibrium data on HNO_3 solutions. This review included the calculation of the Pitzer ion-interaction parameters at 25°C, as well as the first and second derivatives with respect to temperature. These data need to be converted to the temperature-dependent expression in ASPEN PLUS™.

H_2SO_4: Harvie et al. (1984) have accurately fit the osmotic and activity coefficient data for the H_2SO_4-H_2O system at 25°C. This analysis required the bisulfate ion, HSO_4^-, be included. In turn, introducing a bisulfate species required the inclusion of interaction parameters describing H^+-HSO_4^-, Na^+-HSO_4^-, and Na^+-H^+-HSO_4^- ion interactions. In addition, Dickson et al. (1990) have recently evaluated the standard chemical potentials (formation constants) for bisulfate ion in both dilute solution and in concentrated chloride brines to 250°C. Such data need to be included in the ASPEN PLUS™ database.

HF: Hammer (1979) has reviewed much of the data on HF and metal ion fluoride complexes in nitrate solutions. These data, and many of the quoted references, will need to be analyzed in developing the acid dissolution model. Many of the fluoride complexes are, as expected, quite strong.

H_3PO_4: Pitzer and Silvester (1976) have presented a detailed aqueous thermodynamic model for the H_3PO_4-H_2O system valid to high H_3PO_4 concentration (6 molal). These data will be included in the ASPEN PLUS™ database. Additional experimental data may be needed for higher temperatures.

$Al(NO_3)_3$: Although a considerable amount of data is available on the solubility of $Al(NO_3)_3$ in water and in mixed solutions with HNO_3 and $NaNO_3$, no definitive data are available to unambiguously obtain the Al^{3+}-NO_3^- ion-interaction parameters. Therefore, osmotic measurements are planned for FY 1993 to obtain the necessary data to evaluate these parameters.

$Al(NO_2)_3$: No reliable data have been found for determining the Al^{3+}-NO_2^- ion-interaction parameters. Osmotic measurements are planned for FY 1993 to obtain these necessary data.

$Al_2(SO_4)_3$: Reardon (1988) has calculated the necessary ion-interaction parameters for the $Al_2(SO_4)_3$ system at 25°C. These parameters will be included in the ASPEN PLUS™ database. Additional solubility data are available in mixed systems ($Al_2(SO_4)_3$-H_2SO_4, $Al_2(SO_4)_3$-Na_2SO_4, etc.) at 25°C and at higher temperatures. These data need to be analyzed. If necessary, additional solubility or osmotic studies will be conducted.

AlF_3: Al^{3+} interacts strongly with F^- and several Al-F aqueous complex species have been proposed (see the summary of Sanjuan and Michard 1987). A considerable amount of work has been done defining the stability constants for these species in dilute solution. However, much less data are available to model highly concentrated solutions. The most useful data appear to be that of Hammer (1979) covering the temperature range 25°C to 60°C in HF-HNO_3 solutions. In addition, data exist on the solubility of AlF_3 in H_2O over a range of temperatures.

$NaHSO_4$: Harvie et al. (1984) give the necessary ion-interaction parameters at 25°C. Although these are cation-anion (binary) interactions, their evaluation requires common-ion ternary data (i.e., Na_2SO_4-H_2SO_4-H_2O). At least some of these necessary data are available in Linke (1965) over the temperature range (12°C to 97°C). Evaluating these ion interactions involves knowledge of the standard chemical potential of bisulfate ion (see the discussion on H_2SO_4).

4.3 Ternary Data

In addition to the binary chemical systems listed in Table 4.1, a large number of common-ion ternary systems can be defined. As an example, for the system $NaNO_3$-$NaNO_2$-Na_2SO_4-NaF-H_2O (the chemical system involved under both acid and base conditions), six common-ion ternary systems can be defined: $NaNO_3$-$NaNO_2$-H_2O, $NaNO_3$-Na_2SO_4-H_2O, $NaNO_3$-NaF-H_2O, $NaNO_2$-Na_2SO_4-H_2O, $NaNO_2$-NaF-H_2O, and Na_2SO_4-NaF-H_2O. Data from these systems are important both in determining the common-ion ternary Pitzer ion-interaction parameters (i.e., NO_3^--NO_2^-, NO_3^--SO_4^{2-}, Na^+-NO_3^--NO_2^-, etc.) and in determining the standard chemical potentials of mixed salt precipitates including both anions.

Table 4.2 presents a summary of relevant common-ion ternary data identified in this literature review. An impressive amount of experimental data are available for many of the important common-ion ternary systems of importance to waste tank pretreatment problems. These data need to be analyzed and the necessary ion-interaction parameters and standard chemical potentials determined. It is also important to point out that Pitzer ion-interaction parameters determined from common-ion ternary data (i.e., anion-anion, cation-anion-anion, cation-cation, etc.) tend to be much less sensitive to temperature than binary parameters. Thus, even if common-ion ternary data are available only at 25°C, such data will be useful at higher temperatures as well. Also of note in examining Table 4.2 is the general lack of common-ion ternary data for systems containing NO_2 and to a lesser extent $Al(OH)_4^-$. The systems for which experimental studies will be required are discussed in Section 4.4.

4.4 Literature Review Summary

This literature review focused on obtaining the existing Pitzer ion-interaction parameters and necessary experimental data from which to calculate these parameters. Two particular chemical systems were emphasized: the current tank equilibrium model [the system Na^+-NO_3^--NO_2^--SO_4^{2-}-CO_3^{2-}-F^--PO_4^{3-}-OH^--$Al(OH)_4^-$-H_2O] and an acid dissolution model [the chemical system Na^+-H^+-Al^{3+}-NO_3^--NO_2^--SO_4^{2-}-HSO_4^--HF-F^--H_3PO_4-H_2O]. A large number of Pitzer ion-interaction parameters and a large amount of experimental data have been obtained. These data need to be analyzed and the Pitzer ion-interaction parameters determined. In addition, important gaps in the existing experimental data have been identified. These data needs are summarized in Table 4.3. Clearly, the binary data for $NaNO_3$, $NaNO_2$, Na_3PO_4, $Al(NO_3)_3$, and $Al(NO_2)_3$ are the most crucial. As we have described, some of these experiments were initiated in FY 1992.

Table 4.2. Summary of Available Data for Common-Ion Ternary Systems Identified in FY 1992 Literature Review

System	Available Data
$NaNO_3$ - NaOH - H_2O	0°C, 20°C, 25°C
$NaNO_3$ - Na_3PO_4 - H_2O	25°C, 112°C
$NaNO_3$-NaF-H_2O	25°C, 110°C
Na NO_3 - $NaNO_2$ - H_2O	0°C, 21°C, 52°C, 103°C
Na NO_3 - Na_2SO_4 - H_2O	20°C, 100°C
Na NO_3 - Na_2CO_3 - H_2O	25°C, 110°C
$NaNO_3$ - Al $(NO_3)_3$ - H_2O	0°C, 20°C, 40°C, 60°C
Na NO_3 - HNO_3 - H_2O	numerous temperatures
$NaNO_2$ - NaOH - H_2O	20°C, 25°C
$NaNO_2$ - Na_2CO_3 - H_2O	23°C
Na_2SO_4 - NaOH - H_2O	25°C
Na_2SO_4 - Na_3PO_4 - H_2O	25°C
Na_2SO_4 - Na_2CO_3 - H_2O	numerous temperatures
Na_2SO_4-H_2SO_4-H_2O	numerous temperatures
NaF - Na_3PO_4 - H_2O	25°C, 110°C
NaF - NaOH - H_2O	0°C, 20°C, 40°C, 80°C, 94°C
NaF - Na_2CO_3 - H_2O	25°C, 50°C
NaF - AlF_3 - H_2O	25°C, 75°C
NaF - HF - H_2O	0°C, 20°C, 40°C
Na_3PO_4 - NaOH - H_2O	25°C
Na_2CO_3 - NaOH - H_2O	numerous temperatures
Al $(NO_3)_3$ - HNO_3 - H_2O	numerous temperatures
Al $(NO_3)_3$ - Al_2 $(SO_4)_3$ - H_2O	25°C
Al $(NO_3)_3$ - AlF_3 - H_2O	25°C
$Al_2(SO_4)_3$ - Na_2SO_4 - H_2O	0°C, 25°C, 30°C, 42°C
Al_2 $(SO_4)_3$ - H_2SO_4 - H_2O	25°C
Al_2 $(SO_4)_3$ - AlF_3 - H_2O	25°C

Table 4.3. Important Experimental Data Required to Model the Waste Tank Chemical System for Major Constituents

System	Suggested Method	Temperatures
$NaNO_3$	isopiestic	50°C, 75°C, 100°C
$NaNO_2$	isopiestic	50°C, 75°C, 100°C
Na_3PO_4	isopiestic	50°C, 75°C, 100°C
NaF	isopiestic	limited validation
$Al(NO_2)_3$ (a)	isopiestic	25°C to 100°C
$Al(NO_2)_3$ (a)	isopiestic	25°C to 100°C
$Al_2(SO_4)_3$ (a)	isopiestic, solubility	limited validation
$NaNO_2$ - Na_2SO_4 - H_2O	solubility	25°C
$NaNO_2$ - NaF - H_2O	solubility	25°C
$NaNO_2$ - Na_3PO_4 - H_2O	solubility	25°C
$NaNO_3$ - NaOH - $Al(OH)_3$ - H_2O	solubility	25°C
$NaNO_2$ - NaOH - $Al(OH)_3$ - H_2O	solubility	25°C
Na_2SO_4 - NaOH - $Al(OH)_3$ - H_2O	solubility	25°C
Na_2CO_3 - NaOH - $Al(OH)_3$ - H_2O	solubility	25°C

(a) May require limited additions of acid.

5.0 Silica Solubility Studies

Silica is one of the major constituents of concern in developing optimum strategies for waste tank pretreatment options. Most silica-containing compounds, including amorphous silica, SiO_2(am), are insoluble even under strongly acid conditions. Furthermore, scale formation is a particular problem given the large changes in solubility of potential scale-forming minerals such as amorphous silica. Hence, accurate experimental and thermodynamic data are required to predict the solubilities of silicate phases in the waste tanks and wash/leaching solutions.

Silica is one of the most abundant elements in geologic systems, and all aspects of the chemistry of silica have been extensively studied (see Iler 1979 for a review of much of this earlier work). Although this work and more recent studies (Cary et al. 1982; Crerar et al. 1981; Fleming and Crerar 1982; Fournier and Marshall 1983; Marshall and Chen 1982) have shown that a variety of aqueous species, including polymeric species, can exist in aqueous solution, the principal dissolved aqueous silica species, below pH 9, is silicic acid, H_4SiO_4(aq). It is the interactions of silicic acid with the other bulk chemical species (such as Na^+, H^+, NO_3^-, NO_2^-) in the waste tank solutions that will determine the solubility of the potential scale-forming minerals, such as amorphous silica, at least under neutral and acid conditions. Because of the low solubility of most silica compounds, the best means of obtaining these ion-interaction parameters is by analysis of solubility data.

The most useful and extensive set of solubility data for obtaining the ion-interaction parameters includes: 1) the amorphous silica solubility data of Marshall and coworkers (Marshall 1980a,b; Marshall and Warakomski 1980; Chen and Marshall 1982; Marshall and Chen 1982a,b) in $NaNO_3$, NaCl, Na_2SO_4, KNO_3 and other media; 2) the amorphous silica solubility data of Elmer and Nordberg (1958) in HNO_3; and 3) the amorphous silica solubility data in HCl summarized by Linke (1965). Unfortunately, the data of Elmer and Nordberg (1958) do not extend to temperatures below 36°C, and the amorphous silica solubilities given in Linke (1965) for HCl are inconsistent with the dilute solution solubilities reported by Marshall and coworkers. For these reasons, and because of the potential importance of silica in waste tank pretreatment optimization problems, an experimental study was conducted on the solubility of amorphous silica in HNO_3, HCl, and NaOH. These data, when combined with the experimental data in the literature, are essential for the calculation of many of the important ion-interaction parameters for H_4SiO_4(aq) with the bulk ions present in the waste tanks.

The solubility of amorphous silica not only changes significantly with the salt concentration but can also be affected by the particle size, temperature, and other factors. These factors can cause difficulties when amorphous silica solubilities are compared among different investigators. In this study, the solubility of amorphous silica was determined using the same experimental procedure utilized by Marshall and coworkers (see Marshall and Warakomski 1980) in order to ensure that our solubility data are consistent with their extensive experiments in different electrolyte solutions. This procedure allowed the calculation of a consistent and reliable set of H_4SiO_4(aq) ion-interaction parameters valid for many chemical systems.

5.1 Experimental Procedure

The experimental procedure used in this study was the same as that used by Marshall and Warakomski (1980). Briefly, the procedure consisted of suspending 4 g of silica gel (Baker analyzed reagent) in 30-mL of either HNO_3, HCl, NaOH, or $NaNO_3$ placed in 50-mL centrifuge tubes. The HNO_3, HCl, and NaOH solutions ranged in concentration from 0.0001 molal to 2.0 molal. Only four $NaNO_3$ samples were included. These samples were used to check our results against the results of Marshall (1980a). The silica gel had been previously washed with deionized water and air-dried overnight. The silica suspensions were placed on an orbital shaker and continuously shaken. Each suspension was sampled after 7 and 37 days of equilibration.

Sampling consisted of centrifugation at 2000 g for 7 to 10 min followed by filtration through Amicon-type F-25 Centriflo membrane cones with an approximate pore size of 0.0018 μm. The filters were pretreated by soaking and rinsing in deionized water. A small aliquot of the sample was then passed through each filter to saturate any possible adsorption sites (this aliquot was discarded), followed by sufficient solution to analytically determine silica. Silica was analyzed by inductively coupled plasma spectroscopy (ICP).

5.2 Results and Discussion

The results of the $NaNO_3$ samples (Figure 5.1) showed that after 7 days of equilibration our results were in excellent agreement with the data of Marshall (1980a), thus demonstrating consistency among investigators. Such consistency is important especially in studies of amorphous silica solubility, where the results among different investigators can differ by as much as 50% (Marshall 1980a). It is also of interest to compare these experimental results against calculated solubilities using thermodynamic data tabulated by the National Institute of Standards and Technology (Wagman et al. 1982). These calculations clearly show much higher calculated solubilities than are experimentally observed (Figure 5.2). These differences appear to be the result of the tabulated free energy for SiO_2(am) being too high. This once again emphasizes the inaccuracies involved in just arbitrarily selecting thermodynamic data from the literature without a detailed comparison against experimental data.

The observed solubility of amorphous silica in HCl (Figure 5.3) showed that 1) in general the observed solubilities at 7 and 37 days were similar, indicating that equilibrium had been reached in these samples, and 2) that these results were much lower than previously reported values (Linke 1965). That the Linke (1965) values were erroneously high is substantiated by the solubilities in dilute solution being not only much higher than the values reported here but also much higher than the results of Marshall (1980a) in dilute solution (see Figure 5.1). Use of Linke (1965) unreliable experimental data would have resulted in significant errors in our final thermodynamic model. Specifically, in acid chloride solution, use of these data in conjunction with an accurate dissolved silica analysis would have resulted in predictions of no scale formation at 25°C. Such erroneous predictions could have serious consequences in the pretreatment process.

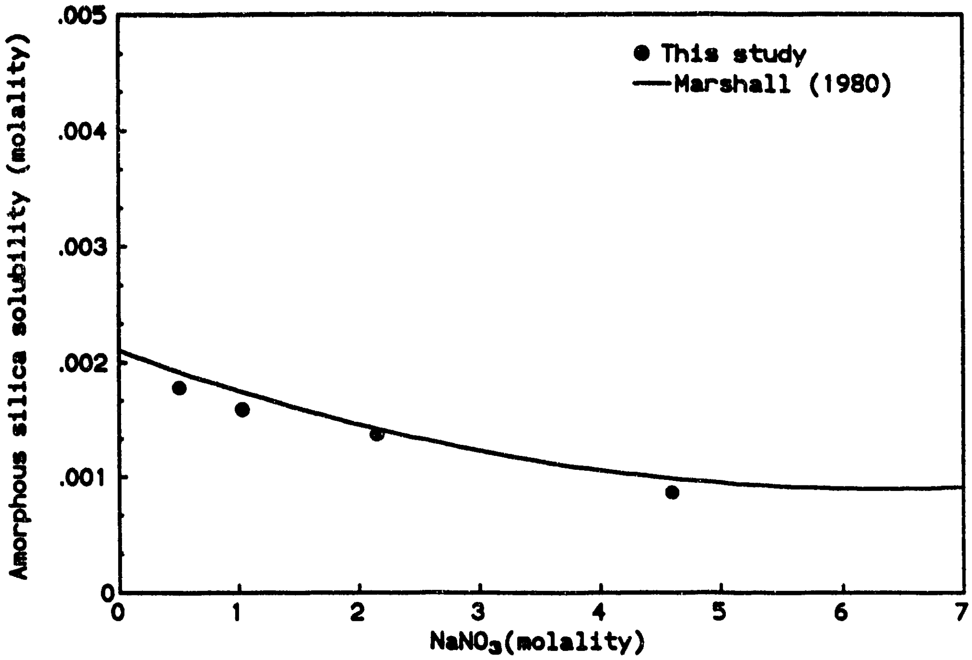


Figure 5.1. Comparison of Experimental Amorphous Silica Solubilities in NaNO$_3$

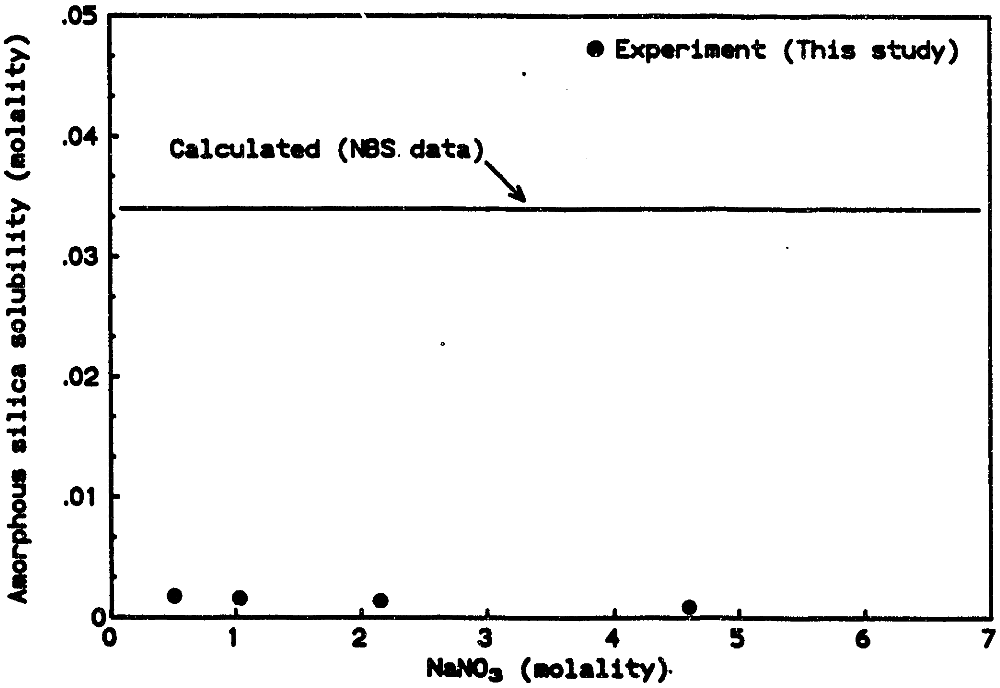


Figure 5.2. Experimental and Calculated Amorphous Silica Solubilities in NaNO$_3$. Calculated solubilities use data from Wagman et al. (1982).

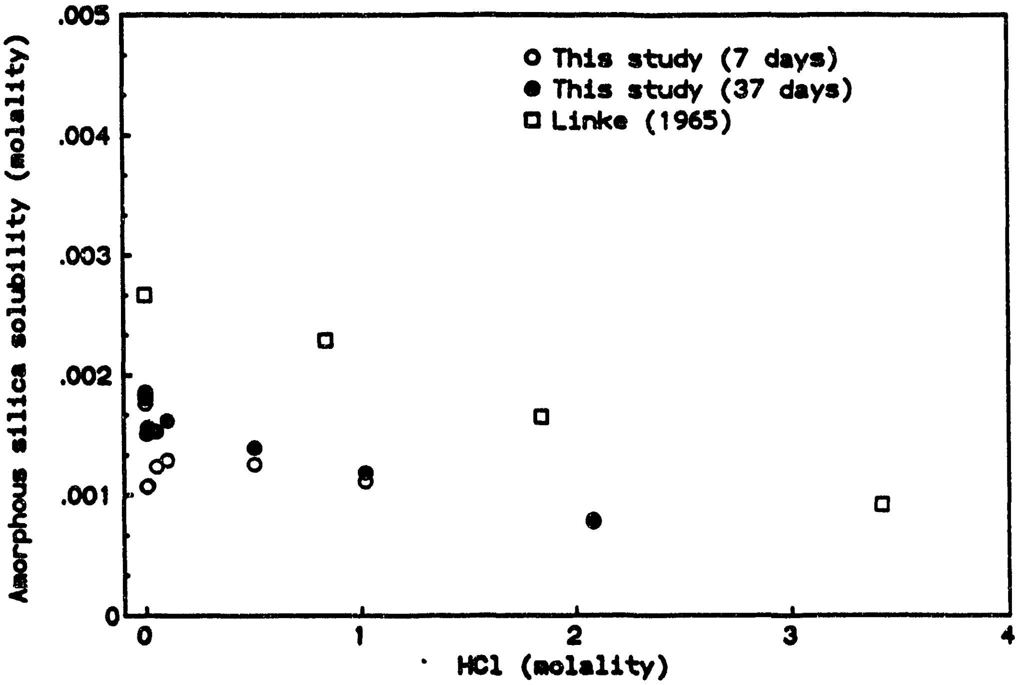


Figure 5.3. Experimental Amorphous Silica Solubilities in HCl at 25°C

The solubility of amorphous silica in HNO_3 (Figure 5.4) showed that 1) the solubility of amorphous silica significantly increased with temperature and decreased with HNO_3 concentration, and 2) the results obtained in this study were consistent with previous investigators who worked at higher temperatures. This latter point is especially significant since previous work using HNO_3 (Elmer and Nordberg 1958) was conducted using porous glass tubes, rather than silica gel, at 36°C and 65°C. Analysis of all of these data in FY 1993 will result in an accurate and reliable model for the $H_4SiO_4(aq)$ ion interactions in acidic solutions. As an initial example, the 25°C HNO_3 solubility data obtained in this study were fit using the Pitzer ion-interaction formalism; only the standard chemical potential of $SiO_2(am)$ and one ion-interaction parameter, $\lambda_{H4SiO4(aq)\text{-}NO3\text{-}}$ were adjusted[(a)]. This calculation yielded $\mu°/RT = -346.08$, and $\lambda_{H4SiO4(aq)\text{-}NO3\text{-}} = 0.14$. The value of $\lambda_{H4SiO4(aq)\text{-}NO3\text{-}}$ was consistent with values for other neutral-anion interactions (Felmy and Weare 1986; Harvie et al. 1984). These parameters represent the experimental data very well (Figure 5.5).

Although the interpretation and modeling of amorphous silica solubilities and ion interactions is straightforward in neutral and acid solutions, it is not the case in base solutions. In base solutions silicic acid can form a variety of both monomeric and polymeric species (Baes and Mesmer 1976; Iler 1979; Sjoberg et al. 1985; Cary et al. 1982; Fleming and Crerar 1982). In addition, all of these species can have specific ion interactions with the bulk ions (such as Na^+, NO_3^-, NO_2^-, SO_4^{2-}) in

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(a) Since measurements can only be made in neutral solutions, one of the parameters must be assigned arbitrarily (Felmy and Weare 1986). We have used the convention of assigning $\lambda_{H4SiO4\text{-}H+}$ equal to zero.

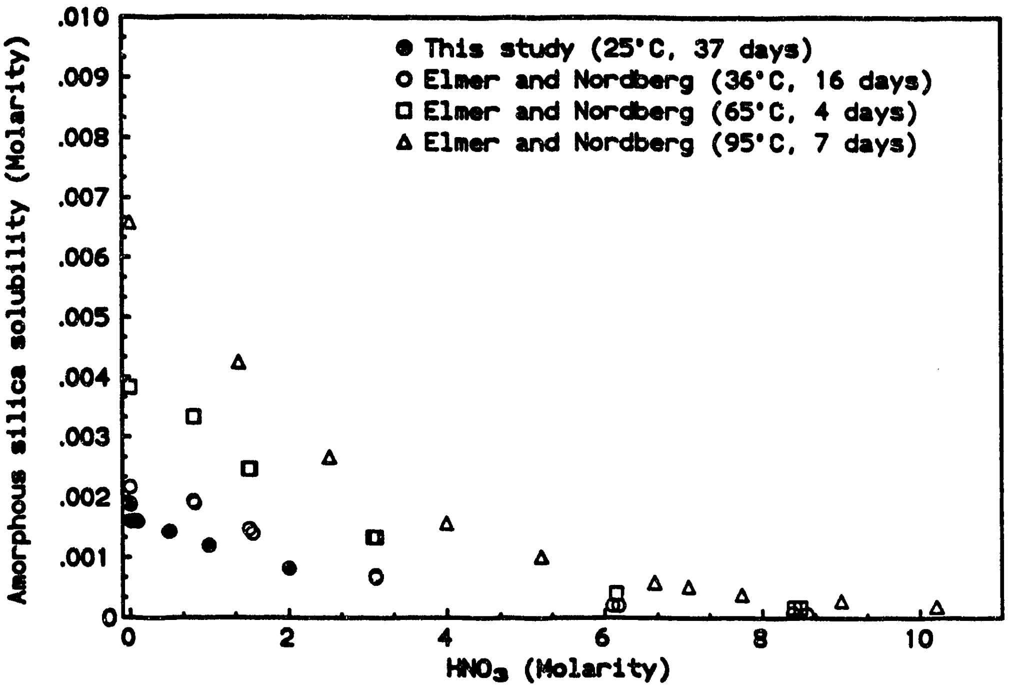

Figure 5.4. Experimental Solubilities of Amorphous Silica in HNO_3 at Different Temperatures

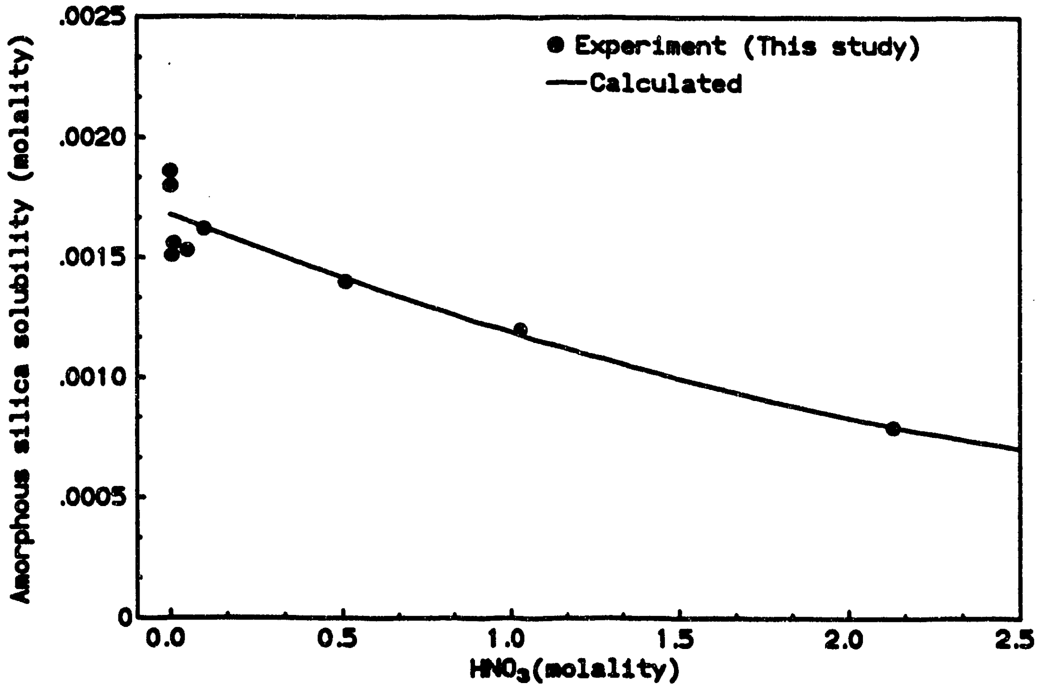

Figure 5.5. Experimental and Calculated Amorphous Silica Solubilities in HNO_3 at 25°C

concentrated solutions such as those found in the waste tanks. Such complex chemical behavior makes it much more difficult to model the equilibria of aqueous silica species under base conditions than under neutral or acid conditions.

In FY 1992, preliminary studies of the solubility of amorphous silica under base conditions were started to 1) establish the range of acid-base (pH) conditions over which the current thermodynamic models for aqueous dissolved silica species are valid, and 2) identify if any other phases, such as sodium silicates, precipitated under strongly base conditions. These data (Table 5.1) show that at relatively low concentrations of added base, 0.05 molal,(a) the aqueous dissolved silica concentration begins to increase as the result of the formation of charged monomeric or polymeric species. At this point the amorphous silica begins to dissolve in a nearly stoichiometric fashion and is completely dissolved at a concentration of 1.0 molal added NaOH. No evidence was found for the formation of insoluble sodium silicate phases, at least after 37 days of equilibration.

A comparison of these solubility data with calculated solubilities using data for $H_3SiO_4^-$ and H_4SiO_4(aq) taken from Wagman et al. (1982) and our previously calculated standard chemical potential for SiO_2(am) calculated from the HNO_3 solubility data shows that the predicted solubilities are consistent with our experimental values, at least at high NaOH concentration (Figure 5.6). However, this agreement may be somewhat fortuitous since it is doubtful that $H_3SiO_4^-$ is the only charged silica species in solution.

Table 5.1. Experimental Data on the Solubility of Amorphous Silica in NaOH, Equilibration Period 37 Days

Concentration of Added Base, molal	Si, molal	Solid Phase Present
0.0001	0.00196	yes
0.0005	0.00195	yes
0.001	0.00195	yes
0.005	0.00205	yes
0.01	0.00234	yes
0.05	0.00818	yes
0.1	0.0239	yes
0.5	0.558	yes
1.0	1.50	no
2.0	1.46	no

(a) This is the total added NaOH concentration. The actual solution pH is considerably different owing to consumption of base by reactions such as $SiO_2(am) + NaOH \rightarrow H_3SiO_4^- + Na^+$.

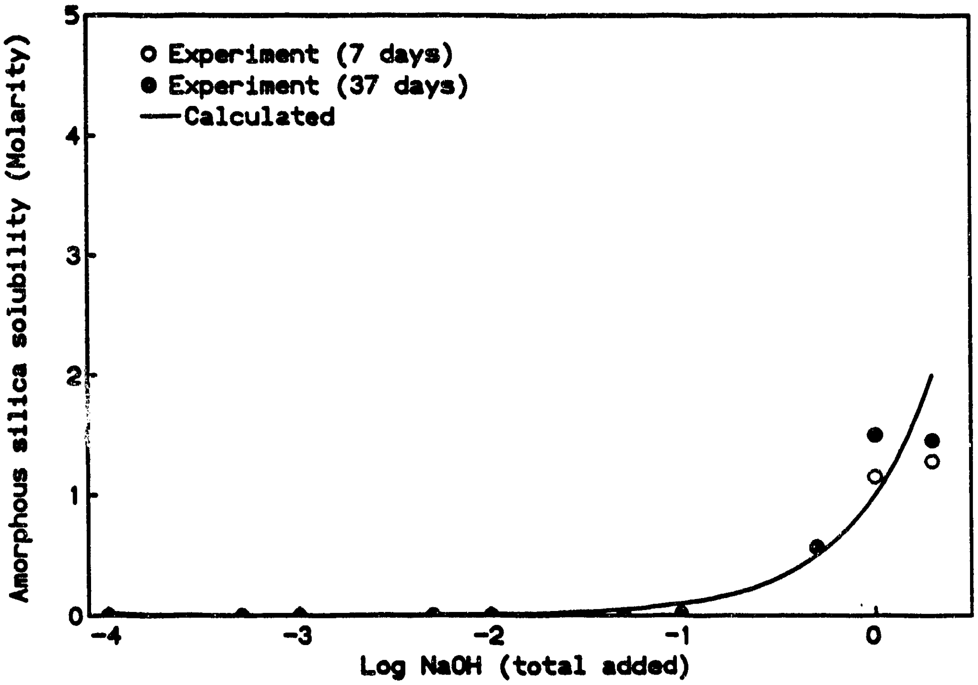

Figure 5.6. Experimental and Calculated Solubilities of Amorphous Silica in NaOH. Calculated solubilities include data from Wagman et al. (1982) for aqueous species only.

5.3 Summary

The experimental studies conducted in FY 1992 have 1) completed the necessary data with which to calculate the $H_4SiO_4(aq)$ ion interactions important in HNO_3 and HCl solutions over a range of temperatures, and 2) established that insoluble sodium silicate phases do not form at high concentrations of added base in the absence of other ions (i.e., Al, Fe, ...). The first result is clearly important in developing our acid leaching model and the second result is important in establishing possible solubility controlling solid phases for silica under base conditions. In particular, previous leaching studies of SST sludge simulant have shown that silica does not readily solubilize even under strong base conditions.

The results presented here strongly indicate that amorphous silica, and in fact any pure SiO_2 phase, cannot be controlling the dissolved silica concentration in such leaching studies. This is consistent with XRD results (Table 3.2), which show the presence of sodium aluminum silicates or sodium aluminum silicate sulfate in selected waste tanks. The solubility data for these phases must be examined. Presently, we are unaware of any data for sodium aluminum silicate sulfate. Therefore, experimental studies may be required to determine the necessary solubility and thermodynamic data for such possible solubility controlling phases under base conditions.

6.0 Conclusions and Recommendations

ASPEN PLUS™, a commercial software package, can be used to rigorously and accurately predict the chemical behavior of SST waste during pretreatment processing. Although SST wastes contain many chemical species, there are relatively few constituents--Na, Al, NO_3, NO_2, PO_4, SO_4, and F--contained in the majority of the waste. These species comprise 86% and 74% of samples from B-110 and U-110 SSTs, respectively. Model development can also be accelerated by only considering specific problems of interest. By focusing on either acid or base conditions, the number of chemical species and chemical reactions that need to be considered is significantly reduced.

In FY 1992, the ASPEN PLUS™ model was acquired and made operational. The database of the model was significantly enhanced to include additional data for $NaNO_3$, $NaNO_2$, NaF, Na_3PO_4, $NaAl(OH)_4$, and several mixed salt solutions. Preliminary water and caustic dissolutions were also performed for a solid containing $NaNO_3$, $NaNO_2$, and NaF phases in the same proportion as B-110 sludge. Results illustrate the advantages of these calculations, including 1) identifying opportunities for more efficient separations and processing, 2) waste minimization, and 3) prediction of feed composition to downstream processes.

An extensive literature review was conducted to obtain existing Pitzer ion-interaction parameters needed to model the tank waste chemical systems; and existing experimental data, such as emf, solubility, and isopiestic were found from which the necessary model parameters can be calculated. In addition, experimental measurements were made on the solubility of amorphous silica primarily in HNO_3 and HCl media where previous data were unreliable or unavailable. Such data are necessary for developing the ion-interaction parameters for H_4SiO_4 (aq) in acid solution.

Continued work should include

- incorporating the remaining information gathered during the literature review conducted this year.
- conducting isopiestic and solubility studies of the chemical systems listed in Table 4.4 in order to fill the gaps in needed information
- testing the model for accuracy using the results from independent experiments. The accuracy of the model will be evaluated, and the need for additional data to improve the calculations will be identified.

7.0 References

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Appendix A

ASPEN PLUS™ Template Input File

```
ITLE 'SLUDGE TREATMENT EVALUATION TEMPLATE 1'

ESCRIPTION      "THIS TEMPLATE CONTAINS A FLOWSHEET FOR MODELING
                 MULTI-STAGE SLUDGE/LIQUID CONTACTING WITH NO
                 RECYCLE OF LIQUID.  ALSO INCLUDED ARE THE PITZER
                 PARAMETERS REQUIRED FOR MODELING ELECTROLYTE
                 SOLID-LIQUID EQUILIBRIUM."

N-UNITS MET TEMP=C PRES=ATM

OMPONENTS H2O H2O / H+ H+ / OH- OH- / &
          NA+ NA+ / NO3- NO3- / NO2- NO2- / F- F- /
          AL+3 AL+3 / 'AL(OH)4-' 'AL(OH)4-'/
          PO4-3 PO4-3 / HPO4-2 HPO4-2 / H2PO4- H2PO4- / H3PO4 H3PO4 /
          SO4-2 SO4-2 / HSO4- HSO4- / H2SO4 H2SO4/
          SIO4-4 SIO4-4 / FE+3 FE+3 / BI+3 FE+3 /
 enter solid species
          NAOH NAOH / NANO3 NANO3 / NANO2 NANO3 / NAF NAF /
          NAPHOS12 FEO / NASULF10 NA2SO4 / BOEMITE 'ALO(OH)' /
          SIO2 SIO2 / 'FEO(OH)' FEO / BIPO4 FEO /
          NAALUM1 NANO3 / NAALUM2 NANO3 / GIBBSITE FEO

ROPERTIES SYSOP16 CHEMISTRY=SLUDGE

ATABANKS AQUEOUS/SOLIDS

HEMISTRY SLUDGE

 FIRST, INCLUDE COMPLETELY DISSOCIATED SPECIES
        DISS NAOH NA+ 1 / OH- 1

 SODIUM SALT PRECIPITATION

        SALT NAALUM1 NA+ 2 / 'AL(OH)4-' 2 / H2O -1.5
        K-SALT NAALUM1 -10
 first guess

        SALT NAALUM2 NA+ 6 / 'AL(OH)4-' 2 / OH- 4
        K-SALT NAALUM2 -32
 first guess

         SALT NACL NA+ 1 / CL- 1
         K-SALT NACL

        SALT NAF NA+ 1 / F- 1
        K-SALT NAF 30.78832 -2370.084 -5.617666
 NaF Solubility Data from Linke Vol. 2 p. 1258  (0-100 C)

        SALT NANO3 NA+ 1 / NO3- 1
        K-SALT NANO3 1245.491 -33988.12 -218.2614 0.3573155
 NaNO3 fit from Mulder (Linke) 0-60 C, with binary parameters at 25 C

        SALT NANO2 NA+ 1 / NO2- 1
        K-SALT NANO2 49.34024 -2920.095 -7.676417
 NaNO2 fit from Bureau/Erdos data in Linke 0-52 C
 Pitzer params were fit only at 25 C

        SALT NAPHOS12 NA+ 3/PO4-3 1/H2O 12
        K-SALT NAPHOS12 -26.72836
 from Eysseltova, J. reviw (Apfel, O. 1911 data)/no Pitzer parameters
```

```
        SALT NASULF10 NA+ 2 / SO4-2 1 / H2O 10
        K-SALT NASULF10 18.191 -9850.
;from Berkeley solubiliity data (Linke Vol 2, p. 1123)

;ALUMINUM SALT PRECIPITATION
        SALT BOEMITE 'AL(OH)4-' 1 / OH- -1 / H2O -1
        K-SALT BOEMITE -1.986
;estimate from NBS Gibbs Free Energy at 25 C

        SALT GIBBSITE 'AL(OH)4-' 1 / OH- -1
        K-SALT GIBBSITE -96.502 2375.35 16.068 -0.01394
;fit from LogK tabulated by Wesolowski (1992) p. 1082

;OTHER SALT PRECIPITATION
        SALT SIO2 SIO4-4 1 / H2O 2 / OH- -4
        K-SALT SIO2 -3.52
;first guess

        SALT 'FEO(OH)' FE+3 1 / OH- 3 / H2O -1
        K-SALT 'FEO(OH)' -25.9
;first guess

        SALT BIPO4 BI+3 1 / PO4-3 1
        K-SALT BIPO4 -52.7
;Zharovskii (1951) Ksp at 18-20 C

PROP-DATA
        IN-UNITS SI

        PROP-LIST       CHARGE
        PVAL BI+3       +3

        PROP-LIST       MW
        PVAL BI+3       208.9804
        PVAL NANO2       68.99527
        PVAL NAPHOS12   380.1231
        PVAL 'FEO(OH)'   88.8537
        PVAL BIPO4      303.95176
        PVAL NAALUM1    208.97822
        PVAL NAALUM2    395.9893
        PVAL GIBBSITE    78.00344
        PVAL NASULF10   322.18914

;BINARY PITZER PARAMETERS FOR AQUEOUS SPECIES
        PROP-LIST      GMPTB0/    GMPTB1/   GMPTC

        BPVAL NA+ 'AL(OH)4-' 0.045017 0 -448.3  -1.3366  0/
                             0.30455  0 -985.9  -2.9187  0/
                            -2.661E-4 0   65.099 0.17457 0
;Na-alum parameters regressed from estimates in Wesolowski (1992) 0-100 C

        BPVAL NA+ CL- 0.07391 0 -257.83 -0.65385 0 /
                      0.27386 7.567E-4 0 0 6.339E-8 /
                      1.609E-3 0 27.255 0.0595435 0
;Greenberg and Moller

        BPVAL NA+ F-    .02151 5.36E-4/.2107 8.7E-4/0
;NaF parameters from Pitzer (1979)
;Linear temperature terms from Silvester & Pitzer (1978)
```

```
        BPVAL NA+ NO2- .0492983/ .1848795/-.002451916
NaNO2 fit from osmotic data at 25 C
no data available for other temperatures

        BPVAL NA+ NO3- .003695436 /.2049175 / -0.5683541E-04
NaNO3 fit from osmotic data at 25 C

        BPVAL NA+ OH- 0.1069 -0.002433 * *  0.315E-5/
                   -0.8749  0.0913    * * -0.1342E-3/
                    0.001063 0.0002101 * * -0.3526E-6
:fit from VLE data (Perry's Handbook, 6th ed.) 0-100 C, 0-10 molal

        BPVAL NA+ PO4-3  0.1781 / -0.0583 / -0.0533
:Pitzer (1979) for 25 C, up to 0.7 m

        BPVAL NA+ HPO4-2 -0.0583 / 1.4655 / 0.0294
:Pitzer (1979) for 25 C, up to 1 m

        BPVAL NA+ H2PO4-  -0.0533 / 0.0396 / 0.00795
:Pitzer (1979) for 25 C, up to 6 m

        BPVAL NA+ SO4-2 0.0175048 0.2283209 -11960.5 -90.313 -9.6E-5 /
                        1.0962602 -0.109861 75.59925 22.86044 6.75E-5/
                        0.0061392 -0.006948 657.2631 3.784364 1.92E-6
;fit from Greenberg and Moller (1989) parameters

        PROP-LIST  GMPTTH
        BPVAL OH- 'AL(OH)4-' 0.014
;Wesolowski (1992) estimate for less than 100 C
        BPVAL NO3- NO2- -0.02069372
;regressed from Linke NaNO2-NaNO3 solubility data at 21 C
        BPVAL OH- NO2- -0.05592618
;regressed from Plekhotkin & Bobrovskaya solubility data at 25 C
        BPVAL OH- NO3- -0.04590266
;regressed from Plekhotkin & Bobrovskaya solubility data at 25 C
        BPVAL OH- F- 0.1218 0.00318
;regressed from Linke solubility data at 0 C, 20 C, 40 C
        BPVAL NO3- F- 0.03005
;regressed from Zhikharev solubility data at 25 C


STREAM SLUDGE TEMP=25 PRES=1 MASS-FLOW=100
        MOLE-FRAC NANO3 0.650 / NANO2 0.053 / NAF 0.027 / &
        NAPHOS12 0.045 / NASULF10 0.028 / BOEMITE 0.011 / &
        SIO2 0.083 / 'FEO(OH)' 0.087 / BIPO4 0.016

STREAM H1LIQ TEMP=25 PRES=1 MOLE-FLOW=10
        MOLE-FLOW H2O 55.51/NAOH 0.1

STREAM H2LIQ TEMP=25 PRES=1 MOLE-FLOW=10
        MOLE-FLOW H2O 55.51/NAOH 0.1

FLOWSHEET
        BLOCK H1 IN=SLUDGE H1LIQ         OUT=H1OUT
        BLOCK S1 IN=H1OUT                OUT=S1LIQ S1SOL
        BLOCK H2 IN=S1SOL H2LIQ          OUT=H2OUT
        BLOCK S2 IN=H2OUT                OUT=S2LIQ S2SOL
        BLOCK M1 IN=S1LIQ S2LIQ          OUT=LIQTOTAL
```

```
LOCK H1 HEATER
       PARAM TEMP=25 PRES=1 MAXIT=100

LOCK H2 HEATER
       PARAM TEMP=25 PRES=1 MAXIT=100

LOCK S1 SEP
       FRAC STREAM=S1LIQ COMPS= H2O H+ OH- NA+ NO3- NO2- F- AL+3   &
          'AL(OH)4-' PO4-3 SO4-2                                   &
          SIO4-4 FE+3 BI+3                                         &
          NANO3 NANO2 NAF NAPHOS12 NASULF10 BOEMITE SIO2 'FEO(OH)'&
          BIPO4 NAALUM1 NAALUM2 GIBBSITE                           &
          FRACS= 1 1 1 1 1 1 1 1 1 1 1 1 1 1                       &
                 0 0 0 0 0 0 0 0 0 0 0 0
       FLASH-SPECS S1LIQ NPHASE=1 PHASE=L
       FLASH-SPECS S1SOL NPHASE=1 PHASE=S

LOCK S2 SEP
       FRAC STREAM=S2LIQ COMPS= H2O H+ OH- NA+ NO3- NO2- F- AL+3   &
          'AL(OH)4-' PO4-3 SO4-2                                   &
          SIO4-4 FE+3 BI+3                                         &
          NANO3 NANO2 NAF NAPHOS12 NASULF10 BOEMITE SIO2 'FEO(OH)'&
          BIPO4 NAALUM1 NAALUM2 GIBBSITE                           &
          FRACS= 1 1 1 1 1 1 1 1 1 1 1 1 1 1                       &
                 0 0 0 0 0 0 0 0 0 0 0 0
       FLASH-SPECS S2LIQ NPHASE=1 PHASE=L
       FLASH-SPECS S2SOL NPHASE=1 PHASE=S

LOCK M1 MIXER
```

Appendix B

Simple ASPEN PLUS™ Water Dissolution Simulation

```
** INPUT ECHO(ES) ***

>CURRENT RUN

 ORIGINAL RUN                              AUGUST 17, 1992
 4:05:33 P.M.                              MONDAY
 INPUT FILE: SMALL1.inp
 OUTPUT PDF: SMALL1   VERSION:  1
 LOCATED IN: C:\FLOWST\SMALL1
 PDF SIZE: FILE (PSIZE)=99999 RECORDS.   IN-CORE =   400 RECORDS.

     TITLE 'FLOWSHEET 1'
     DESCRIPTION      "THIS FLOWSHEET MODELS WATER WASHING OF SOME OF THE
                       COMPONENTS FOUND IN B-110 SLUDGE."
     IN-UNITS MET TEMP=C PRES=ATM
     REPORT NOFLOWSHEET NOPROPERTIES NOBLOCKS
     STREAM-REPORT MASS-FLOW MOLE-FLOW
     COMPONENTS H2O H2O/OH- OH-/NA+ NA+/NO3- NO3-/NO2- NO2-/F- F-/ &
                NANO3 NANO3 / NANO2 NANO3 / NAF NAF

     PROPERTIES SYSOP16 CHEMISTRY=SLUDGE
     DATABANKS AQUEOUS/SOLIDS
     CHEMISTRY SLUDGE
     ;SODIUM SALT PRECIPITATION
             SALT NAF NA+ 1 / F- 1
             K-SALT NAF 30.78832 -2370.084 -5.617666
     ;NaF Solubility Data from Linke Vol. 2 p. 1258  (0-100 C)

             SALT NANO3 NA+ 1 / NO3- 1
             K-SALT NANO3 1245.491 -33988.12 -218.2614 0.3573155
     ;NaNO3 fit from Mulder (Linke) 0-60 C, with binary parameters at 25 C

             SALT NANO2 NA+ 1 / NO2- 1
             K-SALT NANO2 49.34024 -2920.095 -7.676417
     ;NaNO2 fit from Bureau/Erdos data in Linke 0-52 C
     ;Pitzer params were fit only at 25 C

     PROP-DATA
             IN-UNITS SI

             PROP-LIST       MW
             PVAL NANO2       68.99527

     ;BINARY PITZER PARAMETERS FOR AQUEOUS SPECIES
             PROP-LIST      GMPTB0/    GMPTB1/   GMPTC

             BPVAL NA+ F-    .02151 5.36E-4/.2107 8.7E-4/0
     ;NaF parameters from Pitzer (1979)
     ;Linear temperature terms from Silvester & Pitzer (1978)

             BPVAL NA+ NO2- .0492983/ .1848795/-.002451916
     ;NaNO2 fit from osmotic data at 25 C
     ;no data available for other temperatures

```

```
        BPVAL NA+ NO3- .003695436 /.2049175 / -0.5683541E-04
;NaNO3 fit from osmotic data at 25 C

        BPVAL OH- NA+ 0.1069 -0.002433 * *  0.315E-5/
                     -0.8749  0.0913   * * -0.1342E-3/
                      0.001063 0.0002101 * * -0.3526E-6
;fit from VLE data (Perry's Handbook, 6th ed.) 0-100 C, 0-10 molal

;TERNARY PITZER PARAMETERS FOR AQUEOUS SPECIES
        PROP-LIST  GMPTTH
        BPVAL NO3- NO2- -0.02069372
;regressed from Linke NaNO2-NaNO3 solubility data at 21 C
        BPVAL OH- NO2- -0.05592618
;regressed from Plekhotkin & Bobrovskaya solubility data at 25 C
        BPVAL OH- NO3- -0.04590266
;regressed from Plekhotkin & Bobrovskaya solubility data at 25 C
        BPVAL OH- F- 0.1218 0.00318
;regressed from Linke solubility data at 0 C, 20 C, 40 C
        BPVAL NO3- F- 0.03005
;regressed from Zhikharev solubility data at 25 C


STREAM SLUDGE TEMP=25 PRES=1
        MASS-FLOW NANO3 54.42/NANO2 3.60/NAF 0.88

STREAM H1LIQ TEMP=25 PRES=1 MASS-FLOW=4.348
        MOLE-FRAC H2O 1

STREAM H2LIQ TEMP=25 PRES=1 MASS-FLOW=51
        MOLE-FRAC H2O 1

STREAM H3LIQ TEMP=25 PRES=1 MASS-FLOW=15.96
        MOLE-FRAC H2O 1

STREAM H4LIQ TEMP=25 PRES=1 MASS-FLOW=1
        MOLE-FRAC H2O 1

FLOWSHEET
        BLOCK H1 IN=SLUDGE H1LIQ        OUT=H1OUT
        BLOCK S1 IN=H1OUT               OUT=S1LIQ S1SOL
        BLOCK H2 IN=S1SOL H2LIQ         OUT=H2OUT
        BLOCK S2 IN=H2OUT               OUT=S2LIQ S2SOL
        BLOCK H3 IN=S2SOL H3LIQ         OUT=H3OUT
        BLOCK S3 IN=H3OUT               OUT=S3LIQ S3SOL
        BLOCK H4 IN=S3SOL H4LIQ         OUT=H4OUT
        BLOCK S4 IN=H4OUT               OUT=S4LIQ S4SOL
        BLOCK MT IN=S1LIQ S2LIQ S3LIQ S4LIQ  OUT=LIQTOTAL

BLOCK H1 HEATER
        PARAM TEMP=25 PRES=1 MAXIT=500

BLOCK H2 HEATER
        PARAM TEMP=25 PRES=1 MAXIT=500

BLOCK H3 HEATER
        PARAM TEMP=25 PRES=1 MAXIT=500

BLOCK H4 HEATER
        PARAM TEMP=25 PRES=1 MAXIT=500

```

```
 104      BLOCK S1 SEP
 105             FRAC STREAM=S1LIQ COMPS= H2O OH- NA+ NO3- NO2- F- NANO3 NANO2 N
 106                FRACS= 1 1 1 1 1 1 0 0 0
 107             FLASH-SPECS S1LIQ NPHASE=1 PHASE=L
 108             FLASH-SPECS S1SOL NPHASE=1 PHASE=S
 109
 110      BLOCK S2 SEP
 111             FRAC STREAM=S2LIQ COMPS= H2O OH- NA+ NO3- NO2- F- NANO3 NANO2 N
 112                FRACS= 1 1 1 1 1 1 0 0 0
 113             FLASH-SPECS S2LIQ NPHASE=1 PHASE=L
 114             FLASH-SPECS S2SOL NPHASE=1 PHASE=S
 115
 116      BLOCK S3 SEP
 117             FRAC STREAM=S3LIQ COMPS= H2O OH- NA+ NO3- NO2- F- NANO3 NANO2 N
 118                FRACS= 1 1 1 1 1 1 0 0 0
 119             FLASH-SPECS S3LIQ NPHASE=1 PHASE=L
 120             FLASH-SPECS S3SOL NPHASE=1 PHASE=S
 121
 122      BLOCK S4 SEP
 123             FRAC STREAM=S4LIQ COMPS= H2O OH- NA+ NO3- NO2- F- NANO3 NANO2 N
 124                FRACS= 1 1 1 1 1 1 0 0 0
 125             FLASH-SPECS S4LIQ NPHASE=1 PHASE=L
 126             FLASH-SPECS S4SOL NPHASE=1 PHASE=S
 127
 128      BLOCK MT MIXER
 129
*** INPUT TRANSLATOR MESSAGES ***

THIS VERSION OF ASPEN PLUS LICENSED TO BATTELLE PACIFIC NORTHWEST LABS

 *   WARNING IN PHYSICAL PROPERTY SYSTEM WHILE RETRIEVING AND CHECKING
     PARAMETER VALUES                                           (ELEADD.1)
     THE ION-ION PAIR (F- NO2-) NOT FOUND IN THE PITZER DATABANK.
     VALUES FOR THE PITZER PARAMETERS WILL DEFAULT TO ZERO.


*** FLOWSHEET ANALYSIS MESSAGES ***

FLOWSHEET CONNECTIVITY BY STREAMS

  STREAM     SOURCE     DEST           STREAM     SOURCE     DEST
  H1LIQ      ----       H1             SLUDGE     ----       H1
  H2LIQ      ----       H2             H3LIQ      ----       H3
  H4LIQ      ----       H4             H1OUT      H1         S1
  S1LIQ      S1         MT             S1SOL      S1         H2
  H2OUT      H2         S2             S2LIQ      S2         MT
  S2SOL      S2         H3             H3OUT      H3         S3
  S3LIQ      S3         MT             S3SOL      S3         H4
  H4OUT      H4         S4             S4LIQ      S4         MT
  S4SOL      S4         ----           LIQTOTAL   MT         ----

FLOWSHEET CONNECTIVITY BY BLOCKS

  BLOCK        INLETS                         OUTLETS
  H1           SLUDGE H1LIQ                   H1OUT
  S1           H1OUT                          S1LIQ S1SOL
  H2           S1SOL H2LIQ                    H2OUT
  S2           H2OUT                          S2LIQ S2SOL
  H3           S2SOL H3LIQ                    H3OUT
```

```
 S3            H3OUT                           S3LIQ S3SOL
 H4            S3SOL H4LIQ                     H4OUT
 S4            H4OUT                           S4LIQ S4SOL
 MT            S1LIQ S2LIQ S3LIQ S4LIQ         LIQTOTAL

COMPUTATION ORDER FOR THE FLOWSHEET IS:
H1 S1 H2 S2 H3 S3 H4 S4 MT

MODULE SMALL1   IS USED; CREATION DATE 08/17/92 10:35:23:34
LOCATED IN:C:\FLOWST\SMALL1


*** SUMMARY OF ERRORS  ***

                  PHYSICAL
                  PROPERTY  SYSTEM  SIMULATION
TERMINAL ERRORS      0        0         0
  SEVERE ERRORS      0        0         0
         ERRORS      0        0         0
       WARNINGS      1        0         0
SIMULATION PROGRAM MAY BE EXECUTED


************************************************
*  ASPEN PLUS INPUT TRANSLATOR ENDS EXECUTION  *
************************************************

*** CALCULATION TRACE ***

FLOWSHEET 1


SIMULATION CALCULATIONS BEGIN

     ENTHALPY CALCULATION FOR INLET STREAM SLUDGE   OF BLOCK H1
     KODE = 2   NO. TEMP ITER =    1     TEMP =   298.15
     KPHASE =    3 KODE =    2 T =   298.15     P =  0.10133E+06 Q =  0.00000E+0

     ENTHALPY CALCULATION FOR INLET STREAM H1LIQ    OF BLOCK H1
     KODE = 2  NTRIAL =   2  T =   298.2       P =  0.1013E+06  V =  0.0000E+00

     UOS BLOCK H1        MODEL: HEATER
     KODE = 2  NTRIAL =  12  T =   298.2       P =  0.1013E+06  V =  0.0000E+00

     UOS BLOCK S1        MODEL: SEP
     ---FLASH OUTLET STREAM S1LIQ    :
     KODE = 2  NTRIAL =   1  T =   298.2       P =  0.1013E+06  V =  0.0000E+00
     ---FLASH OUTLET STREAM S1SOL    :
     KODE = 2   NO. TEMP ITER =    1     TEMP =   298.15
     KPHASE =    3 KODE =    2 T =   298.15     P =  0.10133E+06 Q =  0.00000E+0

     ENTHALPY CALCULATION FOR INLET STREAM H2LIQ    OF BLOCK H2
     KODE = 2  NTRIAL =   2  T =   298.2       P =  0.1013E+06  V =  0.0000E+00

     UOS BLOCK H2        MODEL: HEATER
     KODE = 2  NTRIAL =   6  T =   298.2       P =  0.1013E+06  V =  0.0000E+00

     UOS BLOCK S2        MODEL: SEP
     ---FLASH OUTLET STREAM S2LIQ    :
     KODE = 2  NTRIAL =   1  T =   298.2       P =  0.1013E+06  V =  0.0000E+00
```

```
   ---FLASH OUTLET STREAM S2SOL    :
   KODE = 2   NO. TEMP ITER =     1      TEMP =   298.15
   KPHASE =    3 KODE =    2 T =   298.15      P =  0.10133E+06 Q =   0.00000E+0

   ENTHALPY CALCULATION FOR INLET STREAM H3LIQ    OF BLOCK H3
   KODE = 2  NTRIAL =   2  T =   298.2       P =  0.1013E+06  V =  0.0000E+00

   UOS BLOCK H3       MODEL: HEATER
   KODE = 2  NTRIAL =   4  T =   298.2       P =  0.1013E+06  V =  0.0000E+00

   UOS BLOCK S3       MODEL: SEP
   ---FLASH OUTLET STREAM S3LIQ    :
   KODE = 2  NTRIAL =   1  T =   298.2       P =  0.1013E+06  V =  0.0000E+00
   ---FLASH OUTLET STREAM S3SOL    :
   KODE = 2   NO. TEMP ITER =     1      TEMP =   298.15
   KPHASE =    3 KODE =    2 T =   298.15      P =  0.10133E+06 Q =   0.00000E+0

   ENTHALPY CALCULATION FOR INLET STREAM H4LIQ    OF BLOCK H4
   KODE = 2  NTRIAL =   2  T =   298.2       P =  0.1013E+06  V =  0.0000E+00

   UOS BLOCK H4       MODEL: HEATER
   KODE = 2  NTRIAL =   2  T =   298.2       P =  0.1013E+06  V =  0.0000E+00

   UOS BLOCK S4       MODEL: SEP
   ---FLASH OUTLET STREAM S4LIQ    :
   KODE = 2  NTRIAL =   1  T =   298.2       P =  0.1013E+06  V =  0.0000E+00

*  WARNING WHILE EXECUTING UNIT OPERATIONS BLOCK: "S4" (MODEL: "SEP")
                                                            (USP03.1)
   OUTLET STREAM "S4SOL" HAS ZERO FLOW. FLASH CALCULATIONS BYPASSED.

   UOS BLOCK MT       MODEL: MIXER
   H-LOOP : NTRIAL =    7 T/V/P =   298.9
   KODE = 1  NTRIAL =   2  T =   298.9       P =  0.1013E+06  V =  0.0000E+00

IMULATION CALCULATIONS COMPLETED

OF UPDATED

EPORT WRITER ENTERED

EPORT GENERATED


** SUMMARY OF ERRORS  ***

                  PHYSICAL
                  PROPERTY   SYSTEM   SIMULATION
ERMINAL ERRORS        0         0          0
 SEVERE ERRORS        0         0          0
        ERRORS        0         0          0
      WARNINGS        0         0          1


********************************************************
  ASPEN PLUS SIMULATION PROGRAM ENDS EXECUTION   *
********************************************************
```

```
ASPEN PLUS   VER: PC-DOS    REL: 8.5-3    INST: PNL-LJS   08/17/92  PAGE 2
                                    FLOWSHEET 1
                                    STREAM SECTION

H1LIQ H1OUT H2LIQ H2OUT H3LIQ
-----------------------------

STREAM ID                  H1LIQ       H1OUT       H2LIQ       H2OUT       H3LIQ
FROM :                     ----        H1          ----        H2          ----
TO   :                     H1          S1          H2          S2          H3

SUBSTREAM: MIXED
PHASE:                     LIQUID      MIXED       LIQUID      MIXED       LIQUID
COMPONENTS: KMOL/HR
  H2O                       0.2413      0.2413      2.8309      2.8309      0.8859
  OH-                       0.0         0.0         0.0         0.0         0.0
  NA+                       0.0         0.1507      0.0         0.5468      0.0
  NO3-                      0.0      9.8419-02      0.0         0.5417      0.0
  NO2-                      0.0      5.2177-02      0.0         0.0         0.0
  F-                        0.0      1.1015-04      0.0      5.1422-03      0.0
  NANO3                     0.0         0.5418      0.0      1.4995-04      0.0
  NANO2                     0.0         0.0         0.0         0.0         0.0
  NAF                       0.0      2.0848-02      0.0      1.5706-02      0.0
COMPONENTS: KG/HR
  H2O                       4.3480      4.3480     51.0000     51.0000     15.9600
  OH-                       0.0         0.0         0.0         0.0         0.0
  NA+                       0.0         3.4647      0.0        12.5718      0.0
  NO3-                      0.0         6.1024      0.0        33.5882      0.0
  NO2-                      0.0         2.4004      0.0         0.0         0.0
  F-                        0.0      2.0927-03      0.0      9.7694-02      0.0
  NANO3                     0.0        46.0548      0.0      1.2745-02      0.0
  NANO2                     0.0         0.0         0.0         0.0         0.0
  NAF                       0.0         0.8753      0.0         0.6594      0.0
TOTAL FLOW:
  KMOL/HR                   0.2413      1.1054      2.8309      3.9405      0.8859
  KG/HR                     4.3480     63.2480     51.0000     97.9302     15.9600
  L/MIN                  7.2674-02      0.5041      0.8524      1.1603      0.2667
STATE VARIABLES:
  TEMP   C                 25.0000     25.0000     25.0000     25.0000     25.0000
  PRES   ATM                1.0000      1.0000      1.0000      1.0000      1.0000
  VFRAC                     0.0         0.0         0.0         0.0         0.0
  LFRAC                     1.0000      0.4909      1.0000      0.9959      1.0000
  SFRAC                     0.0         0.5090      0.0      4.0238-03      0.0
ENTHALPY:
  CAL/MOL               -6.8311+04  -8.5208+04  -6.8311+04  -6.4341+04  -6.8311+04
  CAL/GM                -3791.9127  -1489.2955  -3791.9127  -2588.9557  -3791.9127
  CAL/SEC               -4579.7879  -2.6165+04  -5.3719+04  -7.0427+04  -1.6811+04
ENTROPY:
  CAL/MOL-K               -38.9707    -55.1461    -38.9707    -36.4737    -38.9707
  CAL/GM-K                 -2.1632     -0.9638     -2.1632     -1.4676     -2.1632
DENSITY:
  MOL/CC                 5.5351-02   3.6544-02   5.5351-02   5.6601-02   5.5351-02
  GM/CC                     0.9971      2.0908      0.9971      1.4066      0.9971
AVG MW                     18.0150     57.2136     18.0150     24.8521     18.0150
```

```
ASPEN PLUS    VER: PC-DOS     REL: 8.5-3     INST: PNL-LJS    08/17/92   PAGE 3
                                 FLOWSHEET 1
                                 STREAM SECTION

H3OUT H4LIQ H4OUT LIQTOTAL S1LIQ
--------------------------------

STREAM ID                   H3OUT       H4LIQ       H4OUT       LIQTOTAL    S1LIQ
FROM :                      H3          ----        H4          MT          S1
TO   :                      S3          H4          S4          ----        MT

SUBSTREAM: MIXED
PHASE:                      MIXED       LIQUID      LIQUID      MIXED       MIXED
COMPONENTS: KMOL/HR
  H2O                        0.8859   5.5509-02   5.5509-02      4.0137      0.2413
  OH-                         0.0         0.0         0.0         0.0         0.0
  NA+                     1.5852-02       0.0     4.4060-06      0.7010      0.1507
  NO3-                    1.5011-04       0.0         0.0        0.6402   9.8419-02
  NO2-                        0.0         0.0         0.0     5.2177-02   5.2177-02
  F-                      1.5702-02       0.0     4.4060-06   8.6041-03   1.1015-04
  NANO3                       0.0         0.0         0.0         0.0         0.0
  NANO2                       0.0         0.0         0.0         0.0         0.0
  NAF                     4.4060-06       0.0         0.0     1.2354-02   3.1542-09
COMPONENTS: KG/HR
  H2O                       15.9600      1.0000      1.0000     72.3080      4.3480
  OH-                         0.0         0.0         0.0         0.0         0.0
  NA+                        0.3644       0.0     1.0129-04     16.1171      3.4647
  NO3-                    9.3079-03       0.0         0.0       39.7000      6.1024
  NO2-                        0.0         0.0         0.0        2.4004      2.4004
  F-                         0.2983       0.0     8.3707-05      0.1634   2.0926-03
  NANO3                       0.0         0.0         0.0         0.0         0.0
  NANO2                       0.0         0.0         0.0         0.0         0.0
  NAF                     1.8500-04       0.0         0.0        0.5187   1.3244-07
TOTAL FLOW:
  KMOL/HR                    0.9176   5.5509-02   5.5518-02      5.4282      0.5427
  KG/HR                     16.6322      1.0000      1.0001    131.2078     16.3177
  L/MIN                      0.2665   1.6714-02   1.6714-02      1.5959      0.1594
STATE VARIABLES:
  TEMP   C                  25.0000     25.0000     25.0000     25.7350     25.0000
  PRES   ATM                 1.0000      1.0000      1.0000      1.0000      1.0000
  VFRAC                       0.0         0.0         0.0         0.0         0.0
  LFRAC                      1.0000      1.0000      1.0000      0.9977      1.0000
  SFRAC                   4.8015-06       0.0         0.0     2.2759-03   5.8113-09
ENTHALPY:
  CAL/MOL               -6.8309+04  -6.8311+04  -6.8311+04  -6.4289+04  -5.7375+04
  CAL/GM                -3768.7845  -3791.9127  -3791.8138  -2659.7044  -1908.4354
  CAL/SEC               -1.7412+04  -1053.3090  -1053.4765  -9.6937+04  -8650.3753
ENTROPY:
  CAL/MOL-K                -37.9746    -38.9707    -38.9645    -36.3274    -33.1189
  CAL/GM-K                  -2.0951     -2.1632     -2.1628     -1.5029     -1.1016
DENSITY:
  MOL/CC                 5.7387-02   5.5351-02   5.5361-02   5.6687-02   5.6752-02
  GM/CC                      1.0401      0.9971      0.9973      1.3702      1.7061
AVG MW                      18.1250     18.0150     18.0154     24.1713     30.0639
```

```
S1SOL S2LIQ S2SOL S3LIQ S3SOL
-----------------------------

STREAM ID                 S1SOL        S2LIQ        S2SOL        S3LIQ        S3SOL
FROM :                    S1           S2           S2           S3           S3
TO   :                    H2           MT           H3           MT           H4

SUBSTREAM: MIXED
PHASE:                    SOLID        LIQUID       SOLID        LIQUID       SOLID
COMPONENTS: KMOL/HR
  H2O                      0.0          2.8309       0.0          0.8859       0.0
  OH-                      0.0          0.0          0.0          0.0          0.0
  NA+                      0.0          0.5468       0.0       1.5852-02       0.0
  NO3-                     0.0          0.5417       0.0       1.5011-04       0.0
  NO2-                     0.0          0.0          0.0          0.0          0.0
  F-                       0.0       5.1422-03       0.0       1.5702-02       0.0
  NANO3                    0.5418       0.0       1.4995-04       0.0          0.0
  NANO2                    0.0          0.0          0.0          0.0          0.0
  NAF                   2.0848-02       0.0       1.5706-02       0.0       4.4060-06
COMPONENTS: KG/HR
  H2O                      0.0         51.0000       0.0         15.9600       0.0
  OH-                      0.0          0.0          0.0          0.0          0.0
  NA+                      0.0         12.5718       0.0          0.3644       0.0
  NO3-                     0.0         33.5882       0.0       9.3079-03       0.0
  NO2-                     0.0          0.0          0.0          0.0          0.0
  F-                       0.0       9.7694-02       0.0          0.2983       0.0
  NANO3                   46.0548       0.0       1.2745-02       0.0          0.0
  NANO2                    0.0          0.0          0.0          0.0          0.0
  NAF                      0.8753       0.0          0.6594       0.0       1.8500-04
TOTAL FLOW:
  KMOL/HR                  0.5627       3.9246    1.5856-02       0.9176    4.4060-06
  KG/HR                   46.9302      97.2578       0.6722      16.6320    1.8500-04
  L/MIN                    0.3447       1.1563    4.0163-03       0.2665    1.1003-06
STATE VARIABLES:
  TEMP    C               25.0000      25.0000      25.0000      25.0000      25.0000
  PRES    ATM              1.0000       1.0000       1.0000       1.0000       1.0000
  VFRAC                    0.0          0.0          0.0          0.0          0.0
  LFRAC                    0.0          1.0000       0.0          1.0000       0.0
  SFRAC                    1.0000       0.0          1.0000       0.0          1.0000
ENTHALPY:
  CAL/MOL              -1.1206+05   -6.4046+04   -1.3745+05   -6.8309+04   -1.3771+05
  CAL/GM               -1343.5606   -2584.4446   -3242.2601   -3768.7869   -3279.6656
  CAL/SEC              -1.7515+04   -6.9822+04    -605.4095   -1.7412+04      -0.1685
ENTROPY:
  CAL/MOL-K              -76.3930     -36.5212     -24.7302     -37.9747     -24.2178
  CAL/GM-K                -0.9159      -1.4737      -0.5833      -2.0951      -0.5767
DENSITY:
  MOL/CC                2.7202-02    5.6569-02    6.5799-02    5.7387-02    6.6738-02
  GM/CC                    2.2686       1.4018       2.7895       1.0401       2.8021
AVG MW                    83.4015      24.7811      42.3947      18.1249      41.9880
```

```
S4LIQ S4SOL SLUDGE
------------------

STREAM ID                S4LIQ        S4SOL        SLUDGE
FROM :                   S4           S4           ----
TO   :                   MT           ----         H1

SUBSTREAM: MIXED
PHASE:                   LIQUID       MIXED        SOLID
COMPONENTS: KMOL/HR
  H2O                  5.5509-02      0.0          0.0
  OH-                     0.0         0.0          0.0
  NA+                  4.4060-06      0.0          0.0
  NO3-                    0.0         0.0          0.0
  NO2-                    0.0         0.0          0.0
  F-                   4.4060-06      0.0          0.0
  NANO3                   0.0         0.0          0.6402
  NANO2                   0.0         0.0       5.2177-02
  NAF                     0.0         0.0       2.0958-02
COMPONENTS: KG/HR
  H2O                     1.0000      0.0          0.0
  OH-                     0.0         0.0          0.0
  NA+                  1.0129-04      0.0          0.0
  NO3-                    0.0         0.0          0.0
  NO2-                    0.0         0.0          0.0
  F-                   8.3707-05      0.0          0.0
  NANO3                   0.0         0.0         54.4200
  NANO2                   0.0         0.0          3.6000
  NAF                     0.0         0.0          0.8800
TOTAL FLOW:
  KMOL/HR              5.5518-02      0.0          0.7134
  KG/HR                   1.0001      0.0         58.9000
  L/MIN                1.6714-02      0.0          0.4391
STATE VARIABLES:
  TEMP   C               25.0000    MISSING      25.0000
  PRES   ATM              1.0000    MISSING       1.0000
  VFRAC                   0.0       MISSING       0.0
  LFRAC                   1.0000    MISSING       0.0
  SFRAC                   0.0       MISSING       1.0000
ENTHALPY:
  CAL/MOL              -6.8311+04   MISSING -1.1185+05
  CAL/GM               -3791.8138   MISSING -1354.7584
  CAL/SEC              -1053.4765   MISSING -2.2165+04
ENTROPY:
  CAL/MOL-K              -38.9645   MISSING   -76.8088
  CAL/GM-K                -2.1628   MISSING    -0.9303
DENSITY:
  MOL/CC               5.5361-02    MISSING  2.7074-02
  GM/CC                   0.9973    MISSING     2.2352
AVG MW                   18.0154    MISSING    82.5613
```

Appendix C

Simple ASPEN PLUS™ Caustic Dissolution Simulation

```
*** INPUT ECHO(ES) ***

->CURRENT RUN

 ORIGINAL RUN                             AUGUST 18, 1992
 8:04:29 A.M.                             TUESDAY
 INPUT FILE: SMALL2.inp
 OUTPUT PDF: SMALL2   VERSION:  1
 LOCATED IN: C:\FLOWST\SMALL2
 PDF SIZE: FILE (PSIZE)=99999 RECORDS.   IN-CORE =   400 RECORDS.

    1     TITLE 'FLOWSHEET 1'
    2     DESCRIPTION     "THIS FLOWSHEET MODELS CAUSTIC WASHING OF SOME OF THE
    3                      COMPONENTS FOUND IN B-110 SLUDGE."
    4     IN-UNITS MET TEMP=C PRES=ATM
    5     REPORT NOFLOWSHEET NOPROPERTIES NOBLOCKS
    6     STREAM-REPORT MASS-FLOW MOLE-FLOW
    7     COMPONENTS H2O H2O/OH- OH-/NA+ NA+/NO3- NO3-/NO2- NO2-/F- F-/ &
    8                NANO3 NANO3 / NANO2 NANO3 / NAF NAF /NAOH NAOH
    9
   10     PROPERTIES SYSOP16 CHEMISTRY=SLUDGE
   11     DATABANKS AQUEOUS/SOLIDS
   12     CHEMISTRY SLUDGE
   13             DISS NAOH NA+ 1 / OH- 1
   14     ;SODIUM SALT PRECIPITATION
   15             SALT NAF NA+ 1 / F- 1
   16             K-SALT NAF 30.78832 -2370.084 -5.617666
   17     ;NaF Solubility Data from Linke Vol. 2 p. 1258  (0-100 C)
   18
   19             SALT NANO3 NA+ 1 / NO3- 1
   20             K-SALT NANO3 1245.491 -33988.12 -218.2614 0.3573155
   21     ;NaNO3 fit from Mulder (Linke) 0-60 C, with binary parameters at 25 C
   22
   23             SALT NANO2 NA+ 1 / NO2- 1
   24             K-SALT NANO2 49.34024 -2920.095 -7.676417
   25     ;NaNO2 fit from Bureau/Erdos data in Linke 0-52 C
   26     ;Pitzer params were fit only at 25 C
   27
   28     PROP-DATA
   29             IN-UNITS SI
   30
   31             PROP-LIST       MW
   32             PVAL NANO2       68.99527
   33
   34     ;BINARY PITZER PARAMETERS FOR AQUEOUS SPECIES
   35             PROP-LIST       GMPTB0/    GMPTB1/   GMPTC
   36
   37             BPVAL NA+ F-    .02151 5.36E-4/.2107 8.7E-4/0
   38     ;NaF parameters from Pitzer (1979)
   39     ;Linear temperature terms from Silvester & Pitzer (1978)
   40
   41             BPVAL NA+ NO2- .0492983/ .1848795/-.002451916
   42     ;NaNO2 fit from osmotic data at 25 C
   43     ;no data available for other temperatures
```

```

        BPVAL NA+ NO3- .003695436 /.2049175 / -0.5683541E-04
;NaNO3 fit from osmotic data at 25 C

        BPVAL OH- NA+ 0.1069 -0.002433 * *  0.315E-5/
                     -0.8749  0.0913   * * -0.1342E-3/
                      0.001063 0.0002101 * * -0.3526E-6
;fit from VLE data (Perry's Handbook, 6th ed.) 0-100 C, 0-10 molal

;TERNARY PITZER PARAMETERS FOR AQUEOUS SPECIES
        PROP-LIST  GMPTTH
        BPVAL NO3- NO2- -0.02069372
;regressed from Linke NaNO2-NaNO3 solubility data at 21 C
        BPVAL OH- NO2- -0.05592618
;regressed from Plekhotkin & Bobrovskaya solubility data at 25 C
        BPVAL OH- NO3- -0.04590266
;regressed from Plekhotkin & Bobrovskaya solubility data at 25 C
        BPVAL OH- F- 0.1218 0.00318
;regressed from Linke solubility data at 0 C, 20 C, 40 C
        BPVAL NO3- F- 0.03005
;regressed from Zhikharev solubility data at 25 C


STREAM SLUDGE TEMP=25 PRES=1
        MASS-FLOW NANO3 54.42/NANO2 3.60/NAF 0.38

;0.1 MOLAL CAUSTIC SOLUTION IS ADDED AT EACH STAGE

STREAM H1LIQ TEMP=25 PRES=1 MASS-FLOW=4.34
        MOLE-FRAC H2O 0.9982 / NAOH 0.0018

STREAM H2LIQ TEMP=25 PRES=1 MASS-FLOW=52.4
        MOLE-FRAC H2O 0.9982 / NAOH 0.0018

STREAM H3LIQ TEMP=25 PRES=1 MASS-FLOW=17
        MOLE-FRAC H2O 0.9982 / NAOH 0.0018

STREAM H4LIQ TEMP=25 PRES=1 MASS-FLOW=1
        MOLE-FRAC H2O 0.9982 / NAOH 0.0018

FLOWSHEET
        BLOCK H1 IN=SLUDGE H1LIQ        OUT=H1OUT
        BLOCK S1 IN=H1OUT               OUT=S1LIQ S1SOL
        BLOCK H2 IN=S1SOL H2LIQ         OUT=H2OUT
        BLOCK S2 IN=H2OUT               OUT=S2LIQ S2SOL
        BLOCK H3 IN=S2SOL H3LIQ         OUT=H3OUT
        BLOCK S3 IN=H3OUT               OUT=S3LIQ S3SOL
        BLOCK H4 IN=S3SOL H4LIQ         OUT=H4OUT
        BLOCK S4 IN=H4OUT               OUT=S4LIQ S4SOL
        BLOCK MT IN=S1LIQ S2LIQ S3LIQ S4LIQ  OUT=LIQTOTAL

BLOCK H1 HEATER
        PARAM TEMP=25 PRES=1 MAXIT=500

BLOCK H2 HEATER
        PARAM TEMP=25 PRES=1 MAXIT=500

BLOCK H3 HEATER
        PARAM TEMP=25 PRES=1 MAXIT=500

```

```
104     BLOCK H4 HEATER
105             PARAM TEMP=25 PRES=1 MAXIT=500
106
107     BLOCK S1 SEP
108             FRAC STREAM=S1LIQ COMPS= H2O OH- NA+ NO3- NO2- F- NANO3 NANO2 N
109                FRACS= 1 1 1 1 1 1 0 0 0
110             FLASH-SPECS S1LIQ NPHASE=1 PHASE=L
111             FLASH-SPECS S1SOL NPHASE=1 PHASE=S
112
113     BLOCK S2 SEP
114             FRAC STREAM=S2LIQ COMPS= H2O OH- NA+ NO3- NO2- F- NANO3 NANO2 N
115                FRACS= 1 1 1 1 1 1 0 0 0
116             FLASH-SPECS S2LIQ NPHASE=1 PHASE=L
117             FLASH-SPECS S2SOL NPHASE=1 PHASE=S
118
119     BLOCK S3 SEP
120             FRAC STREAM=S3LIQ COMPS= H2O OH- NA+ NO3- NO2- F- NANO3 NANO2 N
121                FRACS= 1 1 1 1 1 1 0 0 0
122             FLASH-SPECS S3LIQ NPHASE=1 PHASE=L
123             FLASH-SPECS S3SOL NPHASE=1 PHASE=S
124
125     BLOCK S4 SEP
126             FRAC STREAM=S4LIQ COMPS= H2O OH- NA+ NO3- NO2- F- NANO3 NANO2 N
127                FRACS= 1 1 1 1 1 1 0 0 0
128             FLASH-SPECS S4LIQ NPHASE=1 PHASE=L
129             FLASH-SPECS S4SOL NPHASE=1 PHASE=S
130
131     BLOCK MT MIXER
132
*** INPUT TRANSLATOR MESSAGES ***

HIS VERSION OF ASPEN PLUS LICENSED TO BATTELLE PACIFIC NORTHWEST LABS

*   WARNING IN PHYSICAL PROPERTY SYSTEM WHILE RETRIEVING AND CHECKING
    PARAMETER VALUES                                            (ELEADD.1)
    THE ION-ION PAIR (F- NO2-) NOT FOUND IN THE PITZER DATABANK.
    VALUES FOR THE PITZER PARAMETERS WILL DEFAULT TO ZERO.


** FLOWSHEET ANALYSIS MESSAGES ***

LOWSHEET CONNECTIVITY BY STREAMS

 STREAM      SOURCE      DEST            STREAM      SOURCE      DEST
 H1LIQ       ----        H1              SLUDGE      ----        H1
 H2LIQ       ----        H2              H3LIQ       ----        H3
 H4LIQ       ----        H4              H1OUT       H1          S1
 S1LIQ       S1          MT              S1SOL       S1          H2
 H2OUT       H2          S2              S2LIQ       S2          MT
 S2SOL       S2          H3              H3OUT       H3          S3
 S3LIQ       S3          MT              S3SOL       S3          H4
 H4OUT       H4          S4              S4LIQ       S4          MT
 S4SOL       S4          ----            LIQTOTAL    MT          ----

LOWSHEET CONNECTIVITY BY BLOCKS

 BLOCK          INLETS                             OUTLETS
 H1             SLUDGE H1LIQ                       H1OUT
 S1             H1OUT                              S1LIQ S1SOL
```

```
 H2            S1SOL H2LIQ                H2OUT
 S2            H2OUT                      S2LIQ S2SOL
 H3            S2SOL H3LIQ                H3OUT
 S3            H3OUT                      S3LIQ S3SOL
 H4            S3SOL H4LIQ                H4OUT
 S4            H4OUT                      S4LIQ S4SOL
 MT            S1LIQ S2LIQ S3LIQ S4LIQ    LIQTOTAL

OMPUTATION ORDER FOR THE FLOWSHEET IS:
1 S1 H2 S2 H3 S3 H4 S4 MT

ODULE SMALL2   IS USED; CREATION DATE 08/17/92 16:12:53:22
OCATED IN:C:\FLOWST\SMALL2


*** SUMMARY OF ERRORS  ***

                  PHYSICAL
                  PROPERTY  SYSTEM  SIMULATION
ERMINAL ERRORS       0        0         0
 SEVERE ERRORS       0        0         0
        ERRORS       0        0         0
      WARNINGS       1        0         0
IMULATION PROGRAM MAY BE EXECUTED


*******************************************
*  ASPEN PLUS INPUT TRANSLATOR ENDS EXECUTION  *
*******************************************

*** CALCULATION TRACE ***

LOWSHEET 1


IMULATION CALCULATIONS BEGIN

    ENTHALPY CALCULATION FOR INLET STREAM SLUDGE   OF BLOCK H1
    KODE = 2   NO. TEMP ITER =    1     TEMP =   298.15
    KPHASE =    3 KODE =    2 T =   298.15     P =  0.10133E+06 Q =  0.00000E+0

    ENTHALPY CALCULATION FOR INLET STREAM H1LIQ    OF BLOCK H1
    KODE = 2  NTRIAL =   2  T =   298.2      P =  0.1013E+06  V =  0.0000E+00

    UOS BLOCK H1        MODEL: HEATER
    KODE = 2  NTRIAL =  10  T =   298.2      P =  0.1013E+06  V =  0.0000E+00

    UOS BLOCK S1        MODEL: SEP
    ---FLASH OUTLET STREAM S1LIQ    :
    KODE = 2  NTRIAL =   1  T =   298.2      P =  0.1013E+06  V =  0.0000E+00
    ---FLASH OUTLET STREAM S1SOL    :
    KODE = 2   NO. TEMP ITER =    1     TEMP =   298.15
    KPHASE =    3 KODE =    2 T =   298.15     P =  0.10133E+06 Q =  0.00000E+0

    ENTHALPY CALCULATION FOR INLET STREAM H2LIQ    OF BLOCK H2
    KODE = 2  NTRIAL =   2  T =   298.2      P =  0.1013E+06  V =  0.0000E+00

    UOS BLOCK H2        MODEL: HEATER
    KODE = 2  NTRIAL =   6  T =   298.2      P =  0.1013E+06  V =  0.0000E+00
```

```
    UOS BLOCK S2        MODEL: SEP
    ---FLASH OUTLET STREAM S2LIQ    :
    KODE = 2  NTRIAL =    1  T =    298.2       P =  0.1013E+06  V =   0.0000E+00
    ---FLASH OUTLET STREAM S2SOL    :
    KODE = 2   NO. TEMP ITER =     1      TEMP =   298.15
    KPHASE =     3 KODE =     2 T =   298.15      P =  0.10133E+06 Q =   0.00000E+0

    ENTHALPY CALCULATION FOR INLET STREAM H3LIQ    OF BLOCK H3
    KODE = 2  NTRIAL =    2  T =    298.2       P =  0.1013E+06  V =   0.0000E+00

    UOS BLOCK H3        MODEL: HEATER
    KODE = 2  NTRIAL =    4  T =    298.2       P =  0.1013E+06  V =   0.0000E+00

    UOS BLOCK S3        MODEL: SEP
    ---FLASH OUTLET STREAM S3LIQ    :
    KODE = 2  NTRIAL =    1  T =    298.2       P =  0.1013E+06  V =   0.0000E+00
    ---FLASH OUTLET STREAM S3SOL    :
    KODE = 2   NO. TEMP ITER =     1      TEMP =   298.15
    KPHASE =     3 KODE =     2 T =   298.15      P =  0.10133E+06 Q =   0.00000E+0

    ENTHALPY CALCULATION FOR INLET STREAM H4LIQ    OF BLOCK H4
    KODE = 2  NTRIAL =    2  T =    298.2       P =  0.1013E+06  V =   0.0000E+00

    UOS BLOCK H4        MODEL: HEATER
    KODE = 2  NTRIAL =    2  T =    298.2       P =  0.1013E+06  V =   0.0000E+00

    UOS BLOCK S4        MODEL: SEP
    ---FLASH OUTLET STREAM S4LIQ    :
    KODE = 2  NTRIAL =    1  T =    298.2       P =  0.1013E+06  V =   0.0000E+00

 *  WARNING WHILE EXECUTING UNIT OPERATIONS BLOCK: "S4" (MODEL: "SEP")
                                                               (USP03.1)
    OUTLET STREAM "S4SOL" HAS ZERO FLOW. FLASH CALCULATIONS BYPASSED.

    UOS BLOCK MT        MODEL: MIXER
    H-LOOP : NTRIAL =     7 T/V/P =   298.9
    KODE = 1  NTRIAL =    2  T =    298.9       P =  0.1013E+06  V =   0.0000E+00

IMULATION CALCULATIONS COMPLETED

DF UPDATED

EPORT WRITER ENTERED

EPORT GENERATED


** SUMMARY OF ERRORS   ***

                  PHYSICAL
                  PROPERTY  SYSTEM  SIMULATION
ERMINAL ERRORS        0        0         0
 SEVERE ERRORS        0        0         0
        ERRORS        0        0         0
      WARNINGS        0        0         1


**************************************************
  ASPEN PLUS SIMULATION PROGRAM ENDS EXECUTION  *
**************************************************
```

```
ASPEN PLUS   VER: PC-DOS    REL: 8.5-3    INST: PNL-LJS   08/18/92  PAGE 2
                                FLOWSHEET 1
                                STREAM SECTION

H1LIQ H1OUT H2LIQ H2OUT H3LIQ
-----------------------------

STREAM ID                 H1LIQ       H1OUT       H2LIQ       H2OUT       H3LIQ
FROM :                    ----        H1          ----        H2          ----
TO   :                    H1          S1          H2          S2          H3

SUBSTREAM: MIXED
PHASE:                    LIQUID      MIXED       LIQUID      MIXED       LIQUID
COMPONENTS: KMOL/HR
  H2O                      0.2399      0.2399      2.8970      2.8970      0.9399
  OH-                   4.3269-04   4.3269-04   5.2242-03   5.2242-03   1.6949-03
  NA+                   4.3269-04      0.1445   5.2242-03      0.5581   1.6949-03
  NO3-                     0.0      9.1843-02      0.0         0.5478      0.0
  NO2-                     0.0      5.2177-02      0.0         0.0         0.0
  F-                       0.0      1.1305-04      0.0      5.0709-03      0.0
  NANO3                    0.0         0.5484      0.0      5.7145-04      0.0
  NANO2                    0.0         0.0         0.0         0.0         0.0
  NAF                      0.0      2.0845-02      0.0      1.5774-02      0.0
  NAOH                     0.0         0.0         0.0         0.0         0.0
COMPONENTS: KG/HR
  H2O                      4.3226      4.3226     52.1910     52.1910     16.9322
  OH-                   7.3589-03   7.3589-03   8.8849-02   8.8849-02   2.8825-02
  NA+                   9.9474-03      3.3235      0.1201     12.8318   3.8965-02
  NO3-                     0.0         5.6947      0.0        33.9699      0.0
  NO2-                     0.0         2.4004      0.0         0.0         0.0
  F-                       0.0      2.1477-03      0.0      9.6339-02      0.0
  NANO3                    0.0        46.6138      0.0      4.8571-02      0.0
  NANO2                    0.0         0.0         0.0         0.0         0.0
  NAF                      0.0         0.8752      0.0         0.6623      0.0
  NAOH                     0.0         0.0         0.0         0.0         0.0
TOTAL FLOW:
  KMOL/HR                  0.2408      1.0983      2.9075      4.0297      0.9432
  KG/HR                    4.3400     63.2400     52.4000     99.8890     17.0000
  L/MIN                 7.2218-02      0.5038      0.8719      1.1839      0.2828
STATE VARIABLES:
  TEMP    C               25.0000     25.0000     25.0000     25.0000     25.0000
  PRES    ATM              1.0000      1.0000      1.0000      1.0000      1.0000
  VFRAC                    0.0         0.0         0.0         0.0         0.0
  LFRAC                    1.0000      0.4817      1.0000      0.9959      1.0000
  SFRAC                    0.0         0.5183      0.0      4.0563-03      0.0
ENTHALPY:
  CAL/MOL              -6.8268+04  -8.5749+04  -6.8268+04  -6.4355+04  -6.8268+04
  CAL/GM               -3787.9985  -1489.2895  -3787.9985  -2596.2183  -3787.9985
  CAL/SEC              -4566.6427  -2.6162+04  -5.5136+04  -7.2037+04  -1.7888+04
ENTROPY:
  CAL/MOL-K              -38.8794    -55.5415    -38.8794    -36.4455    -38.8794
  CAL/GM-K                -2.1573     -0.9646     -2.1573     -1.4702     -2.1573
DENSITY:
  MOL/CC                5.5576-02   3.6332-02   5.5576-02   5.6727-02   5.5576-02
  GM/CC                    1.0015      2.0918      1.0015      1.4061      1.0015
AVG MW                    18.0221     57.5768     18.0221     24.7879     18.0221
```

```
ASPEN PLUS   VER: PC-DOS     REL: 8.5-3     INST: PNL-LJS    08/18/92  PAGE 3
                                FLOWSHEET 1
                                STREAM SECTION

H3OUT H4LIQ H4OUT LIQTOTAL S1LIQ
--------------------------------

STREAM ID                     H3OUT       H4LIQ       H4OUT       LIQTOTAL    S1LIQ
FROM :                        H3          ----        H4          MT          S1
TO   :                        S3          H4          S4          ----        MT

SUBSTREAM: MIXED
PHASE:                        MIXED       LIQUID      LIQUID      MIXED       MIXED
COMPONENTS: KMOL/HR
  H2O                          0.9399   5.5288-02   5.5288-02     4.1322      0.2399
  OH-                        1.6949-03  9.9698-05   9.9698-05   7.4514-03   4.3269-04
  NA+                        1.7947-02  9.9698-05   1.9327-04     0.7086      0.1445
  NO3-                       5.7145-04    0.0         0.0         0.6402    9.1843-02
  NO2-                         0.0        0.0         0.0       5.2177-02   5.2177-02
  F-                         1.5681-02    0.0       9.3569-05   8.7255-03   1.1304-04
  NANO3                        0.0        0.0         0.0         0.0         0.0
  NANO2                        0.0        0.0         0.0         0.0         0.0
  NAF                        9.3569-05    0.0         0.0       1.2233-02   1.0058-09
  NAOH                         0.0        0.0         0.0         0.0         0.0
COMPONENTS: KG/HR
  H2O                         16.9322     0.9960      0.9960     74.4419      4.3226
  OH-                        2.8825-02  1.6956-03   1.6956-03     0.1267    7.3589-03
  NA+                          0.4126   2.2920-03   4.4432-03    16.2912      3.3235
  NO3-                       3.5433-02    0.0         0.0        39.7000      5.6947
  NO2-                         0.0        0.0         0.0         2.4004      2.4004
  F-                           0.2979     0.0       1.7777-03     0.1657    2.1477-03
  NANO3                        0.0        0.0         0.0         0.0         0.0
  NANO2                        0.0        0.0         0.0         0.0         0.0
  NAF                        3.9288-03    0.0         0.0         0.5136    4.2230-08
  NAOH                         0.0        0.0         0.0         0.0         0.0
TOTAL FLOW:
  KMOL/HR                      0.9758   5.5487-02   5.5674-02     5.5617      0.5290
  KG/HR                       17.7109     1.0000      1.0039    133.6398     15.7509
  L/MIN                        0.2829   1.6640-02   1.6637-02     1.6312      0.1549
STATE VARIABLES:
  TEMP    C                   25.0000    25.0000     25.0000     25.7020     25.0000
  PRES    ATM                  1.0000     1.0000      1.0000      1.0000      1.0000
  VFRAC                        0.0        0.0         0.0         0.0         0.0
  LFRAC                        0.9999     1.0000      1.0000      0.9978      1.0000
  SFRAC                      9.5881-05    0.0         0.0       2.1995-03   1.9010-09
ENTHALPY:
  CAL/MOL                  -6.8264+04 -6.8268+04 -6.8268+04 -6.4351+04 -5.7456+04
  CAL/GM                   -3761.3681 -3787.9985 -3785.9391 -2678.1113 -1929.9857
  CAL/SEC                  -1.8505+04 -1052.2218 -1055.7814 -9.9417+04 -8444.1830
ENTROPY:
  CAL/MOL-K                  -37.9484    -38.8794    -38.7729    -36.3200    -33.0806
  CAL/GM-K                    -2.0909     -2.1573     -2.1502     -1.5115     -1.1112
DENSITY:
  MOL/CC                     5.7487-02  5.5576-02   5.5774-02   5.6825-02   5.6902-02
  GM/CC                        1.0433     1.0015      1.0057      1.3654      1.6939
AVG MW                        18.1486    18.0221     18.0321     24.0285     29.7702
```

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ASPEN PLUS   VER: PC-DOS    REL: 8.5-3    INST: PNL-LJS   08/18/92  PAGE 4
                                  FLOWSHEET 1
                                  STREAM SECTION

S1SOL S2LIQ S2SOL S3LIQ S3SOL
-----------------------------

STREAM ID                S1SOL       S2LIQ       S2SOL       S3LIQ       S3SOL
FROM :                   S1          S2          S2          S3          S3
TO   :                   H2          MT          H3          MT          H4

SUBSTREAM: MIXED
PHASE:                   SOLID       MIXED       SOLID       LIQUID      SOLID
COMPONENTS: KMOL/HR
  H2O                     0.0         2.8970      0.0         0.9399      0.0
  OH-                     0.0      5.2242-03      0.0      1.6949-03      0.0
  NA+                     0.0         0.5581      0.0      1.7947-02      0.0
  NO3-                    0.0         0.5478      0.0      5.7145-04      0.0
  NO2-                    0.0         0.0         0.0         0.0         0.0
  F-                      0.0      5.0708-03      0.0      1.5681-02      0.0
  NANO3                   0.5484   1.6273-07   5.7145-04      0.0         0.0
  NANO2                   0.0         0.0         0.0         0.0         0.0
  NAF                  2.0845-02   3.8339-08   1.5774-02      0.0      9.3569-05
  NAOH                    0.0         0.0         0.0         0.0         0.0
COMPONENTS: KG/HR
  H2O                     0.0        52.1910      0.0        16.9322      0.0
  OH-                     0.0      8.8849-02      0.0      2.8825-02      0.0
  NA+                     0.0        12.8318      0.0         0.4126      0.0
  NO3-                    0.0        33.9699      0.0      3.5433-02      0.0
  NO2-                    0.0         0.0         0.0         0.0         0.0
  F-                      0.0      9.6338-02      0.0         0.2979      0.0
  NANO3                  46.6138   1.3831-05.  4.8571-02      0.0         0.0
  NANO2                   0.0         0.0         0.0         0.0         0.0
  NAF                     0.8752   1.6098-06      0.6623      0.0      3.9288-03
  NAOH                    0.0         0.0         0.0         0.0         0.0
TOTAL FLOW:
  KMOL/HR                 0.5692      4.0134   1.6346-02      0.9757   9.3569-05
  KG/HR                  47.4890     99.1779      0.7109     17.7069   3.9288-03
  L/MIN                   0.3488      1.1796   4.2975-03      0.2829   2.3367-05
STATE VARIABLES:
  TEMP   C               25.0000     25.0000     25.0000     25.0000     25.0000
  PRES   ATM              1.0000      1.0000      1.0000      1.0000      1.0000
  VFRAC                   0.0         0.0         0.0         0.0         0.0
  LFRAC                   0.0         1.0000      0.0         1.0000      0.0
  SFRAC                   1.0000   5.0099-08      1.0000      0.0         1.0000
ENTHALPY:
  CAL/MOL              -1.1204+05  -6.4060+04  -1.3678+05  -6.8257+04  -1.3771+05
  CAL/GM               -1343.1225  -2592.2898  -3144.8724  -3761.4743  -3279.6656
  CAL/SEC              -1.7718+04  -7.1416+04   -621.0321  -1.8501+04     -3.5791
ENTROPY:
  CAL/MOL-K              -76.4165    -36.4876    -26.1120    -37.9497    -24.2178
  CAL/GM-K                -0.9160     -1.4765     -0.6003     -2.0913     -0.5767
DENSITY:
  MOL/CC                2.7195-02   5.6703-02   6.3393-02   5.7486-02   6.6738-02
  GM/CC                    2.2685      1.4012      2.7570      1.0431      2.8021
AVG MW                    83.4202     24.7117     43.4915     18.1463     41.9880
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ASPEN PLUS   VER: PC-DOS     REL: 8.5-3    INST: PNL-LJS    08/18/92  PAGE 5
                                        FLOWSHEET 1
                                        STREAM SECTION

S4LIQ S4SOL SLUDGE
------------------

STREAM ID                   S4LIQ       S4SOL        SLUDGE
FROM :                      S4          S4           ----
TO   :                      MT          ----         H1

SUBSTREAM: MIXED
PHASE:                      LIQUID      MIXED        SOLID
COMPONENTS: KMOL/HR
  H2O                     5.5288-02      0.0          0.0
  OH-                     9.9698-05      0.0          0.0
  NA+                     1.9327-04      0.0          0.0
  NO3-                      0.0          0.0          0.0
  NO2-                      0.0          0.0          0.0
  F-                      9.3569-05      0.0          0.0
  NANO3                     0.0          0.0          0.6402
  NANO2                     0.0          0.0        5.2177-02
  NAF                       0.0          0.0        2.0958-02
  NAOH                      0.0          0.0          0.0
COMPONENTS: KG/HR
  H2O                       0.9960       0.0          0.0
  OH-                     1.6956-03      0.0          0.0
  NA+                     4.4432-03      0.0          0.0
  NO3-                      0.0          0.0          0.0
  NO2-                      0.0          0.0          0.0
  F-                      1.7777-03      0.0          0.0
  NANO3                     0.0          0.0         54.4200
  NANO2                     0.0          0.0          3.6000
  NAF                       0.0          0.0          0.8800
  NAOH                      0.0          0.0          0.0
TOTAL FLOW:
  KMOL/HR                 5.5674-02      0.0          0.7134
  KG/HR                     1.0039       0.0         58.9000
  L/MIN                   1.6637-02      0.0          0.4391
STATE VARIABLES:
  TEMP    C                25.0000     MISSING       25.0000
  PRES    ATM               1.0000     MISSING        1.0000
  VFRAC                     0.0        MISSING        0.0
  LFRAC                     1.0000     MISSING        0.0
  SFRAC                     0.0        MISSING        1.0000
ENTHALPY:
  CAL/MOL                -6.8268+04    MISSING   -1.1185+05
  CAL/GM                 -3785.9391    MISSING   -1354.7584
  CAL/SEC                -1055.7814    MISSING   -2.2165+04
ENTROPY:
  CAL/MOL-K                -38.7729    MISSING     -76.8088
  CAL/GM-K                  -2.1502    MISSING      -0.9303
DENSITY:
  MOL/CC                  5.5774-02    MISSING    2.7074-02
  GM/CC                     1.0057     MISSING       2.2352
AVG MW                     18.0321     MISSING      82.5613
```

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