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ASPEN SIMULATION OF SEED REGENERATION PROCESSES FOR APPLICATION IN COAL-FIRED, OPEN-CYCLE MAGNETOHYDRODYNAMIC POWER SYSTEMS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

James V. Walden
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ABSTRACT

The objective of this effort was to extend the capabilities of Advanced System for Process Engineering (ASPEN) to allow for computer modeling of electrolyte systems. The inherent problem in the ASPEN code was the system's inability to handle the simultaneous chemical and phase equilibrium calculations for electrolyte systems. This problem was broken down into four areas for solution. First, binary interaction parameters had to be developed for various electrolyte systems. This parameter explains the interaction between various electrolyte pairs and is calculated by regressing vapor pressure depression data or boiling point elevation data in the ASPEN Data Regression System (DRS). Literature searches were conducted to find the experimental data for various electrolytes. This information proved to be limited and some of the data were developed by experiments at the University of Tennessee Space Institute (UTSI). This work was begun by another student (Davis, 1985) at UTSI and continued under this project. Second, user models were written that would handle the simultaneous chemical and phase equilibrium calculations for both single and multi-component electrolyte systems. The models had to be written in ASPEN format (ASPEN Technical Reference Manual, Chapter 6) so they could be linked to the ASPEN library. Third, ASPEN user libraries were expanded to incorporate both the new databases and user models making the upgraded system capable of modeling electrolyte systems. Fourth, two

electrolyte schemes were chosen for modeling under this project. The two schemes selected for modeling were chosen for their potential application to the magnetohydrodynamic power generation process (MHD) and because the data needed could either be found in the literature or through experimentation.

The results from this effort showed that the Econoseed Process or preferably the Formate Process from which it is derived should be given additional consideration as a possible scheme for application in the MHD Seed Regeneration system whereas the Hydrated Lime Process should not be given any additional consideration due to the high process water and gross energy requirements. Additional consideration should include development of a process to produce and deliver adequate quantity of calcium formate to the process reactor, sizing of evaporators, and evaluation of various sized spray dryers to completely dry the product potassium formate before recycle back to the MHD combustor.

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LIST OF SYMBOLS

A	Constant (Equation VI.1 Solubility Data Regression)
A_i	Number of atoms in species i
A_{ki}	Number of atoms of element k in species i
aq	Aqueous
B	Constant (Equation VI.1 Solubility Data Regression)
b	Total atoms of an element
C	Constant (Equation VI.1 Solubility Data Regression)
D	Constant (Equation VI.1 Solubility Data Regression)
$f_i^{\cdot}$	Inlet component molar flow rate of component i
F	Total molar flow rate (kmol/sec)
G_i^{ref}	Molar Gibbs free energy of component i in reference state
G_i^{o}	Molar Gibbs free energy for pure component i
G_i^{∞}	Molar Gibbs free energy for component i at infinite dilution
h^l	Enthalpy of liquid
h^v	Enthalpy of vapor
h^s	Enthalpy of solid
Ksp	Solubility Product
L	Liquid phase molar flow rate (kmol/sec)
ln	Natural logarithm
m+	Molality of cation
m-	Molality of anion
m	Number of reactions
n	Number of components
NAT	Number of atomic species
Q	Heat duty
R	Universal gas constant (SI units)

S	Solid phase molar flow rate (kmol/sec)
T	Absolute temperature (K)
V	Vapor phase molar flow rate (kmol/sec)
w_i	Mole fraction of component i in solid phase
x_i	Mole fraction of component i in liquid phase
y_i	Mole fraction of component i in vapor phase
z	Ionic charge number

Greek Letters

μ_i	Chemical potential of component i
ε_j	Equilibrium conversion of component j
ν_{ij}	Stoichiometric coefficient of species i in reaction j
γ_+	Activity coefficient of cation
γ_-	Activity coefficient of anion
$\gamma_\pm$	Mean Ionic Activity Coefficient of electrolyte

Subscripts

i	Component index
j	Reaction or component index
k	Element index

Superscripts

L	Liquid phase
S	Solid phase
V	Vapor phase
ref	Reference state
o	Pure component
∞	Infinite dilution
+	Cation
-	Ion

* Inlet composition

Additional Symbols

↓ Precipitation

NOTE: Each computer program listed in this effort has a internal List of Symbols. Symbols used in ASPEN INPUT files are documented in the ASPEN User's Manual (Graham, 1982).

INTRODUCTION

Under the Department of Energy (DOE) contract, the University of Tennessee Space Institute (UTSI) is developing a prototype open-cycle coal-fired magnetohydrodynamic power system (MHD). In this system a partially ionized feedstock is passed through a magnetic field where a direct current is generated. The feedstock material is a pulverized seed and coal mixture with oxidants. Potassium salts are chosen as the seed material based on the favorable ionization potential of potassium and its commercial availability. After the process stream passes through the magnetic field, high-pressure steam is produced in the downstream components for additional power production. In this type of technology the energy conversion efficiency is higher than the energy conversion efficiency realized in a conventional coal-steam plant. The MHD process also has the built-in capability of removing or controlling the sulfur dioxide and nitrogen oxides emissions found in the flue gases to well below the EPA recommended guidelines. The potassium in the seed material and the sulfur in the coal combine to form potassium sulfate which condenses out as the gas is cooled in the bottoming cycle of the MHD process. Thus, the seed material acts dually by helping to produce additional electrical power in the topping cycle and by removing the sulfur in the bottoming cycle of the process.

Studies at UTSI (Jackson, 1985) have shown that the MHD process can be economically feasible only if more than 90% of the potassium seed is recovered for reuse. Even if the economics of recovery could be overcome, disposal of spent seed would have environmental implications due to the possible presence of potentially toxic trace elements and water soluble K-salts. Since the economics of the process is critical, the logical choice revolves around a process scheme that includes seed recovery. The first economic constraint that seed recovery poses is the quantitative recovery of potassium sulfate from the MHD process. Unfortunately, the recovered seed can not be fed back to the MHD combustor because of potential of increased corrosion of the MHD topping components. Additionally, the system would lose its ability to remove new sulfur from the coal which is one of the most attractive aspects of the MHD process. This would necessitate inclusion of a separate SO_2-scrubbing system to meet EPA emission guidelines. These problems can be overcome by regenerating the recovered seed into a sulfur-free potassium salt. UTSI has identified twenty-three regeneration schemes (Jackson, 1985) that have some potential for application in MHD seed regeneration. Most of these schemes are sodium-based sulfur removal processes used in the pulp and paper industry and in flue gas desulfurization processes. Modifications to these schemes have been made for potassium regeneration. An evaluation of these potential schemes must be made in order to determine which scheme is best suited for use in the MHD process.

One of the tools available to UTSI to determine which regeneration scheme is best suited for the MHD process is the Advanced System for Process Engineering (ASPEN). ASPEN is a publicly available, state-of-the-art process simulator developed at the Massachusetts Institute of Technology during the period 1976-1981 under the sponsorship of the Department of Energy. ASPEN is a good choice for use on the seed regeneration problem for two reasons. First, ASPEN is capable of modeling a wide range of chemical processes and is readily adaptable to extensions for processes that it cannot model. Second, ASPEN is available to UTSI at a low cost. The cost is only that of disk storage and computer time. Both of these reasons make the use of ASPEN appealing for the modeling work to be done.

Before ASPEN could be used to model the candidate regeneration schemes, extensions had to be made to the ASPEN databases and computer code. The database extensions were begun earlier by another student (Davis, 1985) and are continued in this effort. These extensions provide the thermodynamic data of various electrolytes that are needed when the candidate processes are simulated. Binary interaction parameters needed by the various ASPEN computational routines are developed by regressing vapor pressure depression data, boiling point elevation data, and activity coefficient data in the ASPEN Data Regression System (DRS). In some cases literature data were unavailable for various electrolytes and necessary laboratory experiments were performed to create the needed information. Computer code extensions for various

electrolyte schemes were written according to the ASPEN User Model format and were incorporated into the ASPEN User Libraries. These extensions solve simultaneous chemical and phase equilibrium calculations for electrolyte systems and call on other ASPEN library routines to calculate the physical properties of the system based on the binary interaction parameters developed in the ASPEN DRS system.

Once the database and code extensions were completed, two seed regeneration schemes were chosen for modeling. The first was a Hydrated Lime Process (AVCO, 1978). In this process a solution containing potassium sulfate reacts with a calcium hydroxide slurry to form potassium hydroxide and insoluble calcium sulfate (gypsum). After filtering, the potassium hydroxide solution undergoes a carbonation step to form potassium carbonate. After necessary concentration and drying the potassium carbonate is recycled back to the MHD process as the sulfur-free form of seed material. The calcium sulfate is disposed of in a landfill.

The second seed regeneration scheme chosen for modeling was the Econoseed Process. This process was developed and patented by the TRW Corporation (Myers, 1982). The scheme involves a reactor or a mixing tank in which calcium formate and potassium sulfate solutions react to form gypsum and potassium formate. The gypsum is then filtered from the system and the potassium formate is dried to a crystalline form for recycle to the MHD combustor.

These two process were chosen for modeling because the thermodynamic data of these two processes were either known or could be developed easily through relatively simple experimental techniques.

CRANES CREST

CHAPTER I

THE ASPEN SYSTEM

This chapter describes the ASPEN system with particular emphasis on modeling electrolyte systems. The order of this description will be: 1) ASPEN overview; 2) ASPEN Physical Properties System (PPS); 3) ASPEN Data Regression System (DRS); and, 4) ASPEN User Models. Beginning ASPEN users are referred to the ASPEN User's Manual (Graham, 1982) for additional information.

ASPEN Overview

The ASPEN process simulator is a conventional block modular chemical process system with libraries of unit operation model subroutines (UOS) and physical property system subroutines (PPS). The user controls the communication between the UOS and the PPS by specifying property routes in an ASPEN INPUT file. The INPUT file provides the ASPEN process simulator with keywords to follow in order to solve the problem at hand. Figure I.1 shows the format of an ASPEN INPUT file.

The INPUT language consists, hierarchically, of paragraphs, sentences, and individual data entries. Corresponding to this hierarchy are three levels of keywords: primary, secondary, and tertiary (Graham, 1982). It is through primary keywords that specific UOS and PPS subroutines communicate. The task of a UOS subroutine is to compute outlet stream values given equipment parameters,

```
TITLE    'INPUT FILE'
DESCRIPTION  "THIS IS THE BASIC FORMAT OF AN ASPEN INPUT FILE"
;
; COMMENTS ARE PRECEDED BY A SEMI-COLON IN ASPEN
;
IN-UNITS    TEMP=C                      ;IN-UNITS-primary keyword
                                        ;TEMP-tertiary keyword
COMPONENTS id alias/id alias/...        ;primary keyword
PROPERTIES pps option set               ;establishes communication
                                            to UOS
FLOWSHEET                               ;used to input connectivity
STREAM  strm id  PARAM                  ;STREAM-primary keyword
                                        ;PARAM-secondary keyword
BLOCK UOS NAME blck id                  ;BLOCK-primary keyword
                                        ;UOS NAME-defines unit
                                            operation
SIMULATE                                ;Defines end of ASPEN
                                            input file
```

FIGURE I.1: EXAMPLE OF ASPEN INPUT FILE

inlet stream values, and a PPS option set. The PPS can be chosen either on a system-wide basis (global) or for a specific unit operation. The PPS option set will calculate point values for various physical properties, i.e. enthalpies, entropies, fugacities, vapor fraction, etc., based on the UOS equipment parameters and inlet stream conditions. Consequently, the accuracy of the ASPEN output is dependent on the both the user's knowledge of the chemistry of the process to be simulated and ability to convey that knowledge to ASPEN through the INPUT file.

Extensions were needed in both the UOS and PPS subroutines before the ASPEN system could be used to solve the MHD seed regeneration problem. The PPS lacked the thermodynamic data needed to determine the physical properties of the various electrolyte systems and the UOS lacked the logic necessary to simulate precipitation in electrolyte systems. The remainder of this chapter gives a brief overview of the PPS, DRS, and UOS systems and the needed extensions required by ASPEN.

ASPEN Physical Properties System (PPS)

The ASPEN Physical Property System (PPS) is a collection of subroutines that can be called individually or in a specific option set to calculate the point values of various physical properties of a system for a given unit operation model subroutine. Before the PPS can calculate the various physical properties needed, each component's thermodynamic data must be stored in a system database. The ASPEN system has built-in physical property databanks for

most components; however, the user must review the specific ASPEN Unit Operation Models to be used in the simulation to determine which physical and thermodynamic properties are needed. Any missing data must be supplied to the system in user created databanks.

A review of the Aspen Unit Operation Models for this study found that much of the required thermodynamic and physical property data for electrolyte systems were missing. A comprehensive literature search to supply the required thermodynamic data was conducted and two user databanks were created. These two databanks, SOLDAT and AQADAT, provide the solid and aqueous thermodynamic data needed by the ASPEN Data Regression System to develop the physical property parameters needed in the ASPEN Unit Operation Models. The thermodynamic literature search was initiated and completed by another student (Davis, 1985). A copy of these two databanks is located in APPENDIX A. A review of Davis's work and the ASPEN User's Manual (Graham, 1982) will give the beginning ASPEN user the necessary background to determine which thermodynamic and physical property data are required for the simulation and how to create the required ASPEN databanks for missing information.

ASPEN Data Regression System (DRS)

Once the ASPEN Physical Properties System has been supplied with all of the required thermodynamic data the ASPEN DRS can then be used to process the thermodynamic data to develop parameters used in the ASPEN physical property subroutines. In this study, electrolyte thermodynamic data and literature or experimental values for vapor pressure depression, boiling point elevation, and activity coefficients of various electrolyte systems were regressed by the ASPEN DRS system to develop the GMELCC binary interaction parameters used in the Electrolyte Local Composition model. This work was begun by another student (Davis, 1985) and was continued in this effort. The GMELCC binary interaction parameters developed for various electrolyte systems by Davis's study is provided in Table A.1 in Appendix A. A review of Davis's work and the ASPEN User's Manual (Graham, 1982) will give the beginning ASPEN user the necessary background to use the ASPEN DRS system.

ASPEN User Models

A review of the built-in ASPEN User Models found that no model existed that could simulate both the simultaneous chemical and phase equilibria that occurs in electrolyte systems. An ASPEN subroutine named FLASH was available for simulating vapor-liquid equilibria for strong electrolytes. The ASPEN Electrolyte User Model written for this study performs the liquid-solid phase equilibrium calculations based on solubility constraints and then calls the ASPEN FLASH subroutine to perform the vapor-liquid equilibrium

calculations. This model was written in standard ASPEN User Model format and incorporated into the ASPEN system library.

CHAPTER II

THEORY

This chapter will discuss the theory of electrolyte systems with particular emphasis on the MHD Seed Regeneration problem. The order of this description will be: 1) Characterization of Electrolytes; 2) Liquid-Solid Phase Equilibrium in Dilute Aqueous Electrolytes; 3) Theory of Vapor-Liquid-Solid Equilibrium in Electrolyte Systems; and, 4) Assumptions for Electrolytes in MHD Seed Regeneration System.

Characterization of Electrolytes

The physical properties of electrolytic solutions fall into two groups: 1) properties determined by measurements of systems in equilibrium, and, 2) properties determined by measurements of systems in a perturbed state (Harned, 1958). Group one has properties derived from measurements of vapor pressure lowering, boiling point elevation, solubility, specific heat, heat content, the potential of galvanic cells, and surface tension. Group two has properties derived from measurements of diffusion, electrical conductance, and solution viscosity. This study will, however, deal with electrolytes in chemical and phase equilibrium.

There are two basic types of equilibrium electrolyte systems: 1) strong electrolytes, and 2) weak electrolytes. Strong electrolytes dissociate completely into ions when

dissolved in the liquid phase, and exist as solid precipitates if not dissolved. Weak electrolyte systems are more complex as dissociation in the liquid phase is not complete. The undissociated weak electrolytes exist as molecular species. Additionally, dissociation and/or association reactions may occur creating complex ion formations. Thus, in electrolyte systems, there can be precipitates, molecular species from weak electrolytes, and ionic species dissociated from strong or weak electrolytes or formed from side reactions. Dissociation and side reactions occur very rapidly in electrolyte systems and therefore chemical and phase equilibrium are usually assumed.

Liquid-Solid Phase Equilibrium in Dilute Aqueous Electrolyte Solutions

The solubility of chemical species in aqueous solutions is well documented and is used in this study to explain the liquid-solid phase equilibrium of electrolytes. A parameter called the solubility product (Ksp) determines at what concentration a particular electrolyte will precipitate out of solution. The solubility product is a function of composition and activity of the components in solution and is described by the following general equation:

$$Ksp = \gamma_+^{\nu+}\gamma_-^{\nu-}\, m_+^{\nu+} m_-^{\nu-} \qquad \text{(II.1)}$$

Electrolyte systems are usually referred to based on the anionic and cationic stoichiometric coefficients($\nu+:\nu-$) for

the species in the electrolyte system. For example, NaCl is referred to as a 1:1 electrolyte and K2SO4 is referred to as a 2:1 electrolyte. In this study equation II.1 takes on the following $\nu_+:\nu_-$ forms:

1:1 Electrolytes

$$Ksp = \gamma_+ \gamma_- m_+^2 \qquad \text{(II.2)}$$

1:2 Electrolytes

$$Ksp = 4\, \gamma_+ \gamma_-^2 m_+^3 \qquad \text{(II.3)}$$

2:1 Electrolytes

$$Ksp = \gamma_+^2 \gamma_- m_+^3 / 2 \qquad \text{(II.4)}$$

Any interaction between electrolytes and resulting effects on the Ksp parameter were neglected in this study. This is a good approximation because the concentrations of the electrolytes in solution used in this study are very low and thus the interactions between molecules can be considered minimal.

Theory of Vapor-Liquid-Solid Equilibrium In Electrolyte Systems

For any liquid electrolyte phase involving the reaction system $\sum_i^n \sum_j^m \mu_{ij} A_i = 0$ the following constraints must be satisfied (Chen, 1981).

Elemental Balance:

$$\sum_{i}^{n} A_{ki} x_i = b_k \qquad k = 1, \ldots\ldots, NAT \qquad \text{(II.5)}$$

Charge Balance:

$$\sum_{i}^{n} z_i x_i = 0 \qquad \text{(II.6)}$$

Chemical Equilibrium:

$$\sum_{i}^{n} v_{ij} \mu_i = 0 \qquad j = 1, \ldots\ldots, m \qquad \text{(II.7)}$$

If a vapor phase is present, phase equilibrium fugacity constraints apply. If a solid phase is present, solubility constraints also apply. The equations for the vapor-liquid-solid equilibrium of an electrolyte system are as follows.

Chemical Equilibrium:

$$v_{ij} \ln[\gamma_i x_i] = -v_{ij} G_i^{ref}/RT \qquad \text{(II.8)}$$

where the γ_i's are unity at $x = 1$ for solvents and at infinite dilution for solutes. Additionally, the reference state free energy of a solvent is the pure component value G_i^{o}, and for a solute it is the infinite dilution value G_i^{∞}.

Reaction Component Mass Balance:

$$f_i = f_i^{\cdot} + \sum_{j}^{m} \sum_{i}^{n} v_{ij} \varepsilon_j \qquad \text{(II.9)}$$

Constitutive (I):

$$F = \sum_{i}^{n} f_i \qquad \text{(II.10)}$$

Vapor-Liquid Phase equilibrium:

$$\Phi_i^{v} y_i = \Phi_i^{l} x_i \qquad \text{(II.11)}$$

Liquid-Solid Solubility Constraints:

$$K_{sp} = \gamma_{+}^{v+} \gamma_{-}^{v-} m_{+}^{v+} m_{-}^{v-} \qquad \text{(II.12)}$$

Phase Component Mass Balance:

$$x_i L + y_i V + w_i S = f_i \qquad \text{(II.13)}$$

Phase Total Mass Balance:

$$L + V + S = F \qquad \text{(II.14)}$$

Enthalpy Balance:

$$h^{l}L + h^{v}V + h^{s}S = (h^{\cdot}F^{\cdot} + Q)F/F^{\cdot} \qquad \text{(II.15)}$$

Constitutive (II):

$$\Sigma w_i = \Sigma x_i = \Sigma y_i = 1 \qquad \text{(II.16)}$$

Heat of reaction does not appear in equation II.15 because all enthalpy values are element-based. One result of this stoichiometric formulation is that the element and charge balances are automatically satisfied.

The vapor-liquid theoretical development was first suggested for use in the ASPEN system (Chen, 1981) as the basis for the ASPEN User Model FLASH. This algorithm allows for the simulation of the vapor-liquid chemical and phase equilibrium calculations of electrolyte systems. To develop the liquid-solid phase equilibrium extensions that are not in ASPEN but are needed before ASPEN can be used to simulate the MHD Seed Regeneration problem one need only consider the solubility constraints for electrolytes.

Assumptions for Electrolytes in MHD Seed Regeneration System

Due to the complexity of electrolyte systems, several assumptions were made that would minimize the effort required to characterize the various seed regeneration systems under consideration for application in the MHD process.

The first assumption was that the systems under consideration were strong electrolyte systems. Strong electrolytes dissociate completely in solution. This is a good assumption as the systems under consideration will be dilute solutions of electrolytes in water. This assumption was tested using the ASPEN FLASH routine and solubility data of the electrolyte systems to be modeled in this study. The activity coefficients of the various systems were within 2 percent of experimental literature values of activity coefficients reported for these systems.

The second assumption was that the solvent water did not dissociate into hydrogen and hydroxide ions in the solution. This assumption lessened the complexity of the task at hand as it eliminated the many side reactions that are possible in electrolyte systems.

The third assumption was that the electrolyte systems being studied were in chemical and phase equilibrium. This eliminated the need to study diffusion between phases and set the methods by which physical properties for electrolyte systems are to be calculated. This assumption allowed use of the ASPEN DRS system to calculate the binary interaction parameters (GMELCC) needed in the simulation.

The fourth assumption was that the vapor phases of the electrolyte systems being studied here were essentially pure water. For this to be true then the volatility of the electrolytes would have to approach zero in the systems studied. This assumption was tested by experiment on a KHCOO-water system. The results of this experiment showed

that 99.9 percent of the vapor phase was pure water. This allowed use of ASME steam tables to calculate vapor phase properties. The details of this experiment and the results generated are listed in Appendix G.

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CHAPTER III

ASPEN INPUT FILES

The purpose of this chapter is to discuss in detail the formulation of an ASPEN INPUT file. It is very important that the user of the programs developed in this study understand how to translate the solution chemistry of various electrolyte systems into commands that can be understood by the ASPEN system. The interface between the programmer and the ASPEN system occurs in the ASPEN INPUT file. Equally important to the programmer is the knowledge of how and where ASPEN stores the data fed to the system by the INPUT file. The User Model subroutines written to simulate the solution chemistry of electrolyte systems had to access the internally stored component flow rates and physical property data in order to generate an accurate simulation.

Figure III.1 is a sample ASPEN INPUT file. In this example, two electrolyte solutions are fed into a well mixed reactor. The chemical reaction that occurs is:

$$K_2SO_4(aq) + Ca(COOH)_2(aq) \rightarrow 2KCOOH(aq) + CaSO_4(\downarrow) \qquad \text{(III.1)}$$

Dissociation of K_2SO_4 and $Ca(COOH)_2$ into 2K+, SO_4--,Ca++, and 2(COOH)- ions is assumed to be complete in this example.

```
NEW
TITLE  'K2SO4-CA(COOH)2-WATER USER MODEL'
DESCRIPTION "TEST OF A USER MODEL TO HANDLE EVAPORATION
 WITH PRECIPITATION"
;
;      GLOBAL DATA
;
IN-UNITS SI
OUT-UNITS SI
HISTORY MSG-LEVEL SYSTEM=8
;
;      PHYSICAL PROPERTIES
;
COMPONENTS H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
   HCOO- HCOO-/K2SO4 K2SO4/CAH2C2O4 CAH2C2O4/
   CASO4 CASO4
FILES USRPP1A AQADAT USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=ALL/SOLDAT COMPS=ALL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12 / HVMX HVMX12
PROPERTIES SYSOP1 GLOBAL
PROP-DATA
   COMP-LIST                SO4--; H2O-K2SO4 PAIR
   BCVAL GMELCC   1   1  K+      12.27331
   COMP-LIST                 K+   ; K2SO4-H2O PAIR
   BCVAL GMELCC   1   1  SO4--   -6.09492
PROP-DATA
   COMP-LIST                HCOO-; H2O-CAH2C2O4 PAIR
   BCVAL GMELCC   1   1  CA++    14.85465
   COMP-LIST                 CA++ ; CAH2C2O4-H2O PAIR
   BCVAL GMELCC   1   1  HCOO-   -6.394798
FLOWSHEET
   BLOCK FL1 IN=S1 S2       OUT=S3 S4 S5
STREAM S1 TEMP=353.15 PRES=101325.
   MOLE-FLOW H2O 3.7/K+ 0.16072230/SO4-- 0.08036115
STREAM S2 TEMP=353.15 PRES=101325.
   MOLE-FLOW H2O 3.23430557/CA++ 0.08036115/ &
   HCOO- 0.16072230/CAH2C2O4 0.0
BLOCK FL1 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP (K)     PRES (PA)
   REAL     353.15        101325.
   INT 1
;
;  FORTRAN CODE FOLLOWS
;
SIMULATE
```

FIGURE III.1: SAMPLE ASPEN INPUT FILE

The IN-UNITS and OUT-UNITS primary keywords are used to define the units of the input and output information. In this example SI units are used. The COMPONENTS primary keyword is used to define the elements used in the simulation. In this study the true composition approach is used. This means that the flow rates for the components used in the simulation are input in anionic or cationic form. This format will allow for easier manipulation of the data in the Fortran User Models that simulate the solution chemistry of electrolytes. The COMPONENTS keyword is also the method by which ASPEN internally sets up storage arrays for the input information. Table III.1 show two inlet storage arrays called SIN1(NCC+9) and SIN2(NCC+9). The maximum number of inlet arrays is four and is determined by the number of STREAM primary keywords in the ASPEN INPUT file. NCC is the number of conventional components listed in the COMPONENTS keyword. In Figure III.1 NCC is defined as eight. Thus the total length of the input arrays is seventeen. SIN1(1),...,SIN1(8) and SIN2(1),...,SIN2(8) contain the molar flowrates of the inlet components in the order defined by the COMPONENTS keyword with the values defined by the respective STREAM keywords. In this example SIN1(1) is equal to 3.7 kmoles of H_2O per second. SIN-n-(9) is the total molar flow determined by summing up the values in SIN-n-(NCC). SIN-n-(10) and SIN-n-(11) hold the temperature and pressure of the inlet streams as defined by the STREAM keyword.

TABLE III.1: ORDER OF INTERNAL DATA STORAGE WITHIN ASPEN BASED ON SAMPLE INPUT IN FIGURE III.1

INLET STREAM 1		INLET STREAM 2		UNITS
SIN1(1)	= 3.70000	SIN2(1)	= 3.23430	kmol/sec
SIN1(2)	= 0.16072	SIN2(2)	= 0.00000	kmol/sec
SIN1(3)	= 0.08036	SIN2(3)	= 0.00000	kmol/sec
SIN1(4)	= 0.00000	SIN2(4)	= 0.08036	kmol/sec
SIN1(5)	= 0.00000	SIN2(5)	= 0.16072	kmol/sec
SIN1(6)	= 0.00000	SIN2(6)	= 0.00000	kmol/sec
SIN1(7)	= 0.00000	SIN2(7)	= 0.00000	kmol/sec
SIN1(8)	= 0.00000	SIN2(8)	= 0.00000	kmol/sec
SIN1(9)	= 3.94108	SIN2(9)	= 3.47538	kmol/sec
SIN1(10)	= 3.53150E2	SIN2(10)	= 3.53150E2	Kelvin
SIN1(11)	= 1.01325E5	SIN2(11)	= 1.01325E5	Pascals
*SIN1(12)	= 0.00000	*SIN2(12)	= 0.00000	J/kg
*SIN1(13)	= 0.00000	*SIN2(13)	= 0.00000	Vap Frac
*SIN1(14)	= 0.00000	*SIN2(14)	= 0.00000	Liq Frac
*SIN1(15)	= 0.00000	*SIN2(15)	= 0.00000	J/kg/K
*SIN1(16)	= 0.00000	*SIN2(16)	= 0.00000	kg/m3
*SIN1(17)	= 0.00000	*SIN2(17)	= 0.00000	kg/kmol

*NOTE: Values to be calculated by ASPEN PPS System

The loaded stream vectors are then passed to the ASPEN Physical Properties System (PPS) where physical properties for the inlet streams are calculated based on the FILES, PROP-SOURCES, PROP-OPTIONS, PROPERTIES, and PROP-DATA keywords found in the ASPEN INPUT file. In this example the location of the thermodynamic properties datafile for the simulation is given by the FILES keyword in the INPUT file. In this example, AQADAT and SOLDAT are the two files that were created to provide ASPEN thermodynamic data of electrolytes. It should be noted that ASPEN has thermodynamic data for most applications and the use of the FILES keyword is process dependent. The PROP-OPTIONS keyword is used to define the location of the ASPEN PPS subroutines that should be used to calculate the systems physical properties. In this example the ELECTRO subroutine is used to calculate the liquid properties of electrolytes based on the GMELCC parameters developed for this study. The PHIVMX and HVMX subroutines are used to calculate the vapor fugacity coefficient and the vapor enthalpy, respectively, based on ASME Steam Table correlations. These two subroutines were chosen to calculate vapor phase physical properties as greater than 99 percent of the vapor phase will be gaseous water. The PROP-DATA keyword is used to pass the GMELCC parameters to the ASPEN PPS for use in the ELECTRO subroutine. These parameters were developed in the ASPEN DRS and define the binary interaction that occurs between water and various electrolytes. The ASPEN Physical Property System then calculates the point values of the physical properties for the inlet stream and stores this

information in SIN-n-(12),...,SIN-n-(17). The data stored are enthalpy, vapor phase mole fraction, liquid phase mole fraction, entropy, density, and molecular weight, respectively.

The ASPEN Physical Property System sends the loaded stream vector back to the INPUT file and the FLOWSHEET keyword is then addressed. In this example the loaded stream vectors SIN1 and SIN2 are inputs to an ASPEN Unit Operations Model block named FL1. FL1 calls the USRSOL subroutine where the vapor-liquid-solid phase and chemical equilibrium calculations are performed. The output from this subroutine is returned to the ASPEN INPUT file in loaded stream vectors Sout1, Sout2, and Sout3. If convergence criteria are met the results from the simulation are sent to the ASPEN REPORT WRITER SYSTEM. Figure III.2 shows a schematic representation of an ASPEN simulation.

It should be noted that the example INPUT file provides the user with the missing data links necessary to simulate electrolytes. The missing thermodynamic data are provided in the AQADAT and SOLDAT files, the missing binary interaction parameters needed in the ELECTRO PPS subroutine are provided by the PROP-DATA keyword and the link to the subroutine that will calculate the vapor-liquid-solid phase and chemical equilibrium of electrolytes is accessed through the FL1 Block. A detailed description of the program to calculate the vapor-liquid-solid phase and chemical equilibrium will be given in Chapter IV.

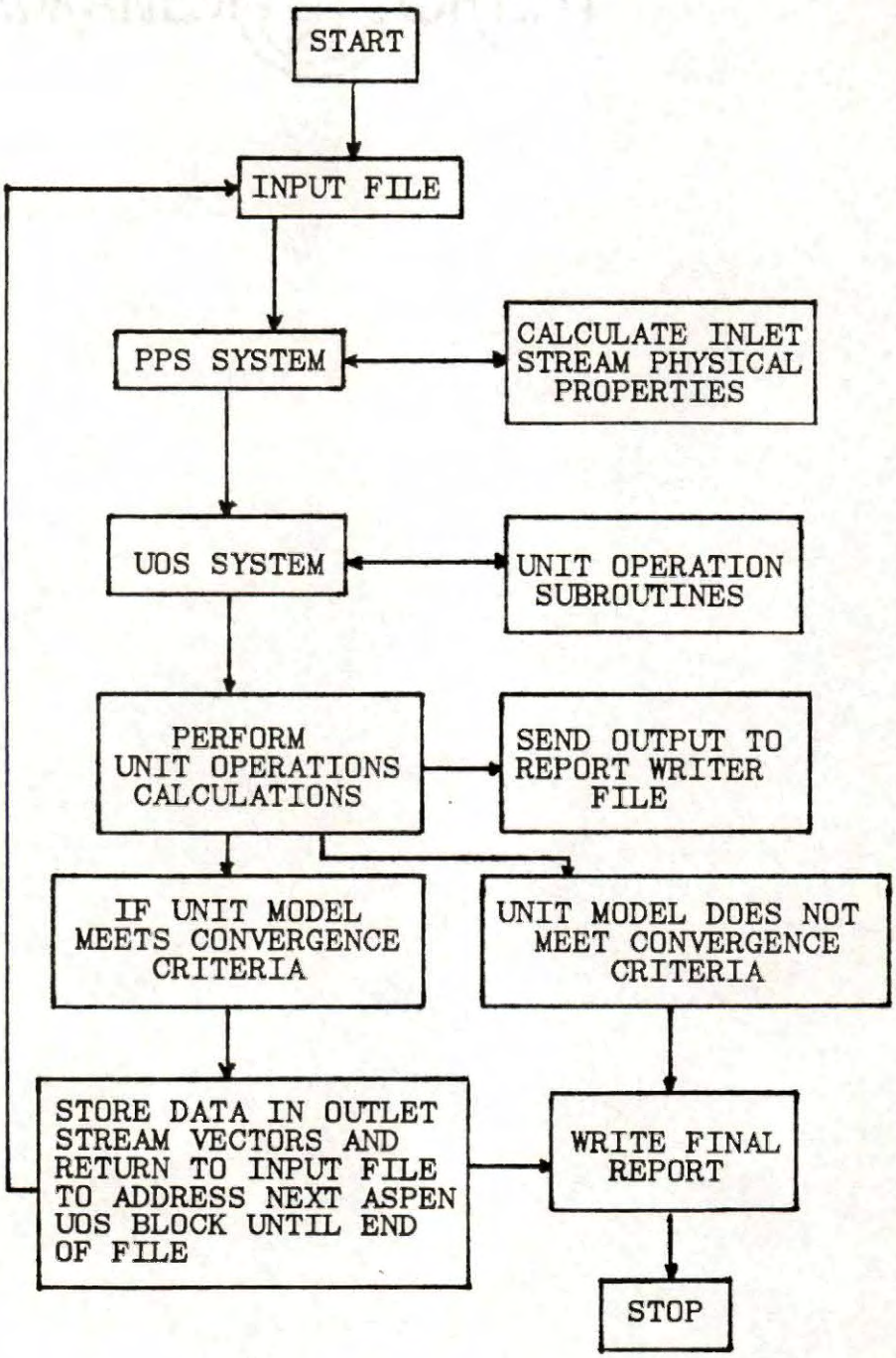


FIGURE III.2: Block Diagram of ASPEN Simulation

Additional information on the structure and development of ASPEN INPUT files can be found in the ASPEN User Manual (Graham, 1982).

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CHAPTER IV

ASPEN USER MODEL TO CALCULATE THE VAPOR-LIQUID-SOLID EQUILIBRIUM IN ELECTROLYTES

The purpose of this chapter is to describe in detail a user model that was written to test the capabilities of ASPEN to model processes that contain electrolytes. The reliability of this model for use in simulating candidate MHD Seed Regeneration Processes will be based on modeling systems for which literature activity coefficient data exist. The assumptions outlined in Chapter II should be reviewed and a determination should be made as to whether complete dissociation is a valid assumption for any future simulations. It should be noted that extensions to these User Models can be made that correct for incomplete dissociation assuming such information can be obtained. In this study it was determined that complete dissociation was a viable approach since partial dissociation data did not exist for most of the electrolyte systems under consideration for use in simulating the candidate MHD Seed Regeneration processes.

Figure IV.1 shows a sample INPUT file that was developed to test the capabilities of ASPEN to model electrolyte systems. In this example the following reaction occurs:

$$NaCl(aq) \rightarrow Na^{+}(aq) + Cl^{-}(aq) \qquad (IV.1)$$

After the ASPEN Physical Property System calculates the

```
NEW
TITLE 'NACL-WATER USER MODEL'
DESCRIPTION "TEST CASE OF KSP USER MODEL TO ACCURATELY
 PREDICT MEAN IONIC ACTIVITY COEFFICIENTS OF ELECTROLYTES"
;
;      GLOBAL DATA
;
IN-UNITS ENG
OUT-UNITS ENG
HISTORY MSG-LEVEL PROPERTIES=8
;
;      PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/NA+ NA+/CL- CL-/NACL NACL
FORMULA H2O H2O/NA+ NA+/CL- CL-/NACL NACL
FILES USRPP1A AQADAT/USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=NA+ CL-/SOLDAT COMPS=NACL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12/HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST              H2O        NACL
   CVAL CHARGE 1    1     0           0
   CVAL CHARGE 1    1     0           0
   CVAL SO25C  1    1     *           *
   CVAL DHAQFM 1    1     *           *
PROP-DATA
   COMP-LIST                          CL-;H2O-NACL PAIR
   BCVAL GMELCC 1   1   NA+    9.7695
   COMP-LIST                          NA+;NACL-H2O PAIR
   BCVAL GMELCC 1   1   CL-   -4.6436
FLOWSHEET
   BLOCK FL1  IN=BRIN OUT=BRIN2
STREAM BRIN TEMP=76. PRES=14.7
   MOLE-FLOW H2O-122.3786/NA+ 1./CL- 1./NACL 0.
BLOCK FL1 USER
   DESCRIPTION "SIMULATE NACL SOLUTION FLASH"
   PARAM NINT=200 NREAL=200 NIW=200 NW=800
;         TEMP(C) MOLALITY  PRES(PA) SLN TYPE
   REAL    25.0      .001     101325     1      &
           25.0      .002     101325     1      &
           25.0      .005     101325     1
   INT 3
SIMULATE
```

FIGURE IV.1: INPUT FILE TO PREDICT ACTIVITY COEFFICIENTS AND Ksp PARAMETERS FOR ELECTROLYTES

inlet physical properties as described in Chaper III, the loaded stream vector is passed to the User Model. The PARAMETER secondary keyword located in Block FL1 is used to pass information used to create work and storage arrays needed to perform the calculations specified in the USRVAP Subroutine. The REAL secondary keyword is used to pass saturation limits based on temperature and pressure dependent solubility data to the USRVAP Subroutine. The INTEGER secondary keyword is used to set the number of loops the subroutine will be called during the simulation.

The USRVAP subroutine is called by Block FL1 to calculate the vapor-liquid-solid phase and chemical equilibrium of electrolytes and is given in Appendix B. In this example the parameters passed to the subroutine from the INPUT file depicted in Figure IV.1 are electrolyte saturation limits and no solid phase is present. This reduces the test case to one of vapor-liquid equilibrium of electrolytes for simplicity. It should be noted that eliminating the solid phase for test purposes introduces no error in this simulation as the purpose of the test case is to determine if the ELECTRO subroutine can accurately predict the activity coefficients of electrolyte solutions. This physical property is the basis for the Ksp parameter described in the theory of electrolytes in Chapter II and will be used to determine if a solid phase is present during simulation of MHD Seed Regeneration schemes. The USRVAP subroutine was written based on the suggested format found in the ASPEN User Manual (Graham, 1982). The USRVAP subroutine contains comment statements designed to allow

other users to follow the logic written in the program. The output from this subroutine will allow for direct comparison with literature and experimental activity coefficient data to determine the accuracy of the model. Additionally, this subroutine calculates the Ksp parameter needed for actual simulation.

CHAPTER V

TESTING THE ASPEN USER MODEL

The purpose of this chapter is to outline the procedure used in testing the validity of the ASPEN User Model described in Chapter IV. Three electrolyte-water systems for which sufficient thermodynamic data are available were used. In each test case temperature dependent concentration data were passed from the ASPEN INPUT file to the ASPEN User Model where the mean ionic activity coefficent for the electrolyte system was calculated. These results were then compared to mean ionic activity coefficient data found in the literature for accuracy. The order of this discussion will be (1) KCl-Water Test Case; (2) KNO3-Water Test Case; (3) NaCl-Water Test Case; and (4) Discussion of Results.

KCl-Water Test Case

This electrolyte system was chosen to test the validity of the ASPEN ELECTROLYTE User Model as sufficient concentration versus activity coefficient data from literature (Hamer, 1972) were available. The literature concentration data were passed from the ASPEN INPUT file to the ASPEN User Model where the respective mean ionic activity coefficients for the KCl-Water electrolyte systems were calculated. The ASPEN calculated mean ionic coefficients were then compared to the literature mean ionic coefficients for accuracy.

Figure V.1 is the ASPEN INPUT file for the KCl-Water electrolyte system. The development of this INPUT file is covered in Chaper IV. This INPUT file accesses the AQADAT and SOLDAT files which contain the thermodynamic information needed for the simulation, provides the GMELCC parameters needed for electrolyte simulation, and passes the concentration data to the ASPEN User Model where the mean ionic activity coefficient is calculated.

Figure V.2 shows a plot of the mean ionic coefficients versus molality for the calculated and literature data sets. Table V.1 shows these same results with the relative percent difference calculated between the data sets. The results shown in Table V.1 and Figure V.2 show an excellent correlation between the calculated and literature mean ionic activity coefficients for the KCl-Water electrolyte system.

KNO3-Water Test Case

This electrolyte system was also chosen to test the validity of the ASPEN ELECTROLYTE User Model as sufficient concentration versus activity coefficient literature data (Hamer, 1972) were available. Figure V.3 is the ASPEN INPUT file for the KNO3-Water electrolyte system. Figure V.4 shows a plot of the mean ionic coefficients versus molality for the calculated and literature data sets. Table V.2 shows these same results with the relative percent difference calculated between the data sets. The

```
NEW
TITLE 'KCL-WATER USER MODEL'
DESCRIPTION "TEST CASE OF KSP USER MODEL TO ACCURATELY
 PREDICT MEAN IONIC ACTIVITY COEFFICIENTS OF ELECTROLYTES"
;
;      GLOBAL DATA
;
IN-UNITS ENG
OUT-UNITS ENG
HISTORY MSG-LEVEL PROPERTIES=8
;
;      PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/K+ K+/CL- CL-/KCL KCL
FORMULA H2O H2O/K+ K+/CL- CL-/KCL KCL
FILES USRPP1A AQADAT/USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=K+ CL-/SOLDAT COMPS=KCL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12/HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST                          CL-;H2O-KCL PAIR
   BCVAL GMELCC 1  1  K+    8.676126
   COMP-LIST                          K+;KCL-H2O PAIR
   BCVAL GMELCC 1  1  CL-   -4.300940
FLOWSHEET
   BLOCK FL1  IN=BRIN OUT=BRIN2
STREAM BRIN TEMP=76. PRES=14.7
   MOLE-FLOW H2O-122.3786/K+ 1./CL- 1./KCL 0.
BLOCK FL1 USER
   DESCRIPTION "SIMULATE KCL SOLUTION FLASH"
   PARAM NINT=200 NREAL=200 NIW=200 NW=800
;        TEMP(C) MOLALITY  PRES(PA) SLN TYPE
   REAL   25.0      .001     101325     1      &
          25.0      .002     101325     1      &
          25.0      .005     101325     1      &
          25.0      .020     101325     1      &
          25.0      .200     101325     1      &
          25.0      .500     101325     1      &
          25.0     1.000     101325     1      &
          25.0     2.000     101325     1
   INT 8
SIMULATE
```

FIGURE V.1: INPUT FILE TO TEST ACCURACY OF ASPEN USER MODEL

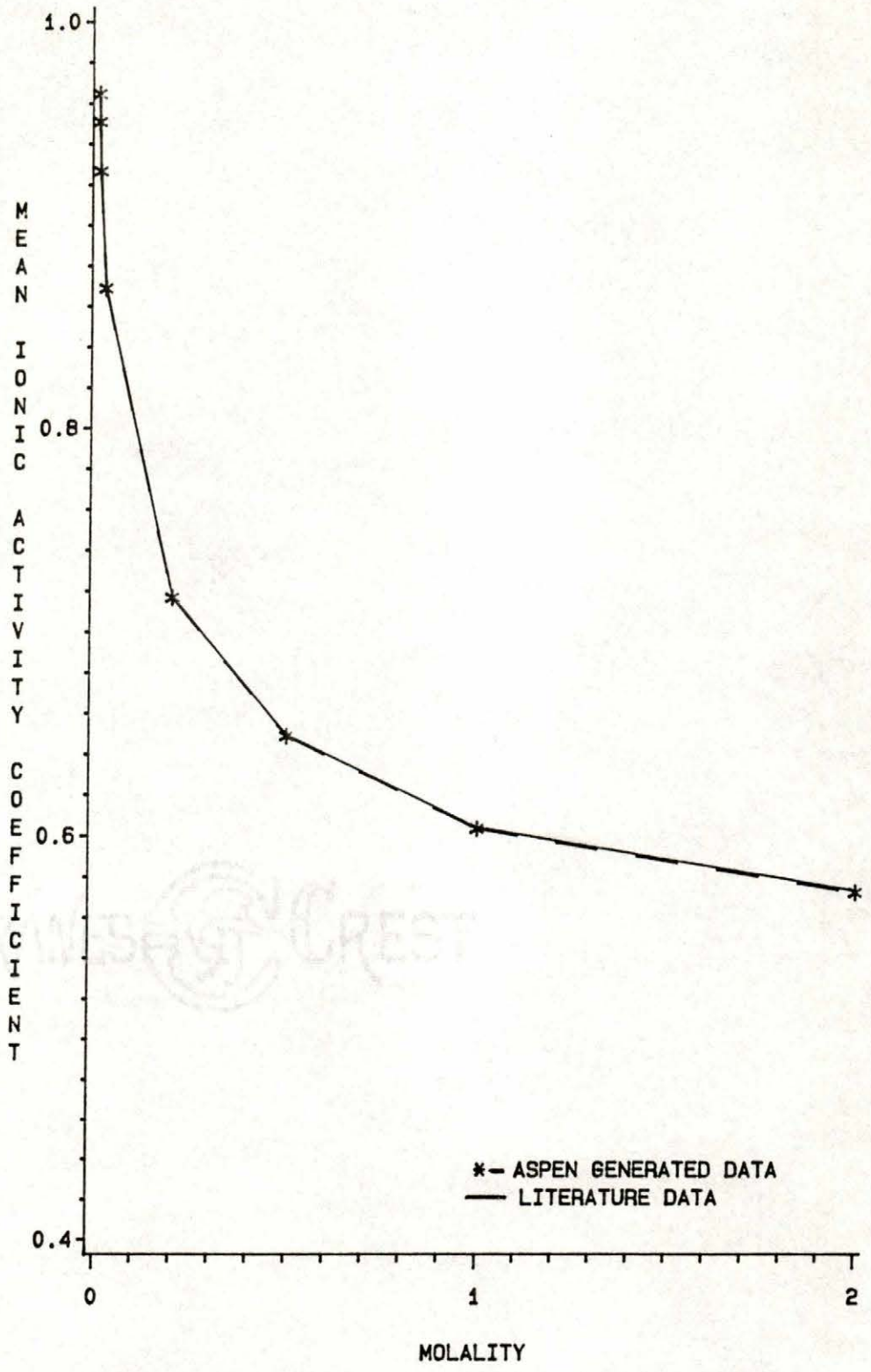


FIGURE V.2: ACTIVITY OF POTASSIUM CHLORIDE IN WATER

TABLE V.1: CALCULATED VERSUS LITERATURE MEAN IONIC ACTIVITY COEFFICIENTS FOR KCl-WATER SOLUTIONS AT 25 DEGREES CELSIUS

MOLALITY	ASPEN CALCULATED ACTIVITY COEFFICIENTS	LITERATURE ACTIVITY COEFFICIENTS (Zemaitis, 1986)	RELATIVE PERCENT DIFFERENCE
.001	0.965	0.965	0.032
.002	0.951	0.951	0.032
.005	0.927	0.927	0.043
.020	0.869	0.869	0.046
.200	0.717	0.717	0.070
.500	0.649	0.649	0.077
1.000	0.603	0.604	0.132
2.000	0.572	0.573	0.192

results shown in Table V.2 and Figure V.4 show an excellent correlation between the calculated and literature mean ionic activity coefficients for the KNO3-Water electrolyte system.

NaCl-Water Test Case

This system was chosen to test the validity of the ASPEN User Model as most previous electrolyte studies have either been based on NaCl or have included NaCl-water data in the studies. A compilation of various sources of NaCl-Water activity coefficient data can be found in the HANDBOOK OF AQUEOUS ELECTROLYTE THERMODYNAMICS (Zemaitis, 1986).

Figure V.5 is the ASPEN INPUT file for the NaCl-Water electrolyte system. Figure V.6 shows a plot of the mean ionic coefficients versus molality for the calculated and literature data sets. Table V.3 shows these same results with the relative percent difference calculated between the data sets. The results shown in Table V.3 and Figure V.6 indicate that the ASPEN User Model simulated this electrolyte system very accurately.

Discussion of Results

The ASPEN Electrolyte User Model is able to predict the activity coefficient for strong electrolytes within 2 percent of the measured activity coefficient for the electrolyte systems studied. The difference between the

```
NEW
TITLE 'KNO3-WATER USER MODEL'
DESCRIPTION "TEST CASE OF KSP USER MODEL TO ACCURATELY
 PREDICT MEAN IONIC ACTIVITY COEFFICIENTS OF ELECTROLYTES"
;
;      GLOBAL DATA
;
IN-UNITS ENG
OUT-UNITS ENG
HISTORY MSG-LEVEL PROPERTIES=8
;
;      PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/K+ K+/NO3- NO3-/KNO3 KNO3
FORMULA H2O H2O/K+ K+/NO3- NO3-/KNO3 KNO3
FILES USRPP1A AQADAT/USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=K+ NO3-/SOLDAT COMPS=KNO3
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12/HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST                          NO3-;H2O-KNO3 PAIR
   BCVAL GMELCC 1  1  K+     7.3130
   COMP-LIST                            K+;KNO3-H2O PAIR
   BCVAL GMELCC 1  1  NO3-  -3.4202
FLOWSHEET
   BLOCK FL1  IN=BRIN OUT=BRIN2
STREAM BRIN TEMP=76. PRES=14.7
   MOLE-FLOW H2O-122.3786/K+ 1./NO3- 1./KNO3 0.
BLOCK FL1 USER
   DESCRIPTION "SIMULATE KNO3 SOLUTION FLASH"
   PARAM NINT=200 NREAL=200 NIW=200 NW=800
;         TEMP(C) MOLALITY  PRES(PA) SLN TYPE
   REAL    25.0      .001     101325     1      &
           25.0      .002     101325     1      &
           25.0      .005     101325     1      &
           25.0      .100     101325     1      &
           25.0      .200     101325     1      &
           25.0      .500     101325     1      &
           25.0     1.000     101325     1      &
           25.0     2.000     101325     1
   INT 8
SIMULATE
```

FIGURE V.3: INPUT FILE TO CALCULATE MEAN IONIC ACTIVITY COEFFICIENT FOR KNO3-WATER SYSTEM

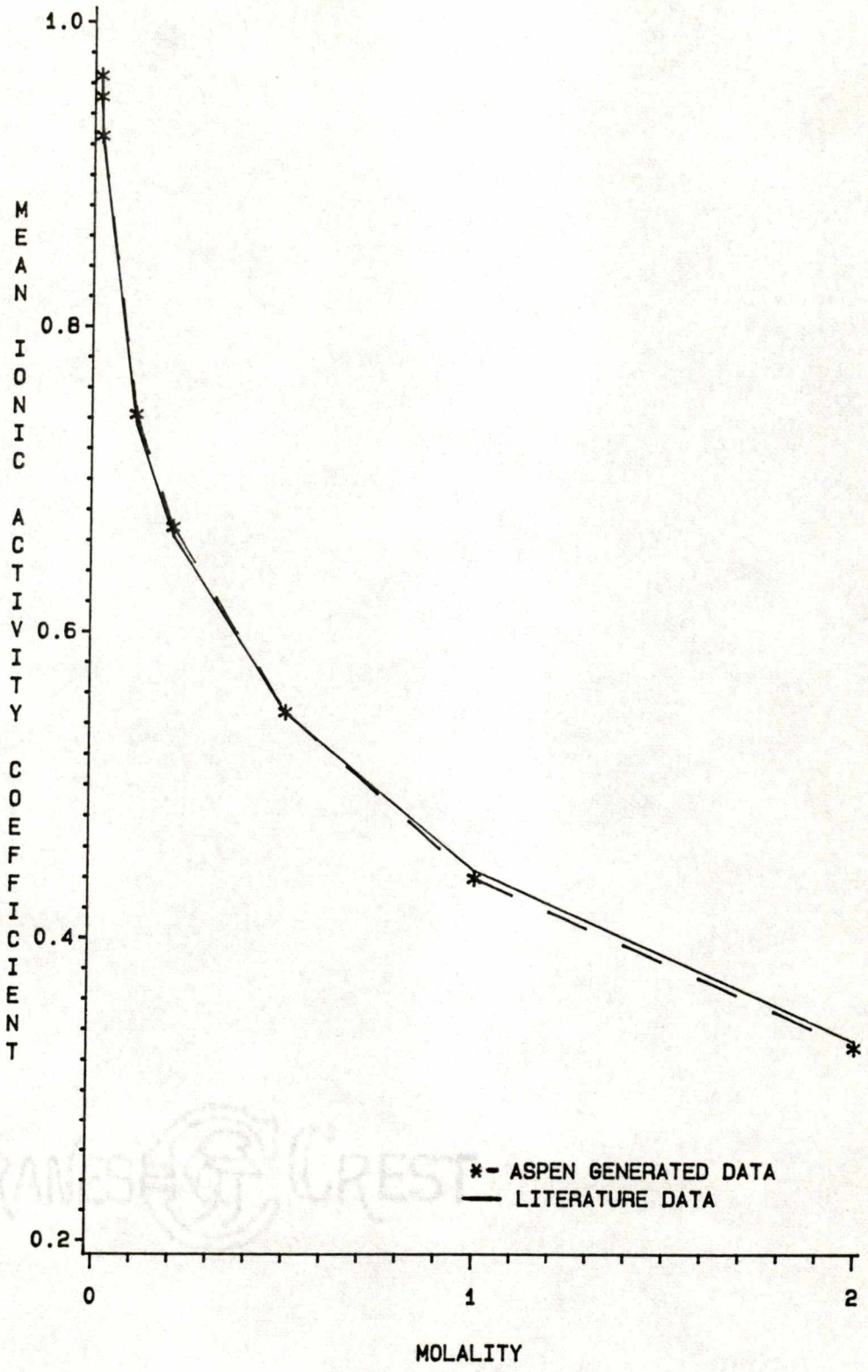


FIGURE V.4: ACTIVITY OF POTASSIUM NITRATE IN WATER

TABLE V.2: CALCULATED VERSUS LITERATURE MEAN IONIC ACTIVITY COEFFICIENTS FOR KNO3-WATER SOLUTIONS AT 25 DEGREES CELSIUS

MOLALITY	ASPEN CALCULATED ACTIVITY COEFFICIENTS	LITERATURE ACTIVITY COEFFICIENTS (Zemaitis, 1986)	RELATIVE PERCENT DIFFERENCE
.001	0.965	0.964	-0.073
.002	0.951	0.950	-0.105
.005	0.925	0.924	-0.141
.100	0.742	0.735	-0.911
.200	0.668	0.662	-0.891
.500	0.547	0.546	-0.128
1.000	0.439	0.444	1.194
2.000	0.328	0.332	1.205

CRANESCREST

```
NEW
TITLE 'NACL-WATER USER MODEL'
DESCRIPTION "TEST CASE OF KSP USER MODEL TO ACCURATELY
 PREDICT MEAN IONIC ACTIVITY COEFFICIENTS OF ELECTROLYTES"
;
;      GLOBAL DATA
;
IN-UNITS ENG
OUT-UNITS ENG
HISTORY MSG-LEVEL PROPERTIES=8
;
;      PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/NA+ NA+/CL- CL-/NACL NACL
FORMULA H2O H2O/NA+ NA+/CL- CL-/NACL NACL
FILES USRPP1A AQADAT/USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=NA+ CL-/SOLDAT COMPS=NACL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12/HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST                          CL-;H2O-NACL PAIR
   BCVAL GMELCC 1   1   NA+    9.7695
   COMP-LIST                          NA+;NACL-H2O PAIR
   BCVAL GMELCC 1   1   CL-   -4.6436
FLOWSHEET
   BLOCK FL1   IN=BRIN OUT=BRIN2
STREAM BRIN TEMP=76. PRES=14.7
   MOLE-FLOW H2O-122.3786/NA+ 1./CL- 1./NACL 0.
BLOCK FL1 USER
   DESCRIPTION "SIMULATE NACL SOLUTION FLASH"
   PARAM NINT=200 NREAL=200 NIW=200 NW=800
;          TEMP(C) MOLALITY  PRES(PA) SLN TYPE
   REAL    25.0      .001     101325     1      &
           25.0      .002     101325     1      &
           25.0      .005     101325     1      &
           25.0      .100     101325     1      &
           25.0      .200     101325     1      &
           25.0      .500     101325     1      &
           25.0     1.000     101325     1      &
           25.0     2.000     101325     1
   INT 8
SIMULATE
```

FIGURE V.5: INPUT FILE TO CALCULATE MEAN IONIC ACTIVITY COEFFICIENT FOR NACL-WATER SYSTEM

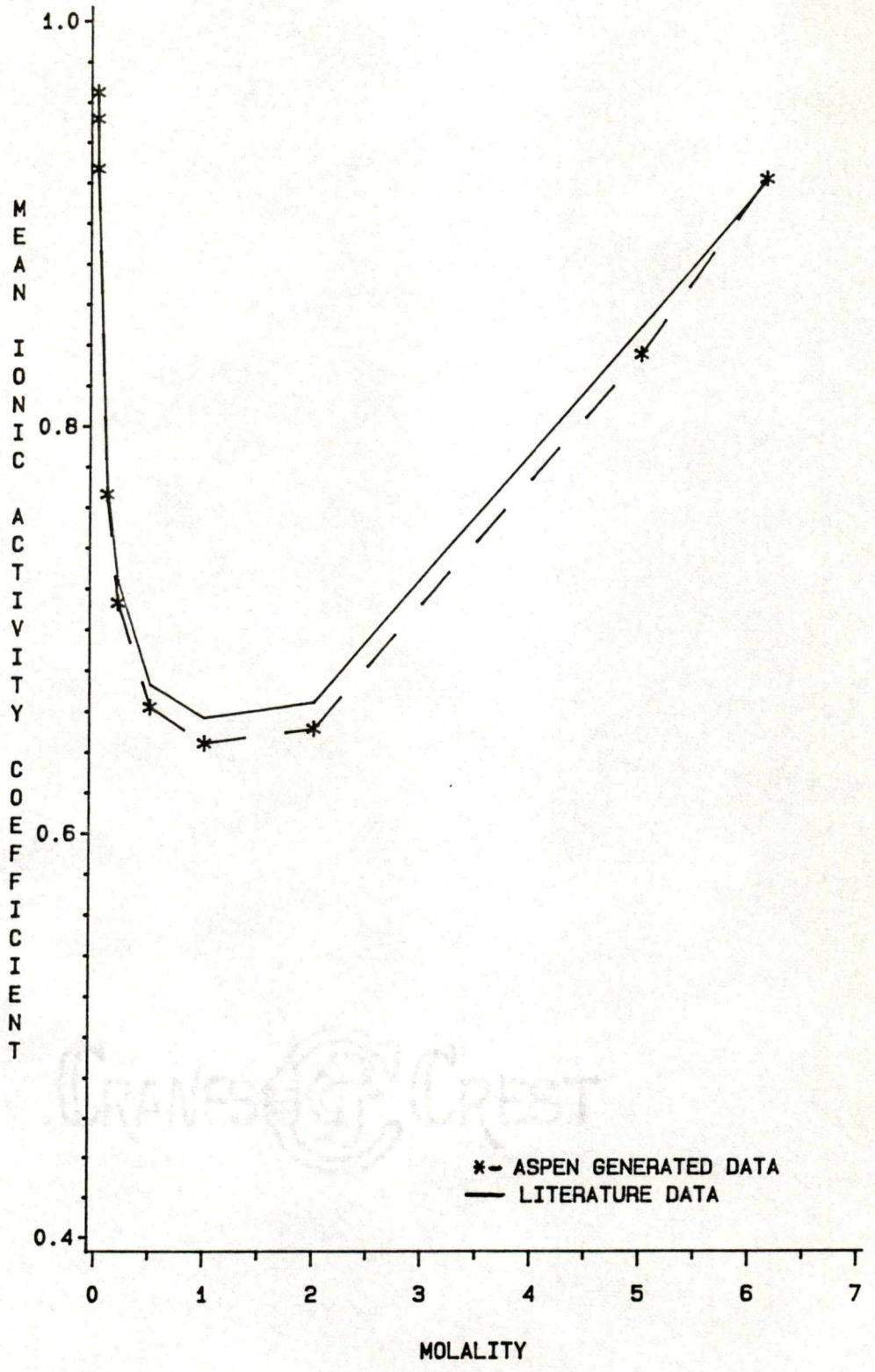


FIGURE V.6: ACTIVITY OF SODIUM CHLORIDE IN WATER

TABLE V.3: CALCULATED VERSUS LITERATURE MEAN IONIC ACTIVITY COEFFICIENTS FOR NaCl-WATER SOLUTIONS AT 25 DEGREES CELSIUS

MOLALITY	ASPEN CALCULATED ACTIVITY COEFFICIENTS	LITERATURE ACTIVITY COEFFICIENTS (Zemaitis, 1986)	RELATIVE PERCENT DIFFERENCE
.001	0.965	0.965	-0.018
.002	0.952	0.951	-0.028
.005	0.927	0.926	-0.045
.100	0.766	0.770	0.531
.200	0.713	0.724	1.528
.500	0.662	0.673	1.629
1.000	0.644	0.657	1.890
2.000	0.651	0.664	1.921
5.000	0.835	0.849	1.560
6.144(sat)	0.922	0.921	-0.142

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measured and calculated mean ionic activity coefficients is tied to the fact that even strong electrolytes do not possibly dissociate completely in solution.

The Ksp parameters developed by this study are a function of composition and activity coefficient and will vary from literature Ksp values by a maximum of 2 percent. This difference is based on the maximum difference between literature and ASPEN generated activity coefficients developed for this study.

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CHAPTER VI

DEVELOPING Ksp PARAMETERS FOR THE MHD SEED REGENERATION SIMULATION

In Chapter V the ability of the ASPEN Electrolyte User Model to accurately predict the activity coefficient of strong electrolytes and, in general, of any electrolyte in an infinite dilution state was demonstrated. This chapter will show the logic added to the USRVAP subroutine, introduced in Chapter IV, that calculates the Ksp parameter for an electrolyte solution. As explained earlier, this parameter defines the maximum electroyte concentration in a particular solution. When comparing various electrolyte systems the Ksp parameter defines which electrolyte will precipitate out of solution first if the molality of the system is changed. The order of discussion for this chapter will be: (1) Ksp Determination for MHD Simulation; (2) Adapting The ASPEN User Model to Incorporate Ksp Parameters; (3) Case Studies; and (4) Discussion of Results.

Ksp Determination for MHD Simulation

The theory of the Ksp parameter was developed in Chapter II and, in general, is defined by equation II.1. The Ksp algorithm is included in the USRVAP subroutine listed in Appendix B. Before potential MHD Seed Regeneration processes can be simulated, Ksp parameters need to be developed for the chemical constituents involved in each process. As described in the Introduction, the two

processes to be modeled are the Hydrated Lime Process and a potassium formate producing process called the Econoseed Process. Based on these two processes, Ksp parameters for potassium sulfate (K_2SO_4), calcium hydroxide ($Ca(OH)_2$), potassium hydroxide (KOH) , potassium carbonate (K_2CO_3), calcium formate ($Ca(HCOO)_2$), calcium sulfate ($CaSO_4$), and potassium formate (KHCOO) are needed.

The approach used in developing the needed Ksp parameters described above was to pass temperature dependent solubility data to the USRVAP subroutine. The algorithm then determined the activity coefficient of the solution and the Ksp parameter was calculated for a particular electrolyte at a particular temperature and concentration. This step was repeated over a range of temperatures. Calculated Ksp values were then correlated over the applicable temperature range using the form:

$$\ln(Ksp) = A + B/T + C*\ln(T) + D*T \qquad \text{(VI.1)}$$

where A, B, C, and D are regression coefficients and T is the temperature in Kelvin. The algorithm used in regressing the Ksp-temperature data is given in APPENDIX C. Figure VI.1 shows the ASPEN INPUT file used to determine the Ksp parameters for potassium sulfate (K_2SO_4). Table VI.1 shows the calculated temperature dependent Ksp values. Table VI.2 shows the regression results for the K_2SO_4 case. Table VI.3 shows the developed Ksp parameters for the

```
TITLE 'K2SO4-WATER USER MODEL'
DESCRIPTION "TEST CASE OF KSP USER MODEL TO ACCURATELY
 PREDICT MEAN IONIC ACTIVITY COEFFICIENTS OF ELECTROLYTES"
;
;      GLOBAL DATA
;
IN-UNITS ENG
OUT-UNITS ENG
HISTORY MSG-LEVEL PROPERTIES=8
;
;      PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/K+ K+/SO4-- SO4--/K2SO4 K2SO4
FORMULA H2O H2O/K+ K+/SO4-- SO4--/K2SO4 K2SO4
FILES USRPP1A AQADAT USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=ALL/SOLDAT COMPS=ALL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12 / HVMX HVMX12
PROPERTIES SYSOP1 GLOBAL
PROP-DATA
   COMP-LIST                          SO4--;H2O-K2SO4 PAIR
   BCVAL GMELCC 1   1  K+    11.3093
   COMP-LIST                            K+    ;K2SO4-H2O PAIR
   BCVAL GMELCC 1   1 SO4-- -5.4028
FLOWSHEET
   BLOCK FL1   IN=BRIN OUT=BRIN2
STREAM BRIN TEMP=76. PRES=14.7
   MOLE-FLOW H2O 122.3786/K+ 1./SO4-- 1./K2SO4 0.
BLOCK FL1 USER
   DESCRIPTION "SIMULATE K2SO4 SOLUTION FLASH"
   SUBROUTINE USRVAP USRRPT
   PARAM NINT=200 NREAL=200 NIW=200 NW=800
;         TEMP(C) SOLUBILITY  PRES(PA) SLN TYPE
   REAL   10.0       8.44      101325     3     &
          20.0      10.00      101325     3     &
          25.0      10.75      101325     3     &
          30.0      11.48      101325     3     &
          40.0      12.86      101325     3     &
          50.0      14.16      101325     3     &
          60.0      15.38      101325     3     &
          70.0      16.49      101325     3     &
          80.0      17.63      101325     3     &
          90.0      18.57      101325     3     &
         100.0      19.42      101325     3
   INT 11
```

FIGURE VI.1: K2SO4 INPUT FILE FOR Ksp DETERMINATION

TABLE VI.1: CALCULATED Ksp VERSUS TEMPERATURE FOR K2SO4-WATER SOLUTIONS AND COMPARISON WITH LITERATURE VALUES

TEMPERATURE (K)	ASPEN CALCULATED Ksp Value	LITERATURE Ksp Value (Goldberg, 1981)	RELATIVE PERCENT DIFFERENCE
283.15	7.578E-03		
293.15	1.185E-02		
298.15	1.463E-02	1.484E-02	1.37
303.15	1.793E-02		
313.15	2.619E-02		
323.15	3.726E-02		
333.15	5.157E-02		
343.15	6.859E-02		
353.15	9.199E-02		
363.15	1.143E-01		
373.15	1.366E-01		

TABLE VI.2: REGRESSION ANALYSIS FOR K2SO4-WATER SOLUTIONS

INTERPOLATION:

TEMPERATURE(K)	ln (Ksp) Experimental	ln (Ksp) Regressed	% Difference
283.15	-4.88	-4.89	-0.24
293.15	-4.43	-4.43	0.02
298.15	-4.22	-4.22	0.13
303.15	-4.02	-4.01	0.18
313.15	-3.64	-3.63	0.27
323.15	-3.29	-3.28	0.16
333.15	-2.96	-2.97	-0.10
343.15	-2.68	-2.68	0.00
353.15	-2.39	-2.42	-1.31
363.15	-2.17	-2.18	-0.49
373.15	-1.99	-1.96	1.35

NOTE:

K2SO4 Ksp NON-LINEAR REGRESSION

EQUATION MODELED:

$$\ln(K_{sp}) = A + B/T + C*\ln(T) + D*T$$

EQUATION COEFFICIENTS:

A = 9.62329E+00
B =-5.00291E+03
C = 1.53550E+00
D =-1.94899E-02

TABLE VI.3: Ksp PARAMETERS FOR MHD SEED REGENERATION SIMULATIONS

COMPONENT	A	B	C	D
K2SO4	9.623E+00	-5.002E+03	1.535E+00	-1.948E-02
KOH	-8.594E+00	-5.269E+03	9.612E+00	-6.027E-02
K2CO3	-8.658E+00	2.989E+03	6.082E-01	4.567E-02
KHCOO	-2.043E+01	6.962E+03	-4.162E+00	9.759E-02
CASO4	-2.220E+01	-7.002E+02	6.557E+00	-6.242E-02
CA(OH)2	5.092E+01	-8.613E+03	3.703E-01	-1.188E-01
CA(HCOO)2	4.472E+00	-1.911E+03	1.563E-02	-1.151E-02

NOTE:

EQUATION MODELED:

$$\ln(K_{sp}) = A + B/T + C*\ln(T) + D*T$$

chemical constituents required in the MHD simulations. A complete listing of the results of each Ksp regression is provided in APPENDIX C.

Adapting The ASPEN User Model to Incorporate Ksp Parameters

Once the Ksp parameters were developed, equation VI.1 was incorporated into the USRVAP subroutine. The completed ASPEN User Model was then incorporated into the ASPEN USER LIBRARY SYSTEM to be called during electroyte simulations. The ASPEN Electrolyte User Model can be found in APPENDIX B. The regression coefficients for a particular electrolyte system can then be passed to the subroutine from the ASPEN INPUT file or included in the subroutine where the system can be tested for solid precipitation. If a solid phase is present, the subroutine separates this phase from the inlet liquid stream, then the FLASH subroutine is called to perform the vapor-liquid equilibrium calculations. A new Ksp parameter is then calculated and compared to the inlet value passed to the subroutine for convergence. If convergence criteria are met the subroutine addresses the next electrolyte constituent in solution. The three phase stream results are passed to the ASPEN REPORT WRITER SYSTEM after completing the vapor-liquid-solid chemical and phase equilibrium calculations and the next block in the ASPEN INPUT file is addressed.

Case Studies

Six case studies were evaluated to determine the accuracy of the User Model. The input files for each of the six case studies are presented in APPENDIX D.

In case study one, excess potassium sulfate is fed into a mixed reactor containing water. The User Model determines the amount of potassium sulfate that will completely dissociate into potassium and sulfate ions. The insoluble material will be placed in an exit solids stream. This process is repeated at a variety of temperatures. The results from this simulation were compared to literature values for potassium sulfate and are given in Table VI.4.

Case studies two, three, and four are identical to case study one except that the studies involve mixtures of calcium formate in water, calcium sulfate in water, and potassium formate in water, respectively. The results of these simulations can be found in Tables VI.5, VI.6, and VI.7.

Case studies five and six test the User Model's ability to predict the common ion affect on electrolyte solubility. In case study five, sodium sulfate is mixed with a saturated solution of potassium sulfate in water. The inlet concentration of sodium sulfate and potassium sulfate were held constant during this simulation while the solvent concentrations based on solubility constraints were reduced as the temperature of the solution increased. The addition of sodium sulfate to these solutions caused the

TABLE VI.4: CALCULATED SOLUBILITY VERSUS TEMPERATURE FOR K2SO4-WATER SOLUTIONS AND COMPARISON WITH LITERATURE VALUES

TEMPERATURE (K)	ASPEN CALCULATED SOLUBILITY WT %	REPORTED SOLUBILITY WT % (Seidell, 1948)	RELATIVE PERCENT DIFFERENCE
298.15	10.75	10.75	0.01
313.15	12.87	12.86	-0.07
328.15	14.76	14.77	0.05
343.15	16.47	16.49	0.14
358.15	18.02	18.10	0.42
373.15	19.47	19.42	-0.24

TABLE VI.5: CALCULATED SOLUBILITY VERSUS TEMPERATURE FOR CA(HCOO)2-WATER SOLUTIONS AND COMPARISON WITH LITERATURE VALUES

TEMPERATURE (K)	ASPEN CALCULATED SOLUBILITY WT %	REPORTED SOLUBILITY WT % (Seidell, 1948)	RELATIVE PERCENT DIFFERENCE
298.15	14.28	14.31	0.15
313.15	14.54	14.56	0.12
328.15	14.79	14.81	0.10
343.15	15.04	15.05	0.11
358.15	15.28	15.30	0.14
373.15	15.52	15.53	0.07

TABLE VI.6: CALCULATED SOLUBILITY VERSUS TEMPERATURE FOR CASO4-WATER SOLUTIONS AND COMPARISON WITH LITERATURE VALUES

TEMPERATURE (K)	ASPEN CALCULATED SOLUBILITY WT %	REPORTED SOLUBILITY WT % (Seidell, 1948)	RELATIVE PERCENT DIFFERENCE
298.15	0.74	0.76	2.52
313.15	0.58	0.58	0.86
328.15	0.44	0.43	-1.62
343.15	0.34	0.34	0.89
358.15	0.25	0.26	0.78

TABLE VI.7: CALCULATED SOLUBILITY VERSUS TEMPERATURE FOR KHCOO-WATER SOLUTIONS AND COMPARISON WITH LITERATURE VALUES

TEMPERATURE (K)	ASPEN CALCULATED SOLUBILITY WT %	REPORTED SOLUBILITY WT % (Seidell, 1948)	RELATIVE PERCENT DIFFERENCE
298.15	77.47	77.65	0.23
313.15	78.89	79.48	0.74
328.15	81.07	81.46	0.47
343.15	83.80	83.75	-0.06
358.15	86.75	86.04	-0.83
373.15	89.68	88.53	-1.29

forced precipitation of potassium ions from solution. The solubility of potassium sulfate at various temperatures in these solutions was then calculated and compared to literature values for accuracy. The results from this simulation are given in Table VI.8. In case study six, potassium hydroxide is mixed with a saturated solution of potassium sulfate in water. The inlet concentration of potassium hydroxide and potassium sulfate were held constant during this simulation while the solvent concentrations based on solubility constraints were reduced as the temperature of the solution increased. The addition potassium hydroxide to these solutions casued the forced precipitation of sulfate ions. The results from this simulation are given in Table VI.9.

Discussion of Results

The case studies show that the ASPEN User Model is capable of accurately calculating the solubility of various electrolytes in water. The maximum relative percent difference in these studies was 2.5 percent (CaSO4 case study) with the average relative percent difference below 1.0 percent. Based on this, it is believed that the ASPEN User Model could provide a satisfactory simulation (within 1-2 percent) of the underlying solution chemistry for the two test cases to be modeled for application in MHD Seed Regeneration.

TABLE VI.8: CALCULATED SOLUBILITY VERSUS TEMPERATURE FOR K2SO4-WATER SOLUTIONS AND COMPARISON WITH LITERATURE VALUES-COMMON ION AFFECT DUE TO ADDITION OF NA2SO4

TEMPERATURE (K)	ASPEN CALCULATED SOLUBILITY WT %	REPORTED SOLUBILITY WT % (Seidell, 1948)	RELATIVE PERCENT DIFFERENCE
298.15	10.77	10.75	-0.26
313.15	12.90	12.86	-0.32
328.15	14.79	14.77	-0.16
343.15	16.49	16.49	-0.05
358.15	18.05	18.10	0.23
373.15	19.50	19.42	-0.41

NOTE:

K+/Na+ molar ratio is 150/1

TABLE VI.9: CALCULATED SOLUBILITY VERSUS TEMPERATURE FOR K2SO4-WATER SOLUTIONS AND COMPARISON WITH LITERATURE VALUES-COMMON ION AFFECT DUE TO ADDITION OF KOH

TEMPERATURE (K)	ASPEN CALCULATED SOLUBILITY WT %	REPORTED SOLUBILITY WT % (Seidell, 1948)	RELATIVE PERCENT DIFFERENCE
298.15	10.72	10.75	0.26
313.15	12.84	12.86	0.13
328.15	14.73	14.77	0.23
343.15	16.44	16.49	0.29
358.15	17.99	18.10	0.55
373.15	19.44	19.42	-0.10

NOTE:

SO4--/OH- molar ratio is 125/1

CHAPTER VII

ASPEN SIMULATION OF THE MHD SEED REGENERATION PROCESSES

The purpose of this chapter is to provide the background and logic behind the development of the two ASPEN INPUT files needed to simulate two of the potential seed regeneration processes for application to the MHD technology. The order of discussion will be (1) Simulation Basis; (2) Econoseed Process; and (3) Hydrated Lime Process.

Simulation Basis

The basis listed in the previous UTSI work (Jackson, 1985) will be used in these two simulations. This basis includes a 2260 mega Watt thermal feedstock, a 1000 mega Watt electric MHD facility, and a 111,000 pounds K_2SO_4 per hour waste stream to be regenerated.

Econoseed Process

The Econoseed Process which is part of the commercially applied Formate Process, was developed and patented by TRW, Inc. (Meyers, 1982). The chemistry of this process is:

$$K_2SO_4 + Ca(HCOO)_2 + 2H_2O \quad \text{--->}$$
$$CaSO_4\text{-}2H_2O \downarrow + 2HCOOK \qquad \text{(VII.1)}$$

A possible processing scheme is shown in Figure VII.1 and

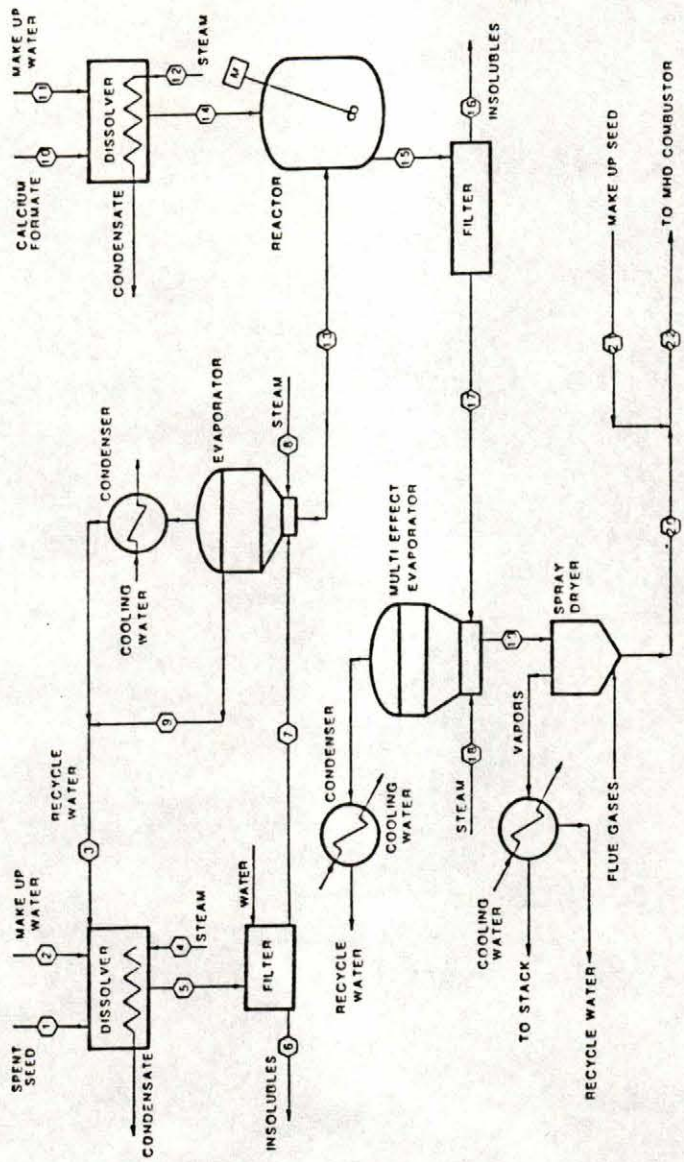


FIGURE VII.1: SCHEMATIC FOR ECONOSEED PROCESS

involves a reactor in which water soluble calcium formate and potassium sulfate react to form water insoluble calcium sulfate (gypsum) and soluble potassium formate. After the insoluble calcium sulfate is removed from the system the potassium formate is dried to a crystalline form and recycled to the MHD combustor.

The ASPEN INPUT file used to simulate the Econoseed Process is given in APPENDIX E. Figure VII.2 translates the INPUT file into block diagram format. It should be noted that the INPUT file calls both AQADAT and SOLDAT to retrieve the thermodynamic data needed to calculate physical properties. Additionally, the GMELCC parameters developed by this study are included for calculating the vapor-liquid equilibrium of electrolyte systems. Further, the Ksp coefficients are included in the USRSOL subroutine to provide for the liquid-solid phase calculations.

The ASPEN simulation was carried out and the results of interest are shown in Table VII.1. These results will be discussed in detail in Chapter VIII. A detailed ASPEN generated report file of this simulation is given in APPENDIX E.

Hydrated Lime Process

This process is currently being used in various forms in a number of flue gas desulfurization applications for sodium systems. A possible flow diagram for the Hydrated Lime Process is shown in Figure VII.3. The chemistry of the process is:

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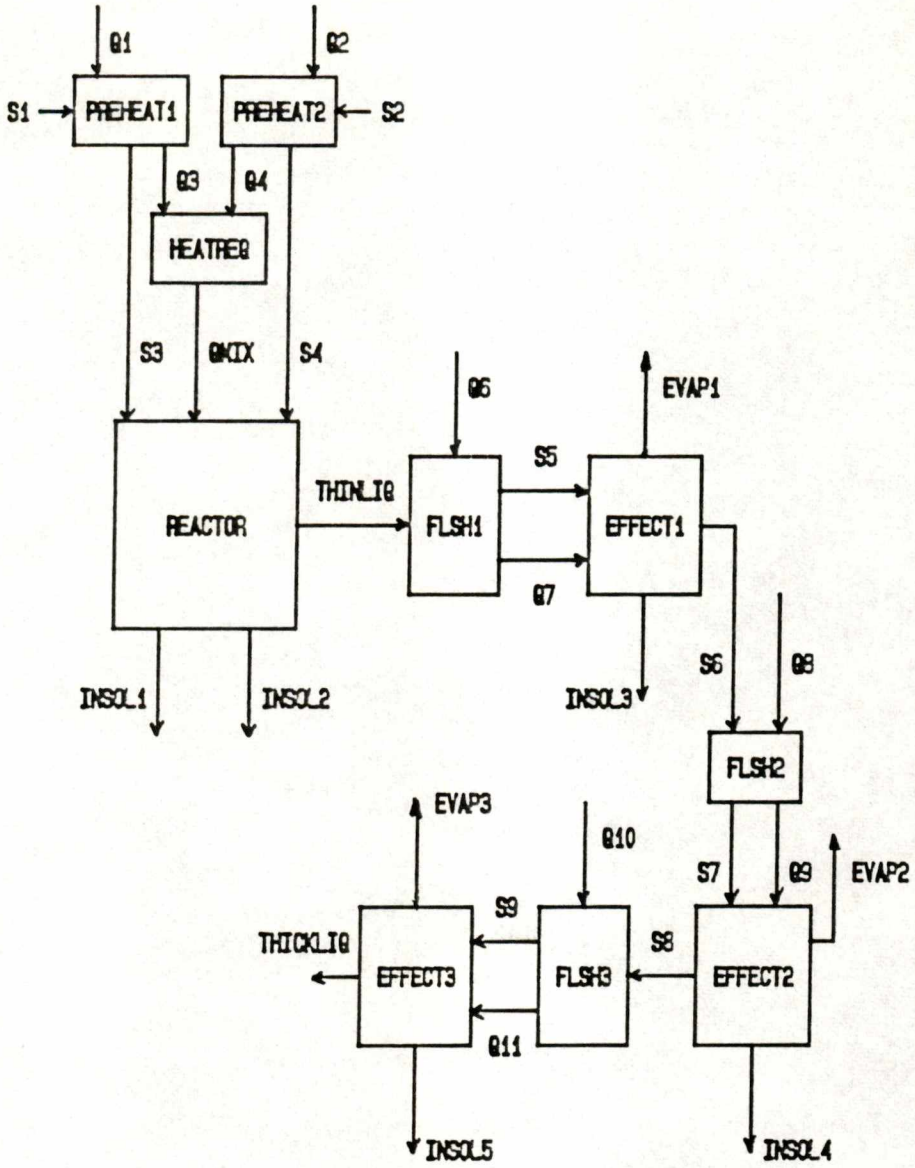


FIGURE VII.2: BLOCK DIAGRAM OF ECONOSEED INPUT FILE

TABLE VII.1: ECONOSEED SIMULATION RESULTS

Parameter (Units)	Value
Process Water to dissolve K2SO4 and Ca(HCOO)2 (lb/hr)	5.36E+05
Gross Heat Requirement for Process (BTU/hr)	1.16E+09
Preheat inlet water from 25 to 80 degrees Celsius with 10 lb. inlet steam (lb/hr)	5.50E+04
Multi-effect Evaporator Steam Requirements with 70 lb. inlet steam (lb/hr)	2.98E+05
Evaporator Economy	1.80E+00
Inlet KHCOO concentration to Evaporators (mass fraction)	1.67E-01
Outlet KHCOO concentration from Evaporators to Spray Dryers (mass fraction)	7.62E-01

NOTE: These results do not include possible credits available for internal recycle streams.

NOTE: Evaporator economy is defined at the inlet process water mass flow rate divided by the required evaporator steam mass flow rate needed for concentrating the process stream.

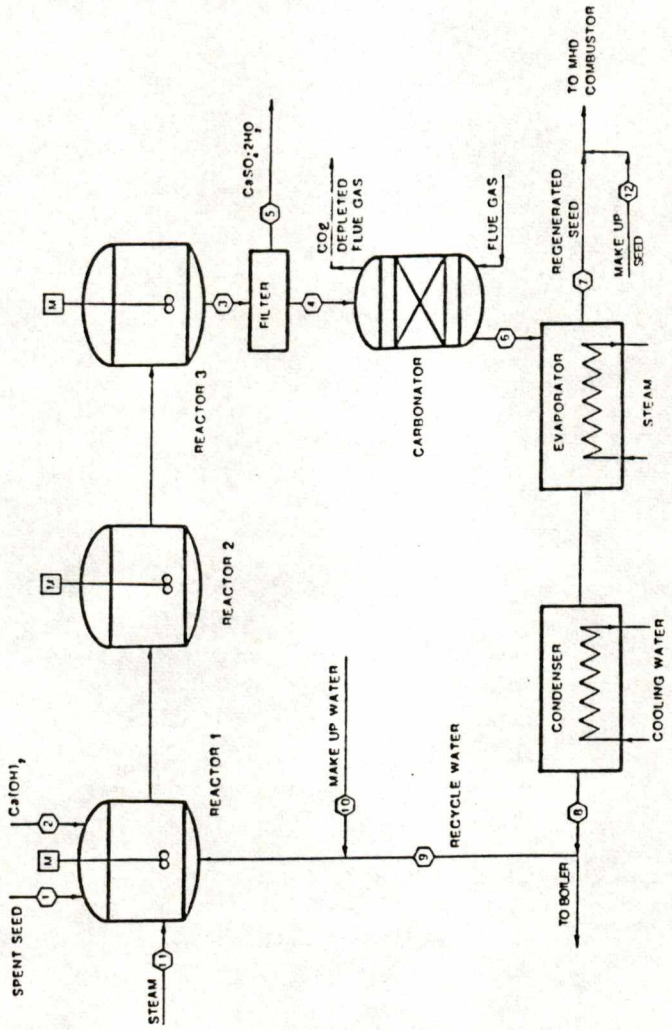


FIGURE VII.3: SCHEMATIC FOR HYDRATED LIME PROCESS

$$K_2SO_4 + Ca(OH)_2 + 2H_2O \longrightarrow 2KOH + CaSO_4 \cdot 2H_2O \downarrow \qquad \text{(VI.2)}$$

The causticizing reaction (equation VI.2) must be kept above 302 degrees Farenheit to avoid the formation of insoluble double salts and thus this system requires a pressurized reactor (AVCO, 1978). A tanks-in-series reactor model will be used to maximize the conversion of the products. It should be noted that the AVCO concept of this process also included the following equation:

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O \qquad \text{(VI.3)}$$

A carbonator (equation VI.3) is not needed for application in the MHD Seed Regeneration system as KOH can be recycled back to the MHD combustor as the regenerated seed. In an effort to minimize process utility cost the carbonation reaction will not be considered in this study.

The ASPEN INPUT file used to simulate the Hydrated Lime Process is located in APPENDIX F. Figure VII.4 translates the input file into block diagram format. It should be noted that the INPUT file calls both AQADAT and SOLDAT to retrieve the thermodynamic data needed to calculate physical properties. Additionally, the GMELCC parameters developed by this study are included for calculating the vapor-liquid equilíbrium of electrolyte systems. Further, the Ksp coefficients are included in the USRSOL subroutine to provide for the liquid-solid phase calculations.

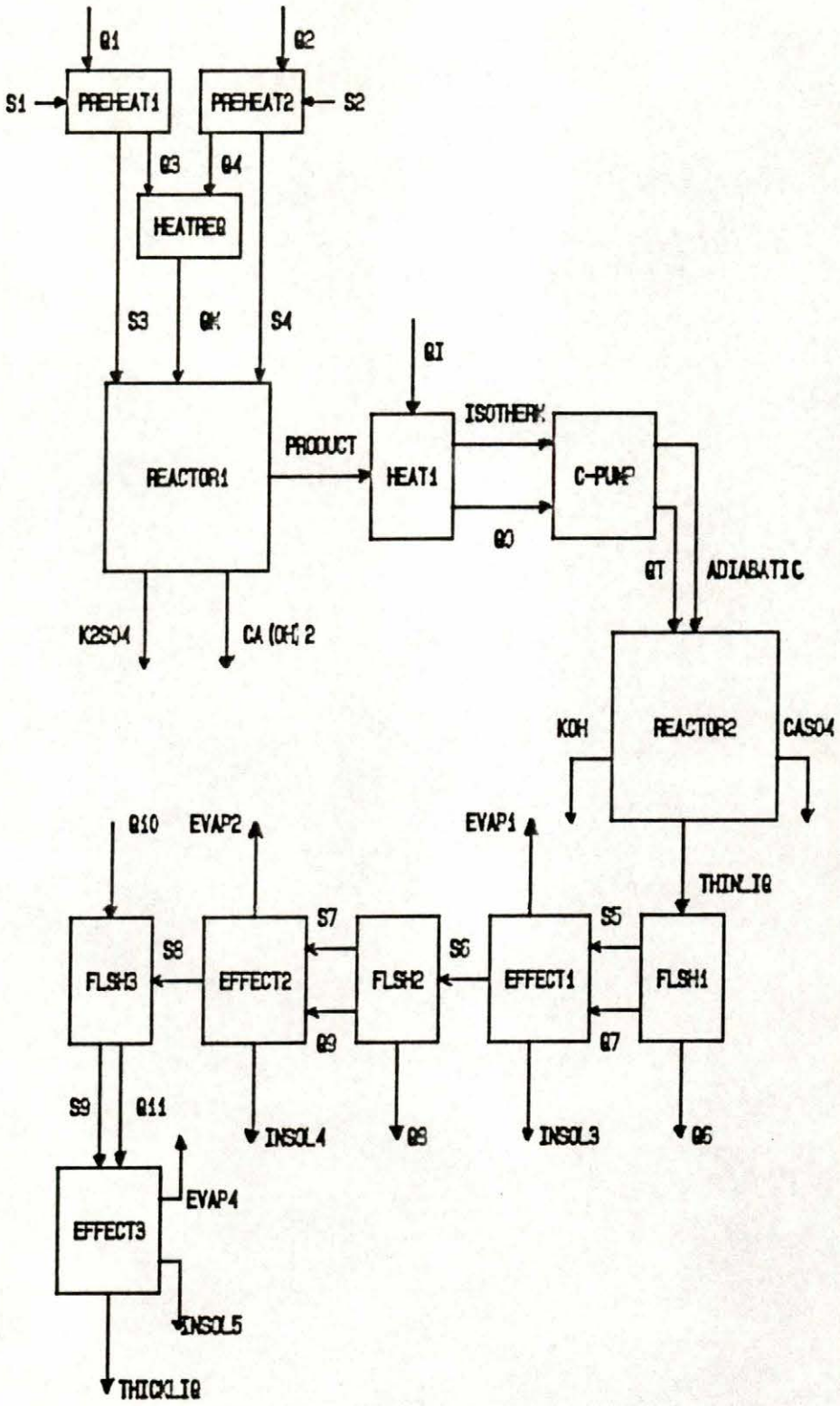


FIGURE VII.4: BLOCK DIAGRAM OF HYDRATED LIME INPUT FILE

The ASPEN simulation was carried out and the results of interest are shown in Table VII.2. These results will be discussed in detail in Chapter VIII. A detailed ASPEN generated report file of this simulation is given in APPENDIX F.

TABLE VII.2: HYDRATED LIME SIMULATION RESULTS

Parameter (Units)	Value
Process Water to dissolve K2SO4 and Ca(OH)2 (lb/hr)	3.61E+07
Gross Heat Requirement for Process (BTU/hr)	1.04E+11
Preheat inlet water from 25 to 50 degrees Celsius with 10 lb. inlet steam (lb/hr)	1.65E+06
Multi-effect Evaporator Steam Requirements with 1000 lb. inlet steam (lb/hr)	2.38E+07
Evaporator Economy	1.52E+00
Inlet KOH concentration to Evaporators (mass fraction)	1.90E-03
Outlet KOH concentration from Evaporators to Spray Dryer (mass fraction)	7.06E-01

NOTE: These results do not include possible credits for internal recycle streams.

NOTE: Evaporator economy is defined at the inlet process water mass flow rate divided by the required evaporator steam mass flow rate needed for concentrating the process stream.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this chapter is to summarize the key results developed in this study and to recommend areas for additional work. The order of discussion will be (1) ASPEN Extensions and Recommendations; and (2) Simulation Results and Recommendations.

ASPEN Extensions and Recommendations

In this study extensions were made to the public domain version of ASPEN that allow for simulations that involve the vapor-liquid-solid equilibrium of electrolytes in water. The model has proven to be accurate to within 2 percent for the electrolytes studied. This includes predictions of both activity coefficient and water solubility of electrolytes. Additional work that should be considered to enhance this model revolves around literature searches to extend the thermodynamic databases for electrolytes. This would allow Ksp parameters to be developed for other electrolytes of interest. Additionally, since dissociation of electrolytes is rarely complete, dissociation data either generated in the laboratory or found through literature searches could be included in the model to improve the accuracy of the activity coefficient model, if desired.

Simulation Results and Recommendations

The results of the Econoseed and Hydrated Lime studies show the importance of computer simulations in chemical process design. In the Econoseed Process calcium formate, which is moderately soluble, is used as the reactant with potassium sulfate to form calcium sulfate, which is highly insoluble. In the Hydrated Lime Process calcium hydroxide, which is highly insoluble, is used as the reactant with potassium sulfate to form calcium sulfate, which is highly insoluble. A comparision of the simulation results presented in Tables VII.1 and VII.2 show that the Hydrated Lime Process requires 67 times the amount of process water used in the dissolver stage than does the Econoseed Process. Additionally, the Hydrated Lime Process requires 90 times more gross energy to perform the preheat and evaporation stages than does the Econoseed Process. While the product potassium hydroxide is less heat sensitive than potassium formate, the process water and gross heat requirements for the respective process make the Hydrated Lime Process infeasible for further consideration as a possible MHD Seed Regeneration scheme.

The results of the simulations show that the Econoseed Process or the Formate Process from which it is derived should be given additional consideration as a potential seed regeneration scheme. Three additional areas of further study include development of process to supply calcium formate to reactor, evaluation of spray dryer system to completely dry the potassium formate product to a

crystalline state for recycle back to the MHD combustor, and overall process economics for the Econoseed Process.

The results from the Econoseed Process simulation were compared to the results predicted by an earlier UTSI study (Jackson, 1985) for completeness. Both studies accounted for greater than 99 percent regeneration of potassium ions into potassium formate with the Econoseed Process. Process water requirements were similiar for both studies.

In an effort to provide experimental validity to the results reported by this study, several evaporation studies were conducted with potassium formate and water to establish vapor-liquid equilibrium data. This information is outlined in Appendix G and Tables G.1 and G.2 and verfies that greater than 99.9% of the vapor phase was gaseous water and that electrolyte dissociation in the liquid phase was virtually complete. Additionally, the data in Table G.2 show that the thermodynamic data and physical property sets used in this simulation are able to accurately describe the potassium formate-water system.

The simulations show that improvements in process water requirements and gross energy requirements can be realized by evaluating candidate schemes whose reactant solubility is close to that of potassium sulfate. Additionally, improvements in evaporator exit concentration can be realized by evaluating reactor products that are less heat sensitive than potassium formate; however, this must be weighed against the economics of various sized spray dryer systems.

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BIBLIOGRAPHY

BIBLIOGRAPHY

"ASPEN PLUS Electrolyte Manual". Cambridge: Aspen Technology, 1983.

"ASPEN PLUS Notes on Interfaces and User Models". Cambridge: Aspen Technology, 1985.

AVCO Everett Research Laboratory, Inc. "Engineering Test Facility Conceptual Design - Final Report - Parts 1 and 2". Prepared for the U. S. Department of Energy under Contract Report number EF77C012614, June 1978.

Barker, R. E., et. al. "ASPEN Input and Report Files for the Modeling of the Tri-State Liquifaction Process". Oak Ridge: Oak Ridge National Laboratory, 1984.

Barnes, Ivan and Speltz, Velma (editors). U. S. Geological Survey. Translation of a Russian Report "Handbook of Thermodynamic Data". Springfield: National Technical Information Service, Department of Commerce, 1974.

Chen, C. C. "Computer Simulation of Chemical Processes with Electrolytes". D. S. Dissertation. Cambridge: Massachusetts Institute of Technology, 1980.

Davis, Stephan Rowan. "Implementation of ASPEN Electrolyte Routines and Aqueous and Solid Component User Databases for Application to MHD Seed Regeneration". M. S. Thesis. Tullahoma: The University of Tennessee Space Institute, 1985.

Goldberg, R. N. "Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Thirty-Six Uni-Bivalent Electrolytes". Washington, D. C.: Journal of Physical and Chemical Reference Data, Volume 10, No. 3, pages 671-764, 1981.

Graham, L. E. (editor). "ASPEN User Manual". Cambridge: Massachusetts Institute of Technology, 1982.

Harned, Herbert S., et. al. The Physical Chemistry of Electrolytic Solutions. New York: Reinhold Publishing Corporation, 1958.

Jackson, D., et. al. "Evaluation of Seed Regeneration Process for Coal Fired MHD Power Plants". Prepared for the U. S. Department of Energy under Contract Report number DEAC0279ET10815. Tullahoma: The University of Tennessee Space Institute, July 1985.

McCabe, Warren L., et. al. Unit Operations of Chemical Engineering. 4th Edition. New York: McGraw-Hill Book Company, 1985.

Myers, R. A. and W. D. Hart. "TRW Econoseed Process for Regeneration of Spent MHD Seed". Presented at the 20th Symposium of Engineering Aspects of Magnetohydrodynamics, Irvine, CA, June 1982.

Resibois, Pierre M. V. Electrolyte Theory. New York: Harper and Row, 1968.

Seidell,A. Solubilities of Inorganic and Organic Compounds. 3rd ed., Volume 2. New York: Van Nostrand, 1948.

Sheth, A. C., et. al. "Seed Recovery and Regeneration in Coal-Fired, Open-Cycle Magnetohydrodynamic Systems". Tullahoma: The University of Tennessee Space Institute, 1983.

Zemaitis, Jr., Joseph F., et. al. Handbook of Aqueous Electrolyte Thermodynamics. New York: Design Institute for Physical Property Data sponsored by the American Institute of Chemical Engineers, 1986.

APPENDICES

APPENDIX A

THERMODYNAMIC DATABASES AND

GMELCC PARAMETERS

```
;
;AQADAT DATABASE
;
TITLE 'CREATION OF AN ELECTROLYTE DATA BASE'
FILE ASPENPP2 ASPENPP2 OLD / ASPENPCD ASPENPCD
WRFILE ASPENPP2 SESAME
NEW-COMP 'K+' K+/'CA++' CA++/'NA+' NA+/'H+' H+/'CL-' CL-/
  'NO3-' NO3-/'SO4--' SO4--/'OH-' OH-/'CO3--' CO3--/
  'HCO3-' HCO3-/'HCOO-' HCOO-/'S--' S--/'HS-' HS-/
  'HSO4-' HSO4-/'KSO4-' KSO4-/'HSO3-' HSO3-/'CO' CO/
  'CO2' CO2/'HCL' HCL/'CH2O2' CH2O2/'H2S' H2S/'O2' O2/
  'O2S' O2S/'NO' NO/'NO2' NO2/'O3S' O3S
NEW-PROP MW 1/TC 1/PC 1/VC 1/ZC 1/CHARGE 1/IONTYP 1/DHFORM 1/
  DHAQFM 1/SO25C 1/PLXANT 9/DHVLWT 5/DGFORM 1/CPIG 11
COPY ASPENPCD COMPS=HCL H2S NO NO2 O2 O2S O3S CO CO2 CH2O2
  PROPS=MW TC PC VC ZC CPIG PLXANT DHFORM DGFORM DHVLWT
PROP-DATA
  PROP-LIST  CHARGE 1 0/IONTYP 1 0/DHAQFM 1 0/SO25C 1 0
  PVAL 'CO'     0  /  0  /  -1.2096D8  /  10.46D4
  PVAL 'CO2'    0  /  0  /  -4.1380D8  /  11.76D4
  PVAL 'HCL'    0  /  0  /  -1.6716D8  /   5.65D4
  PVAL 'CH2O2'  0  /  0  /  -4.2543D8  /  16.30D4
  PVAL 'H2S'    0  /  0  /  -0.3970D8  /  12.10D4
  PVAL 'O2'     0  /  0  /  -0.1170D8  /  11.09D4
  PVAL 'O2S'    0  /  0  /  -3.2298D8  /  16.19D4
  PVAL 'O3S'    0  /  0  /      *      /      *
  PVAL 'NO'     0  /  0  /      *      /      *
  PVAL 'NO2'    0  /  0  /      *      /      *
PROP-DATA
  PROP-LIST  MW 1 0/TC 1 0/PC 1 0/VC 1 0/ZC 1 0/CHARGE 1 0/
    IONTYP 1 0
  PVAL 'K+'      39.102/647.3/.2205D8/.0559/.229/ 1/1
  PVAL 'CA++'    40.080/647.3/.2205D8/.0559/.229/ 2/1
  PVAL 'NA+'     22.990/647.3/.2205D8/.0559/.229/ 1/1
  PVAL 'H+'       1.008/647.3/.2205D8/.0559/.229/ 1/1
  PVAL 'CL-'     35.453/647.3/.2205D8/.0559/.229/-1/2
  PVAL 'NO3-'    62.005/647.3/.2205D8/.0559/.229/-1/3
  PVAL 'SO4--'   96.062/647.3/.2205D8/.0559/.229/-2/3
  PVAL 'OH-'     17.007/647.3/.2205D8/.0559/.229/-1/3
  PVAL 'CO3--'   60.009/647.3/.2205D8/.0559/.229/-2/3
  PVAL 'HCO3-'   61.017/647.3/.2205D8/.0559/.229/-1/3
  PVAL 'HCOO-'   45.018/647.3/.2205D8/.0559/.229/-1/4
  PVAL 'S--'     32.064/647.3/.2205D8/.0559/.229/-2/2
  PVAL 'HS-'     33.072/647.3/.2205D8/.0559/.229/-1/2
  PVAL 'HSO4-'   97.070/647.3/.2205D8/.0559/.229/-1/3
  PVAL 'KSO4-'  135.164/647.3/.2205D8/.0559/.229/-1/3
  PVAL 'HSO3-'   81.070/647.3/.2205D8/.0559/.229/-1/3
PROP-DATA
  PROP-LIST  DHFORM 1 0/DHAQFM 1 0/SO25C 1 0
  PVAL 'K+'       5.4126D8/-2.5238D8/10.25D4
  PVAL 'CA++'     7.7425D8/-5.4283D8/-5.31D4
  PVAL 'NA+'      6.0936D8/-2.4012D8/ 5.90D4
  PVAL 'H+'      15.2804D8/      0D0/    0D0
  PVAL 'CL-'     -2.3313D8/-1.6716D8/ 5.65D4
  PVAL 'NO3-'          *   /-2.0500D8/14.64D4
  PVAL 'SO4--'         *   /-9.0927D8/ 2.01D4
  PVAL 'OH-'     -1.4350D8/-2.2999D8/-1.07D4
```

```
  PVAL 'CO3--'          *    /-6.7714D8/-5.69D4
  PVAL 'HCO3-'          *    /-6.9199D8/ 9.12D4
  PVAL 'HCOO-'          *    /-4.2555D8/ 9.20D4
  PVAL 'S--'            *    / 0.3310D8/-1.46D4
  PVAL 'HS-'            *    /-0.1760D8/ 6.28D4
  PVAL 'HSO4-'          *    /-8.8734D8/13.18D4
  PVAL 'KSO4-'          *   /-11.5742D8/15.10D4
  PVAL 'HSO3-'          *    /-6.2622D8/13.97D4
PROP-DATA
  PROP-LIST  DGFORM 1 0/DHVLWT 1 0/CPIG 1 0
  PVAL 'K+'     */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'CA++'   */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'NA+'    */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'H+'     */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'CL-'    */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'NO3-'   */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'SO4--'  */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'OH-'    */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'CO3--'  */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'HCO3-'  */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'HCOO-'  */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'S--'    */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'HS-'    */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'HSO4-'  */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'KSO4-'  */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
  PVAL 'HSO3-'  */2D7 298 * * */2.08D4 0 0 0 0 0 0 2D3 * * *
PROP-DATA
  PROP-LIST           PLXANT 1 0
  PVAL 'K+'     -1D30 0 * * * * * * *
  PVAL 'CA++'   -1D30 0 * * * * * * *
  PVAL 'NA+'    -1D30 0 * * * * * * *
  PVAL 'H+'     -1D30 0 * * * * * * *
  PVAL 'CL-'    -1D30 0 * * * * * * *
  PVAL 'NO3-'   -1D30 0 * * * * * * *
  PVAL 'SO4--'  -1D30 0 * * * * * * *
  PVAL 'OH-'    -1D30 0 * * * * * * *
  PVAL 'CO3--'  -1D30 0 * * * * * * *
  PVAL 'HCO3-'  -1D30 0 * * * * * * *
  PVAL 'HCOO-'  -1D30 0 * * * * * * *
  PVAL 'S--'    -1D30 0 * * * * * * *
  PVAL 'HS-'    -1D30 0 * * * * * * *
  PVAL 'HSO4-'  -1D30 0 * * * * * * *
  PVAL 'KSO4-'  -1D30 0 * * * * * * *
  PVAL 'HSO3-'  -1D30 0 * * * * * * *
PRINT-DIR AQADAT
PRINT-DATA AQADAT
END-INPUT
```

```
;
;SOLDAT DATABASE
;
TITLE 'CREATION OF A SOLIDS DATA BANK'
FILE USRPP1B SOLDAT NEW
WRFILE SOLDAT
NEW-COMP 'CAC03' CAC03/'CAH2C2O4' CAH2C2O4/'CAN2O6' CAN2O6/
  'CAO2H2' CAO2H2/'CAS04' CAS04/'CACL2' CACL2/'C' C/
  'K2C03' K2C03/'KCL' KCL/'KHC03' KHC03/'KHC00' KHC00/
  'KHS' KHS/'KN03' KN03/'KOH' KOH/'K2S' K2S/'K2S04' K2S04/
  'NACL' NACL/'NA2C03' NA2C03/'NAHC03' NAHC03/'NAN03' NAN03/
  'NAOH' NAOH/'NA2S04' NA2S04/'KC2H302' KC2H302/
  'CAN206D4' CAN206D4/'CAS04D2' CAS04D2/'K2C03D1P5' K2C03D1P5
NEW-PROP MW 1/DHSFRM 1/DGSFRM 1/TBP 1/TFP 1/PSANT 5/
  CPS01 8/VSPOLY 7
PROP-DATA
  PROP-LIST          MW 1  / DHSFRM 1 / DGSFRM 1
  PVAL 'CAC03'      100.0894/-12.0692D8/-11.2879D8
  PVAL 'CAH2C2O4'   130.1160/-13.8660D8/     *
  PVAL 'CAN2O6'     164.0898/ -9.3839D8/ -7.4307D8
  PVAL 'CAO2H2'      74.0948/ -9.8609D8/ -8.9849D8
  PVAL 'CAS04'      136.1416/-14.2080D8/-13.0898D8
  PVAL 'CACL2'      110.9860/ -7.9590D8/ -7.4810D8
  PVAL 'C'           12.0112/       0D0/       0D0
  PVAL 'K2C03'      138.2134/-11.5102D8/-10.6350D8
  PVAL 'KCL'         74.5550/ -4.3675D8/ -4.0914D8
  PVAL 'KHC03'      100.1194/ -9.6320D8/ -8.6350D8
  PVAL 'KHC00'       84.1200/ -6.7973D8/     *
  PVAL 'KHS'         72.1740/ -2.6510D8/     *
  PVAL 'KN03'       101.1060/ -4.9463D8/ -3.9486D8
  PVAL 'KOH'         56.1094/ -4.2476D8/ -3.7908D8
  PVAL 'K2S'        110.2680/ -3.8070D8/ -3.6400D8
  PVAL 'K2S04'      174.2656/-14.3779D8/-13.2137D8
  PVAL 'NACL'        58.4428/ -4.1115D8/ -3.8414D8
  PVAL 'NA2C03'     105.9890/-11.3068D8/-10.4444D8
  PVAL 'NAHC03'      84.0072/ -9.5081D8/ -8.5100D8
  PVAL 'NAN03'       84.9947/ -4.6785D8/ -3.6700D8
  PVAL 'NAOH'        39.9972/ -4.2560D8/ -3.7949D8
  PVAL 'NA2S04'     142.0412/-13.8708D8/-12.7016D8
  PVAL 'KC2H302'     98.1472/ -7.2800D8/     *
  PVAL 'CAN206D4'   236.1510/-21.3233D8/-17.7170D8
  PVAL 'CAS04D2'    172.1720/-20.2263D8/-17.9730D8
  PVAL 'K2C03D1P5'  165.2400/-16.0920D8/-14.3250D8
;PROP-DATA
  PROP-LIST  TBP 1/TFP 1/CPS01 8
  PVAL 'CAC03'      1172/1172/ 8.188D4 0 0 0 0 0 0 2D3
  PVAL 'CAH2C2O4'    373/ 373/ 2.080D4 0 0 0 0 0 0 2D3
  PVAL 'CAN2O6'      834/ 834/14.937D4 0 0 0 0 0 0 2D3
  PVAL 'CAO2H2'      853/ 853/ 8.749D4 0 0 0 0 0 0 2D3
  PVAL 'CAS04'      1723/1723/ 9.904D4 0 0 0 0 0 0 2D3
  PVAL 'CACL2'      1873/1045/ 7.259D4 0 0 0 0 0 0 2D3
  PVAL 'C'          3925/3925/ 0.853D4 0 0 0 0 0 0 2D3
  PVAL 'K2C03'      1164/1164/11.443D4 0 0 0 0 0 0 2D3
  PVAL 'KCL'        1773/1049/ 5.130D4 0 0 0 0 0 0 2D3
```

```
   PVAL 'KHCO3'        373/ 373/ 2.080D4 0 0 0 0 0 0 2D3
   PVAL 'KHCOO'        441/ 441/ 2.080D4 0 0 0 0 0 0 2D3
   PVAL 'KHS'          728/ 728/ 7.531D4 0 0 0 0 0 0 2D3
   PVAL 'KNO3'         673/ 607/10.740D4 0 0 0 0 0 0 2D3
   PVAL 'KOH'         1593/ 633/ 6.490D4 0 0 0 0 0 0 2D3
   PVAL 'K2S'         1113/1113/ 2.080D4 0 0 0 0 0 0 2D3
   PVAL 'K2SO4'       1962/1342/13.146D4 0 0 0 0 0 0 2D3
   PVAL 'NACL'        1686/1074/ 5.050D4 0 0 0 0 0 0 2D3
   PVAL 'NA2CO3'      1124/1124/11.230D4 0 0 0 0 0 0 2D3
   PVAL 'NAHCO3'       543/ 543/ 8.761D4 0 0 0 0 0 0 2D3
   PVAL 'NANO3'        653/ 580/ 9.288D4 0 0 0 0 0 0 2D3
   PVAL 'NAOH'        1663/ 591/ 5.954D4 0 0 0 0 0 0 2D3
   PVAL 'NA2SO4'      1157/1157/12.820D4 0 0 0 0 0 0 2D3
   PVAL 'KC2H3O2'      565/ 565/12.661D4 0 0 0 0 0 0 2D3
   PVAL 'CAN2O6D4'     405/ 316/45.053D4 0 0 0 0 0 0 2D3
   PVAL 'CASO4D2'      440/ 401/18.602D4 0 0 0 0 0 0 2D3
   PVAL 'K2CO3D1P5'    436/ 401/22.737D4 0 0 0 0 0 0 2D3
;PROP-DATA
   PROP-LIST                PSANT 1  /      VSPOLY 1
   PVAL 'CACO3'        -1D30 0 * * */ 3.693D-2 0 0 0 0 0 1D3
   PVAL 'CAH2C2O4'     -1D30 0 * * */ 6.470D-2 0 0 0 0 0 1D3
   PVAL 'CAN2O6'       -1D30 0 * * */ 6.553D-2 0 0 0 0 0 1D3
   PVAL 'CAO2H2'       -1D30 0 * * */ 3.308D-2 0 0 0 0 0 1D3
   PVAL 'CASO4'        -1D30 0 * * */ 4.599D-2 0 0 0 0 0 1D3
   PVAL 'CACL2'        -1D30 0 * * */ 6.052D-2 0 0 0 0 0 1D3
   PVAL 'C'            -1D30 0 * * */ 0.534D-2 0 0 0 0 0 1D3
   PVAL 'K2CO3'        -1D30 0 * * */ 5.692D-2 0 0 0 0 0 1D3
   PVAL 'KCL'          -1D30 0 * * */ 3.758D-2 0 0 0 0 0 1D3
   PVAL 'KHCO3'        -1D30 0 * * */ 4.614D-2 0 0 0 0 0 1D3
   PVAL 'KHCOO'        -1D30 0 * * */ 4.404D-2 0 0 0 0 0 1D3
   PVAL 'KHS'          -1D30 0 * * */ 4.271D-2 0 0 0 0 0 1D3
   PVAL 'KNO3'         -1D30 0 * * */ 4.794D-2 0 0 0 0 0 1D3
   PVAL 'KOH'          -1D30 0 * * */ 2.745D-2 0 0 0 0 0 1D3
   PVAL 'K2S'          -1D30 0 * * */ 6.109D-2 0 0 0 0 0 1D3
   PVAL 'K2SO4'        -1D30 0 * * */ 6.546D-2 0 0 0 0 0 1D3
   PVAL 'NACL'         -1D30 0 * * */ 2.699D-2 0 0 0 0 0 1D3
   PVAL 'NA2CO3'       -1D30 0 * * */ 2.308D-2 0 0 0 0 0 1D3
   PVAL 'NAHCO3'       -1D30 0 * * */ 3.891D-2 0 0 0 0 0 1D3
   PVAL 'NANO3'        -1D30 0 * * */ 3.759D-2 0 0 0 0 0 1D3
   PVAL 'NAOH'         -1D30 0 * * */ 1.878D-2 0 0 0 0 0 1D3
   PVAL 'NA2SO4'       -1D30 0 * * */ 5.300D-2 0 0 0 0 0 1D3
   PVAL 'KC2H3O2'      -1D30 0 * * */ 6.251D-2 0 0 0 0 0 1D3
   PVAL 'CAN2O6D4'     -1D30 0 * * */12.460D-2 0 0 0 0 0 1D3
   PVAL 'CASO4D2'      -1D30 0 * * */ 7.421D-2 0 0 0 0 0 1D3
   PVAL 'K2CO3D1P5'    -1D30 0 * * */ 8.088D-2 0 0 0 0 0 1D3
PRINT-DIR SOLDAT
PRINT-DATA SOLDAT
END-INPUT
```

Table A.1: GMELCC PARAMETER VALUES AND STANDARD DEVIATIONS

COMPONENT NAME	PARAMETER ESTIMATE	STANDARD DEVIATION
NA+ CL-	9.7695	0.2376E-01
CL- NA+	-4.7052	0.6398E-02
NA+ NO3-	7.5853	0.1336E-01
NO3- NA+	-3.8782	0.3341E-02
NA+ OH-	11.5711	0.3319E-02
OH- NA+	-4.9976	0.2448E-02
NA+ CO3--	9.2104	0.1211E-01
CO3-- NA+	-4.8249	0.4158E-02
NA+ SO4--	9.7423	0.5437E-01
SO4-- NA+	-4.9341	0.1913E-01
NA+ HCO3-	8.2208	0.2036E-01
HCO3- NA+	-4.1175	0.5748E-02
K+ OH-	10.8050	0.1834E-01
OH- K+	-5.2144	0.2647E-02
K+ CL-	9.3662	0.2992E-01
CL- K+	-4.4424	0.7297E-02
K+ NO3-	7.3130	0.3063E-01
NO3- K+	-3.4202	0.1129E-01
K+ CO3--	10.8544	0.1723E-01
CO3-- K+	-5.4726	0.2773E-02
K+ SO4--	11.6593	0.7707E-01
SO4-- K+	-5.7928	0.2911E-01
K+ HCO3-	8.4924	0.1988E-01
HCO3- K+	-4.2523	0.5289E-02
CA++ CL-	11.7474	0.2570E-01
CL- CA++	-6.0221	0.4155E-02
CA++ NO3-	8.8413	0.8740E-01
NO3- CA++	-4.9984	0.2574E-01
CA++ HCO2-	14.8546	0.9109E-01
HCO2- CA++	-6.3948	0.2842E-01

APPENDIX B

ELECTROLYTE USER MODELS

CRANESHOT CREST

```
      SUBROUTINE USRVAP(NSIN,NINFI,SIN1,SIN2,SIN3,SIN4,
     1  SINFI,NSOUT,NINFO,SOUT1,SOUT2,SOUT3,SOUT4,SINFO,
     2  NSUBS,IDXSUB,ITYPE,NINT,INT,NREAL,REAL,IDS,NPO,
     3  NBOPST,NIW,IW,NW,W,NSIZE,SIZE)
C
C     DESCRIPTION OF VARIABLES IN ARGUMENT LIST
C
C     VAR             DESCRIPTION AND RANGE
C
C     NSIN            NO. INLET STREAMS (MAX=5)
C     NINFI           NO. INLET INFO. STREAMS (0 OR 1)
C     SIN1            INLET STREAM 1
C     SIN2            INLET STREAM 2
C     SIN3            INLET STREAM 3
C     SIN4            INLET STREAM 4
C     SINFI           INLET INFORMATION STREAM
C     NSOUT           NO. OUTLET STREAMS (MAX=5)
C     NINFO           NO. OUTLET INFO. STREAMS (0 OR 1)
C     SOUT1           OUTLET STREAM 1
C     SOUT2           OUTLET STREAM 2
C     SOUT3           OUTLET STREAM 3
C     SOUT4           OUTLET STREAM 4
C     SINFO           OUTLET INFORMATION STREAM
C     NSUBS           NO. SUBSTRMS (ALL STRMS MUST BE SAME!)
C     IDXSUB          INDEX VECTOR OF LENGTH NSUBS
C     ITYPE           SUBSTREAM TYPE VECTOR OF LENGTH NSUBS
C     NINT            LENGTH OF INTEGER ARRAY
C     INT             INTEGER ARRAY
C     NREAL           LENGTH OF REAL ARRAY
C     REAL            REAL ARRAY
C     IDS             ARRAY ID'S TO WRITE TO (HIST/REP FILE)
C     NPO             NO. PHYSICAL PROPERTY OPTION SETS (=2)
C     NBOPST          ARRAY OF PP OPTION SET POINTERS
C     NIN             LENGTH OF INTEGER WORK ARRAY
C     IW              INTEGER WORK ARRAY
C     NW              LENGTH OF REAL WORK ARRAY
C     W               REAL WORK ARRAY
C     NSIZE           LENGTH OF SIZE ARRAY
C     SIZE            SIZE ARRAY
C     ITEMP           POSITION VECTOR
C     IMOLE           POSITION VECTOR
C     IPRES           POSITION VECTOR
C     ICOUNT          POSITION VECTOR
C     POUT            OUTLET PRESSURE
C     TIN             INLET TEMPERATURE
C     COUNT           ELECTROLYTE TYPE
C     KGMH2O          WEIGHT OF H2O IN KILOGRAMS
C     KMOLST          KILOMOLES OF SALT PRESENT
C     VP              NUMBER OF POSITIVE IONS
C     VM              NUMBER OF NEGATIVE IONS
```

```
C      V                TOTAL NUMBER OF IONS
CC     GAMPM            MEAN IONIC ACTIVITY COEFFICIENT
CC     MOLPM            MEAN IONIC MOLALITY OF SOLUTION
C
C      DECLARATIONS
C
       IMPLICIT REAL * 8 (A-H,O-Z)
       REAL KGMH2O,KMOLST,M,MP,MM,MOLPM,MOLM,MOLP,KSP
       INTEGER COUNT
C
CC     DIMENSIONS
C
       DIMENSION SIN1(1),SIN2(1),SIN3(1),SIN4(1),SINFI(1),
     1SOUT1(1),SOUT2(1),SOUT3(1),SOUT4(1),SINFO(1),
     2IDXSUB(NSUBS),ITYPE(NSUBS),INT(NINT),REAL(NREAL),
     3EDS(2,13),NBOPST(3,NPO),IW(NIW),W(NW),SIZE(NSIZE),
     4RETN(500),IRETN(7),NBOPS1(3,1),DUMMY(10)
C
CC     COMMONS
C
       COMMON/USER/RMISS,IMISS,NGBAL,IPASS,IRESTR,ICONV,
     1LMSG,LPMSG,KFLAG,NHSTRY,NRPT,NTRMNL,ISIZE
       COMMON/NCOMP/NCC,NNCC
       COMMON/IDSCC/INSCC(2,1)
       COMMON/IDSNCC/IDSNCC(2,1)
       COMMON/IDXCC/IDXCC(1)
       COMMON/IDXNCC/IDXNCC(1)
       COMMON/MW/XMW(1)
       COMMON/RPTGLP/IREPFL,ISUB(10)
       COMMON/CHARGE/CHARGE(1)
       COMMON/DHAQFM/DHAQFM(1)
       COMMON/IONTYP/IONTYP(1)
       COMMON/S025C/S025C(1)
       COMMON/GMELCA/GMELCA(1)
       COMMON/GMELCB/GMELCB(1)
       COMMON/GMELCC/GLEMCC(1)
       COMMON/GMELCD/GMELCD(1)
       COMMON/GAMMA/GAMMA(1)
       COMMON/GAMUS/GAMUS(1)
       COMMON/GAMMAS/GAMMAS(1)
       COMMON/GAMPC/GAMPC(1)
       COMMON/GAMPC1/GAMPC1(1)
       COMMON/GAMSPC/GAMSPC(1)
       COMMON/VLION/VLION(2,1)
C
CC     EXECUTABLE STATEMENTS AND EXPLANATION OF ACTIONS
CC
CC
CC     LOAD STREAM VARIABLES INTO SOUT1
C
       N=NCC+9
```

```
      DO 100 I=1,N
         SOUT1(I)=SIN1(I)
  100 CONTINUE
      DO 200 I=1,3
         NBOPS1(I,1)=NBOPST(I,1)
  200 CONTINUE
      NDATA=INT(1)
      DO 300 I=1,NDATA
C
C     THESE STATEMENTS INITIALIZE THE VARIABLES
C     FOR EACH DATA SET
C
          SOUT1(1)=SIN1(1)
          ITEMP=I*4-3
          IMOLE=I*4-2
          IPRES=I*4-1
          ICOUNT=I*4
C
C     READ THE DATA FROM THE CRYVAP.INP FILE
C
          POUT=REAL(IPRES)
          TIN=REAL(ITEMP)
          COUNT=REAL(ICOUNT)
C
C     CONVERT THE TEMPERATURE FROM CENTIGRADE TO KELVINS
C     AND CONVERT THE MOLALITY TO FLOW RATE OF IONS IN
C     KMOLES/SECOND
C
          TIN=TIN+273.15
          KGMH2O=SOUT1(1)*XMW(1)*3600.0
          KMOLST=REAL(IMOLE)
C
C     COUNT DIRECTS THE PROGRAM TO THE CORRECT EQUATION
C     FOR CONVERSION OF MOLALITY TO FLOW RATE DEPENDING
C     ON ELECTROLYTE TYPE (i.e 1:1,1:2,2:1, OR 2:2)
C
          IF (COUNT.EQ.1) GO TO 310
          IF (COUNT.EQ.2) GO TO 320
          IF (COUNT.EQ.3) GO TO 330

C
C     ASSUMPTION:  COMPLETE IONIZATION OF SALT
C     COUNT=1 REPRESENTS CONVERSION FOR 1:1 ELECTROLYTES
C     (i.e, NACL DECOMPOSES INTO NA+ AND CL-)
C
  310     SOUT1(2)=KMOLST/3600.0
          SOUT1(3)=KMOLST/3600.0
          GO TO 340
```

```
C
C       COUNT=2 REPRESENTS CONVERSION FOR 2:1 ELECTROLYTES
C       (i.e, NA2SO4 DECOMPOSES INTO 2NA+ AND SO4--)
C
  320       SOUT1(2)=2*KMOLST/3600.0
            SOUT1(3)=KMOLST/3600.0
            GO TO 340
C
C       COUNT=3 REPRESENTS CONVERSION FOR 1:2 ELECTROLYTES
C       (i.e, CACL2 DECOMPOSES INTO CA++ AND 2CL-)
  330       SOUT1(2)=KMOLST/3600.0
            SOUT1(3)=2*KMOLST/3600.0
  340       CONTINUE
C
C       CALL ASPEN FLASH ROUTINE TO CALCULATE THE MEAN IONIC
C       ACTIVITY COEFFICIENT OF THE SOLUTION
C
            CALL FLASH(SOUT1,NSUBS,IDXSUB,ITYPE,NBOPS1,2,2,
     1           1,30,1.D-4,TIN,POUT,0.D0,LMSG,LPMSG,IRESTR,
     2           IPASS,RETN,IRETN,LCFLAG)
C
C       CALCULATE MEAN IONIC ACTIVITY COEFFICIENT AND MEAN
C       IONIC MOLALITY
C
            IF (COUNT.EQ.1) GO TO 350
            IF (COUNT.EQ.2) GO TO 360
            IF (COUNT.EQ.3) GO TO 370
  350       VP=1.0
            VM=1.0
            GO TO 380
  360       VP=2.0
            VM=1.0
            GO TO 380
  370       VP=1.0
            VM=2.0
  380       CONTINUE

            MOLP=SOUT1(2)*1000.0*3600.0/KGMH20
            MOLM=SOUT1(3)*1000.0*3600.0/KGMH20
            MOLPM=((MOLP**VP)*(MOLM**VM))
            GAMPM=((EXP(GAMMA(2))**VP)*(EXP(GAMMA(3))**VM))
C
C     CALCULATE SOLUBILITY PRODUCT (Ksp)
C
       KSP=MOLPM*GAMPM

C
C     THIS DATA IS THEN SENT TO A REGRESSION ROUTINE FOR NON-
C     LINEAR INTERPOLATION.
C
```

```
C
C     INSERT WRITE STATEMENTS
C
  300 CONTINUE
      RETURN
      END
```

CRANE CREST

```
      SUBROUTINE USRSOL(NSIN,NINFI,SIN1,SIN2,SIN3,SIN4,
     1  SINFI,NSOUT,NINFO,SOUT1,SOUT2,SOUT3,SOUT4,SINFO,
     2  NSUBS,IDXSUB,ITYPE,NINT,INT,NREAL,REAL,IDS,NPO,
     3  NBOPST,NIW,IW,NW,W,NSIZE,SIZE)
C
C     DESCRIPTION OF VARIABLES IN ARGUMENT LIST
C
C     VAR             DESCRIPTION AND RANGE
C
C     NSIN            NO. INLET STREAMS (MAX=5)
C     NINFI           NO. INLET INFO. STREAMS (0 OR 1)
C     SIN1            INLET STREAM 1
C     SIN2            INLET STREAM 2
C     SIN3            INLET STREAM 3
C     SIN4            INLET STREAM 4
C     SINFI           INLET INFORMATION STREAM
C     NSOUT           NO. OUTLET STREAMS (MAX=5)
C     NINFO           NO. OUTLET INFO. STREAMS (0 OR 1)
C     SOUT1           OUTLET STREAM 1
C     SOUT2           OUTLET STREAM 2
C     SOUT3           OUTLET STREAM 3
C     SOUT4           OUTLET STREAM 4
C     SINFO           OUTLET INFORMATION STREAM
C     NSUBS           NO. SUBSTRMS (ALL STRMS MUST BE SAME!)
C     IDXSUB          INDEX VECTOR OF LENGTH NSUBS
C     ITYPE           SUBSTREAM TYPE VECTOR OF LENGTH NSUBS
C     NINT            LENGTH OF INTEGER ARRAY
C     INT             INTEGER ARRAY
C     NREAL           LENGTH OF REAL ARRAY
C     REAL            REAL ARRAY
C     IDS             ARRAY ID'S TO WRITE TO (HIST/REP FILE)
C     NPO             NO. PHYSICAL PROPERTY OPTION SETS (=2)
C     NBOPST          ARRAY OF PP OPTION SET POINTERS
C     NIN             LENGTH OF INTEGER WORK ARRAY
C     IW              INTEGER WORK ARRAY
C     NW              LENGTH OF REAL WORK ARRAY
C     W               REAL WORK ARRAY
C     NSIZE           LENGTH OF SIZE ARRAY
C     SIZE            SIZE ARRAY
C     ITEMP           POSITION VECTOR
C     IPRES           POSITION VECTOR
C     POUT            OUTLET PRESSURE
C     TIN             INLET TEMPERATURE
C     KGMH2O          WEIGHT OF H2O IN KILOGRAMS
C     KSP             SOLUBILITY PRODUCT
C     DUMMY           DUMMY STREAMS FOR VARIABLE MANIPULATIONS
C
C     DECLARATIONS
C
      IMPLICIT REAL * 8 (A-H,O-Z)
      REAL KGMH2O,KSP1,KSP2,KSP3,KSP4
      REAL KKSP1,KKSP2,KKSP3,KKSP4


C
C     DIMENSIONS
C
      DIMENSION SIN1(1),SIN2(1),SIN3(1),SIN4(1),SINFI(1),
```

```
     1SOUT1(1),SOUT2(1),SOUT3(1),SOUT4(1),SINFO(1),
     2IDXSUB(NSUBS),ITYPE(NSUBS),INT(NINT),REAL(NREAL),
     3EDS(2,13),NBOPST(3,NPO),IW(NIW),W(NW),SIZE(NSIZE),
     4RETN(500),IRETN(7),NBOPS1(3,1),DUMMY(17),DUMMY1(17),
     5DUMMY2(17),DUMMY3(17),DUMMY4(17)
C
CC      COMMONS
C
       COMMON/USER/RMISS,IMISS,NGBAL,IPASS,IRESTR,ICONV,
     1LMSG,LPMSG,KFLAG,NHSTRY,NRPT,NTRMNL,ISIZE
       COMMON/NCOMP/NCC,NNCC
       COMMON/IDSCC/INSCC(2,1)
       COMMON/IDSNCC/IDSNCC(2,1)
       COMMON/IDXCC/IDXCC(1)
       COMMON/IDXNCC/IDXNCC(1)
       COMMON/MW/XMW(1)
       COMMON/RPTGLP/IREPFL,ISUB(10)
       COMMON/CHARGE/CHARGE(1)
       COMMON/DHAQFM/DHAQFM(1)
       COMMON/IONTYP/IONTYP(1)
       COMMON/SO25C/SO25C(1)
       COMMON/GMELCA/GMELCA(1)
       COMMON/GMELCB/GMELCB(1)
       COMMON/GMELCC/GMELCC(1)
       COMMON/GMELCD/GMELCD(1)
       COMMON/GAMMA/GAMMA(1)
       COMMON/GAMUS/GAMUS(1)
       COMMON/GAMMAS/GAMMAS(1)
       COMMON/GAMPC/GAMPC(1)
       COMMON/GAMPC1/GAMPC1(1)
       COMMON/GAMSPC/GAMSPC(1)
       COMMON/VLION/VLION(2,1)
C
CC      EXECUTABLE STATEMENTS AND EXPLANATION OF ACTIONS
C
       N=NCC+9


       DO 200 I=1,3
          NBOPS1(I,1)=NBOPST(I,1)
  200  CONTINUE
       NDATA=INT(1)
       DO 480 I=1,NDATA
C
CC      THESE STATEMENTS INITIALIZE THE VARIABLES
CC      FOR EACH DATA SET
C

          ITEMP=I*2-1
          IPRES=I*2

       SIN3(NCC+1)=0.0
       SIN4(NCC+1)=0.0

       IF(SIN1(NCC+1).EQ.0.0)THEN

          DO 201 J=1,NCC+9
```

```
            SIN1(J)=0.0

201   CONTINUE
      ENDIF

      IF(SIN2(NCC+1).EQ.0.0)THEN

          DO 202 J=1,NCC+9

              SIN2(J)=0.0

202   CONTINUE
      ENDIF

      IF(SIN3(NCC+1).EQ.0.0)THEN

          DO 203 J=1,NCC+9

              SIN3(J)=0.0

203   CONTINUE
      ENDIF

      IF(SIN4(NCC+1).EQ.0.0)THEN

          DO 204 J=1,NCC+9

              SIN4(J)=0.0

204   CONTINUE
      ENDIF

      DO 205 J=NCC+1,NCC+9

              SOUT1(J)=0.0
              SOUT2(J)=0.0
              SOUT3(J)=0.0
              SOUT4(J)=0.0

205   CONTINUE
C
C     READ THE DATA FROM THE ECONOSEED.INP FILE
C
          POUT=REAL(IPRES)
          TIN=REAL(ITEMP)

C
C     LOAD SOLUBILITY PRODUCT PARAMETERS
C
C     K2SO4 PARAMETERS
C
      A1=9.62329E+00
      B1=-5.00291E+03
      C1=1.53550E+00
      D1=-1.94899E-02
C
C     CA(HCOO)2 PARAMETERS
C
```

```
      A2=4.47205E+00
      B2=-1.91144E+03
      C2=1.56345E-02
      D2=-1.15162E-02
C
C     CASO4 PARAMETERS
C
      A3 =-2.22084E+01
      B3 =-7.00252E+02
      C3 = 6.55774E+00
      D3 =-6.24281E-02

C
C     KHCOO PARAMETERS
C
      A4 =-2.04368E+01
      B4 = 6.96256E+03
      C4 =-4.16275E+00
      D4 = 9.75974E-02

C
C     CALCULATE SOLUBILITY PRODUCTS FOR NO PRECIPITATION
C
      KSP1=EXP(A1 + B1/TIN +C1*LOG(TIN) +D1*TIN)
      KSP2=EXP(A2 + B2/TIN +C2*LOG(TIN) +D2*TIN)
      KSP3=EXP(A3 + B3/TIN +C3*LOG(TIN) +D3*TIN)
      KSP4=EXP(A4 + B4/TIN +C4*LOG(TIN) +D4*TIN)
C
C     ADD CONSTITUENTS FOR COMMON ION AFFECT
C
      DO 206 J=1,NCC+1
         DUMMY(J)=SIN1(J)+SIN2(J)+SIN3(J)+SIN4(J)
 206  CONTINUE
      DUMMY(NCC+2)=(SIN1(NCC+2)+SIN2(NCC+2)+SIN3(NCC+2)
     1+SIN4(NCC+2))/NSIN
      DUMMY(NCC+3)=(SIN1(NCC+3)+SIN2(NCC+3)+SIN3(NCC+3)
     1+SIN4(NCC+3))/NSIN
      DUMMY(NCC+4)=(SIN1(NCC+4)+SIN2(NCC+4)+SIN3(NCC+4)
     1+SIN4(NCC+4))
      DUMMY(NCC+5)=(SIN1(NCC+5)+SIN2(NCC+5)+SIN3(NCC+5)
     1+SIN4(NCC+5))/NSIN
      DUMMY(NCC+6)=(SIN1(NCC+6)+SIN2(NCC+6)+SIN3(NCC+6)
     1+SIN4(NCC+6))/NSIN
      DUMMY(NCC+7)=(SIN1(NCC+7)+SIN2(NCC+7)+SIN3(NCC+7)
     1+SIN4(NCC+7))
      DUMMY(NCC+8)=(SIN1(NCC+8)+SIN2(NCC+8)+SIN3(NCC+8)
     1+SIN4(NCC+8))
      DUMMY(NCC+9)=(SIN1(NCC+9)*SIN1(NCC+1)/DUMMY(NCC+1))+
     1(SIN2(NCC+9)*SIN2(NCC+1)/DUMMY(NCC+1))+(SIN3(NCC+9)*
     2SIN3(NCC+1)/DUMMY(NCC+1))+(SIN4(NCC+9)*SIN4(NCC+1)/
     4DUMMY(NCC+1))

C
C     SEPARATE INTO K2SO4 ELECTROLYTE STREAM FOR Ksp FLASH
C     CALCULATIONS
C
```

```
      DUMMY1(1)=DUMMY(1)
      DUMMY1(2)=DUMMY(2)
      DUMMY1(3)=DUMMY(3)
      DO 220 K=1,1000
      DO 210 J=4,N
         DUMMY1(J)=0.0
  210 CONTINUE
      DUMMY1(NCC+1)=DUMMY(1)+DUMMY(2)+DUMMY(3)
      DUMMY1(NCC+2)=DUMMY(NCC+2)
      DUMMY1(NCC+3)=DUMMY(NCC+3)
      DUMMY1(NCC+9)=(DUMMY1(1)*XMW(1)+DUMMY1(2)*XMW(2)+
     1DUMMY1(3)*XMW(3))/DUMMY1(NCC+1)
C
C     CHECK K2SO4 FOR INITIAL PRECIPITATION
C
      CALL FLASH(DUMMY1,NSUBS,IDXSUB,ITYPE,NBOPST,2,2,
     1          KPHASE,30,1.D-4,TIN,POUT,GUESS,LMSG,LPMSG,0,
     2          IPASS,RETN,IRETN,LCFLAG)

      KGMH2O=DUMMY1(1)*XMW(1)/1000.0
      KKSP1=((DUMMY1(2)/KGMH2O)**2.0)*(DUMMY1(3)/KGMH2O)*
     1((EXP(GAMMA(2)))**2.0)*(EXP(GAMMA(3)))

C
C        NO COMMON IONS
C
      IF(SIN3(2).EQ.0.0.AND.(DUMMY(2)/DUMMY(3)).EQ.2)THEN
C
C     SEPARATE OUT PRECIPITATES
C
        IF(KKSP1.GT.KSP1)THEN

          VARIABLE=(KKSP1-KSP1)/KSP1
          IF(VARIABLE.GT.5.0) THEN

            DUMMY1(2)=DUMMY1(2)-0.010
            DUMMY1(3)=DUMMY1(3)-0.005
            SOUT2(2)=SOUT2(2)+0.010
            SOUT2(3)=SOUT2(3)+0.005

          ELSEIF(VARIABLE.LT.5.0)THEN

            IF(VARIABLE.LT.5.0.AND.VARIABLE.GT.0.5)THEN

              DUMMY1(2)=DUMMY1(2)-0.0010
              DUMMY1(3)=DUMMY1(3)-0.0005
              SOUT2(2)=SOUT2(2)+0.0010
              SOUT2(3)=SOUT2(3)+0.0005

            ELSEIF(VARIABLE.LT.0.5)THEN

              DUMMY1(2)=DUMMY1(2)-0.00010
              DUMMY1(3)=DUMMY1(3)-0.00005
              SOUT2(2)=SOUT2(2)+0.00010
              SOUT2(3)=SOUT2(3)+0.00005

            ENDIF
```

```
            ENDIF
C
C       NO PRECIPITATES
C
            ELSEIF(KSP1.GE.KKSP1)THEN

               SOUT1(1)=DUMMY1(1)
               SOUT1(2)=DUMMY1(2)
               SOUT1(3)=DUMMY1(3)

            ENDIF
C
C       COMMON ION AFFECT--FORCED PRECIPITATION
C
        ELSEIF(SIN3(2).GT.0.0.OR.(DUMMY(2)/DUMMY(3).GT.2))THEN
C
C       SEPARATE OUT PRECIPITATES
C
            IF(KKSP1.GT.KSP1)THEN

              DUMMY1(3)=DUMMY1(3)-0.00005
              SOUT2(3)=SOUT2(3)+0.00005
C
C       NO PRECIPITATES
C
            ELSEIF(KSP1.GE.KKSP1)THEN

              SOUT1(1)=DUMMY1(1)
              SOUT1(2)=DUMMY1(2)
              SOUT1(3)=DUMMY1(3)

            ENDIF
        ENDIF
        IF((KKSP1-KSP1).LE.0.0)GO TO 230
  220   CONTINUE
  230   CONTINUE
C
C       SEPARATE INTO CA(HCOO)2 ELECTROLYTE STREAM FOR Ksp
C       FLASH CALCULATIONS
C
        DUMMY2(1)=DUMMY(1)
        DUMMY2(2)=0.0
        DUMMY2(3)=0.0
        DUMMY2(4)=DUMMY(4)
        DUMMY2(5)=DUMMY(5)
        DO 250 K=1,1000
        DO 240 J=6,N
           DUMMY2(J)=0.0
  240   CONTINUE
        DUMMY2(NCC+1)=DUMMY2(1)+DUMMY2(4)+DUMMY2(5)
        DUMMY2(NCC+2)=DUMMY(NCC+2)
        DUMMY2(NCC+3)=DUMMY(NCC+3)
        DUMMY2(NCC+9)=(DUMMY2(1)*XMW(1)+DUMMY2(4)*XMW(4)+
       1DUMMY2(5)*XMW(5))/DUMMY2(NCC+1)
C
C       CHECK CA(HCOO)2 FOR INITIAL PRECIPITATION
C
        CALL FLASH(DUMMY2,NSUBS,IDXSUB,ITYPE,NBOPST,2,2,
```

```
     1          KPHASE,30,1.D-4,TIN,POUT,GUESS,LMSG,LPMSG,0,
     2          IPASS,RETN,IRETN,LCFLAG)

      KGMH2O=DUMMY2(1)*XMW(1)/1000.0
      KKSP2=((DUMMY2(5)/KGMH2O)**2.0)*(DUMMY2(4)/KGMH2O)*
     1((EXP(GAMMA(3)))**2.0)*(EXP(GAMMA(2)))

C
C         NO COMMON IONS
C
      IF(SIN3(5).EQ.0.0.AND.(DUMMY(5)/DUMMY(4)).EQ.2)THEN
C
C     SEPARATE OUT PRECIPITATES
C
         IF(KKSP2.GT.KSP2)THEN

           VARIABLE=(KKSP2-KSP2)/KSP2
           IF(VARIABLE.GT.5.0) THEN

             DUMMY2(5)=DUMMY2(5)-0.010
             DUMMY2(4)=DUMMY2(4)-0.005
             SOUT2(5)=SOUT2(5)+0.010
             SOUT2(4)=SOUT2(4)+0.005

           ELSEIF(VARIABLE.LT.5.0)THEN

             IF(VARIABLE.LT.5.0.AND.VARIABLE.GT.0.5)THEN

               DUMMY2(5)=DUMMY2(5)-0.0010
               DUMMY2(4)=DUMMY2(4)-0.0005
               SOUT2(5)=SOUT2(5)+0.0010
               SOUT2(4)=SOUT2(4)+0.0005


             ELSEIF(VARIABLE.LT.0.5)THEN

               DUMMY2(5)=DUMMY2(5)-0.00010
               DUMMY2(4)=DUMMY2(4)-0.00005
               SOUT2(5)=SOUT2(5)+0.00010
               SOUT2(4)=SOUT2(4)+0.00005

             ENDIF

           ENDIF


C
C     NO PRECIPITATES
C
         ELSEIF(KSP2.GE.KKSP2)THEN

            SOUT1(4)=DUMMY2(4)
            SOUT1(5)=DUMMY2(5)

         ENDIF
C
C     COMMON ION AFFECT FORCED PRECIPITATION
C
```

```
      ELSEIF(SIN3(5).GT.0.0.OR.(DUMMY(5)/DUMMY(4).GT.2))THEN
C
CC    SEPARATE OUT PRECIPITATES
C
          IF(KKSP2.GT.KSP2)THEN

            DUMMY2(4)=DUMMY2(4)-0.00005
            SOUT2(4)=SOUT2(4)+0.00005
C
CC    NO PRECIPITATES
C
          ELSEIF(KSP2.GE.KKSP2)THEN

            SOUT1(4)=DUMMY2(4)
            SOUT1(5)=DUMMY2(5)

          ENDIF
      ENDIF
      IF((KKSP2-KSP2).LE.0.0)GO TO 260
  250 CONTINUE
  260 CONTINUE
C
CC    THE REMAINING WATER SOLUBLE IONS UNDERGO THE
CC    FOLLOWING REACTION.  ASSUMPTION 100% CONVERSION
C
CC       K2SO4 +CA(HCOO)2 ----> CASO4 + 2KHCOO
C
CC    DETERMINE IF THE CASO4 REACTANT IS WATER SOLUBLE
C
      DUMMY3(1)=SOUT1(1)
      DUMMY3(2)=0.0
      DUMMY3(3)=SOUT1(3)
      DUMMY3(4)=SOUT1(4)
      DUMMY3(5)=0.0
      DO 280 K=1,10000
      DO 270 J=6,N
         DUMMY3(J)=0.0
  270 CONTINUE
      DUMMY3(NCC+1)=DUMMY3(1)+DUMMY3(4)+DUMMY3(3)
      DUMMY3(NCC+2)=DUMMY(NCC+2)
      DUMMY3(NCC+3)=DUMMY(NCC+3)
      DUMMY3(NCC+9)=(DUMMY3(1)*XMW(1)+DUMMY3(4)*XMW(4)+
     1DUMMY3(3)*XMW(3))/DUMMY3(NCC+1)
C
CC    CHECK CASO4 FOR PRECIPITATION
C

      IF(DUMMY3(3).LE.1.0E-6.OR.DUMMY3(4).LE.1.0E-6)THEN

        SOUT1(1)=DUMMY3(1)
        SOUT1(3)=DUMMY3(3)
        SOUT1(4)=DUMMY3(4)
        GO TO 290

      ELSEIF(DUMMY3(3).GE.1.0E-5.OR.DUMMY3(4).GE.1.0E-5)THEN


          KGMH2O=DUMMY3(1)*XMW(1)/1000.0
```

```
            KKSP3=(DUMMY3(3)/KGMH2O)*(DUMMY3(4)/KGMH2O)
C
C       SEPARATE OUT PRECIPITATES
C
          IF(KKSP3.GT.KSP3)THEN

            VARIABLE=(KKSP3-KSP3)/KSP3
            IF(VARIABLE.GT.5.0) THEN

              DUMMY3(3)=DUMMY3(3)-0.0010
              DUMMY3(4)=DUMMY3(4)-0.0010
              SOUT3(3)=SOUT3(3)+0.0010
              SOUT3(4)=SOUT3(4)+0.0010

            ELSEIF(VARIABLE.LT.5.0)THEN

              IF(VARIABLE.LT.5.0.AND.VARIABLE.GT.0.5)THEN

                DUMMY3(3)=DUMMY3(3)-0.00010
                DUMMY3(4)=DUMMY3(4)-0.00010
                SOUT3(3)=SOUT3(3)+0.00010
                SOUT3(4)=SOUT3(4)+0.00010


              ELSEIF(VARIABLE.LT.0.5)THEN

                DUMMY3(3)=DUMMY3(3)-0.000010
                DUMMY3(4)=DUMMY3(4)-0.000010
                SOUT3(3)=SOUT3(3)+0.000010
                SOUT3(4)=SOUT3(4)+0.000010


              ENDIF

            ENDIF


C
C       NO PRECIPITATES
C
          ELSEIF(KSP3.GE.KKSP3)THEN

             SOUT1(1)=DUMMY3(1)
             SOUT1(3)=DUMMY3(3)
             SOUT1(4)=DUMMY3(4)

          ENDIF
        ENDIF
        IF((KKSP3-KSP3).LE.0.0)GO TO 290
 280    CONTINUE
 290    CONTINUE

C
C       DETERMINE IF THE KHCOO REACTANT IS WATER SOLUBLE
C
        DUMMY4(1)=SOUT1(1)
        DUMMY4(2)=SOUT1(2)
```

```
      DUMMY4(3)=0.0
      DUMMY4(4)=0.0
      DUMMY4(5)=SOUT1(5)
      DO 310 K=1,10000
      DO 300 J=6,N
         DUMMY4(J)=0.0
  300 CONTINUE
      DUMMY4(NCC+1)=DUMMY4(1)+DUMMY4(2)+DUMMY4(5)
      DUMMY4(NCC+2)=DUMMY(NCC+2)
      DUMMY4(NCC+3)=DUMMY(NCC+3)
      DUMMY4(NCC+9)=(DUMMY4(1)*XMW(1)+DUMMY4(2)*XMW(2)+
     1DUMMY4(5)*XMW(5))/DUMMY4(NCC+1)
C
C     CHECK KHCOO FOR PRECIPITATION
C
      CALL FLASH(DUMMY4,NSUBS,IDXSUB,ITYPE,NBOPST,2,2,
     1          KPHASE,30,1.D-4,TIN,POUT,GUESS,LMSG,LPMSG,0,
     2          IPASS,RETN,IRETN,LCFLAG)

      KGMH2O=DUMMY4(1)*XMW(1)/1000.0
      KKSP4=(DUMMY4(5)/KGMH2O)*(DUMMY4(2)/KGMH2O)*
     1(EXP(GAMMA(3)))*(EXP(GAMMA(2)))


C
C     SEPARATE OUT PRECIPITATES
C
      IF(KKSP4.GT.KSP4)THEN

           VARIABLE=(KKSP4-KSP4)/KSP4
           IF(VARIABLE.GT.5.0) THEN

             DUMMY4(2)=DUMMY4(4)-0.0010
             DUMMY4(5)=DUMMY4(5)-0.0010
             SOUT3(2)=SOUT3(2)+0.0010
             SOUT3(5)=SOUT3(5)+0.0010

           ELSEIF(VARIABLE.LT.5.0)THEN

             IF(VARIABLE.LT.5.0.AND.VARIABLE.GT.0.5)THEN

               DUMMY4(2)=DUMMY4(4)-0.00010
               DUMMY4(5)=DUMMY4(5)-0.00010
               SOUT3(2)=SOUT3(2)+0.00010
               SOUT3(5)=SOUT3(5)+0.00010

             ELSEIF(VARIABLE.LT.0.5)THEN

               DUMMY4(2)=DUMMY4(4)-0.000010
               DUMMY4(5)=DUMMY4(5)-0.000010
               SOUT3(2)=SOUT3(2)+0.000010
               SOUT3(5)=SOUT3(5)+0.000010


             ENDIF

           ENDIF
```

```
C
C       NO PRECIPITATES
C
        ELSEIF(KSP4.GE.KKSP4)THEN


          SOUT1(2)=DUMMY4(2)
          SOUT1(5)=DUMMY4(5)

        ENDIF
        IF((KKSP2-KSP2).LE.0.0)GO TO 320
  310   CONTINUE
  320   CONTINUE
  400   CONTINUE
C
C       SUM UP VARIABLES FOR RETURN TO ASPEN INPUT FILE
C
        DO 410 J=1,NCC

           SOUT1(NCC+1)=SOUT1(NCC+1)+SOUT1(J)
           SOUT2(NCC+1)=SOUT2(NCC+1)+SOUT2(J)
           SOUT3(NCC+1)=SOUT3(NCC+1)+SOUT3(J)
           SOUT4(NCC+1)=SOUT4(NCC+1)+SOUT4(J)

  410   CONTINUE


C
C       CALCULATE EXIT TEMPERATURE
C
           SOUT1(NCC+2)=SIN1(NCC+2)
           SOUT2(NCC+2)=SIN1(NCC+2)
           SOUT3(NCC+2)=SIN1(NCC+2)

C
C       CALCULATE EXIT PRESSURE
C
           SOUT1(NCC+3)=SIN1(NCC+3)
           SOUT2(NCC+3)=SIN1(NCC+3)
           SOUT3(NCC+3)=SIN1(NCC+3)

C
C       CALCULATE AVERAGE MOLECULAR WEIGHTS
C
        IF(SOUT1(NCC+1).EQ.0.0)GO TO 420
        SOUT1(NCC+9)=(SOUT1(1)*XMW(1) + SOUT1(2)*XMW(2) +
       1SOUT1(3)*XMW(3) + SOUT1(4)*XMW(4) + SOUT1(5)*XMW(5) +
       2SOUT1(6)*XMW(6) + SOUT1(7)*XMW(7) + SOUT1(8)*XMW(8))/
       3SOUT1(NCC+1)
  420   CONTINUE

        IF(SOUT2(NCC+1).EQ.0.0)GO TO 430
        SOUT2(NCC+9)=(SOUT2(1)*XMW(1) + SOUT2(2)*XMW(2) +
       1SOUT2(3)*XMW(3) + SOUT2(4)*XMW(4) + SOUT2(5)*XMW(5) +
       2SOUT2(6)*XMW(6) + SOUT2(7)*XMW(7) + SOUT2(8)*XMW(8))/
       3SOUT2(NCC+1)
  430   CONTINUE
```

```
      IF(SOUT3(NCC+1).EQ.0.0)GO TO 440
      SOUT3(NCC+9)=(SOUT3(1)*XMW(1) + SOUT3(2)*XMW(2) +
     1SOUT3(3)*XMW(3) + SOUT3(4)*XMW(4) + SOUT3(5)*XMW(5) +
     2SOUT3(6)*XMW(6) + SOUT3(7)*XMW(7) + SOUT3(8)*XMW(8))/
     3SOUT3(NCC+1)
 440  CONTINUE

C
C     CALCULATE SPECIFIC ENTHALPY---CONVERT TO WATTS
C
      DUMMY(NCC+4)=SIN1(NCC+4)*SIN1(NCC+1)*SIN1(NCC+9)+
     1SIN2(NCC+4)*SIN2(NCC+1)*SIN2(NCC+9)+SIN3(NCC+4)*
     2SIN3(NCC+1)*SIN3(NCC+9)+SIN4(NCC+4)*SIN4(NCC+1)*
     3SIN4(NCC+9)+SINFI(1)

      IF(SOUT1(NCC+1).EQ.0.0)THEN
        GO TO 450
      ELSEIF(SOUT1(NCC+1).GT.0.0)THEN
        SOUT1(NCC+4)=(DUMMY(NCC+4)*SOUT1(NCC+1)/DUMMY(NCC+1))/
     1(SOUT1(NCC+1)*SOUT1(NCC+9))
      ENDIF
 450  CONTINUE

      IF(SOUT2(NCC+1).EQ.0.0)THEN
        GO TO 460
      ELSEIF(SOUT2(NCC+1).GT.0.0)THEN
        SOUT2(NCC+4)=(DUMMY(NCC+4)*SOUT2(NCC+1)/DUMMY(NCC+1))/
     1(SOUT2(NCC+1)*SOUT2(NCC+9))
      ENDIF
 460  CONTINUE

      IF(SOUT3(NCC+1).EQ.0.0)THEN
        GO TO 470
      ELSEIF(SOUT3(NCC+1).GT.0.0)THEN
        SOUT3(NCC+4)=(DUMMY(NCC+4)*SOUT3(NCC+1)/DUMMY(NCC+1))/
     1(SOUT3(NCC+1)*SOUT3(NCC+9))
      ENDIF
 470  CONTINUE
C
C     DETERMINE MOLAR VAPOR FRACTION
C
      SOUT1(NCC+5)=0.0
      SOUT2(NCC+5)=0.0
      SOUT3(NCC+5)=0.0
      SOUT4(NCC+5)=0.0
C
C     DETERMINE MOLAR LIQUID FRACTION
      SOUT1(NCC+6)=1.0
      SOUT2(NCC+5)=0.0
      SOUT3(NCC+5)=0.0
      SOUT4(NCC+5)=0.0

 480  CONTINUE
      RETURN
      END
```

```
C
C     THIS BLOCK SETS THE TEMPERATURE FOR THE HEAT EXCHANGER
C     IN BLOCK H2.  IF TOO MUCH HEAT IS ADDED THEN THE
C     DESIRED PRODUCT (POTASSIUM FORMATE) WILL PRECIPITATE
C     OUT OF SOLUTION.
C

      SUBROUTINE USRFLH(NSIN,NINFI,SIN1,SIN2,SIN3,SIN4,
     1  SINFI,NSOUT,NINFO,SOUT1,SOUT2,SOUT3,SOUT4,SINFO,
     2  NSUBS,IDXSUB,ITYPE,NINT,INT,NREAL,REAL,IDS,NPO,
     3  NBOPST,NIW,IW,NW,W,NSIZE,SIZE)
C
C     DESCRIPTION OF VARIABLES IN ARGUMENT LIST
C
C     VAR             DESCRIPTION AND RANGE
C
C     NSIN            NO. INLET STREAMS (MAX=5)
C     NINFI           NO. INLET INFO. STREAMS (0 OR 1)
C     SIN1            INLET STREAM 1
C     SIN2            INLET STREAM 2
C     SIN3            INLET STREAM 3
C     SIN4            INLET STREAM 4
C     SINFI           INLET INFORMATION STREAM
C     NSOUT           NO. OUTLET STREAMS (MAX=5)
C     NINFO           NO. OUTLET INFO. STREAMS (0 OR 1)
C     SOUT1           OUTLET STREAM 1
C     SOUT2           OUTLET STREAM 2
C     SOUT3           OUTLET STREAM 3
C     SOUT4           OUTLET STREAM 4
C     SINFO           OUTLET INFORMATION STREAM
C     NSUBS           NO. SUBSTRMS (ALL STRMS MUST BE SAME!)
C     IDXSUB          INDEX VECTOR OF LENGTH NSUBS
C     ITYPE           SUBSTREAM TYPE VECTOR OF LENGTH NSUBS
C     NINT            LENGTH OF INTEGER ARRAY
C     INT             INTEGER ARRAY
C     NREAL           LENGTH OF REAL ARRAY
C     REAL            REAL ARRAY
C     IDS             ARRAY ID'S TO WRITE TO (HIST/REP FILE)
C     NPO             NO. PHYSICAL PROPERTY OPTION SETS (=2)
C     NBOPST          ARRAY OF PP OPTION SET POINTERS
C     NIN             LENGTH OF INTEGER WORK ARRAY
C     IW              INTEGER WORK ARRAY
C     NW              LENGTH OF REAL WORK ARRAY
C     W               REAL WORK ARRAY
C     NSIZE           LENGTH OF SIZE ARRAY
C     SIZE            SIZE ARRAY
C     ITEMP           POSITION VECTOR
C     IPRES           POSITION VECTOR
C     POUT            OUTLET PRESSURE
C     TIN             INLET TEMPERATURE
C     KGMH2O          WEIGHT OF H2O IN KILOGRAMS
C     KSP             SOLUBILITY PRODUCT
C     DUMMY           DUMMY STREAMS FOR VARIABLE MANIPULATIONS
C
C     DECLARATIONS
C
      IMPLICIT REAL * 8 (A-H,O-Z)
      REAL KGMH2O,KSP1,KSP2,KSP3,KSP4
```

```
      REAL KKSP1,KKSP2,KKSP3,KKSP4

C
CC     DIMENSIONS
C
       DIMENSION SIN1(1),SIN2(1),SIN3(1),SIN4(1),SINFI(1),
     1SOUT1(1),SOUT2(1),SOUT3(1),SOUT4(1),SINFO(1),
     2IDXSUB(NSUBS),ITYPE(NSUBS),INT(NINT),REAL(NREAL),
     3EDS(2,13),NBOPST(3,NPO),IW(NIW),W(NW),SIZE(NSIZE),
     4RETN(500),IRETN(7),NBOPS1(3,1),DUMMY(17),DUMMY1(17),
     5DUMMY2(17),DUMMY3(17),DUMMY4(17)
C
CC     COMMONS
C
       COMMON/USER/RMISS,IMISS,NGBAL,IPASS,IRESTR,ICONV,
     1LMSG,LPMSG,KFLAG,NHSTRY,NRPT,NTRMNL,ISIZE
       COMMON/NCOMP/NCC,NNCC
       COMMON/IDSCC/INSCC(2,1)
       COMMON/IDSNCC/IDSNCC(2,1)
       COMMON/IDXCC/IDXCC(1)
       COMMON/IDXNCC/IDXNCC(1)
       COMMON/MW/XMW(1)
       COMMON/RPTGLP/IREPFL,ISUB(10)
       COMMON/CHARGE/CHARGE(1)
       COMMON/DHAQFM/DHAQFM(1)
       COMMON/IONTYP/IONTYP(1)
       COMMON/S025C/S025C(1)
       COMMON/GMELCA/GMELCA(1)
       COMMON/GMELCB/GMELCB(1)
       COMMON/GMELCC/GMELCC(1)
       COMMON/GMELCD/GMELCD(1)
       COMMON/GAMMA/GAMMA(1)
       COMMON/GAMUS/GAMUS(1)
       COMMON/GAMMAS/GAMMAS(1)
       COMMON/GAMPC/GAMPC(1)
       COMMON/GAMPC1/GAMPC1(1)
       COMMON/GAMSPC/GAMSPC(1)
       COMMON/VLION/VLION(2,1)
C
CC     EXECUTABLE STATEMENTS AND EXPLANATION OF ACTIONS
C
       N=NCC+9


       DO 200 I=1,3
          NBOPS1(I,1)=NBOPST(I,1)
  200  CONTINUE
       NDATA=INT(1)
       DO 480 I=1,NDATA
C
CC     THESE STATEMENTS INITIALIZE THE VARIABLES
CC     FOR EACH DATA SET
C

          ITEMP=I*2-1
          IPRES=I*2
```

```
      IF(SIN1(NCC+1).EQ.0.0)THEN
          DO 201 J=NCC+1,NCC+9
             SIN1(J)=0.0
  201 CONTINUE
      ENDIF
      IF(SIN2(NCC+1).EQ.0.0)THEN
          DO 202 J=NCC+1,NCC+9
             SIN2(J)=0.0
  202 CONTINUE
      ENDIF
      IF(SIN3(NCC+1).EQ.0.0)THEN
          DO 203 J=NCC+1,NCC+9
             SIN3(J)=0.0
  203 CONTINUE
      ENDIF
      IF(SIN4(NCC+1).EQ.0.0)THEN
          DO 204 J=NCC+1,NCC+9
             SIN4(J)=0.0
  204 CONTINUE
      ENDIF
      DO 205 J=NCC+1,NCC+9
             SOUT1(J)=0.0
             SOUT2(J)=0.0
             SOUT3(J)=0.0
             SOUT4(J)=0.0
  205 CONTINUE
C
C     READ THE DATA FROM THE ECONOSEED.INP FILE
C
          POUT=REAL(IPRES)
          TIN=REAL(ITEMP)
C
C     LOAD SOLUBILITY PRODUCT PARAMETERS
C
C
C     CASO4 PARAMETERS
C
      A3 =-2.22084E+01
```

```
      B3 =-7.00252E+02
      C3 = 6.55774E+00
      D3 =-6.24281E-02

C
C     KHCOO PARAMETERS
C

      A4 =-2.04368E+01
      B4 = 6.96256E+03
      C4 =-4.16275E+00
      D4 = 9.75974E-02

C
C     CALCULATE SOLUBILITY PRODUCTS FOR NO PRECIPITATION
C

      KSP3=EXP(A3 + B3/TIN +C3*LOG(TIN) +D3*TIN)
      KSP4=EXP(A4 + B4/TIN +C4*LOG(TIN) +D4*TIN)
C
C     SEPARATE VAPOR AND LIQUID STREAMS
C
      SOUT2(1)=SIN1(NCC+1)*SIN1(NCC+5)
      SOUT1(1)=SIN1(1)-SOUT2(1)

C
C     DETERMINE IF THE CASO4 REACTANT IS WATER SOLUBLE
C
      DUMMY3(1)=SOUT1(1)
      DUMMY3(2)=0.0
      DUMMY3(3)=SIN1(3)
      DUMMY3(4)=SIN1(4)
      DUMMY3(5)=0.0
      DO 280 K=1,10000
      DO 270 J=6,N
         DUMMY3(J)=0.0
 270  CONTINUE
C
C     THIS NEXT SECTION REMOVES THE INFINITE AMOUNT OF CASO4
C     THAT REMAINS SOLUBLE IN WATER AT ANY TEMPERATURE.
C     INSIGNIFANT FOR THIS SIMULATION
C
      IF(DUMMY3(3).LE.1E-4.AND.DUMMY3(4).LE.1E-4)THEN

        SOUT3(3)=SOUT3(3)+DUMMY3(3)
        SOUT3(4)=SOUT3(4)+DUMMY3(4)
        SOUT1(3)=0.0
        SOUT1(4)=0.0
        GO TO 290

      ENDIF
      DUMMY3(NCC+1)=DUMMY3(1)+DUMMY3(4)+DUMMY3(3)
      DUMMY3(NCC+2)=SIN1(NCC+2)
      DUMMY3(NCC+3)=SIN1(NCC+3)
      DUMMY3(NCC+9)=(DUMMY3(1)*XMW(1)+DUMMY3(4)*XMW(4)+
     1DUMMY3(3)*XMW(3))/DUMMY3(NCC+1)
C
C     CHECK CASO4 FOR PRECIPITATION
```

```
C
      IF(DUMMY3(3).LE.1.0E-6.OR.DUMMY3(4).LE.1.0E-6)THEN

        SOUT1(1)=DUMMY3(1)
        SOUT1(3)=DUMMY3(3)
        SOUT1(4)=DUMMY3(4)
        GO TO 290

      ELSEIF(DUMMY3(3).GE.1.0E-5.OR.DUMMY3(4).GE.1.0E-5)THEN


          KGMH20=DUMMY3(1)*XMW(1)/1000.0
          KKSP3=(DUMMY3(3)/KGMH20)*(DUMMY3(4)/KGMH20)
C
C     SEPARATE OUT PRECIPITATES
C
         IF(KKSP3.GT.KSP3)THEN

          VARIABLE=(KKSP3-KSP3)/KSP3
           IF(VARIABLE.GT.5.0)  THEN

            DUMMY3(3)=DUMMY3(3)-0.00010
            DUMMY3(4)=DUMMY3(4)-0.00010
            SOUT3(3)=SOUT3(3)+0.00010
            SOUT3(4)=SOUT3(4)+0.00010

           ELSEIF(VARIABLE.LT.5.0)THEN

            IF(VARIABLE.LT.5.0.AND.VARIABLE.GT.0.5)THEN

              DUMMY3(3)=DUMMY3(3)-0.000010
              DUMMY3(4)=DUMMY3(4)-0.000010
              SOUT3(3)=SOUT3(3)+0.000010
              SOUT3(4)=SOUT3(4)+0.000010


            ELSEIF(VARIABLE.LT.0.5)THEN

              DUMMY3(3)=DUMMY3(3)-0.0000010
              DUMMY3(4)=DUMMY3(4)-0.0000010
              SOUT3(3)=SOUT3(3)+0.0000010
              SOUT3(4)=SOUT3(4)+0.0000010


            ENDIF

           ENDIF


C
C     NO PRECIPITATES
C
         ELSEIF(KSP3.GE.KKSP3)THEN

           SOUT1(1)=DUMMY3(1)
           SOUT1(3)=DUMMY3(3)
           SOUT1(4)=DUMMY3(4)
```

```
         ENDIF
       ENDIF
       IF((KKSP3-KSP3).LE.0.0)GO TO 290
 280   CONTINUE
 290   CONTINUE

C
C      DETERMINE IF THE KHCOO REACTANT IS WATER SOLUBLE
C
       DUMMY4(1)=SOUT1(1)
       DUMMY4(2)=SIN1(2)
       DUMMY4(3)=0.0
       DUMMY4(4)=0.0
       DUMMY4(5)=SIN1(5)
       DO 310 K=1,100000
       DO 300 J=6,N
          DUMMY4(J)=0.0
 300   CONTINUE
       DUMMY4(NCC+1)=DUMMY4(1)+DUMMY4(2)+DUMMY4(5)
       DUMMY4(NCC+2)=SIN1(NCC+2)
       DUMMY4(NCC+3)=SIN1(NCC+3)
       DUMMY4(NCC+9)=(DUMMY4(1)*XMW(1)+DUMMY4(2)*XMW(2)+
      1DUMMY4(5)*XMW(5))/DUMMY4(NCC+1)
C
C      CHECK KHCOO FOR PRECIPITATION
C
       CALL FLASH(DUMMY4,NSUBS,IDXSUB,ITYPE,NBOPST,2,2,
      1          KPHASE,30,1.D-4,TIN,POUT,GUESS,LMSG,LPMSG,0,
      2          IPASS,RETN,IRETN,LCFLAG)

       KGMH2O=DUMMY4(1)*XMW(1)/1000.0
       KKSP4=(DUMMY4(5)/KGMH2O)*(DUMMY4(2)/KGMH2O)*
      1(EXP(GAMMA(3)))*(EXP(GAMMA(2)))


C
C      SEPARATE OUT PRECIPITATES
C
       IF(KKSP4.GT.KSP4)THEN

            VARIABLE=(KKSP4-KSP4)/KSP4
            IF(VARIABLE.GT.5.0)  THEN

              DUMMY4(2)=DUMMY4(2)-0.0010
              DUMMY4(5)=DUMMY4(5)-0.0010
              SOUT3(2)=SOUT3(2)+0.0010
              SOUT3(5)=SOUT3(5)+0.0010

            ELSEIF(VARIABLE.LT.5.0)THEN

              IF(VARIABLE.LT.5.0.AND.VARIABLE.GT.0.5)THEN

                DUMMY4(2)=DUMMY4(2)-0.00010
                DUMMY4(5)=DUMMY4(5)-0.00010
                SOUT3(2)=SOUT3(2)+0.00010
                SOUT3(5)=SOUT3(5)+0.00010
```

```
                ELSEIF(VARIABLE.LT.0.5)THEN

                  DUMMY4(2)=DUMMY4(2)-0.000010
                  DUMMY4(5)=DUMMY4(5)-0.000010
                  SOUT3(2)=SOUT3(2)+0.000010
                  SOUT3(5)=SOUT3(5)+0.000010


                ENDIF

              ENDIF


C
C       NO PRECIPITATES
C
        ELSEIF(KSP4.GE.KKSP4)THEN


          SOUT1(2)=DUMMY4(2)
          SOUT1(5)=DUMMY4(5)

        ENDIF
        IF((KKSP4-KSP4).LE.0.0)GO TO 320
  310   CONTINUE
  320   CONTINUE
  400   CONTINUE
C
C       SUM UP VARIABLES FOR RETURN TO ASPEN INPUT FILE
C
        DO 410 J=1,NCC

            SOUT1(NCC+1)=SOUT1(NCC+1)+SOUT1(J)
            SOUT2(NCC+1)=SOUT2(NCC+1)+SOUT2(J)
            SOUT3(NCC+1)=SOUT3(NCC+1)+SOUT3(J)
            SOUT4(NCC+1)=SOUT4(NCC+1)+SOUT4(J)

  410   CONTINUE


C
C       CALCULATE EXIT TEMPERATURE
C
            SOUT1(NCC+2)=SIN1(NCC+2)
            SOUT2(NCC+2)=SIN1(NCC+2)
            SOUT3(NCC+2)=SIN1(NCC+2)

C
C       CALCULATE EXIT PRESSURE
C
            SOUT1(NCC+3)=SIN1(NCC+3)
            SOUT2(NCC+3)=SIN1(NCC+3)
            SOUT3(NCC+3)=SIN1(NCC+3)

C
C       CALCULATE AVERAGE MOLECULAR WEIGHTS
C
        IF(SOUT1(NCC+1).EQ.0.0)GO TO 420
```

```
      SOUT1(NCC+9)=(SOUT1(1)*XMW(1) + SOUT1(2)*XMW(2) +
     1SOUT1(3)*XMW(3) + SOUT1(4)*XMW(4) + SOUT1(5)*XMW(5) +
     2SOUT1(6)*XMW(6) + SOUT1(7)*XMW(7) + SOUT1(8)*XMW(8))/
     3SOUT1(NCC+1)
  420 CONTINUE

      IF(SOUT2(NCC+1).EQ.0.0)GO TO 430
      SOUT2(NCC+9)=(SOUT2(1)*XMW(1) + SOUT2(2)*XMW(2) +
     1SOUT2(3)*XMW(3) + SOUT2(4)*XMW(4) + SOUT2(5)*XMW(5) +
     2SOUT2(6)*XMW(6) + SOUT2(7)*XMW(7) + SOUT2(8)*XMW(8))/
     3SOUT2(NCC+1)
  430 CONTINUE

      IF(SOUT3(NCC+1).EQ.0.0)GO TO 440
      SOUT3(NCC+9)=(SOUT3(1)*XMW(1) + SOUT3(2)*XMW(2) +
     1SOUT3(3)*XMW(3) + SOUT3(4)*XMW(4) + SOUT3(5)*XMW(5) +
     2SOUT3(6)*XMW(6) + SOUT3(7)*XMW(7) + SOUT3(8)*XMW(8))/
     3SOUT3(NCC+1)
  440 CONTINUE

C
C     CALCULATE SPECIFIC ENTHALPY---CONVERT TO WATTS
C
      DUMMY(NCC+4)=SIN1(NCC+4)*SIN1(NCC+1)*SIN1(NCC+9)+
     1SIN2(NCC+4)*SIN2(NCC+1)*SIN2(NCC+9)+SIN3(NCC+4)*
     2SIN3(NCC+1)*SIN3(NCC+9)+SIN4(NCC+4)*SIN4(NCC+1)*
     3SIN4(NCC+9)+SINFI(1)

      IF(SOUT1(NCC+1).EQ.0.0)THEN
        GO TO 450
      ELSEIF(SOUT1(NCC+1).GT.0.0)THEN
        SOUT1(NCC+4)=(DUMMY(NCC+4)*SOUT1(NCC+1)/SIN1(NCC+1))/
     1(SOUT1(NCC+1)*SOUT1(NCC+9))
      ENDIF
  450 CONTINUE

      IF(SOUT2(NCC+1).EQ.0.0)THEN
        GO TO 460
      ELSEIF(SOUT2(NCC+1).GT.0.0)THEN
        SOUT2(NCC+4)=(DUMMY(NCC+4)*SOUT2(NCC+1)/SIN1(NCC+1))/
     1(SOUT2(NCC+1)*SOUT2(NCC+9))
      ENDIF
  460 CONTINUE

      IF(SOUT3(NCC+1).EQ.0.0)THEN
        GO TO 470
      ELSEIF(SOUT3(NCC+1).GT.0.0)THEN
        SOUT3(NCC+4)=(DUMMY(NCC+4)*SOUT3(NCC+1)/SIN1(NCC+1))/
     1(SOUT3(NCC+1)*SOUT3(NCC+9))
      ENDIF
  470 CONTINUE
C
C     DETERMINE MOLAR VAPOR FRACTION
C
      SOUT1(NCC+5)=0.0
      SOUT2(NCC+5)=1.0
      SOUT3(NCC+5)=0.0
      SOUT4(NCC+5)=0.0
```

```
C
C       DETERMINE MOLAR LIQUID FRACTION
C
        SOUT1(NCC+6)=1.0
        SOUT2(NCC+6)=0.0
        SOUT3(NCC+6)=0.0
        SOUT4(NCC+6)=0.0

 480    CONTINUE
        RETURN
        END
```

CRANES CREST

APPENDIX C

REGRESSION ANALYSIS

CRANES CREST

```
c
c       REGRESSION FORTRAN PROGRAM
c
c
c       This is a program that will regress the non-linear
c       Solubility Product of various electrolytes in water.
c       The data is entered through an auxiliary file named
c       for100.dat.  When the program is run the number of
c       data points to be read is entered interactively.
c
        dimension x(20),s(20),t(20),b(20,20),y(300),z(300)
        dimension pd(300)
        dimension y1(300),y2(300),y3(300),y4(300),y5(300)
        integer v
        type *,'Number of Data Points'
        accept 100,n
  100   format(I5)
        v=3
        x(1)=1.0
        do 200 i=1,n
           open(unit=2,name='for100.dat',type='old')
           read(2,*)y(i),PD(I)
           z(i)=log(pd(i))
  200   continue
        do 300 i=1,n
           x(2)=1./y(i)*1000.
           x(3)=log(y(i))
           x(4)=y(i)/100.
           x(v+2)=z(i)
           do 400 k=1,v+1
              do 500 l=1,v+2
                 b(k,l)=b(k,l)+x(k)*x(l)
                 s(k)=b(k,v+2)
  500         continue
  400      continue
           s(v+2)=s(v+2)+x(v+2)*x(v+2)
  300   continue
        do 600 i=2,v+1
           t(i)=b(1,i)
  600   continue
        do 700 i=1,v+1
           j=i
  800      if(b(j,i).ne.0)go to 900
           j=j+1
           if(j.le.v+1)go to 800
           write(106,150)
  150      format('no unique solution!!!')
           go to 1700
  900      do 1000 k=1,v+2
              bb=b(i,k)
```

```
                b(i,k)=b(j,k)
                b(j,k)=bb
1000          continue
              zz=1./b(i,i)
              do 1100 k=1,v+2
                b(i,k)=zz*b(i,k)
1100          continue
              do 1200 j=1,v+1
                if(j.eq.i)go to 1200
                zz=-b(j,i)
                do 1300 k=1,v+2
                  b(j,k)=b(j,k)+zz*b(i,k)
1300            continue
1200          continue
 700       continue
           write(106,250)
 250       format(10x,' EQUATION COEFFICIENTS:')
           write(106,*)'  '
           write(106,*)'  '
           write(106,350)b(1,v+2)
 350       format(10x,'A =',1pe12.5)
           write(106,351)(b(2,v+2)*1000.0)
 351       format(10x,'B =',1pe12.5)
           write(106,352)b(3,v+2)
 352       format(10x,'C =',1pe12.5)
           write(106,353)(b(4,v+2)/100.0)
 353       format(10x,'D =',1pe12.5)
           write(106,*)'  '
           write(106,850)
 850       format('  interpolation ',/,5x,
     1' Temp (k)    Exp.    Cal.       % difference'
     2,/,'          ln(ksp) ln(ksp)')
           do 1600 i=1,n
              tt=y(i)
              xx=b(1,v+2)+b(2,v+2)*1000./tt+b(3,v+2)
     1*log(tt)+b(4,v+2)*tt/100.
              q=((z(i)-xx)/z(i))*100.
              write(106,950)tt,z(i),xx,q
 950          format(7x,f10.2,7x,f10.4,7x,f10.4,7x,f10.4)
1600       continue
1700       stop
           end
```

TABLE C.1: REGRESSION ANALYSIS FOR CA(HCOO)2-WATER SOLUTIONS

INTERPOLATION:

TEMPERATURE(K)	ln (Ksp) Experimental	ln (Ksp) Regressed	% Difference
293.15	-5.33	-5.33	-0.04
313.15	-5.15	-5.14	0.06
333.15	-5.01	-5.01	0.05
353.15	-4.90	-4.91	-0.14
373.15	-4.85	-4.85	0.06

NOTE:

CA(HCOO)2 Ksp NON-LINEAR REGRESSION

EQUATION MODELED:

$$\ln(Ksp) = A + B/T + C*\ln(T) + D*T$$

EQUATION COEFFICIENTS:

A = 4.472E+00
B =-1.911E+03
C = 1.563E-02
D =-1.151E-02

TABLE C.2: REGRESSION ANALYSIS FOR CA(OH)2-WATER SOLUTIONS

INTERPOLATION:

TEMPERATURE(K)	ln (Ksp) Experimental	ln (Ksp) Regressed	% Difference
283.15	-10.97	-11.06	-0.80
288.15	-11.17	-11.12	0.47
298.15	-11.28	-11.29	-0.09
303.15	-11.45	-11.40	0.36
313.15	-11.79	-11.67	0.97
323.15	-12.06	-12.00	0.48
333.15	-12.23	-12.38	-1.22
343.15	-12.59	-12.80	-1.68
353.15	-13.46	-13.27	1.42

NOTE:

CA(OH)2 Ksp NON-LINEAR REGRESSION

EQUATION MODELED:

$$\ln(K_{sp}) = A + B/T + C*\ln(T) + D*T$$

EQUATION COEFFICIENTS:

A = 5.092E+01
B =-8.613E+03
C = 3.703E-01
D =-1.188E-01

TABLE C.3: REGRESSION ANALYSIS FOR CASO4-WATER SOLUTIONS

INTERPOLATION:

TEMPERATURE(K)	ln (Ksp) Experimental	ln (Ksp) Regressed	% Difference
278.35	-5.31	-5.18	2.33
287.65	-5.35	-5.47	-2.09
294.85	-5.62	-5.69	-1.36
302.45	-5.95	-5.94	0.10
307.65	-6.09	-6.12	-0.35
317.95	-6.50	-6.47	0.48
333.15	-7.10	-7.01	1.17
343.65	-7.39	-7.40	-0.13
354.15	-7.81	-7.80	0.20
368.65	-8.30	-8.36	-0.69
369.65	-8.42	-8.40	0.22

NOTE:

CASO4 Ksp NON-LINEAR REGRESSION

EQUATION MODELED:

$$\ln(Ksp) = A + B/T + C*\ln(T) + D*T$$

EQUATION COEFFICIENTS:

A =-2.220E+01
B =-7.002E+02
C = 6.557E+00
D =-6.242E-02

TABLE C.4: REGRESSION ANALYSIS FOR KHCOO-WATER SOLUTIONS

INTERPOLATION:

TEMPERATURE(K)	ln (Ksp) Experimental	ln (Ksp) Regressed	% Difference
291.15	8.22	8.27	-0.64
303.15	8.38	8.33	0.65
323.15	8.64	8.59	0.63
343.15	9.02	9.04	-0.14
363.15	9.45	9.63	-1.96
373.15	10.13	9.98	1.39

NOTE:

KHCOO Ksp NON-LINEAR REGRESSION

EQUATION MODELED:

$$\ln(Ksp) = A + B/T + C*\ln(T) + D*T$$

EQUATION COEFFICIENTS:

A =-2.043E+01
B = 6.962E+03
C =-4.162E+00
D = 9.759E-02

TABLE C.5: REGRESSION ANALYSIS FOR K2CO3-WATER SOLUTIONS

INTERPOLATION:

TEMPERATURE(K)	ln (Ksp) Experimental	ln (Ksp) Regressed	% Difference
283.15	18.26	18.26	0.01
293.15	18.39	18.38	0.03
298.15	18.46	18.45	0.05
303.15	18.53	18.52	0.03
313.15	18.65	18.68	-0.15
323.15	18.83	18.86	-0.16
333.15	19.06	19.06	0.00
343.15	19.30	19.27	0.13
353.15	19.52	19.50	0.10
363.15	19.75	19.74	0.06
373.15	19.97	19.99	-0.13

NOTE:

K2CO3 Ksp NON-LINEAR REGRESSION

EQUATION MODELED:

$$\ln(Ksp) = A + B/T + C*\ln(T) + D*T$$

EQUATION COEFFICIENTS:

A =-8.658E+00
B = 2.989E+03
C = 6.082E-01
D = 4.567E-02

TABLE C.6: REGRESSION ANALYSIS FOR KOH-WATER SOLUTIONS

INTERPOLATION:

TEMPERATURE(K)	ln (Ksp) Experimental	ln (Ksp) Regressed	% Difference
284.65	9.96	10.06	-0.93
298.15	10.47	10.53	-0.57
306.15	10.98	10.76	1.98
313.15	11.03	10.94	0.84
338.45	11.29	11.42	-1.10
353.15	11.43	11.59	-1.36
373.15	11.84	11.71	1.03

NOTE:

KOH Ksp NON-LINEAR REGRESSION

EQUATION MODELED:

$$\ln(Ksp) = A + B/T + C*\ln(T) + D*T$$

EQUATION COEFFICIENTS:

A =-8.594E+00
B =-5.269E+03
C = 9.612E+00
D =-6.027E-02

TABLE C.7: REGRESSION ANALYSIS FOR K2SO4-WATER SOLUTIONS

INTERPOLATION:

TEMPERATURE(K)	ln (Ksp) Experimental	ln (Ksp) Regressed	% Difference
283.15	-4.88	-4.89	-0.24
293.15	-4.43	-4.43	0.02
298.15	-4.22	-4.21	0.13
303.15	-4.02	-4.01	0.18
313.15	-3.64	-3.63	0.27
323.15	-3.28	-3.28	0.16
333.15	-2.96	-2.96	-0.10
343.15	-2.67	-2.67	0.00
353.15	-2.38	-2.41	-1.31
363.15	-2.16	-2.17	-0.49
373.15	-1.99	-1.96	1.35

NOTE:

K2SO4 Ksp NON-LINEAR REGRESSION

EQUATION MODELED:

$$\ln(Ksp) = A + B/T + C*\ln(T) + D*T$$

EQUATION COEFFICIENTS:

A = 9.623E+00
B =-5.002E+03
C = 1.535E+00
D =-1.948E-02

CRANES CREST

APPENDIX D

CASE STUDIES

```
;
;CASE STUDY 1:  INPUT FILE
;
TITLE 'Case Study One - Potassium Sulfate Solubility'
DESCRIPTION "TEST OF Ksp USER MODEL TO HANDLE
     PRECIPITATION"
;
;  GLOBAL DATA
;
IN-UNITS SI
OUT-UNITS ENG
RUN-CONTROL MAX-TIME=450
HISTORY MSG-LEVEL SYSTEM=8
;
;  PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
 HCOO- HCOO-/NA+ NA+
FORMULA    H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
 HCOO- HCOO-/NA+ NA+
FILES USRPP1A AQADAT / USRPP1B SOLDAT
PROP-SOURCES
  GLOBAL AQADAT COMPS=ALL/SOLDAT COMPS=ALL
PROP-OPTIONS SYSOPA ELECTRO &
  PHIVMX PHIVMX12 / HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST                      SO4--;H2O-K2SO4 PAIR
   BCVAL GMELCC 1  1  K+   11.3093
   COMP-LIST                        K+   ;K2SO4-H2O PAIR
   BCVAL GMELCC 1  1 SO4-- -5.4028
PROP-DATA
   COMP-LIST                   HCOO-  ;H2O-CAHCOO2 PAIR
   BCVAL GMELCC 1  1 CA++   14.8546
   COMP-LIST                   CA++   ;CAHCOO2-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-  -6.3948
PROP-DATA
   COMP-LIST                      HCOO-;H2O-KHCOO PAIR
   BCVAL GMELCC 1  1  K+     8.145
   COMP-LIST                        K+ ;KHCOO-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-  -4.182
FLOWSHEET
   BLOCK REACTOR1    IN=S1 OUT=LIQ1 INSOL11 INSOL21
   BLOCK REACTOR2    IN=S2 OUT=LIQ2 INSOL12 INSOL22
   BLOCK REACTOR3    IN=S3 OUT=LIQ3 INSOL13 INSOL23
   BLOCK REACTOR4    IN=S4 OUT=LIQ4 INSOL14 INSOL24
   BLOCK REACTOR5    IN=S5 OUT=LIQ5 INSOL15 INSOL25
   BLOCK REACTOR6    IN=S6 OUT=LIQ6 INSOL16 INSOL26
STREAM S1 TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 3./ K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S2 TEMP=313.15 PRES=101325.
   MOLE-FLOW H2O 3./ K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
```

```
STREAM S3 TEMP=328.15 PRES=101325.
   MOLE-FLOW H2O 3./ K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S4 TEMP=343.15 PRES=101325.
   MOLE-FLOW H2O 3./K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.
STREAM S5 TEMP=358.15 PRES=101325.
   MOLE-FLOW H2O 3./ K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S6 TEMP=373.15 PRES=101325.
   MOLE-FLOW H2O 3./ K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
BLOCK REACTOR1 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     298.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR2 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     313.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR3 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     328.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR4 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     343.15           101325.
   INT 1
```

```
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR5 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     358.15          101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR6 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     373.15          101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
SIMULATE
```

```
;
;CASE STUDY 2:  INPUT FILE
;
 TITLE 'Case Study Two - Calcium Formate Solubility'
DESCRIPTION "TEST OF Ksp USER MODEL TO HANDLE
      PRECIPITATION"
;
;  GLOBAL DATA
;
IN-UNITS SI
OUT-UNITS ENG
RUN-CONTROL MAX-TIME=250
HISTORY MSG-LEVEL SYSTEM=8
;
;  PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-
FORMULA    H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-
FILES USRPP1A AQADAT / USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=ALL/SOLDAT COMPS=ALL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12 / HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST                      SO4--;H2O-K2SO4 PAIR
   BCVAL GMELCC 1  1  K+   11.3093
   COMP-LIST                      K+   ;K2SO4-H2O PAIR
   BCVAL GMELCC 1  1 SO4-- -5.4028
PROP-DATA
   COMP-LIST                      HCOO-  ;H2O-CAHCOO2 PAIR
   BCVAL GMELCC 1  1 CA++   14.8546
   COMP-LIST                      CA++   ;CAHCOO2-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-  -6.3948
PROP-DATA
   COMP-LIST                     HCOO-;H2O-KHCOO PAIR
   BCVAL GMELCC 1  1  K+     8.145
   COMP-LIST                     K+ ;KHCOO-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-  -4.182
FLOWSHEET
   BLOCK REACTOR1    IN=S1  OUT=LIQ1 INSOL11 INSOL21
   BLOCK REACTOR2    IN=S2  OUT=LIQ2 INSOL12 INSOL22
   BLOCK REACTOR3    IN=S3  OUT=LIQ3 INSOL13 INSOL23
   BLOCK REACTOR4    IN=S4  OUT=LIQ4 INSOL14 INSOL24
   BLOCK REACTOR5    IN=S5  OUT=LIQ5 INSOL15 INSOL25
   BLOCK REACTOR6    IN=S6  OUT=LIQ6 INSOL16 INSOL26
STREAM S1 TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 2.750 / K+ 0.0/ SO4-- 0.0/
     CA++ 0.08036115/HCOO- 0.16072230
STREAM S2 TEMP=313.15 PRES=101325.
   MOLE-FLOW H2O 2.750 / K+ 0.0/ SO4-- 0.0/
     CA++ 0.08036115/HCOO- 0.16072230
```

```
STREAM S3 TEMP=328.15 PRES=101325.
   MOLE-FLOW H2O 2.750 / K+ 0.0/ SO4-- 0.0/
     CA++ 0.08036115/HCOO- 0.16072230
STREAM S4 TEMP=343.15 PRES=101325.
   MOLE-FLOW H2O 2.750 / K+ 0.0/ SO4-- 0.0/
     CA++ 0.08036115/HCOO- 0.16072230
STREAM S5 TEMP=358.15 PRES=101325.
   MOLE-FLOW H2O 2.750 / K+ 0.0/ SO4-- 0.0/
     CA++ 0.08036115/HCOO- 0.16072230
STREAM S6 TEMP=373.15 PRES=101325.
   MOLE-FLOW H2O 2.750 / K+ 0.0/ SO4-- 0.0/
     CA++ 0.08036115/HCOO- 0.16072230
BLOCK REACTOR1 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL     298.15         101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR2 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL     313.15         101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR3 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL     328.15         101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR4 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL     343.15         101325.
   INT 1
```

```
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR5 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     358.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR6 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     373.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
SIMULATE
```

```
;
;CASE STUDY 3:  INPUT FILE
;
TITLE 'Case Study Three - Calcium Sulfate Solubility'
DESCRIPTION "TEST OF Ksp USER MODEL TO HANDLE
    PRECIPITATION"
;
;  GLOBAL DATA
;
IN-UNITS SI
OUT-UNITS ENG
RUN-CONTROL MAX-TIME=250
HISTORY MSG-LEVEL SYSTEM=8
;
;  PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-
FORMULA    H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-
FILES USRPP1A AQADAT / USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=ALL/SOLDAT COMPS=ALL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12 / HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST                    SO4--;H2O-K2SO4 PAIR
   BCVAL GMELCC 1  1  K+   11.3093
   COMP-LIST                    K+   ;K2SO4-H2O PAIR
   BCVAL GMELCC 1  1 SO4-- -5.4028
PROP-DATA
   COMP-LIST                  HCOO-  ;H2O-CAHCOO2 PAIR
   BCVAL GMELCC 1  1 CA++   14.8546
   COMP-LIST                  CA++   ;CAHCOO2-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-  -6.3948
PROP-DATA
   COMP-LIST                    HCOO-;H2O-KHCOO PAIR
   BCVAL GMELCC 1  1  K+     8.145
   COMP-LIST                     K+ ;KHCOO-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-  -4.182
FLOWSHEET
   BLOCK REACTOR1    IN=S1  OUT=LIQ1 INSOL11 INSOL21
   BLOCK REACTOR2    IN=S2  OUT=LIQ2 INSOL12 INSOL22
   BLOCK REACTOR3    IN=S3  OUT=LIQ3 INSOL13 INSOL23
   BLOCK REACTOR4    IN=S4  OUT=LIQ4 INSOL14 INSOL24
   BLOCK REACTOR5    IN=S5  OUT=LIQ5 INSOL15 INSOL25
   BLOCK REACTOR6    IN=S6  OUT=LIQ6 INSOL16 INSOL26
STREAM S1 TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 2.0 / K+ 0.0/ SO4-- 0.08036115/
     CA++ 0.08036115/HCOO- 0.0
STREAM S2 TEMP=313.15 PRES=101325.
   MOLE-FLOW H2O 2.0 / K+ 0.0/ SO4-- 0.08036115/
     CA++ 0.08036115/HCOO- 0.0
```

```
STREAM S3 TEMP=328.15 PRES=101325.
   MOLE-FLOW H2O 2.0 / K+ 0.0/ SO4-- 0.08036115/
     CA++ 0.08036115/HCOO- 0.0
STREAM S4 TEMP=343.15 PRES=101325.
   MOLE-FLOW H2O 2.0 / K+ 0.0/ SO4-- 0.08036115/
     CA++ 0.08036115/HCOO- 0.0
STREAM S5 TEMP=358.15 PRES=101325.
   MOLE-FLOW H2O 2.0 / K+ 0.0/ SO4-- 0.08036115/
     CA++ 0.08036115/HCOO- 0.0
STREAM S6 TEMP=373.15 PRES=101325.
   MOLE-FLOW H2O 2.0 / K+ 0.0/ SO4-- 0.08036115/
     CA++ 0.08036115/HCOO- 0.0
BLOCK REACTOR1 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)         PRES(PA)
   REAL     298.15          101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR2 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)         PRES(PA)
   REAL     313.15          101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR3 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)         PRES(PA)
   REAL     328.15          101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR4 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)         PRES(PA)
   REAL     343.15          101325.
   INT 1
```

```
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR5 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     358.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR6 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     373.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
SIMULATE
```

```
;
;CASE STUDY 4:  INPUT FILE
;
TITLE 'Case Study Four - Potassium Formate Solubility'
DESCRIPTION "TEST OF Ksp USER MODEL TO HANDLE
     PRECIPITATION"
;
;  GLOBAL DATA
;
IN-UNITS SI
OUT-UNITS ENG
RUN-CONTROL MAX-TIME=250
HISTORY MSG-LEVEL SYSTEM=8
;
;  PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-
FORMULA    H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-
FILES USRPP1A AQADAT / USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=ALL/SOLDAT COMPS=ALL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12 / HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST                      SO4--;H2O-K2SO4 PAIR
   BCVAL GMELCC 1  1  K+   11.3093
   COMP-LIST                       K+   ;K2SO4-H2O PAIR
   BCVAL GMELCC 1  1 SO4-- -5.4028
PROP-DATA
   COMP-LIST                    HCOO-  ;H2O-CAHCOO2 PAIR
   BCVAL GMELCC 1  1 CA++   14.8546
   COMP-LIST                    CA++   ;CAHCOO2-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-  -6.3948
PROP-DATA
   COMP-LIST                      HCOO-;H2O-KHCOO PAIR
   BCVAL GMELCC 1  1  K+     8.145
   COMP-LIST                        K+ ;KHCOO-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-  -4.182
FLOWSHEET
   BLOCK REACTOR1    IN=S1  OUT=LIQ1 INSOL11 INSOL21
   BLOCK REACTOR2    IN=S2  OUT=LIQ2 INSOL12 INSOL22
   BLOCK REACTOR3    IN=S3  OUT=LIQ3 INSOL13 INSOL23
   BLOCK REACTOR4    IN=S4  OUT=LIQ4 INSOL14 INSOL24
   BLOCK REACTOR5    IN=S5  OUT=LIQ5 INSOL15 INSOL25
   BLOCK REACTOR6    IN=S6  OUT=LIQ6 INSOL16 INSOL26
STREAM S1 TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 0.0750 / K+ 0.16072230/ SO4-- 0.0/
     CA++ 0.0/HCOO- 0.16072230
STREAM S2 TEMP=313.15 PRES=101325.
   MOLE-FLOW H2O 0.0750 / K+ 0.16072230/ SO4-- 0.0/
     CA++ 0.0/HCOO- 0.16072230
```

```
STREAM S3 TEMP=328.15 PRES=101325.
   MOLE-FLOW H2O 0.0750 / K+ 0.16072230/ SO4-- 0.0/
     CA++ 0.0/HCOO- 0.16072230
STREAM S4 TEMP=343.15 PRES=101325.
   MOLE-FLOW H2O 0.0750 / K+ 0.16072230/ SO4-- 0.0/
     CA++ 0.0/HCOO- 0.16072230
STREAM S5 TEMP=358.15 PRES=101325.
   MOLE-FLOW H2O 0.0750 / K+ 0.16072230/ SO4-- 0.0/
     CA++ 0.0/HCOO- 0.16072230
STREAM S6 TEMP=373.15 PRES=101325.
   MOLE-FLOW H2O 0.0750 / K+ 0.16072230/ SO4-- 0.0/
     CA++ 0.0/HCOO- 0.16072230
BLOCK REACTOR1 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     298.15          101325.
   INT 1
;
;     FORTRAN CODE FOLLOWS
;
BLOCK REACTOR2 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     313.15          101325.
   INT 1
;
;     FORTRAN CODE FOLLOWS
;
BLOCK REACTOR3 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     328.15          101325.
   INT 1
;
;     FORTRAN CODE FOLLOWS
;
BLOCK REACTOR4 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     343.15          101325.
   INT 1
```

```
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR5 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     358.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR6 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     373.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
SIMULATE
```

```
;
;CASE STUDY 5:  INPUT FILE
;
TITLE 'Case Study Five - Common Ion Affect -
    Selective Precipitation of Potassium Ions'
DESCRIPTION "TEST OF Ksp USER MODEL TO HANDLE
      PRECIPITATION"
;
;  GLOBAL DATA
;
IN-UNITS SI
OUT-UNITS ENG
RUN-CONTROL MAX-TIME=450
HISTORY MSG-LEVEL SYSTEM=8
;
;  PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-/NA+ NA+
FORMULA    H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-/NA+ NA+
FILES USRPP1A AQADAT / USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=ALL/SOLDAT COMPS=ALL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12 / HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST                      SO4--;H2O-K2SO4 PAIR
   BCVAL GMELCC 1  1  K+   11.3093
   COMP-LIST                        K+   ;K2SO4-H2O PAIR
   BCVAL GMELCC 1  1 SO4-- -5.4028
PROP-DATA
   COMP-LIST                   HCOO-   ;H2O-CAHCOO2 PAIR
   BCVAL GMELCC 1  1 CA++    14.8546
   COMP-LIST                   CA++    ;CAHCOO2-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-   -6.3948
PROP-DATA
   COMP-LIST                      HCOO-;H2O-KHCOO PAIR
   BCVAL GMELCC 1  1  K+      8.145
   COMP-LIST                        K+ ;KHCOO-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-   -4.182
FLOWSHEET
   BLOCK REACTOR1     IN=S1 S1A OUT=LIQ1 INSOL11 INSOL21
   BLOCK REACTOR2     IN=S2 S2A OUT=LIQ2 INSOL12 INSOL22
   BLOCK REACTOR3     IN=S3 S3A OUT=LIQ3 INSOL13 INSOL23
   BLOCK REACTOR4     IN=S4 S4A OUT=LIQ4 INSOL14 INSOL24
   BLOCK REACTOR5     IN=S5 S5A OUT=LIQ5 INSOL15 INSOL25
   BLOCK REACTOR6     IN=S6 S6A OUT=LIQ6 INSOL16 INSOL26
STREAM S1 TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 6.435603 / K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S1A TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 0.01/NA+ 0.001078/ SO4-- 0.000539
```

```
STREAM S2 TEMP=313.15 PRES=101325.
   MOLE-FLOW H2O 5.244156 / K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S2A TEMP=313.15 PRES=101325.
   MOLE-FLOW H2O 0.01/NA+ 0.001078/ SO4-- 0.000539
STREAM S3 TEMP=328.15 PRES=101325.
   MOLE-FLOW H2O 4.471660 / K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S3A TEMP=328.15 PRES=101325.
   MOLE-FLOW H2O 0.01/NA+ 0.001078/ SO4-- 0.000539
STREAM S4 TEMP=343.15 PRES=101325.
   MOLE-FLOW H2O 3.928541/ K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.
STREAM S4A TEMP=343.15 PRES=101325.
   MOLE-FLOW H2O 0.01/NA+ 0.001078/ SO4-- 0.000539
STREAM S5 TEMP=358.15 PRES=101325.
   MOLE-FLOW H2O 3.521058 / K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S5A TEMP=358.15 PRES=101325
   MOLE-FLOW H2O 0.01/NA+ 0.001078/ SO4-- 0.000539
STREAM S6 TEMP=373.15 PRES=101325.
   MOLE-FLOW H2O 3.201630 / K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S6A TEMP=373.15 PRES=101325.
   MOLE-FLOW H2O 0.01/NA+ 0.001078/ SO4-- 0.000539
BLOCK REACTOR1 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     298.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR2 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     313.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR3 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     328.15           101325.
   INT 1
```

```
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR4 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     343.15          101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR5 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     358.15          101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR6 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     373.15          101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
SIMULATE
```

```
;
;CASE STUDY 6:  INPUT FILE
;
TITLE 'Case Study Six - Common Ion Affect -
       Selective Precipitation of Sulfate Ions '
DESCRIPTION "TEST OF Ksp USER MODEL TO HANDLE
      PRECIPITATION"
;
;  GLOBAL DATA
;
IN-UNITS SI
OUT-UNITS ENG
RUN-CONTROL MAX-TIME=450
HISTORY MSG-LEVEL SYSTEM=8
;
;  PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-/OH- OH-
FORMULA    H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-/OH- OH-
FILES USRPP1A AQADAT / USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=ALL/SOLDAT COMPS=ALL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12 / HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST                    SO4--;H2O-K2SO4 PAIR
   BCVAL GMELCC 1  1  K+   11.3093
   COMP-LIST                     K+   ;K2SO4-H2O PAIR
   BCVAL GMELCC 1  1 SO4-- -5.4028
PROP-DATA
   COMP-LIST                  HCOO-  ;H2O-CAHCOO2 PAIR
   BCVAL GMELCC 1  1 CA++   14.8546
   COMP-LIST                  CA++   ;CAHCOO2-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-  -6.3948
PROP-DATA
   COMP-LIST                    HCOO-;H2O-KHCOO PAIR
   BCVAL GMELCC 1  1  K+     8.145
   COMP-LIST                      K+ ;KHCOO-H2O PAIR
   BCVAL GMELCC 1  1 HCOO-  -4.182
FLOWSHEET
   BLOCK REACTOR1    IN=S1 S1A OUT=LIQ1 INSOL11 INSOL21
   BLOCK REACTOR2    IN=S2 S2A OUT=LIQ2 INSOL12 INSOL22
   BLOCK REACTOR3    IN=S3 S3A OUT=LIQ3 INSOL13 INSOL23
   BLOCK REACTOR4    IN=S4 S4A OUT=LIQ4 INSOL14 INSOL24
   BLOCK REACTOR5    IN=S5 S5A OUT=LIQ5 INSOL15 INSOL25
   BLOCK REACTOR6    IN=S6 S6A OUT=LIQ6 INSOL16 INSOL26
STREAM S1 TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 6.435603 / K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S1A TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 0.01/K+  0.000639/OH-  0.000639
```

```
STREAM S2 TEMP=313.15 PRES=101325.
   MOLE-FLOW H2O 5.244156 / K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S2A TEMP=313.15 PRES=101325.
   MOLE-FLOW H2O 0.01/K+  0.000639/OH-  0.000639
STREAM S3 TEMP=328.15 PRES=101325.
   MOLE-FLOW H2O 4.471660 / K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S3A TEMP=328.15 PRES=101325.
   MOLE-FLOW H2O 0.01/K+  0.000639/OH-  0.000639
STREAM S4 TEMP=343.15 PRES=101325.
   MOLE-FLOW H2O 3.928541/ K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.
STREAM S4A TEMP=343.15 PRES=101325.
   MOLE-FLOW H2O 0.01/K+  0.000639/OH-  0.000639
STREAM S5 TEMP=358.15 PRES=101325.
   MOLE-FLOW H2O 3.521058 / K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S5A TEMP=358.15 PRES=101325
   MOLE-FLOW H2O 0.01/K+  0.000639/OH-  0.000639
STREAM S6 TEMP=373.15 PRES=101325.
   MOLE-FLOW H2O 3.201630 / K+ 0.16072230/ SO4-- 0.08036115/
     CA++ 0.0/HCOO- 0.0
STREAM S6A TEMP=373.15 PRES=101325.
   MOLE-FLOW H2O 0.01/K+  0.000639/OH-  0.000639
BLOCK REACTOR1 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL    298.15         101325.
   INT 1
;
;     FORTRAN CODE FOLLOWS
;
BLOCK REACTOR2 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL    313.15         101325.
   INT 1
;
;     FORTRAN CODE FOLLOWS
;
BLOCK REACTOR3 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL    328.15         101325.
   INT 1
```

```
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR4 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     343.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR5 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     358.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK REACTOR6 USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     373.15           101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
SIMULATE
```

APPENDIX E

SIMULATION OF ECONOSEED PROCESS

CRAMES CREST

```
;
;ECONOSEED INPUT FILE
;
NEW
TITLE 'SIMULATION OF ECONOSEED PROCESS'
DESCRIPTION "TEST OF Ksp USER MODEL TO
 HANDLE EVAPORATION AND PRECIPITATION"
;
;  GLOBAL DATA
;
IN-UNITS SI
OUT-UNITS ENG
RUN-CONTROL MAX-TIME=250
HISTORY MSG-LEVEL SYSTEM=8
;
;  PHYSICAL PROPERTIES SECTION
;
COMPONENTS H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-
FORMULA    H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  HCOO- HCOO-
FILES USRPP1A AQADAT / USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=ALL/SOLDAT COMPS=ALL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12 / HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST                  SO4--;H2O-K2SO4 PAIR
   BCVAL GMELCC 1   1  K+    11.3093
   COMP-LIST                  K+    ;K2SO4-H2O PAIR
   BCVAL GMELCC 1   1 SO4-- -5.4028
PROP-DATA
   COMP-LIST              HCOO-   ;H2O-CAHCOO2 PAIR
   BCVAL GMELCC 1   1 CA++    14.8546
   COMP-LIST              CA++    ;CAHCOO2-H2O PAIR
   BCVAL GMELCC 1   1 HCOO-   -6.3948
PROP-DATA
   COMP-LIST                  HCOO-;H2O-KHCOO PAIR
   BCVAL GMELCC 1   1  K+      8.145
   COMP-LIST                   K+ ;KHCOO-H2O PAIR
   BCVAL GMELCC 1   1 HCOO-   -4.182
DEF-STREAMS HEAT Q1 Q2 Q3 Q4 QMIX Q6 Q7 Q8 Q9 Q10 Q11
FLOWSHEET
;
;  DISSOLVER AND REACTOR BLOCKS
;
BLOCK PREHEAT1 IN=S1 Q1       OUT=S3 Q3
BLOCK PREHEAT2 IN=S2 Q2       OUT=S4 Q4
BLOCK HEATREQ  IN=Q3 Q4       OUT=QMIX
BLOCK REACTOR  IN=S3 S4 QMIX OUT=THINLIQ INSOL1 INSOL2
```

```
;
;  MULTI-EFFECT EVAPORATOR BLOCKS
;
BLOCK FLSH1    IN=THINLIQ Q6 OUT=S5 Q7
BLOCK EFFECT1 IN=S5 Q7       OUT=S6 EVAP1 INSOL3
BLOCK FLSH2    IN=S6 Q8      OUT=S7 Q9
BLOCK EFFECT2 IN=S7 Q9       OUT=S8 EVAP2 INSOL4
BLOCK FLSH3    IN=S8 Q10     OUT=S9 Q11
BLOCK EFFECT3 IN=S9 Q11      OUT=THICKLIQ EVAP3 INSOL5
;
STREAM S1 TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 0.750 / K+ 0.16072230/
     SO4-- 0.08036115/ CA++ 0.0/HCOO- 0.0
STREAM S2 TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 3.00/ K+ 0.0/ SO4-- 0.0/
     CA++ 0.08036115/HCOO- 0.16072230
BLOCK PREHEAT1 HEATER
   PARAM TEMP=353.15 PRES=101325.
BLOCK PREHEAT2 HEATER
   PARAM TEMP=353.15 PRES=101325.
BLOCK HEATREQ MIXER
BLOCK REACTOR USER
   DESCRIPTION "SIMULATE KCOOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL     353.15         101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
;
;  THE FOLLOWING BLOCKS ACT AS A MULTI-EFFECT
;  EVAPORATOR REMOVING FIRST THE INSOLUBLE CASO4
;  THEN CONCENTRATING THE REMAINING LIQUOR TO
;  APPROXIMATELY 80% KHCOOH 20% H2O.
;
BLOCK FLSH1 HEATER
   PARAM TEMP=376.7 PRES=101325.
BLOCK EFFECT1 USER
   DESCRIPTION "SIMULATE MULTI-EFFECT
       EVAPORATOR EFFECT 2"
   SUBROUTINE USRFLH USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL     376.7          101325.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK FLSH2 HEATER
   PARAM TEMP=380.18 PRES=101325.
```

```
BLOCK EFFECT2 USER
   DESCRIPTION "SIMULATE MULTI-EFFECT
        EVAPORATOR EFFECT 3"
   SUBROUTINE USRFLH USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     380.18           101325.
   INT 1
;
;    FORTRAN CODE FOLLOWS
;
BLOCK FLSH3 HEATER
   PARAM TEMP=412.83 PRES=101325.
BLOCK EFFECT3 USER
   DESCRIPTION "SIMULATE MULTI-EFFECT
         EVAPORATOR EFFECT 1"
   SUBROUTINE USRFLH USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)          PRES(PA)
   REAL     412.83           101325.
   INT 1
;
;     FORTRAN CODE FOLLOWS
;
SIMULATE
```

ECONOSEED REPORT

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SIMULATION OF ECONOSEED PROCESS
RUN CONTROL SECTION

RUN CONTROL INFORMATION

TYPE OF RUN: NEW

INPUT FILE NAME:USER0051:[U858446.ASPEN]ECONOSEED.INP;1

OUTPUT PROBLEM DATA FILE NAME: ECON
VERSION NO. 1
LOCATED IN: U$D2:[U858446.ASPEN]

PDF SIZE USED FOR INPUT TRANSLATION:
NUMBER OF FILE RECORDS (PSIZE) = 200
NUMBER OF IN-CORE RECORDS = 400
PSIZE NEEDED FOR SIMULATION = 66

CALLING PROGRAM NAME: ECON
LOCATED IN: U$D2:[U858446.ASPEN]

SIMULATION REQUESTED FOR ENTIRE FLOWSHEET

DESCRIPTION

TEST OF Ksp USER MODEL TO HANDLE EVAPORATION
AND PRECIPITATION

BLOCK STATUS

```
**************************************************
*                                                *
* ALL UNIT OPERATION BLOCKS WERE COMPLETED NORMALLY *
*                                                *
**************************************************
```

FLOWSHEET CONNECTIVITY BY STREAMS

STREAM	SOURCE	DEST	STREAM	SOURCE	DEST
Q1	----	PREHEAT1	S1	----	PREHEAT1
Q2	----	PREHEAT2	S2	----	PREHEAT2
Q6	----	FLSH1	Q8	----	FLSH2
Q10	----	FLSH3	S3	PREHEAT1	REACTOR
Q3	PREHEAT1	HEATREQ	S4	PREHEAT2	REACTOR
Q4	PREHEAT2	HEATREQ	QMIX	HEATREQ	REACTOR
THINLIQ	REACTOR	FLSH1	INSOL1	REACTOR	----
INSOL2	REACTOR	----	S5	FLSH1	EFFECT1
Q7	FLSH1	EFFECT1	S6	EFFECT1	FLSH2
EVAP1	EFFECT1	----	INSOL3	EFFECT1	----
S7	FLSH2	EFFECT2	Q9	FLSH2	EFFECT2
S8	EFFECT2	FLSH3	EVAP2	EFFECT2	----
INSOL4	EFFECT2	----	S9	FLSH3	EFFECT3
Q11	FLSH3	EFFECT3	THICKLIQ	EFFECT3	----
EVAP3	EFFECT3	----	INSOL5	EFFECT3	----

FLOWSHEET CONNECTIVITY BY BLOCKS

BLOCK	INLETS	OUTLETS
PREHEAT1	S1 Q1	S3 Q3
PREHEAT2	S2 Q2	S4 Q4
HEATREQ	Q3 Q4	QMIX
REACTOR	S3 S4 QMIX	THINLIQ INSOL1 INSOL2
FLSH1	THINLIQ Q6	S5 Q7
EFFECT1	S5 Q7	S6 EVAP1 INSOL3
FLSH2	S6 Q8	S7 Q9
EFFECT2	S7 Q9	S8 EVAP2 INSOL4
FLSH3	S8 Q10	S9 Q11
EFFECT3	S9 Q11	THICKLIQ EVAP3 INSOL5

COMPUTATIONAL SEQUENCE

SEQUENCE USED WAS:
PREHEAT2 PREHEAT1 HEATREQ REACTOR FLSH1 EFFECT1
FLSH2 EFFECT2 FLSH3 EFFECT3

OVERALL FLOWSHEET BALANCE

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
CONVENTIONAL COMPONENTS (LBMOL/HR)			
H2O	29762.4	29762.4	-0.152793E-16
K+	1275.60	1275.60	0.000000E+00
SO4--	637.798	637.798	0.245092E-15
CA++	637.798	637.798	0.245092E-15
HCOO-	1275.60	1275.60	0.000000E+00
TOTAL BALANCE			
MOLE (LBMOL/HR)	33589.2	33589.2	-0.270770E-16
MASS (LB/HR)	730333.	730333.	0.000000E+00
ENTHALPY (BTU/HR)	-0.442657E+10	-0.442657E+10	0.000000E+00

COMPONENTS

ID	TYPE	FORMULA	NAME OR ALIAS	REPORT NAME
H2O	C	H2O	H2O	H2O
K+	C	K+	K+	K+
SO4--	C	SO4--	SO4--	SO4--
CA++	C	CA++	CA++	CA++
HCOO-	C	HCOO-	HCOO-	HCOO-

SIMULATION OF ECONOSEED PROCESS
U-O-S BLOCK SECTION

BLOCK: EFFECT1 MODEL: USER

SIMULATE MULTI-EFFECT EVAPORATOR EFFECT 2
INLET STREAMS: S5 Q7
OUTLET STREAMS: S6 EVAP1 INSOL3
PROPERTY OPTION SET: SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	32335.7	32335.7	0.000000E+00
MASS (LB/HR)	645006.	645006.	0.000000E+00
ENTHALPY (BTU/HR)	-0.426138E+10	-0.426138E+10	0.000000E+00

BLOCK: EFFECT2 MODEL: USER

SIMULATE MULTI-EFFECT EVAPORATOR EFFECT 3
INLET STREAMS: S7 Q9
OUTLET STREAMS: S8 EVAP2 INSOL4
PROPERTY OPTION SET: SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	23028.1	23028.1	-0.197475E-16
MASS (LB/HR)	476695.	476695.	0.000000E+00
ENTHALPY (BTU/HR)	-0.303477E+10	-0.303477E+10	0.392811E-16

BLOCK: EFFECT3 MODEL: USER

SIMULATE MULTI-EFFECT EVAPORATOR EFFECT 1
INLET STREAMS: S9 Q11
OUTLET STREAMS: THICKLIQ EVAP3 INSOL5
PROPERTY OPTION SET: SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	13735.8	13735.8	-0.165534E-16
MASS (LB/HR)	309049.	309049.	0.000000E+00
ENTHALPY (BTU/HR)	-0.181018E+10	-0.181018E+10	0.329275E-16

BLOCK: FLSH1 MODEL: HEATER

INLET STREAM(S):	THINLIQ Q6
OUTLET STREAM:	S5
OUTLET HEAT STREAM:	Q7
PROPERTY OPTION SET:	SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	32335.7	32335.7	0.000000E+00
MASS (LB/HR)	645006.	645006.	0.000000E+00
ENTHALPY (BTU/HR)	-0.426138E+10	-0.426138E+10	0.000000E+00

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	218.390
SPECIFIED PRESSURE	PSI	14.6959
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	218.39
OUTLET PRESSURE	PSI	14.696
HEAT DUTY	BTU/HR	0.46720E+09
VAPOR FRACTION		0.28745

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.92042	0.88832	1.0000	1.1257
K+	0.39449E-01	0.55363E-01	0.00000E+00	0.00000E+00
SO4--	0.34145E-03	0.47920E-03	0.00000E+00	0.00000E+00
CA++	0.34145E-03	0.47920E-03	0.00000E+00	0.00000E+00
HCOO-	0.39449E-01	0.55363E-01	0.00000E+00	0.00000E+00

BLOCK: FLSH2 MODEL: HEATER

INLET STREAM(S):	S6	Q8
OUTLET STREAM:	S7	
OUTLET HEAT STREAM:	Q9	
PROPERTY OPTION SET:	SYSOPA	

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	23028.1	23028.1	0.000000E+00
MASS (LB/HR)	476695.	476695.	0.152633E-16
ENTHALPY (BTU/HR)	-0.303477E+10	-0.303477E+10	-0.196406E-16

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	224.654
SPECIFIED PRESSURE	PSI	14.6959
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	224.65
OUTLET PRESSURE	PSI	14.696
HEAT DUTY	BTU/HR	0.36594E+09
VAPOR FRACTION		0.40332

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.88880	0.81363	1.0000	1.2291
K+	0.55393E-01	0.92835E-01	0.00000E+00	0.00000E+00
SO4--	0.20788E-03	0.34839E-03	0.00000E+00	0.00000E+00
CA++	0.20788E-03	0.34839E-03	0.00000E+00	0.00000E+00
HCOO-	0.55393E-01	0.92835E-01	0.00000E+00	0.00000E+00

BLOCK: FLSH3 MODEL: HEATER

INLET STREAM(S):	S8	Q10
OUTLET STREAM:	S9	
OUTLET HEAT STREAM:	Q11	
PROPERTY OPTION SET:	SYSOPA	

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	13735.8	13735.8	0.000000E+00
MASS (LB/HR)	309049.	309049.	-0.235431E-16
ENTHALPY (BTU/HR)	-0.181018E+10	-0.181018E+10	0.000000E+00

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	283.424
SPECIFIED PRESSURE	PSI	14.6959
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	283.42
OUTLET PRESSURE	PSI	14.696
HEAT DUTY	BTU/HR	0.27090E+09
VAPOR FRACTION		0.67892

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.81391	0.42044	1.0000	2.3785
K+	0.92867E-01	0.28923	0.00000E+00	0.00000E+00
SO4--	0.17747E-03	0.55273E-03	0.00000E+00	0.00000E+00
CA++	0.17747E-03	0.55273E-03	0.00000E+00	0.00000E+00
HCOO-	0.92867E-01	0.28923	0.00000E+00	0.00000E+00

BLOCK: HEATREQ MODEL: MIXER

INLET STREAM(S):	Q3	Q4
OUTLET STREAM:	QMIX	
PROPERTY OPTION SET:	SYSOPA	

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE ENTHALPY (BTU/HR)	-0.539968E+08	-0.539968E+08	0.000000E+00

BLOCK: PREHEAT1 MODEL: HEATER

INLET STREAM(S):	S1	Q1
OUTLET STREAM:	S3	
OUTLET HEAT STREAM:	Q3	
PROPERTY OPTION SET:	SYSOPA	

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	7865.87	7865.87	0.000000E+00
MASS (LB/HR)	218386.	218386.	0.000000E+00
ENTHALPY (BTU/HR)	-0.111796E+10	-0.111796E+10	0.000000E+00

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	176.000
SPECIFIED PRESSURE	PSI	14.6959
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	176.00
OUTLET PRESSURE	PSI	14.696
HEAT DUTY	BTU/HR	0.85244E+07
VAPOR FRACTION		0.00000E+00

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.75675	0.75675	1.0000	0.27754
K+	0.16217	0.16217	0.00000E+00	0.00000E+00
SO4--	0.81084E-01	0.81084E-01	0.00000E+00	0.00000E+00

BLOCK: PREHEAT2 MODEL: HEATER

INLET STREAM(S):	S2	Q2
OUTLET STREAM:	S4	
OUTLET HEAT STREAM:	Q4	
PROPERTY OPTION SET:	SYSOPA	

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	25723.3	25723.3	0.000000E+00
MASS (LB/HR)	511947.	511947.	0.000000E+00
ENTHALPY (BTU/HR)	-0.330861E+10	-0.330861E+10	0.000000E+00

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	176.000
SPECIFIED PRESSURE	PSI	14.6959
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	176.00
OUTLET PRESSURE	PSI	14.696
HEAT DUTY	BTU/HR	0.45472E+08
VAPOR FRACTION		0.00000E+00

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.92562	0.92562	1.0000	0.43604
CA++	0.24795E-01	0.24795E-01	0.00000E+00	0.00000E+00
HCOO-	0.49589E-01	0.49589E-01	0.00000E+00	0.00000E+00

BLOCK: REACTOR MODEL: USER

SIMULATE KCOOH-CASO4 CHEMISTRY

INLET STREAMS:	S3	S4	QMIX
OUTLET STREAMS:	THINLIQ	INSOL1	INSOL2
PROPERTY OPTION SET:	SYSOPA		

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	33589.2	33589.2	0.000000E+00
MASS (LB/HR)	730333.	730333.	0.000000E+00
ENTHALPY (BTU/HR)	-0.442657E+10	-0.442657E+10	0.000000E+00

Q1 Q10 Q11 Q2

STREAM ID	Q1	Q10	Q11	Q2
FROM :	----	----	FLSH3	----
TO :	PREHEAT1	FLSH3	EFFECT3	PREHEAT2
CLASS:	HEAT	HEAT	HEAT	HEAT
STREAM ATTRIBUTES:				
HEAT				
Q BTU/HR	0.0	0.0	-2.7090+08	0.0

Q3 Q4 Q6 Q7

STREAM ID	Q3	Q4	Q6	Q7
FROM :	PREHEAT1	PREHEAT2	----	FLSH1
TO :	HEATREQ	HEATREQ	FLSH1	EFFECT1
CLASS:	HEAT	HEAT	HEAT	HEAT
STREAM ATTRIBUTES:				
HEAT				
Q BTU/HR	-8.5244+06	-4.5472+07	0.0	-4.6720+08

Q8 Q9 QMIX

STREAM ID	Q8	Q9	QMIX
FROM :	----	FLSH2	HEATREQ
TO :	FLSH2	EFFECT2	REACTOR
CLASS:	HEAT	HEAT	HEAT
STREAM ATTRIBUTES:			
HEAT			
Q BTU/HR	0.0	-3.6594+08	-5.3997+07

EVAP1 EVAP2 EVAP3

STREAM ID	EVAP1	EVAP2	EVAP3
FROM :	EFFECT1	EFFECT2	EFFECT3
TO :	----	----	----
SUBSTREAM: MIXED			
PHASE:	VAPOR	VAPOR	VAPOR
COMPONENTS: LBMOL/HR			
H2O	9295.0469	9287.6341	9325.4344
K+	0.0	0.0	0.0
SO4--	0.0	0.0	0.0
CA++	0.0	0.0	0.0
HCOO-	0.0	0.0	0.0
TOTAL FLOW:			
LBMOL/HR	9295.0469	9287.6341	9325.4344
LB/HR	1.6746+05	1.6733+05	1.6801+05
STATE VARIABLES:			
TEMP F	218.3900	224.6540	283.4240
PRES PSI	14.6959	14.6959	14.6959
VFRAC	1.0000	1.0000	1.0000
LFRAC	0.0	0.0	0.0
SFRAC	0.0	0.0	0.0
ENTHALPY:			
BTU/LBMOL	-1.3179+05	-1.3179+05	-1.3179+05
BTU/LB	-7314.9191	-7314.9191	-7314.9191
BTU/HR	-1.2250+09	-1.2240+09	-1.2290+09
ENTROPY:			
BTU/LBMOL-R	0.0	0.0	0.0
BTU/LB-R	0.0	0.0	0.0
DENSITY:			
LBMOL/CUFT	0.0	0.0	0.0
LB/CUFT	0.0	0.0	0.0
AVG MW	18.0160	18.0160	18.0160

INSOL1 INSOL2

STREAM ID	INSOL1	INSOL2
FROM :	REACTOR	REACTOR
TO :	----	----
SUBSTREAM: MIXED		
PHASE:	MIXED	MIXED
COMPONENTS: LBMOL/HR		
H2O	0.0	0.0
K+	0.0	0.0
SO4--	0.0	626.7566
CA++	0.0	626.7566
HCOO-	0.0	0.0
TOTAL FLOW:		
LBMOL/HR	0.0	1253.5132
LB/HR	0.0	8.5328+04
STATE VARIABLES:		
TEMP F	176.0000	176.0000
PRES PSI	14.6959	14.6959
VFRAC	0.0	0.0
LFRAC	0.0	0.0
SFRAC	1.0000	1.0000
ENTHALPY:		
BTU/LBMOL	0.0	-1.3179+05
BTU/LB	0.0	-1936.0076
BTU/HR	0.0	-1.6519+08
ENTROPY:		
BTU/LBMOL-R	0.0	0.0
BTU/LB-R	0.0	0.0
DENSITY:		
LBMOL/CUFT	0.0	0.0
LB/CUFT	0.0	0.0
AVG MW	0.0	68.0708

INSOL3 INSOL4 INSOL5

STREAM ID FROM : TO :	INSOL3 EFFECT1 ----	INSOL4 EFFECT2 ----	INSOL5 EFFECT3 ----
SUBSTREAM: MIXED PHASE:	MIXED	MIXED	MIXED
COMPONENTS: LBMOL/HR			
H2O	0.0	0.0	0.0
K+	0.0	0.0	0.0
SO4--	6.2541	2.3492	2.4377
CA++	6.2541	2.3492	2.4377
HCOO-	0.0	0.0	0.0
TOTAL FLOW:			
LBMOL/HR	12.5081	4.6985	4.8755
LB/HR	851.4396	319.8301	331.8777
STATE VARIABLES:			
TEMP F	218.3900	224.6540	283.4240
PRES PSI	14.6959	14.6959	14.6959
VFRAC	0.0	0.0	0.0
LFRAC	0.0	0.0	0.0
SFRAC	1.0000	1.0000	1.0000
ENTHALPY:			
BTU/LBMOL	-1.3179+05	-1.3179+05	-1.3179+05
BTU/LB	-1936.0076	-1936.0076	-1936.0076
BTU/HR	-1.6484+06	-6.1919+05	-6.4252+05
ENTROPY:			
BTU/LBMOL-R	0.0	0.0	0.0
BTU/LB-R	0.0	0.0	0.0
DENSITY:			
LBMOL/CUFT	0.0	0.0	0.0
LB/CUFT	0.0	0.0	0.0
AVG MW	68.0708	68.0708	68.0708

SIMULATION OF ECONOSEED PROCESS
STREAM SECTION

S1 S2

STREAM ID	S1	S2
FROM :	----	----
TO :	PREHEAT1	PREHEAT2
SUBSTREAM: MIXED		
PHASE:	LIQUID	LIQUID
COMPONENTS: LBMOL/HR		
H2O	5952.4811	2.3810+04
K+	1275.5953	0.0
SO4--	637.7976	0.0
CA++	0.0	637.7976
HCOO-	0.0	1275.5953
TOTAL FLOW:		
LBMOL/HR	7865.8740	2.5723+04
LB/HR	2.1839+05	5.1195+05
STATE VARIABLES:		
TEMP F	77.0000	77.0000
PRES PSI	14.6959	14.6959
VFRAC	0.0	0.0
LFRAC	1.0000	1.0000
SFRAC	0.0	0.0
ENTHALPY:		
BTU/LBMOL	-1.4213+05	-1.2862+05
BTU/LB	-5119.2077	-6462.7894
BTU/HR	-1.1180+09	-3.3086+09
ENTROPY:		
BTU/LBMOL-R	-119.5504	-62.6212
BTU/LB-R	-4.3060	-3.1465
DENSITY:		
LBMOL/CUFT	3.7492	2.9715
LB/CUFT	104.0905	59.1392
AVG MW	27.7637	19.9021

S3 S4 S5

STREAM ID	S3	S4	S5
FROM :	PREHEAT1	PREHEAT2	FLSH1
TO :	REACTOR	REACTOR	EFFECT1
SUBSTREAM: MIXED			
PHASE:	LIQUID	LIQUID	MIXED
COMPONENTS: LBMOL/HR			
H2O	5952.4811	2.3810+04	2.9762+04
K+	1275.5953	0.0	1275.5953
SO4--	637.7976	0.0	11.0411
CA++	0.0	637.7976	11.0411
HCOO-	0.0	1275.5953	1275.5953
TOTAL FLOW:			
LBMOL/HR	7865.8740	2.5723+04	3.2336+04
LB/HR	2.1839+05	5.1195+05	6.4501+05
STATE VARIABLES:			
TEMP F	176.0000	176.0000	218.3900
PRES PSI	14.6959	14.6959	14.6959
VFRAC	0.0	0.0	0.2875
LFRAC	1.0000	1.0000	0.7125
SFRAC	0.0	0.0	0.0
ENTHALPY:			
BTU/LBMOL	-1.4104+05	-1.2686+05	-1.1734+05
BTU/LB	-5080.1739	-6373.9670	-5882.3851
BTU/HR	-1.1094+09	-3.2631+09	-3.7942+09
ENTROPY:			
BTU/LBMOL-R	-103.3217	-55.2945	-40.8191
BTU/LB-R	-3.7215	-2.7783	-2.0464
DENSITY:			
LBMOL/CUFT	3.6533	2.8955	7.0130-03
LB/CUFT	101.4286	57.6268	0.1399
AVG MW	27.7637	19.9021	19.9472

S6 S7 S8

STREAM ID	S6	S7	S8
FROM :	EFFECT1	FLSH2	EFFECT2
TO :	FLSH2	EFFECT2	FLSH3
SUBSTREAM: MIXED			
PHASE:	LIQUID	MIXED	LIQUID
COMPONENTS: LBMOL/HR			
H2O	2.0467+04	2.0467+04	1.1180+04
K+	1275.5953	1275.5953	1275.5953
SO4--	4.7870	4.7870	2.4377
CA++	4.7870	4.7870	2.4377
HCOO-	1275.5953	1275.5953	1275.5953
TOTAL FLOW:			
LBMOL/HR	2.3028+04	2.3028+04	1.3736+04
LB/HR	4.7669+05	4.7669+05	3.0905+05
STATE VARIABLES:			
TEMP F	218.3900	224.6540	224.6540
PRES PSI	14.6959	14.6959	14.6959
VFRAC	0.0	0.4033	0.0
LFRAC	1.0000	0.5967	1.0000
SFRAC	0.0	0.0	0.0
ENTHALPY:			
BTU/LBMOL	-1.3179+05	-1.1589+05	-1.3179+05
BTU/LB	-6366.2855	-5598.6151	-5857.2587
BTU/HR	-3.0348+09	-2.6688+09	-1.8102+09
ENTROPY:			
BTU/LBMOL-R	0.0	-42.8355	0.0
BTU/LB-R	0.0	-2.0693	0.0
DENSITY:			
LBMOL/CUFT	0.0	4.9556-03	0.0
LB/CUFT	0.0	0.1026	0.0
AVG MW	20.7005	20.7005	22.4995

S9 THICKLIQ THINLIQ

STREAM ID	S9	THICKLIQ	THINLIQ
FROM :	FLSH3	EFFECT3	REACTOR
TO :	EFFECT3	----	FLSH1
SUBSTREAM: MIXED			
PHASE:	MIXED	LIQUID	LIQUID
COMPONENTS: LBMOL/HR			
H2O	1.1180+04	1854.2901	2.9762+04
K+	1275.5953	1275.5953	1275.5953
SO4--	2.4377	0.0	11.0411
CA++	2.4377	0.0	11.0411
HCOO-	1275.5953	1275.5953	1275.5953
TOTAL FLOW:			
LBMOL/HR	1.3736+04	4405.4807	3.2336+04
LB/HR	3.0905+05	1.4071+05	6.4501+05
STATE VARIABLES:			
TEMP F	283.4240	283.4240	176.0000
PRES PSI	14.6959	14.6959	14.6959
VFRAC	0.6789	0.0	0.0
LFRAC	0.3211	1.0000	1.0000
SFRAC	0.0	0.0	0.0
ENTHALPY:			
BTU/LBMOL	-1.1206+05	-1.3179+05	-1.3179+05
BTU/LB	-4980.6962	-4126.0677	-6606.7262
BTU/HR	-1.5393+09	-5.8058+08	-4.2614+09
ENTROPY:			
BTU/LBMOL-R	-44.7561	0.0	0.0
BTU/LB-R	-1.9892	0.0	0.0
DENSITY:			
LBMOL/CUFT	2.7128-03	0.0	0.0
LB/CUFT	6.1038-02	0.0	0.0
AVG MW	22.4995	31.9398	19.9472

APPENDIX F

SIMULATION OF HYDRATED LIME PROCESS

CRANES CREST

```
;
;HYDRATED LIME INPUT FILE
;
NEW
TITLE 'SIMULATION OF HYDRATED LIME PROCESS'
DESCRIPTION "TEST OF Ksp USER MODEL TO HANDLE
  EVAPORATION AND PRECIPITATION"
;  GLOBAL DATA
IN-UNITS SI
OUT-UNITS ENG
RUN-CONTROL MAX-TIME=250
HISTORY MSG-LEVEL SYSTEM=8
;  PHYSICAL PROPERTIES SECTION
COMPONENTS H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  OH- OH-
FORMULA    H2O H2O/K+ K+/SO4-- SO4--/CA++ CA++/
  OH- OH-
FILES USRPP1A AQADAT / USRPP1B SOLDAT
PROP-SOURCES
   GLOBAL AQADAT COMPS=ALL/SOLDAT COMPS=ALL
PROP-OPTIONS SYSOPA ELECTRO &
   PHIVMX PHIVMX12 / HVMX HVMX12
PROPERTIES SYSOPA GLOBAL
PROP-DATA
   COMP-LIST                    SO4--;H2O-K2SO4 PAIR
   BCVAL GMELCC 1  1  K+    11.3093
   COMP-LIST                    K+    ;K2SO4-H2O PAIR
   BCVAL GMELCC 1  1 SO4--  -5.4028
PROP-DATA
   COMP-LIST                    OH-   ;H2O-CAHCO02 PAIR
   BCVAL GMELCC 1  1 CA++    8.851
   COMP-LIST                    CA++    ;CAHCO02-H2O PAIR
   BCVAL GMELCC 1  1 OH-    -4.598
PROP-DATA
   COMP-LIST                   OH-;H2O-KOH PAIR
   BCVAL GMELCC 1  1  K+    10.8050
   COMP-LIST                    K+ ;KOH-H2O PAIR
   BCVAL GMELCC 1  1 OH-    -5.2144
DEF-STREAMS HEAT Q1 Q2 Q3 Q4 QM Q6 Q7 Q8 Q9 Q10 Q11 &
    QI QO QT
FLOWSHEET
;
;  DISSOLVER AND REACTOR BLOCKS
;
BLOCK PREHEAT1   IN=S1  Q1        OUT=S3 Q3
BLOCK PREHEAT2   IN=S2  Q2        OUT=S4 Q4
BLOCK HEATREQ    IN=Q3  Q4        OUT=QM
BLOCK REACTOR1   IN=S3  S4 QM     OUT=PRODUCT K2SO4 CAOH2
BLOCK HEAT1      IN=PRODUCT QI    OUT=ISOTHERM QO
BLOCK C-PUMP     IN=ISOTHERM QO   OUT=ADIABATIC QT
BLOCK REACTOR2   IN=ADIABATIC QT OUT=THINLIQ KOH CASO4
;
;  MULTI-EFFECT EVAPORATOR BLOCKS
```

```
;
BLOCK FLSH1      IN=THINLIQ Q6 OUT=S5 Q7
BLOCK EFFECT1    IN=S5 Q7      OUT=S6 EVAP1 INSOL3
BLOCK FLSH2      IN=S6 Q8      OUT=S7 Q9
BLOCK EFFECT2    IN=S7 Q9      OUT=S8 EVAP2 INSOL4
BLOCK FLSH3      IN=S8 Q10     OUT=S9 Q11
BLOCK EFFECT3    IN=S9 Q11     OUT=THICKLIQ EVAP3 INSOL5
;
STREAM S1 TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 0.750 / K+ 0.16072230/
     SO4-- 0.08036115/ CA++ 0.0/OH- 0.0
STREAM S2 TEMP=298.15 PRES=101325.
   MOLE-FLOW H2O 252.00/ K+ 0.0/ SO4-- 0.0/
     CA++ 0.08036115/OH- 0.16072230
BLOCK PREHEAT1 HEATER
   PARAM TEMP=323.15 PRES=101325.
BLOCK PREHEAT2 HEATER
   PARAM TEMP=323.15 PRES=101325.
BLOCK HEATREQ MIXER
BLOCK REACTOR1 USER
   DESCRIPTION "SIMULATE KOH-CASO4 CHEMISTRY"
   SUBROUTINE USRSOL USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL     323.15         101325.
   INT 1
;
;     FORTRAN CODE FOLLOWS
;
;
BLOCK HEAT1 HEATER
   PARAM TEMP=430.0  PRES=101325.
BLOCK C-PUMP HEATER
   PARAM TEMP=430.0  PRES=570000.
BLOCK REACTOR2 USER
   DESCRIPTION "SIMULATE KOH-CASO4 CHEMISTRY"
   SUBROUTINE USRFLH USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRESS(PA)
   REAL     430.0          570000.
   INT 1
;
;     FORTRAN CODE FOLLOWS
;
;
;  THE FOLLOWING BLOCKS ACT AS A MULTI-EFFECT
;  EVAPORATOR REMOVING FIRST THE INSOLUBLE CASO4
;  THEN CONCENTRATING THE REMAINING LIQUOR TO
;  APPROXIMATELY 80% KOH 20% H2O.
;
```

CRANES CREST

```
BLOCK FLSH1 HEATER
   PARAM TEMP=430.064 PRES=570000.
BLOCK EFFECT1 USER
   DESCRIPTION "SIMULATE MULTI-EFFECT
          EVAPORATOR EFFECT 2"
   SUBROUTINE USRFLH USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL     430.064          570000.
   INT 1
;
;      FORTRAN CODE FOLLOWS
;
BLOCK FLSH2 HEATER
   PARAM TEMP=430.124 PRES=570000.
BLOCK EFFECT2 USER
   DESCRIPTION "SIMULATE MULTI-EFFECT
          EVAPORATOR EFFECT 3"
   SUBROUTINE USRFLH USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL     430.124          570000.
   INT 1
;
;    FORTRAN CODE FOLLOWS
;
BLOCK FLSH3 HEATER
   PARAM TEMP=560.0 PRES=570000.
BLOCK EFFECT3 USER
   DESCRIPTION "SIMULATE MULTI-EFFECT
          EVAPORATOR EFFECT 1"
   SUBROUTINE USRFLH USRRPT
   PARAM NINT=100 NREAL=100 NIW=100 NW=400
;          TEMP(K)        PRES(PA)
   REAL     560.0          570000.
   INT 1
;
;     FORTRAN CODE FOLLOWS
;
SIMULATE
```

HYDRATED LIME REPORT

SIMULATION OF HYDRATED LIME PROCESS
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```
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                SIMULATION OF HYDRATED LIME PROCESS
                      RUN CONTROL SECTION

RUN CONTROL INFORMATION
-----------------------

TYPE OF RUN: NEW

INPUT FILE NAME: USER0051:[U858446.ASPEN]LIME.INP;50

OUTPUT PROBLEM DATA FILE NAME: LIME      VERSION NO.    1
LOCATED IN:                    U$D2:[U858446.ASPEN]


PDF SIZE USED FOR INPUT TRANSLATION:
  NUMBER OF FILE RECORDS (PSIZE) =    200
  NUMBER OF IN-CORE RECORDS      =    400
PSIZE NEEDED FOR SIMULATION      =     74

CALLING PROGRAM NAME:            LIME.INP
LOCATED IN:                      U$D2:[U858446.ASPEN]

SIMULATION REQUESTED FOR ENTIRE FLOWSHEET

DESCRIPTION
-----------

    TEST OF Ksp USER MODEL TO HANDLE EVAPORATION
        AND PRECIPITATION

BLOCK STATUS
------------

************************************************************
*                                                          *
* ALL UNIT OPERATION BLOCKS WERE COMPLETED NORMALLY        *
*                                                          *
************************************************************
```

SIMULATION OF HYDRATED LIME PROCESS
FLOWSHEET SECTION

FLOWSHEET CONNECTIVITY BY STREAMS

STREAM	SOURCE	DEST	STREAM	SOURCE	DEST
Q1	----	PREHEAT1	S1	----	PREHEAT1
Q2	----	PREHEAT2	S2	----	PREHEAT2
QI	----	HEAT1	Q6	----	FLSH1
Q8	----	FLSH2	Q10	----	FLSH3
S3	PREHEAT1	REACTOR1	Q3	PREHEAT1	HEATREQ
S4	PREHEAT2	REACTOR1	Q4	PREHEAT2	HEATREQ
QM	HEATREQ	REACTOR1	PRODUCT	REACTOR1	HEAT1
K2SO4	REACTOR1	----	CAOH2	REACTOR1	----
ISOTHERM	HEAT1	C-PUMP	Q0	HEAT1	C-PUMP
ADIABATI	C-PUMP	REACTOR2	QT	C-PUMP	REACTOR2
THINLIQ	REACTOR2	FLSH1	KOH	REACTOR2	----
CASO4	REACTOR2	----	S5	FLSH1	EFFECT1
Q7	FLSH1	EFFECT1	S6	EFFECT1	FLSH2
EVAP1	EFFECT1	----	INSOL3	EFFECT1	----
S7	FLSH2	EFFECT2	Q9	FLSH2	EFFECT2
S8	EFFECT2	FLSH3	EVAP2	EFFECT2	----
INSOL4	EFFECT2	----	S9	FLSH3	EFFECT3
Q11	FLSH3	EFFECT3	THICKLIQ	EFFECT3	----
EVAP3	EFFECT3	----	INSOL5	EFFECT3	----

FLOWSHEET CONNECTIVITY BY BLOCKS

BLOCK	INLETS	OUTLETS
PREHEAT1	S1 Q1	S3 Q3
PREHEAT2	S2 Q2	S4 Q4
HEATREQ	Q3 Q4	QM
REACTOR1	S3 S4 QM	PRODUCT K2SO4 CAOH2
HEAT1	PRODUCT QI	ISOTHERM Q0
C-PUMP	ISOTHERM Q0	ADIABATI QT
REACTOR2	ADIABATI QT	THINLIQ KOH CASO4
FLSH1	THINLIQ Q6	S5 Q7
EFFECT1	S5 Q7	S6 EVAP1 INSOL3
FLSH2	S6 Q8	S7 Q9
EFFECT2	S7 Q9	S8 EVAP2 INSOL4
FLSH3	S8 Q10	S9 Q11
EFFECT3	S9 Q11	THICKLIQ EVAP3 INSOL5

COMPUTATIONAL SEQUENCE

SEQUENCE USED WAS:
PREHEAT2 PREHEAT1 HEATREQ REACTOR1 HEAT1 C-PUMP
REACTOR2 FLSH1 EFFECT1 FLSH2 EFFECT2 FLSH3 EFFECT3

OVERALL FLOWSHEET BALANCE

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
CONVENTIONAL COMPONENTS (LBMOL/HR)			
H2O	0.200599E+07	0.200599E+07	-0.145085E-16
K+	1275.60	1275.60	0.000000E+00
SO4--	637.798	637.798	0.891245E-16
CA++	637.798	637.798	0.891245E-16
OH-	1275.60	1275.60	0.000000E+00
TOTAL BALANCE			
MOLE (LBMOL/HR)	0.200981E+07	0.200981E+07	0.000000E+00
MASS (LB/HR)	0.362982E+08	0.362982E+08	0.000000E+00
ENTHALPY (BTU/HR)	-0.247317E+12	-0.247317E+12	0.462729E-16

COMPONENTS

ID	TYPE	FORMULA	NAME OR ALIAS	REPORT NAME
H2O	C	H2O	H2O	H2O
K+	C	K+	K+	K+
SO4--	C	SO4--	SO4--	SO4--
CA++	C	CA++	CA++	CA++
OH-	C	OH-	OH-	OH-

BLOCK: C-PUMP MODEL: HEATER

INLET STREAM(S):	ISOTHERM QO
OUTLET STREAM:	ADIABATI
OUTLET HEAT STREAM:	QT
PROPERTY OPTION SET:	SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	0.200981E+07	0.200981E+07	0.000000E+00
MASS (LB/HR)	0.362982E+08	0.362982E+08	0.000000E+00
ENTHALPY (BTU/HR)	-0.247317E+12	-0.247317E+12	0.000000E+00

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	314.330
SPECIFIED PRESSURE	PSI	82.6715
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	314.33
OUTLET PRESSURE	PSI	82.672
HEAT DUTY	BTU/HR	-0.33127E+11
VAPOR FRACTION		0.00000E+00

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.99810	0.99810	1.0000	1.0009
K+	0.63468E-03	0.63468E-03	0.00000E+00	0.00000E+00
SO4--	0.31734E-03	0.31734E-03	0.00000E+00	0.00000E+00
CA++	0.31734E-03	0.31734E-03	0.00000E+00	0.00000E+00
OH-	0.63468E-03	0.63468E-03	0.00000E+00	0.00000E+00

BLOCK: EFFECT1 MODEL: USER

SIMULATE MULTI-EFFECT EVAPORATOR EFFECT 2
INLET STREAMS: S5 Q7
OUTLET STREAMS: S6 EVAP1 INSOL3
PROPERTY OPTION SET: SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	0.200885E+07	0.200885E+07	0.000000E+00
MASS (LB/HR)	0.362324E+08	0.362324E+08	-0.257041E-16
ENTHALPY (BTU/HR)	-0.247198E+12	-0.247198E+12	0.308634E-16

BLOCK: EFFECT2 MODEL: USER

SIMULATE MULTI-EFFECT EVAPORATOR EFFECT 3
INLET STREAMS: S7 Q9
OUTLET STREAMS: S8 EVAP2 INSOL4
PROPERTY OPTION SET: SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	0.134578E+07	0.134578E+07	0.000000E+00
MASS (LB/HR)	0.242815E+08	0.242815E+08	0.191776E-16
ENTHALPY (BTU/HR)	-0.165605E+12	-0.165605E+12	0.000000E+00

BLOCK: EFFECT3 MODEL: USER

SIMULATE MULTI-EFFECT EVAPORATOR EFFECT 1
INLET STREAMS: S9 Q11
OUTLET STREAMS: THICKLIQ EVAP3 INSOL5
PROPERTY OPTION SET: SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	677177.	677177.	0.214891E-16
MASS (LB/HR)	0.122308E+08	0.122308E+08	-0.190364E-16
ENTHALPY (BTU/HR)	-0.833299E+11	-0.833299E+11	0.000000E+00

BLOCK: FLSH1 MODEL: HEATER

INLET STREAM(S):	THINLIQ Q6
OUTLET STREAM:	S5
OUTLET HEAT STREAM:	Q7
PROPERTY OPTION SET:	SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	0.200885E+07	0.200885E+07	0.000000E+00
MASS (LB/HR)	0.362324E+08	0.362324E+08	0.000000E+00
ENTHALPY (BTU/HR)	-0.247198E+12	-0.247198E+12	0.000000E+00

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	314.445
SPECIFIED PRESSURE	PSI	82.6715
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	314.45
OUTLET PRESSURE	PSI	82.672
HEAT DUTY	BTU/HR	0.19789E+11
VAPOR FRACTION		0.33002

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.99858	0.99788	1.0000	1.0023
K+	0.63499E-03	0.94778E-03	0.00000E+00	0.00000E+00
SO4--	0.76663E-04	0.11443E-03	0.00000E+00	0.00000E+00
CA++	0.76663E-04	0.11443E-03	0.00000E+00	0.00000E+00
OH-	0.63499E-03	0.94778E-03	0.00000E+00	0.00000E+00

BLOCK: FLSH2 MODEL: HEATER

INLET STREAM(S):	S6	Q8
OUTLET STREAM:	S7	
OUTLET HEAT STREAM:	Q9	
PROPERTY OPTION SET:	SYSOPA	

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	0.134578E+07	0.134578E+07	0.000000E+00
MASS (LB/HR)	0.242815E+08	0.242815E+08	-0.191776E-16
ENTHALPY (BTU/HR)	-0.165605E+12	-0.165605E+12	0.230349E-16

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	314.553
SPECIFIED PRESSURE	PSI	82.6715
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	314.55
OUTLET PRESSURE	PSI	82.672
HEAT DUTY	BTU/HR	0.16979E+11
VAPOR FRACTION		0.49674

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.99795	0.99593	1.0000	1.0041
K+	0.94785E-03	0.18834E-02	0.00000E+00	0.00000E+00
SO4--	0.76508E-04	0.15202E-03	0.00000E+00	0.00000E+00
CA++	0.76508E-04	0.15202E-03	0.00000E+00	0.00000E+00
OH-	0.94785E-03	0.18834E-02	0.00000E+00	0.00000E+00

SIMULATION OF HYDRATED LIME PROCESS
U.O.S. SECTION

BLOCK: FLSH3 MODEL: HEATER

INLET STREAM(S):	S8	Q10
OUTLET STREAM:	S9	
OUTLET HEAT STREAM:	Q11	
PROPERTY OPTION SET:	SYSOPA	

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	677177.	677177.	0.000000E+00
MASS (LB/HR)	0.122308E+08	0.122308E+08	0.190364E-16
ENTHALPY (BTU/HR)	-0.833299E+11	-0.833299E+11	-0.228891E-16

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	548.330
SPECIFIED PRESSURE	PSI	82.6715
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	548.33
OUTLET PRESSURE	PSI	82.672
HEAT DUTY	BTU/HR	0.15471E+11
VAPOR FRACTION		0.99364

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.99608	0.38409	1.0000	2.6035
K+	0.18837E-02	0.29597	0.00000E+00	0.00000E+00
SO4--	0.76265E-04	0.11983E-01	0.00000E+00	0.00000E+00
CA++	0.76265E-04	0.11983E-01	0.00000E+00	0.00000E+00
OH-	0.18837E-02	0.29597	0.00000E+00	0.00000E+00

BLOCK: HEAT1 MODEL: HEATER

INLET STREAM(S):	PRODUCT QI
OUTLET STREAM:	ISOTHERM
OUTLET HEAT STREAM:	QO
PROPERTY OPTION SET:	SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	0.200981E+07	0.200981E+07	0.000000E+00
MASS (LB/HR)	0.362982E+08	0.362982E+08	0.000000E+00
ENTHALPY (BTU/HR)	-0.247317E+12	-0.247317E+12	0.154243E-16

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	314.330
SPECIFIED PRESSURE	PSI	14.6959
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	314.33
OUTLET PRESSURE	PSI	14.696
HEAT DUTY	BTU/HR	0.41756E+11
VAPOR FRACTION		0.99606

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.99810	0.51733	1.0000	1.9330
K+	0.63468E-03	0.16089	0.00000E+00	0.00000E+00
SO4--	0.31734E-03	0.80445E-01	0.00000E+00	0.00000E+00
CA++	0.31734E-03	0.80445E-01	0.00000E+00	0.00000E+00
OH-	0.63468E-03	0.16089	0.00000E+00	0.00000E+00

BLOCK: HEATREQ MODEL: MIXER

INLET STREAM(S):	Q3 Q4
OUTLET STREAM:	QM
PROPERTY OPTION SET:	SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE ENTHALPY (BTU/HR)	-0.161997E+10	-0.161997E+10	0.000000E+00

CRANES CREST

BLOCK: PREHEAT1 MODEL: HEATER

INLET STREAM(S):	S1	Q1
OUTLET STREAM:	S3	
OUTLET HEAT STREAM:	Q3	
PROPERTY OPTION SET:	SYSOPA	

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	7865.87	7865.87	0.000000E+00
MASS (LB/HR)	218386.	218386.	0.000000E+00
ENTHALPY (BTU/HR)	-0.111796E+10	-0.111796E+10	0.266577E-16

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	122.000
SPECIFIED PRESSURE	PSI	14.6959
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	122.00
OUTLET PRESSURE	PSI	14.696
HEAT DUTY	BTU/HR	0.38535E+07
VAPOR FRACTION		0.00000E+00

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.75675	0.75675	1.0000	0.71872E-01
K+	0.16217	0.16217	0.00000E+00	0.00000E+00
SO4--	0.81084E-01	0.81084E-01	0.00000E+00	0.00000E+00

BLOCK: PREHEAT2 MODEL: HEATER

INLET STREAM(S): S2 Q2
OUTLET STREAM: S4
OUTLET HEAT STREAM: Q4
PROPERTY OPTION SET: SYSOPA

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	0.200195E+07	0.200195E+07	0.000000E+00
MASS (LB/HR)	0.360799E+08	0.360799E+08	0.000000E+00
ENTHALPY (BTU/HR)	-0.246200E+12	-0.246200E+12	0.000000E+00

*** INPUT DATA ***

TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	F	122.000
SPECIFIED PRESSURE	PSI	14.6959
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***

OUTLET TEMPERATURE	F	122.00
OUTLET PRESSURE	PSI	14.696
HEAT DUTY	BTU/HR	0.16161E+10
VAPOR FRACTION		0.00000E+00

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
H2O	0.99904	0.99904	1.0000	0.12189
CA++	0.31859E-03	0.31859E-03	0.00000E+00	0.00000E+00
OH-	0.63718E-03	0.63718E-03	0.00000E+00	0.00000E+00

BLOCK: REACTOR1 MODEL: USER

SIMULATE KOH-CASO4 CHEMISTRY

INLET STREAMS:	S3	S4	QM
OUTLET STREAMS:	PRODUCT	K2SO4	CAOH2
PROPERTY OPTION SET:	SYSOPA		

	*** MASS AND ENERGY BALANCE *** IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	0.200981E+07	0.200981E+07	0.000000E+00
MASS (LB/HR)	0.362982E+08	0.362982E+08	0.256575E-16
ENTHALPY (BTU/HR)	-0.247317E+12	-0.247317E+12	0.000000E+00

BLOCK: REACTOR2 MODEL: USER

SIMULATE KOH-CASO4 CHEMISTRY

INLET STREAMS:	ADIABATI	QT	
OUTLET STREAMS:	THINLIQ	KOH	CASO4
PROPERTY OPTION SET:	SYSOPA		

	*** MASS AND ENERGY BALANCE *** IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (LBMOL/HR)	0.200981E+07	0.200981E+07	0.144809E-16
MASS (LB/HR)	0.362982E+08	0.362982E+08	0.000000E+00
ENTHALPY (BTU/HR)	-0.247317E+12	-0.247317E+12	0.000000E+00

Q1 Q10 Q11 Q2

STREAM ID	Q1	Q10	Q11	Q2
FROM :	----	----	FLSH3	----
TO :	PREHEAT1	FLSH3	EFFECT3	PREHEAT2
CLASS:	HEAT	HEAT	HEAT	HEAT
STREAM ATTRIBUTES: HEAT				
Q BTU/HR	0.0	0.0	-1.5471+10	0.0

Q3 Q4 Q6 Q7

STREAM ID	Q3	Q4	Q6	Q7
FROM :	PREHEAT1	PREHEAT2	----	FLSH1
TO :	HEATREQ	HEATREQ	FLSH1	EFFECT1
CLASS:	HEAT	HEAT	HEAT	HEAT
STREAM ATTRIBUTES: HEAT				
Q BTU/HR	-3.85835+06	1.6161+09	0.0	-1.9789+10

Q8 Q9 QI QM

STREAM ID	Q8	Q9	QI	QM
FROM :	----	FLSH2	----	HEATREQ
TO :	FLSH2	EFFECT2	HEAT1	REACTOR1
CLASS:	HEAT	HEAT	HEAT	HEAT
STREAM ATTRIBUTES: HEAT				
Q BTU/HR	0.0	-1.6979+10	0.0	-1.6200+09

Q0 QT

STREAM ID	Q0	QT
FROM:	HEAT1	C-PUMP
TO:	C-PUMP	REACTOR
CLASS:	HEAT	HEAT
STREAM ATTRIBUTES: HEAT		
Q BTU/HR	-4.1756+10	-8.6292+09

SIMULATION OF HYDRATED LIME PROCESS
STREAM SECTION

ADIABATI CAOH2 CASO4

STREAM ID	ADIABATI	CAOH2	CASO4
FROM :	C-PUMP	REACTOR1	REACTOR2
TO :	REACTOR2	----	----
SUBSTREAM: MIXED			
PHASE:	LIQUID	MIXED	MIXED
COMPONENTS: LBMOL/HR			
H2O	2.0060+06	0.0	0.0
K+	1275.5953	0.0	0.0
SO4--	637.7976	0.0	483.7939
CA++	637.7976	0.0	483.7939
OH-	1275.5953	0.0	0.0
TOTAL FLOW:			
LBMOL/HR	2.0098+06	0.0	967.5877
LB/HR	3.6298+07	0.0	6.5864+04
STATE VARIABLES:			
TEMP F	314.3300	122.0000	314.3300
PRES PSI	82.6715	14.6959	82.6715
VFRAC	0.0	0.0	0.0
LFRAC	1.0000	0.0	0.0
SFRAC	0.0	1.0000	1.0000
ENTHALPY:			
BTU/LBMOL	-1.1876+05	0.0	-1.2305+05
BTU/LB	-6575.7527	0.0	-1807.7498
BTU/HR	-2.3869+11	0.0	-1.1907+08
ENTROPY:			
BTU/LBMOL-R	-32.6721	0.0	0.0
BTU/LB-R	-1.8090	0.0	0.0
DENSITY:			
LBMOL/CUFT	3.1601	0.0	0.0
LB/CUFT	57.0725	0.0	0.0
AVG MW	18.0605	0.0	68.0708

EVAP1 EVAP2

STREAM ID	EVAP1	EVAP2
FROM :	EFFECT1	EFFECT2
TO :	----	----
SUBSTREAM: MIXED		
PHASE:	VAPOR	VAPOR
COMPONENTS: LBMOL/HR		
H2O	6.6296+05	6.6850+05
K+	0.0	0.0
SO4--	0.0	0.0
CA++	0.0	0.0
OH-	0.0	0.0
TOTAL FLOW:		
LBMOL/HR	6.6296+05	6.6850+05
LB/HR	1.1944+07	1.2044+07
STATE VARIABLES:		
TEMP F	314.4452	314.5532
PRES PSI	82.6715	82.6715
VFRAC	1.0000	1.0000
LFRAC	0.0	0.0
SFRAC	0.0	0.0
ENTHALPY:		
BTU/LBMOL	-1.2305+05	-1.2305+05
BTU/LB	-6830.3162	-6830.3162
BTU/HR	-8.1581+10	-8.2262+10
ENTROPY:		
BTU/LBMOL-R	0.0	0.0
BTU/LB-R	0.0	0.0
DENSITY:		
LBMOL/CUFT	0.0	0.0
LB/CUFT	0.0	0.0
AVG MW	18.0160	18.0160

EVAP3 INSOL3 INSOL4

STREAM ID	EVAP3	INSOL3	INSOL4
FROM :	EFFECT3	EFFECT1	EFFECT2
TO :	----	----	----
SUBSTREAM: MIXED			
PHASE:	VAPOR	MIXED	MIXED
COMPONENTS: LBMOL/HR			
H2O	6.7287+05	0.0	0.0
K+	0.0	0.0	0.0
SO4--	0.0	51.0405	51.3183
CA++	0.0	51.0405	51.3183
OH-	0.0	0.0	0.0
TOTAL FLOW:			
LBMOL/HR	6.7287+05	102.0811	102.6366
LB/HR	1.2122+07	6948.7410	6986.5587
STATE VARIABLES:			
TEMP F	548.3300	314.4452	314.5532
PRES PSI	82.6715	82.6715	82.6715
VFRAC	1.0000	0.0	0.0
LFRAC	0.0	0.0	0.0
SFRAC	0.0	1.0000	1.0000
ENTHALPY:			
BTU/LBMOL	-1.2305+05	-1.2305+05	-1.2305+05
BTU/LB	-6830.3162	-1807.7498	-1807.7498
BTU/HR	-8.2800+10	-1.2562+07	-1.2630+07
ENTROPY:			
BTU/LBMOL-R	0.0	0.0	0.0
BTU/LB-R	0.0	0.0	0.0
DENSITY:			
LBMOL/CUFT	0.0	0.0	0.0
LB/CUFT	0.0	0.0	0.0
AVG MW	18.0160	68.0708	68.0708

INSOL5 ISOTHERM

STREAM ID	INSOL5	ISOTHERM
FROM :	EFFECT3	HEAT1
TO :	----	C-PUMP
SUBSTREAM: MIXED		
PHASE:	MIXED	MIXED
COMPONENTS: LBMOL/HR		
H2O	0.0	2.0060+06
K+	0.0	1275.5953
SO4--	51.6449	637.7976
CA++	51.6449	637.7976
OH-	0.0	1275.5953
TOTAL FLOW:		
LBMOL/HR	103.2898	2.0098+06
LB/HR	7031.0216	3.6298+07
STATE VARIABLES:		
TEMP F	548.3300	314.3300
PRES PSI	82.6715	14.6959
VFRAC	0.0	0.9961
LFRAC	0.0	3.9448-03
SFRAC	1.0000	0.0
ENTHALPY:		
BTU/LBMOL	-1.2305+05	-1.0228+05
BTU/LB	-1807.7498	-5663.1174
BTU/HR	-1.2710+07	-2.0556+11
ENTROPY:		
BTU/LBMOL-R	0.0	-8.0673
BTU/LB-R	0.0	-0.4467
DENSITY:		
LBMOL/CUFT	0.0	1.7763-03
LB/CUFT	0.0	3.2081-02
AVG MW	68.0708	18.0605

K2SO4 KOH PRODUCT

STREAM ID	K2SO4	KOH	PRODUCT
FROM :	REACTOR1	REACTOR2	REACTOR1
TO :	----	----	HEAT1
SUBSTREAM: MIXED			
PHASE:	MIXED	VAPOR	LIQUID
COMPONENTS: LBMOL/HR			
H2O	0.0	0.0	2.0060+06
K+	0.0	0.0	1275.5953
SO4--	0.0	0.0	637.7976
CA++	0.0	0.0	637.7976
OH-	0.0	0.0	1275.5953
TOTAL FLOW:			
LBMOL/HR	0.0	0.0	2.0098+06
LB/HR	0.0	0.0	3.6298+07
STATE VARIABLES:			
TEMP F	122.0000	314.3300	122.0000
PRES PSI	14.6959	82.6715	14.6959
VFRAC	0.0	1.0000	0.0
LFRAC	0.0	0.0	1.0000
SFRAC	1.0000	0.0	0.0
ENTHALPY:			
BTU/LBMOL	0.0	0.0	-1.2305+05
BTU/LB	0.0	0.0	-6813.4823
BTU/HR	0.0	0.0	-2.4732+11
ENTROPY:			
BTU/LBMOL-R	0.0	0.0	0.0
BTU/LB-R	0.0	0.0	0.0
DENSITY:			
LBMOL/CUFT	0.0	0.0	0.0
LB/CUFT	0.0	0.0	0.0
AVG MW	0.0	0.0	18.0605

S1 S2

STREAM ID	S1	S2
FROM :	----	----
TO :	PREHEAT1	PREHEAT2
SUBSTREAM: MIXED		
PHASE:	LIQUID	LIQUID
COMPONENTS: LBMOL/HR		
H2O	5952.4811	2.0000+06
K+	1275.5953	0.0
SO4--	637.7976	0.0
CA++	0.0	637.7976
OH-	0.0	1275.5953
TOTAL FLOW:		
LBMOL/HR	7865.8740	2.0019+06
LB/HR	2.1839+05	3.6080+07
STATE VARIABLES:		
TEMP F	77.0000	77.0000
PRES PSI	14.6959	14.6959
VFRAC	0.0	0.0
LFRAC	1.0000	1.0000
SFRAC	0.0	0.0
ENTHALPY:		
BTU/LBMOL	-1.4213+05	-1.2298+05
BTU/LB	-5119.2077	-6823.7375
BTU/HR	-1.1180+09	-2.4620+11
ENTROPY:		
BTU/LBMOL-R	-119.5504	-39.1723
BTU/LB-R	-4.3060	-2.1735
DENSITY:		
LBMOL/CUFT	3.7492	3.4603
LB/CUFT	104.0905	62.3635
AVG MW	27.7637	18.0224

S3 S4 S5

STREAM ID	S3	S4	S5
FROM :	PREHEAT1	PREHEAT2	FLSH1
TO :	REACTOR1	REACTOR1	EFFECT1
SUBSTREAM: MIXED			
PHASE:	LIQUID	LIQUID	MIXED
COMPONENTS: LBMOL/HR			
H2O	5952.4811	2.0000+06	2.0060+06
K+	1275.5953	0.0	1275.5953
SO4--	637.7976	0.0	154.0038
CA++	0.0	637.7976	154.0038
OH-	0.0	1275.5953	1275.5953
TOTAL FLOW:			
LBMOL/HR	7865.8740	2.0019+06	2.0088+06
LB/HR	2.1839+05	3.6080+07	3.6232+07
STATE VARIABLES:			
TEMP F	122.0000	122.0000	314.4452
PRES PSI	14.6959	14.6959	82.6715
VFRAC	0.0	0.0	0.3300
LFRAC	1.0000	1.0000	0.6700
SFRAC	0.0	0.0	0.0
ENTHALPY:			
BTU/LBMOL	-1.4164+05	-1.2217+05	-1.1320+05
BTU/LB	-5101.5624	-6778.9448	-6276.4226
BTU/HR	-1.1141+09	-2.4458+11	-2.2741+11
ENTROPY:			
BTU/LBMOL-R	-111.5519	-37.7080	-25.4743
BTU/LB-R	-4.0179	-2.0923	-1.4124
DENSITY:			
LBMOL/CUFT	3.7150	3.4288	2.9963-02
LB/CUFT	103.1415	61.7950	0.5404
AVG MW	27.7637	18.0224	18.0364

S6 S7 S8

STREAM ID	S6	S7	S8
FROM :	EFFECT1	FLSH2	EFFECT2
TO :	FLSH2	EFFECT2	FLSH3
SUBSTREAM: MIXED			
PHASE:	MIXED	MIXED	MIXED
COMPONENTS: LBMOL/HR			
H2O	1.3430+06	1.3430+06	6.7452+05
K+	1275.5953	1275.5953	1275.5953
SO4--	102.9632	102.9632	51.6449
CA++	102.9632	102.9632	51.6449
OH-	1275.5953	1275.5953	1275.5953
TOTAL FLOW:			
LBMOL/HR	1.3458+06	1.3458+06	6.7718+05
LB/HR	2.4281+07	2.4281+07	1.2231+07
STATE VARIABLES:			
TEMP F	314.4452	314.5532	314.5532
PRES PSI	82.6715	82.6715	82.6715
VFRAC	0.1084	0.4967	2.7476-02
LFRAC	0.8916	0.5033	0.9725
SFRAC	0.0	0.0	0.0
ENTHALPY:			
BTU/LBMOL	-1.2305+05	-1.1044+05	-1.2305+05
BTU/LB	-6820.2125	-6120.9397	-6813.1266
BTU/HR	-1.6560+11	-1.4863+11	-8.3330+10
ENTROPY:			
BTU/LBMOL-R	0.0	-21.9834	0.0
BTU/LB-R	0.0	-1.2184	0.0
DENSITY:			
LBMOL/CUFT	0.0	1.9968-02	0.0
LB/CUFT	0.0	0.3603	0.0
AVG MW	18.0427	18.0427	18.0615

S9 THICKLIQ THINLIQ

STREAM ID	S9	THICKLIQ	THINLIQ
FROM :	FLSH3	EFFECT3	REACTOR2
TO :	EFFECT3	----	FLSH1
SUBSTREAM: MIXED			
PHASE:	MIXED	MIXED	LIQUID
COMPONENTS: LBMOL/HR			
H2O	6.7452+05	1655.3653	2.0060+06
K+	1275.5953	1275.5953	1275.5953
SO4--	51.6449	0.0	154.0038
CA++	51.6449	0.0	154.0038
OH-	1275.5953	1275.5953	1275.5953
TOTAL FLOW:			
LBMOL/HR	6.7718+05	4206.5558	2.0088+06
LB/HR	1.2231+07	1.0140+05	3.6232+07
STATE VARIABLES:			
TEMP F	548.3300	548.3300	314.3300
PRES PSI	82.6715	82.6715	82.6715
VFRAC	0.9936	7.8283-03	0.0
LFRAC	6.3644-03	0.9922	1.0000
SFRAC	0.0	0.0	0.0
ENTHALPY:			
BTU/LBMOL	-1.0021+05	-1.2305+05	-1.2305+05
BTU/LB	-5548.2074	-5105.1117	-6822.5819
BTU/HR	-6.7859+10	-5.1764+08	-2.4720+11
ENTROPY:			
BTU/LBMOL-R	-9.2532	0.0	0.0
BTU/LB-R	-0.5123	0.0	0.0
DENSITY:			
LBMOL/CUFT	7.6914-03	0.0	0.0
LB/CUFT	0.1389	0.0	0.0
AVG MW	18.0615	24.1043	18.0364

APPENDIX G

VAPOR-LIQUID EQUILIBRIUM DATA

FOR KHCOO-WATER SYSTEM

CRANES CREST

LABORATORY EXPERIMENT TO DETERMINE KHCOO-WATER BOILING POINT ELEVATION CURVE AND DISTILLATE ANALYSIS

An experiment was performed to develop a boiling point elevation curve and a distillate analysis during evaporation for a potassium formate-water solution. The assumption to be tested with this experiment was that while concentrating a potassium formate-water solution the vapor phase generated would be greater than 99 percent water. If this assumption proved to be correct then the ASME Steam Tables used during the ASPEN simulation of the Econoseed Process would accurately define the physical properties of the vapor phase and the steam requirements generated during the ASPEN simulation would be reasonable.

In this experiment a 2.4M (mass fraction KHCOO 0.1667) solution of potassium formate-water was prepared at room temperature. The solution was then heated in an erlenmeyer flask to approximately 310 degrees F. This temperature was chosen as the limit as potassium formate decomposes at approximately 315 degress F. The boiling point elevation and solution concentrations were calculated based on the assumption that the volality of potassium formate in water approaches zero. Concentration versus boiling point elevation data are given in Table G.1 and are compared to the ASPEN generated boiling point elevation of various potassium formate-water solutions. The vapor phase was

passed through a condenser and the resulting distillate was collected for analysis. The outlet concentration of the heated solution (assuming y_{KHCOO} equals zero) was calculated to be 58M based on a weight by difference calculation between the original solution and the resulting distillate. The distillate was then analyzed for total water, concentration of potassium ions in solution, concentration of formate ions in solution, and total organic carbon in solution. The results from these analyses is given in Table G.2.

The results verify the assumption that the vapor phase is greater than 99 percent water and suggests that the steam required to concentrate the potassium formate-water solution is reasonable. Additionally, the boiling point elevation curve generated by the experiment compares favorably with the boiling point elevation curve generated with ASPEN suggesting that the simulation results are reasonable.

GRANGE CREST

TABLE G.1: POTASSIUM FORMATE-WATER
VAPOR-LIQUID EQUILIBRIUM
BOILING POINT ELEVATION CURVE

CONCENTRATION (MASS FRACTION)	EXPERIMENTAL BOILING POINT (F)	ASPEN GENERATED BOILING POINT (F)
0.21073	217.43	218.30
0.24989	219.23	220.29
0.28552	221.39	221.62
0.36991	226.43	225.74
0.39943	229.31	227.85
0.45373	234.17	232.29
0.49895	238.67	236.65
0.56996	247.85	245.20
0.66454	265.67	260.69
0.79675	303.47	296.38

TABLE G.2: POTASSIUM FORMATE-WATER VAPOR-LIQUID EQUILIBRIUM DISTILLATE ANALYSIS

ANALYSIS (METHOD)	CONCENTRATION	ACCURACY
TOTAL WATER (Volumetric Analysis)	99.9 %	0.1 %
FORMATE (Dionex-ion chromatography)	18 ppm	2 ppm
POTASSIUM (Flame atomic absorption)	14 ppm	5 ppm
TOTAL ORGANIC CARBON (Infrared absorption)	10 ppm	5 ppm

NOTE: ANALYSES WERE COMPLETED BY AN ORGANIC CHEMICAL LABORATORY AT TENNESSEE EASTMAN COMPANY

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VITA

James V. Walden was born in Bethesda, MD on July 20, 1951. He graduated from Jacksonville Sr. High School in Jacksonville, NC in June of 1969. After a two year tour of duty with the Army during the Vietnam War, he began a career as an air traffic controller with the government.

In January 1982, Mr. Walden returned to school to pursue a Bachelor of Science degree in Chemical Engineering. In June of 1985, he was awarded a Bachelor of Science degree in Chemical Engineering from the University of Tennessee in Knoxville.

In June of 1985, Mr. Walden entered the University of Tennessee Space Institute where he began pursuit of a Master of Science degree in Chemical Engineering.

In July of 1986, Mr. Walden completed the course work associated with his degree and began full time employment as a Chemical Engineer with Tennessee Eastman Company in Kingsport, TN working in the Coal Gasification Department.

Mr. Walden is married to the former Jennifer Hasty of East Point, Georgia.