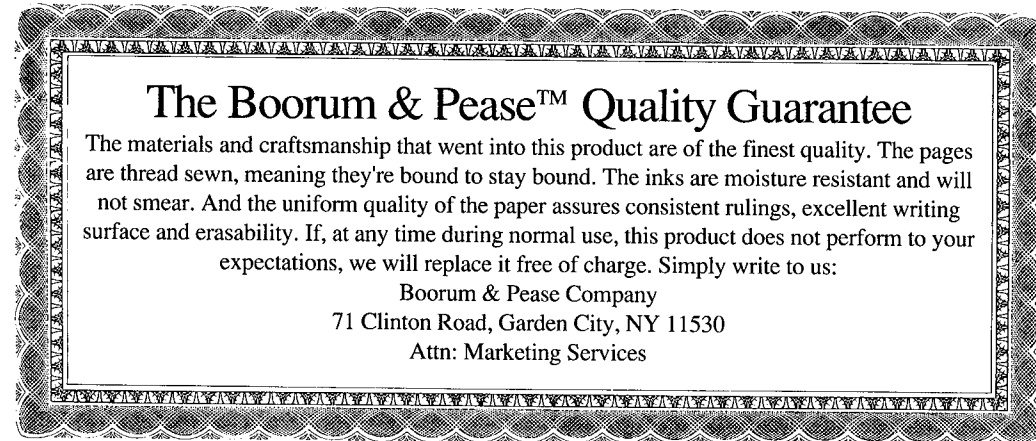


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#### Contents

#### Page

Geochemistry Research Project

1

The purpose of this notebook is to formally document codes and calculations associated with the geochemistry research project, particularly for the modeling task.

Initial entries are by

William M. Murphy (WMM)

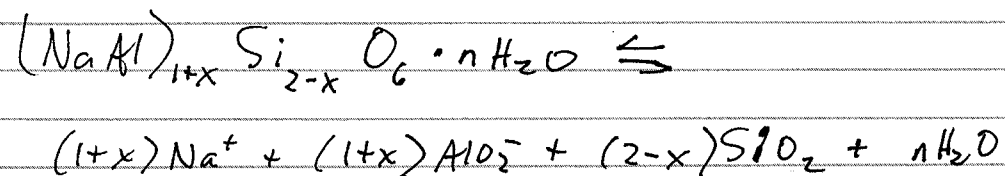
and Christopher J. Goulet (CJG)  
(acting on behalf of Murphy).

WMM 6/9/92

and Jennifer A. Roberts (JAR)  
(acting on behalf of Murphy)

## IASDRE (Integrated Analcime Stoichiometric Dissolution Rate Equation)

The IASDRE code is a FORTRAN program written and maintained to perform calculations and solve the dissolution rate equation for the Analcime-Clinoptilolite Dissolution Tests (ACDT) in the geochemistry research project. It was developed in January, 1992 by Christopher Goulet and William M. Murphy. ISADRE32 is a revised version, and will be used interchangeably with IASDRE. The dissolution of analcime can be written



where  $x$  represents the variance from the ideal stoichiometry of analcime for the given sample.

The dissolution rate equation can be written as

$$\frac{d\xi}{dt} = k^*s \left[ 1 - \left( \frac{Q}{K} \right)^{1/\sigma} \right]$$

where  $\xi$  = reaction progress

$k^*s$  = apparent rate constant times surface area of reactant

$Q$  = activity product

and  $K$  = equilibrium constant

As reported in the annual report for the calendar year 1991 by William M. Murphy, the rate equation

(cont'd) → CJG 6/9/92

can be integrated analytically to give:

$$\int_{t_i}^{t_{i+1}} dt = \int_{u(t_i)}^{u(t_{i+1})} \frac{du}{A+Bu} = \frac{1}{B} \ln \left| \frac{A+Bu}{A+Bu} \right|_{u(t_i)}^{u(t_{i+1})}$$

where  $\sigma$  for the rate equation equals 3

and  $u = n_{Si,R} - n_{Si,E}$  or the total number of moles of  $Si$  released in dissolution minus the total number of moles of  $Si$  extracted during sampling intervals. The above solution to the rate equation was used in the IASDRE code.

The name of the source code is IASDRE32.FOR

The "3" signifies that the value of  $\sigma$  in the dissolution rate equation was 3 for the code evaluations.

The "2" signifies that 2 values of  $k^*s$  were used in the code to correct for a dual reaction mechanism caused by decreasing surface area of reactive material. This is reported in the 1991 annual report in the "Interpretation of Rate Data" under the Kinetic Analysis in Chapter 2. CJG 6/9/92

For a complete theoretical development see chapter 2.2 of CNWRA 91-01A, the annual report referenced above. ISADRE32 was used for the data regression shown in Fig. 2-13 of that report. WMM 6/10/92



The value of "A" in the solution is given as:

$$A = (2-x) K^* S$$

and "B" is given as:

$$B = -(2-x) K^* S \left[ \frac{\chi_{SiO_2}^{2-x} \chi_{SiO_2}^{2-x} (a_{Na^+} \chi_{AlO_2^-} \chi_{AlO_2^-} \frac{(1+x)^{1+x}}{(2-x)^{1+x}})}{K W^3} \right]^{1/5}$$

For the IASDRE32 code,  
the values for

$$\chi_{SiO_2}, \chi_{SiO_2}, \chi_{AlO_2^-}, \chi_{AlO_2^-}, a_{Na^+}$$

were taken from calculations made using  
the EQ3/6 software package.

Experimental conditions were placed in  
the EQ3 input deck and EQ3 was  
run to calculate the above values.

$\chi_{SiO_2}$  was calculated to be .6931

$\chi_{SiO_2}$  was calculated to be 1.0

$\chi_{AlO_2^-}$  was calculated to be .9991

$\chi_{AlO_2^-}$  was calculated to be .7705

$a_{Na^+}$  was calculated to be .08334

The value of  $a_{Na^+}$  however, was later  
corrected for non-constant activities of the  
activity of  $Na^+$ .

The values for  $\chi_{SiO_2}$ ,  $\chi_{SiO_2}$ ,  $\chi_{AlO_2^-}$  and  $\chi_{AlO_2^-}$   
remained approximately constant in speciation  
calculations using EQ3. CJ 1/19/92

$$\text{Since } a_{Na^+} = [Na^+] \gamma_{Na^+},$$

the value for  $\gamma_{Na^+}$  can be calculated  
accurately with EQ3 and the correction  
for non-constant  $a_{Na^+}$  can be reflected  
in varying  $Na^+$  concentration.

$[Na^+]$  is given/assigned the variable name  
"CON- $Na$ " in IASDRE32.

CON- $Na$  was calculated at any time  $t$  as:

$$\text{CON-} Na = (\text{Initial moles } Na^+) + \frac{(1.0+x) \text{ (moles Si Released)}}{(2.0-x)} - \text{Moles } Na^+ \text{ removed}$$

(Mass of Water at time  $t$ )

The initial moles of  $Na^+$ ,  $Na\_moles\_init$  in  
IASDRE32 is calculated as:

$$Na\_moles\_init = (\text{initial concentration}) \times (\text{initial water mass})$$

The initial concentration of sodium was  
measured to be .11 molal and the  
initial water mass for sample ACD72A  
was measured to be .99975 kg.

CJ 6/19/92

See note on page 24 concerning the  
EQ3/6 data base.

WJ 6/10/92

synthesized WJ 6/10/92



The cumulative amount of  $\text{Na}^+$  removed from solution was calculated in IASDRE32 at every experimental sampling period (the only time water is extracted) as:

$$(\text{Na-rem-tot})_{t_{i+1}} = (\text{Na-rem-tot})_{t_i} + (\text{con-Na}) * \left( \frac{\text{Mass of Water}}{\text{Extracted}} \right)$$

The mass of water extracted at each sampling point can be calculated easily using experimental measurements. Since the mass of water was measured before and after sampling, the mass of water extracted at time  $t$  is given by:

$$\text{Mass of Water Extracted} = (\text{Mass}_{\text{H}_2\text{O}} \text{ before}) - (\text{Mass}_{\text{H}_2\text{O}} \text{ after})$$

Values for  $k^*s$  used in IASDRE32 were calculated from graphical representation of the experimental data.

$(k^*s)_1$  is equal to the initial slope of

the graph of  $\xi$  v time. This slope was calculated using experimental data entered in MICROSOFT EXCEL spreadsheets and CRICKET GRAPH graphics software.

SEE FIGURES IN 1991 annual report.

$(k^*s)$  was measured to be  $4e^{-12}$ .  
calculated  $CSA$  6/19/92

6/19/92  
CJD

A secondary mechanism in the dissolution reaction requires that a second value of  $k^*s$  be used for the interval of the reaction in which the reactive material (surface area) has been depleted.

Again, using MICROSOFT EXCEL (filename on the Mac is ACDTIA) and CRICKET GRAPH, the  $(k^*s)_2$  was calculated using the slope of the graph  $\xi$  v. time.

$(k^*s)_2$  was calculated to be  $5e^{-13}$ .

The value for  $W$ , the mass of water, used in IASDRE32 was taken from the experimental measurements which can also be found in MICROSOFT EXCEL (ACDTIA).

At any theoretical time  $t$  the mass of water  $W$  was approximated as the mass of water after the most recent experimental sampling interval. See notes below re: evaporation.

WM 6/10/92 CJD 6/19/92

A new variable  $W_{H_2O} + t_{im}$ , was introduced to calculate the mass of water at any time, including between sampling intervals. The evaporation that occurred was linearly interpolated throughout each non-sampling time interval. The calculated mass of water was thus the mass of water after the previous sampling minus the fraction of time transpired until the next sampling interval times ( $x$ ) the total evaporation for that interval.

CJD 6/19/92



The value for  $x$ , the correction for the non-ideal stoichiometry of the analcime sample was calculated using data measured by inductively coupled plasma emission spectroscopy (ICP) as reported in the 1991 annual report.

From the data reported in Table 2-1 of the 1991 annual report, the following calculations were made:

oxide	(average wt/100g)	(moles/100g)	(moles cation/100g)	(moles O/100g)
SiO <sub>2</sub>	54.33	.9042	.9042	1.8084
Al <sub>2</sub> O <sub>3</sub>	23.84	.2338	.4676	.7014
TiO <sub>2</sub>	.004	5.007e <sup>-5</sup>	5.007e <sup>-5</sup>	1.001e <sup>-4</sup>
Fe <sub>2</sub> O <sub>3</sub>	.05	3.131e <sup>-4</sup>	6.262e <sup>-4</sup>	9.393e <sup>-4</sup>
MgO	.038	9.429e <sup>-4</sup>	9.429e <sup>-4</sup>	9.429e <sup>-4</sup>
CaO	.002	3.566e <sup>-5</sup>	3.566e <sup>-5</sup>	3.566e <sup>-5</sup>
Na <sub>2</sub> O	14.354	.2315	.4630	.2315
K <sub>2</sub> O	.028	2.973e <sup>-4</sup>	5.946e <sup>-4</sup>	2.973e <sup>-4</sup>

TOTAL  
moles O/100g

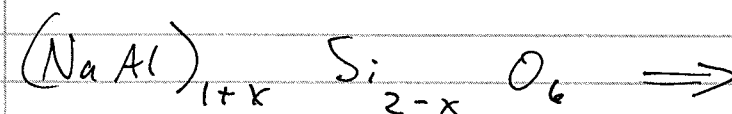
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CJD  
6/9/92

oxide	moles O/100g	moles cation
SiO <sub>2</sub>	1.8084 $\cdot \frac{6}{2.744} = 1.977$ CJD 6/9/92 3.955	1.977
Al <sub>2</sub> O <sub>3</sub>	.7014 $\cdot \frac{6}{2.744} = 1.023$ CJD 6/9/92 1.534	1.023
TiO <sub>2</sub>	1.001e <sup>-4</sup> $\cdot \frac{6}{2.744} = 1.095e^{-4}$ CJD 6/9/92 2.189e <sup>-4</sup>	1.095e <sup>-4</sup>
Fe <sub>2</sub> O <sub>3</sub>	9.393e <sup>-4</sup> $\cdot \frac{6}{2.744} = 1.369e^{-3}$ CJD 6/9/92 2.054e <sup>-3</sup>	1.369e <sup>-3</sup>
MgO	9.429e <sup>-4</sup> $\cdot \frac{6}{2.744} = 2.062e^{-3}$	2.062e <sup>-3</sup>
CaO	3.566e <sup>-5</sup> $\cdot \frac{6}{2.744} = 7.799e^{-5}$	7.799e <sup>-5</sup>
Na <sub>2</sub> O	.2315 $\cdot \frac{6}{2.744} = 1.013$ CJD 6/9/92 .5063	1.013
K <sub>2</sub> O	2.973e <sup>-4</sup> $\cdot \frac{6}{2.744} = 1.300e^{-3}$ CJD 6/9/92 6.502e <sup>-4</sup>	1.300e <sup>-3</sup>

Ideal Analcime: NaAlSi<sub>2</sub>O<sub>6</sub> · H<sub>2</sub>O

Experimental Analcime: Na<sub>1.013</sub>Al<sub>1.023</sub>Si<sub>1.977</sub>O<sub>6</sub> · H<sub>2</sub>O



$$1.013 = 1+x \quad x = .013$$

$$1.023 = 1+x \quad x = .023$$

$$1.977 = 2-x \quad x = .023$$

$$\frac{(.013 + .023 + .023)}{3} = .0197 \approx .02 \quad \text{CJD 6/9/92}$$



The equilibrium constant,  $K$ , was calculated using results from EQ3 equilibrium aqueous speciation calculations performed on the ACDT "A" Series and also the Analcime Solubility Experiments, ASE1, 2, 3, and 4,

The logarithmic activity diagram in Figure 2-14 of the 1991 annual report shows  $\text{LOG}(a_{\text{SiO}_2})$  v.  $\text{LOG}([a_{\text{Na}^+}][a_{\text{AlO}_2^-}])$  for the ACDT and ASE data.

The law of mass action for dissolution of analcime with the analytically determined composition can be written in logarithmic form as:

$$\log([a_{\text{Na}^+}][a_{\text{AlO}_2^-}]) = \frac{-1.98}{1.02} \log(a_{\text{SiO}_2}) + \frac{\log K}{1.02}$$

Using Cricket Graph software on the Mac, the above relationship was used to calculate a value of  $\log K$  from the graph of  $\log(a_{\text{SiO}_2})$  v  $\log([a_{\text{Na}^+}][a_{\text{AlO}_2^-}])$ ,

$\left(\frac{-1.98}{1.02}\right)$  corresponds to the slope of the graph

and  $\frac{\log K}{1.02}$  corresponds to the y-intercept of the graph.

Using a line with the above given slope, with final values for ASE data falling on the line (the line is also an interpretation of the solubility cont'd

CS 9/26/10/92

limit of analcime), the y-intercept was calculated to be  $= 15.147$  CS 9/26/10/92

$$\frac{\log K}{1.02} = 14.56$$

which corresponds to a  $\log K = 14.85$ .

$$\text{and } K = 1.41 \times 10^{-15}$$

The concentration of chloride was also calculated in IASDRE32, based on a linear interpolation of the evaporation which took place between each sampling interval. ~~Chloride concentration was monitored here to compare the results with experimental chloride concentrations which are somewhat sporadic and probably less accurate.~~

~~incorrect, this was true for Na.~~ WY 6/10/92

The code IASDRE32 itself is uncomplicated. It involves the pickup of two input files, a series of calculations, and a series of writes to several output files. No external subroutine calls are made. 6/10/92 CJD

Chlorine values were used for complete aqueous speciations with EQ3.

WY 6/10/92



IASDRE32 begins by declaring all real variables as "doubleprecision" types. This will improve accuracy for the desired calculations. Integer locations and filename locations are next declared. Filenames are declared as PARAMETERS so their values will not change during execution of the program.

The first file to be read is the input file of constants.

The code reads from the file a string of 80 characters. If the first character of the line is "#", then the process is continued with the next line from the input file being read. In the input file, all lines other than the line of constants to be read begin with a "#." Users are warned that a "#" must begin any comment line or line other than that one which contains the constants.

When the line of constants is reached, the variables:

$k^*S$ ,  $\gamma_{SiO_2}$ ,  $\chi_{SiO_2}$ ,  $\gamma_{Al_2O_3}$ ,  $\chi_{Al_2O_3}$ ,  $K$ ,  $X$ ,

$con\_Na$ ,  $\gamma_{Na}$ ,  $(k^*S)_2$ , mech-time,  $con\_cl$

are read. "Con-Na" and "con-cl" are initial concentrations based on initial experimental conditions. "Mech-time" is the time at which the secondary rate constant  $(k^*S)_2$  will supercede the initial rate constant  $k^*S$ . "Mech-time" was calculated from Cricket Graphs of experimental data, using the slope of the graph of Si moles released v. time to determine "mech-time."

CJN  
6/10/92

Mech-time must be in seconds. It was calculated to be 300 hours or 1.08e6 seconds. Values for the input constants were checked to Aft<sup>CSP</sup><sub>6/10/92</sub> ensure that variables had been read and passed properly.

After reading the file of constants, the experimental data file is read. This file includes three columns of data: the mass of water before sampling at time  $t$  ( $wh_2O_{be}$ ) the mass of water after sampling at time  $t$  ( $wh_2O_{af}$ ) and the time of the sampling (exptim).

As with the file of constants the experimental data file is read line by line until the first character of the line is not a "#."

Then, the data is read into three arrays with 50 elements each. A counter called file-size is incremented each time a set of experimental data is read. This keeps a count of the number of sampling records in the file. The experimental time table in the file is in units of hours. CJN 6/10/92

Cricket graph was not used for calculations or regressions, only for plotting. The solubility and rate data were interpreted as described in CNWRA-01. WMY 6/10/92



For the solution to the integrated equation, the experimental time values must be in units of seconds. A conversion factor of 3600.0 is multiplied by each element in the array (exptim).

Units of time in the experimental data file are in units of hours for convenience and legibility.

The algorithm for reading the experimental data continues to read from the file until a negative number is read.

A flag of -1 is used in the file to mark the end of the experimental input data.

After both input files have been read successfully, they were checked using write statements in the main program to ensure the correct reading and passing of variables and their values.

The next stage of the program involves initializing all variables that are not read as input.

All variables are initialized to 0 except wh2otim, the mass of water at any time t. Wh2otim is initialized to the initial mass of water as read from the experimental data file.

CJD 6/10/92

Another variable, expnum, is initialized to 1. This variable will keep track of which sampling interval is being considered by the code. Expnum is incremented when the experimental time from a sampling period is passed by the time calculated by the code (variable name "time").

Once variables have been initialized the code is ready to run. It first calculates values for B, con-Na, and max-soln.

The value of B is the same as that found on page 4 of this notebook.

The concentration of Na at any time is the same as that given on page 5 of this notebook.

Max-soln is a variable which represents the maximum theoretical number of moles of Si in solution:

$$\text{Max-soln} = \text{wh2otim} \left[ \frac{K (2-x)^{1+x}}{(\text{con-Na } V_{\text{Na}} (1+x) V_{\text{H}_2\text{O}})^{1+x} \left( \frac{V_{\text{SiO}_2}}{V_{\text{H}_2\text{O}}} \right)^{2-x}} \right]^{1/3}$$

All three values (B, con-Na, max-soln) will vary with each iteration of the code since wh2otim and con-Na will vary. CJD 6/10/92



The logical, theoretical basis for the code is as follows:

$$\int_{t_i}^{t_{i+1}} dt = \int_{u(t_i)}^{u(t_{i+1})} \frac{du}{A+Bu} = \frac{1}{B} \ln \left| \frac{A+Bu}{u(t_i)} \right|^{u(t_{i+1})}$$

$$= \int_{\text{molso1n1}}^{\text{molso1n2}} dt$$

By giving the code values for "u" at times  $t_i$  and  $t_{i+1}$ , the program can generate values for  $dt$ , or the amount of time elapsed in the interval.

Again, "u" represents the total amount of  $S_i$  (moles) released minus the total amount of  $S_i$  (moles) extracted in sampling. In other words "u" is the number of moles in the solution at any time  $t$ . A variable called `molso1n1` represents  $u$  at time  $t_i$ . A variable called `molso1n2` represents  $u$  at time  $t_{i+1}$ .

What IASDRE32 must do is to choose a stepsize which will augment the current value of `molso1n1` to create a `molso1n2`. Then the code can integrate over these limits and return a value for  $dt$ . CJ 4/10/92

When the code calculates  $dt$  (variable name in IASDRE32 is "delttime"), the value is added to the previous value of time and the ordered pair (time, `molso1n2`) can be plotted to produce the graph of moles in solution as a function of time.

Since the total number of moles released equals the total number of moles in solution plus the total number of moles extracted during all previous intervals, a plot of moles released ( $S_i$  or  $A_i$ ) as a function of time can be generated.

The first step of the actual calculations is to set the limits of integration, `molso1n1` and `molso1n2`.

The initial value of `molso1n1` equals zero since the analcime sample has just been added and has yet to begin dissolving. The initial value of `molso1n2`, the upper limit of integration, is equal to `molso1n1` plus a certain stepsize, which may vary during the execution of the code.

The initial and default stepsize was set at  $1.0 \times 10^{-8}$  moles, a value small enough to produce a sufficient number of iterations in the code.

CJ 4/10/92



The variable  $\text{molsoln2}$  is set to  $\text{molsoln1}$  plus the stepsize.

A check is then made to ensure that  $\text{molsoln2}$  does not exceed the maximum theoretically possible number of moles in solution.

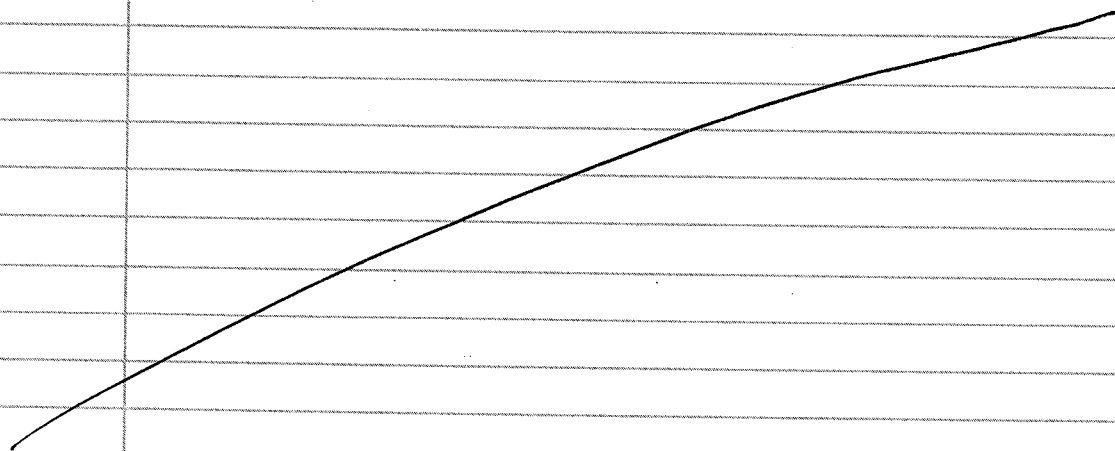
If  $\text{molsoln2}$  is too large, it is decreased and the stepsize is also decreased.

The new value of  $\text{molsoln2}$  is the average of the old  $\text{molsoln2}$  and  $\text{molsoln1}$ . In other words, the new stepsize ~~is~~<sup>is</sup> taken is half as great as the previous stepsize.

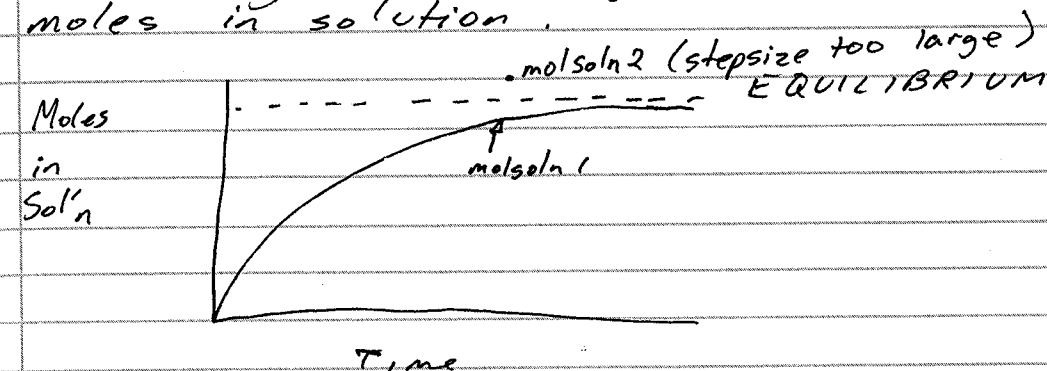
The new value of stepsize then becomes the difference between the new  $\text{molsoln2}$  and  $\text{molsoln1}$ .

A precautionary measure was implemented to ensure that  $\text{molsoln2}$  would never be smaller than  $\text{molsoln1}$ . In other words, the stepsize will not be allowed to become negative. If it does, the code prints an error message and halts.

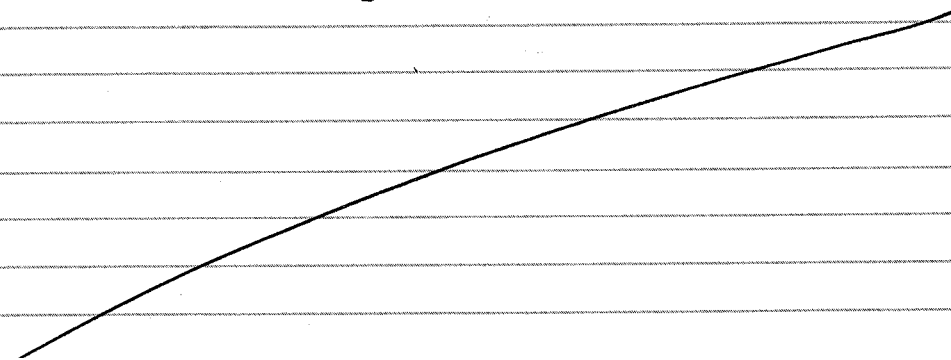
Once the code has legitimate values for  $\text{molsoln1}$  and  $\text{molsoln2}$ , it proceeds to evaluate the integral. CJD 6/10/92



When the integral is evaluated, a value for  $\text{delttime}$  is generated. Before continuing, the code checks to see if  $\text{delttime}$  is negative. If so, the stepsize taken was too large. Conceptually, an oversized step which produces a negative delta time corresponds to stepping over the equilibrium value for moles in solution.



If  $\text{delttime}$  is negative, the code resets time to its previous value (before evaluation of integral) and decreases the value of the variable stepsize by a factor of 10. The code then evaluates the integral again this time with the smaller stepsize from  $\text{molsoln1}$  to  $\text{molsoln2}$ . The process is repeated (up to 10 iterations) until the value of  $\text{delttime}$  is positive. If stepsize is decreased by 10 orders of magnitude and  $\text{delttime}$  is still negative, the code halts since it has reached the approximate equilibrium boundary. CJD 6/10/92



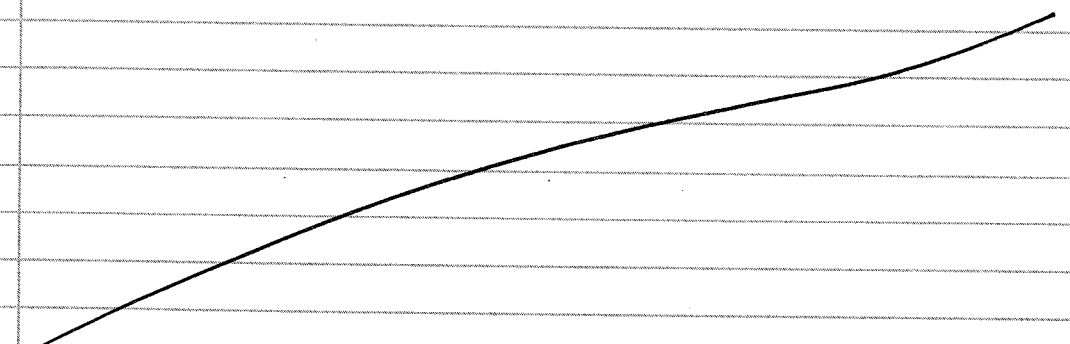


The code continues to take small steps, evaluating the integral over each small interval until the calculated time (time + deltime after each evaluation) exceeds the next experimental sampling time. When the code has "stepped over" a sampling period it retreats and takes a fraction of its previous step until it falls just short of the experimental sampling time in question.

At this time the code advances to the next experimental sampling set of data, advancing experimental time (exp-time), mass of water before sampling (wh2obe), and mass of water after sampling (wh2oaf).

The code then ~~code~~<sup>CJD 6/10/92</sup> continues its integrations over small stepsizes advancing the experimental data arrays as the calculated times fall<sup>CJD 6/10/92</sup> into the experimental intervals of sampling.

After each evaluation of the integral, if the value returned is valid, the value of molsoh1 (lower limit of integration) is replaced by the value of molsoh2. Then molsoh2 is increased by the appropriate stepsize and the code continues. CJD 6/10/92



Whenever an experimental sampling period is stepped over, certain calculations are necessary in addition to advancing the experimental data arrays.

The total number of moles removed from the system due to sampling (variable name "molrem-tot") is increased by the amount of water removed in the sampling period times the molality at the time of sampling.

The value of molsoh1 is decreased by the amount of moles removed during the given sampling period (molality \* mass of water extracted).

The variable wh2otim, which represents the mass of water at any time  $t$  is advanced to the value of the mass of water (experimental) after the sample in question is taken.

CJD 6/10/92

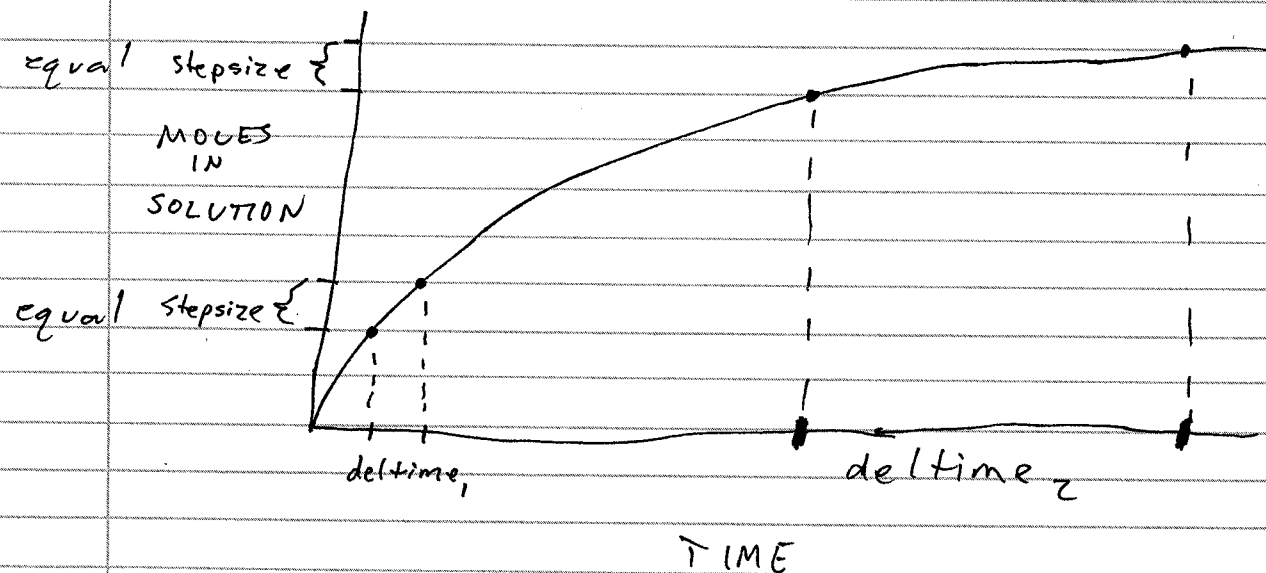


Before going on to the next iteration of the code, the program decides whether or not to print the current values of variables to their respective output files.

Since a large amount of iterations are being performed, speed of execution, efficiency, and disk space require that only a fraction of the iterations be written to files as output.

Every 50<sup>th</sup> iteration will print when the solution is far from equilibrium.

When the solution gets closer to equilibrium, however, the value of  $\text{delttime}$  becomes very large for a small stepsize from  $\text{molso1}$  to  $\text{molso2}$ .



A correction to the print interval algorithm was added to print every iteration as the calculated solution approaches/nears equilibrium. CJD. 4/10/92

If the instantaneous slope of the graph of moles released v. time is less than three tenths ( $\frac{3}{10}$ ) of its initial slope, the code assumes it is nearing equilibrium and it prints after each iteration, writing variable values to files.

When the calculated time finally gets to the last experimental sampling set of data the code prints a message and exits without calculating the integral again.

The output files created and their contents are:

na.out	Total moles of Na released at time t
al.out	" " " Al " " " "
si.out	" " " Si " " " "
si-conc.out	concentration of Si at time t
hours.out	time in hours at time t

CJD 6/10/92

Results from the IASDRE32 code, which incorporates an analytical solution to the integral to be performed, were compared with results from NIADRE, a code which uses numerical integration to solve the problem. The values generated by each code were indistinguishable from one another, verifying the techniques used in solving the differential equation, using both analytical and numerical integration. CJD 6/10/92



For EO3 calculations in support of geochemical modeling for the CNWRA 91-01A chapter 2.2 the data0.com.R7 version of the data base was used with the following modifications:

- The  $p_{\text{dot}}$  value at  $0^{\circ}\text{C}$  was corrected to 0.0374 to fix a typographical error in the original data base
- The  $\text{H}_3\text{SiO}_4^-$  aqueous species was removed from the data base because it is redundant with  $\text{HSiO}_3^-$ .
- The  $\text{NaH}_3\text{SiO}_4$  aqueous species was removed because it is redundant with  $\text{NaHSiO}_3$
- Clinoptilolite data from Kerrick were entered to test its solubility.

CM/6/10/92

## NIADRE (Numerically Integrated Analcime Dissolution Rate Equation)

NIADRE is a FORTRAN code written for use on the CCFVAX for the purpose of solving the Analcime Dissolution Rate Equation for the ACDT data using numerical integration techniques. The code was also used to verify the results of the IASDRE32 code which solved the same problem using analytical integration techniques.

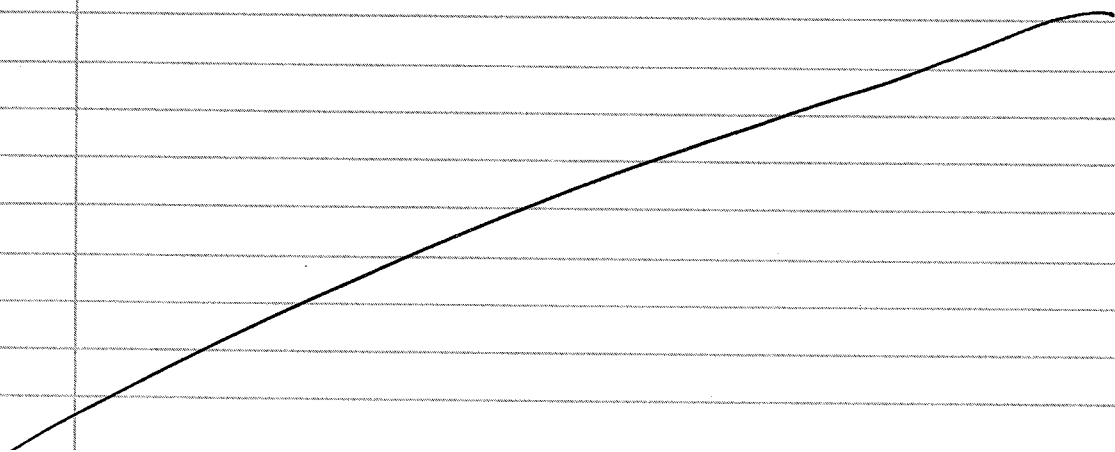
NIADRE incorporates a Runge-Kutta numerical integrator, which is found in four external subroutines.

SUBROUTINE DERIVS is a user supplied routine which provides Runge-Kutta the ordinary differential equations to be solved. DERIVS is found in a separate file called 'derivs.for' which is link to the main program before execution.

C.J.D. 6/11/92

SUBROUTINE RK4 is the "algorithm" routine of Runge-Kutta. It is the routine that performs the actual integration. RK4 is found in the file 'rk4.for' which is linked to the main program before execution.

SUBROUTINE RKQC is the "stepper" routine of Runge-Kutta. To perform the integration, Runge-Kutta needs a beginning time and an end time to act as its lower and upper limits of integration. RKQC determines these limits by taking tiny steps in time over which Runge-Kutta will integrate. NIADRE incorporates a Runge-Kutta method with adaptive stepsize corrections. This means RKQC will take as large a step as it can while remaining within a user-supplied level of accuracy (accuracy variable is eps, for epsilon). The stepsize will adapt as needed for any particular iteration, increasing or decreasing. Two user-supplied variables, HMIN and HMAX, are the smallest and largest stepsizes allowed by the user, respectively. RKQC is found in a file called 'rkqc.for' and is linked before execution. C J 2 6/11/92

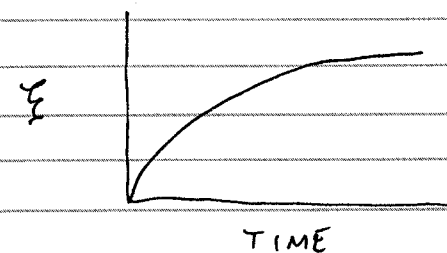


SUBROUTINE ODEINT is the "driver" routine of Runge-Kutta. It is called by the main program and it makes the initial calls to DERIVS and RKQC. ODEINT is found in the file 'odeint.for' and is linked to the main program before execution.

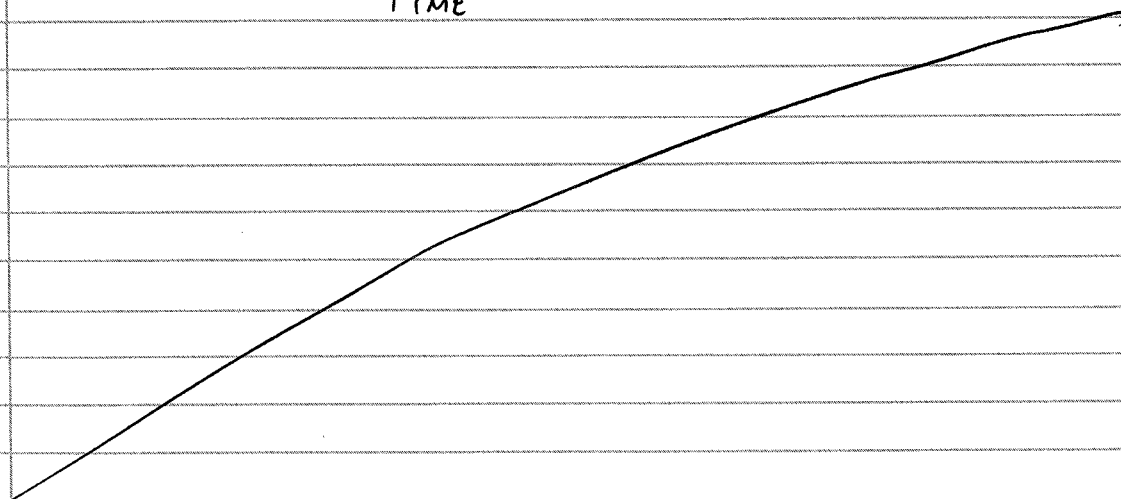
NIADRE takes the differential equation or equations that are input in SUBROUTINE DERIVS and solves for them. The primary differential equation NIADRE was used to solve was:

$$\frac{dI}{dt} = k * S [1 - (Q/K)^{1/5}]$$

NIADRE calculates a value for  $I$  over the time interval requested by the user, who provides only the above differential equation and any related equations and the time interval to integrate over. A plot of  $I$  v. TIME can then be created and compared with experimental data.



C J 2





NIADRE picks up two input files when execution begins.

An input file of constants to be used is found in 'const.in'.

Values for:

$K^*S$ ,  $\gamma_{SiO_2}$ ,  $\gamma_{SiO_2}$ ,  $\gamma_{AlO_3}$ ,  $\gamma_{AlO_3}$ ,  $\gamma_{Na^+}$ ,  $\gamma_{Na^+}$ ,  $K$ , and  $x$

were determined in the same way as in the IASDRE32 code (described on pages 4-10 of this notebook).

A value for sigma ( $\sigma$ ), which is found in the primary differential equation, is also read in from the constants file.  $\sigma$  was varied in different test runs of NIADRE using  $\sigma = 1, 2, 3$ . When  $\sigma = 3$ , the results of NIADRE are indistinguishable from those of IASDRE32, which analytically solves for the equation when  $\sigma = 3$ .

Initial concentrations for Al, Na, and Si <sup>CSJ 6/11/92</sup> are also read from 'const.in'.

con-Al-init = 0.0

con-Si-init = 0.0

con-Na-init = .11

Initial concentrations of Al and Si equal 0.0 since the analcime has not begun to dissolve at time=0. Initial concentration of Na equals .11 since the initial solution contained .10 M NaCl and .010 M NaHCO<sub>3</sub> CSJ 6/11/92

NIADRE next picks up an experimental data file which contains three columns to be read in as arrays of 50 elements each. These columns are: experimental time (exp-time), (h<sub>2</sub>O-mass) - the mass of water at a particular experimental time, and the cumulative mass of water extracted through sampling (h<sub>2</sub>O-ext).

To prevent a discontinuity in the function of water mass as a function of time, the sampling period was given a value of 0.1 hours for each sampling time.

In contrast with the IASDRE32 code, in which each experimental time of sampling had a value for water mass before and after, the NIADRE has only one array for water mass. For each sampling period there are two times given, one corresponding to the time at the beginning of the sample and the other corresponding to the end of the sample period (0.1 hours later).

The experimental data file is found in 'water.ary'

#	Water Period	Sample Time (hours)	Water Mass (kg)	Water Mass Extracted (cumulative) (kg) (sampling only)
1		0.0000	0.0000	0.0000
2		48.1170	0.9966	0.0000
3		48.2170	0.9463	0.0503
4		95.4170	0.9462	0.0503
5		95.5170	0.8955	0.1009
6		168.2500	0.8953	0.1009
7		168.3500	0.8448	0.1515
8		261.0670	0.8445	0.1515
9		261.1670	0.7937	0.2022
10		357.7167	0.7935	0.2022
11		357.8167	0.7427	0.2529
12		496.7500	0.7422	0.2529
13		496.8500	0.6917	0.3035
14		593.5000	0.6913	0.3035
15		593.6000	0.6405	0.3542
16		712.4500	0.6400	0.3542
17		712.5500	0.5893	0.4049
18		833.5170	0.5888	0.4049
19		833.6170	0.5382	0.4556

EXAMPLE  
OF  
'WATER.ARY'  
INPUT  
FILE

CSJ  
6/11/92

The next stage of NIADRE involves the initialization of variables. The values for the four differential equations to be used are set to 0:

$$\begin{aligned} \frac{dF}{dt} &= 0.0 && \rightarrow \text{Change in reaction progress with time} \\ \frac{dN_{Al,E}}{dt} &= 0.0 && \rightarrow \text{Change in cumulative number of moles of Al extracted} \\ \frac{dN_{Na,E}}{dt} &= 0.0 && \rightarrow \text{Change in cumulative number of moles of Na extracted} \\ \frac{dN_{Si,E}}{dt} &= 0.0 && \rightarrow \text{Change in cumulative number of moles of Si extracted} \end{aligned}$$

Values for these four differential equations must be provided to Runge-Kutta by the user in SUBROUTINE DERIVS. Runge-Kutta then integrates with respect to time and generates values for  $F$ ;  $N_{Al,E}$ ;  $N_{Na,E}$ ;  $N_{Si,E}$ .

Values for  $F$ ,  $N_{Al,E}$ ,  $N_{Na,E}$ , and  $N_{Si,E}$  must also be initialized to 0.0.

The initial number of moles in solution of Al, Na, and Si is also needed so these initializations are made:

$$\begin{aligned} Al_{init} &= h2O\_mass(1) * con\_Al_{init} \\ Na_{init} &= h2O\_mass(1) * con\_Na_{init} \\ Si_{init} &= h2O\_mass(1) * con\_Si_{init} \end{aligned}$$

Experimental data indicate that there was an initial preferential release of aluminum in the ACDT experiments (see FIGURE 2-10 of CNWRA 91-01A).  $Al_{init}$  has therefore been re-initialized to  $1e^{-6}$  to correspond with the experimental data.

CJD  
6/11/92

The next segment of code is the initialization of variables required by the Runge-Kutta routines.

H1, the initial guess for a time stepsize is set to .1 hours and then converted to units of seconds.

HMIN, the smallest allowed stepsize is set to 0.0.

The degree of accuracy desired,  $eps$ , is set to  $1.0e^{-6}$ , which corresponds reasonably with experimental data.

HMAX, the maximum allowed stepsize is set to .1 hours and converted to sec; this is to ensure that Runge-Kutta will "step" into each sample period. Successful runs show that the code does in fact step into each sampling period. The initial mass of water is set to  $wh2O = wh2O\_mass(1)$ , the initial experimental water mass.

Additionally, a print interval is set and an iteration loop is established. Since the experimental time runs for approximately 5000 hours, NIADRE breaks up this time into 500 intervals of 10 hours each. It is through each of these 500 intervals of 10 hours that Runge-Kutta integrates using adaptive stepsizes. Since the maximum allowed stepsize is .1 hours, each interval will contain at least 100 iterations performed by Runge-Kutta.

CJY 6/11/92



To save space on disk and increase speed and efficiency of execution, NIADRE does not print at the end of all 500 intervals. The print interval was modified to facilitate printing a total of 100 calculated data points to output files, occurring at equally spaced intervals of 50 hours.

After each 50 hours the values returned by the SUBROUTINE ODEINT will be printed to output files.

After each iteration of NIADRE, whether the values were written to file or not, the running calculated time is incremented by another 10 hours.

Values returned by the Runge-Kutta routines are for reaction progress ( $\xi$ ) and the cumulative number of moles extracted for the species Al, Na, and Si.

In addition to these values the cumulative number of moles released (Al, Na, and Si) can be calculated as:

$$\begin{aligned} \text{Al}_{\text{rel}} &= \text{Al}_{\text{init}} + (1.0 \times \xi) \\ \text{Na}_{\text{rel}} &= \text{Na}_{\text{init}} + (1.0 \times \xi) \\ \text{Si}_{\text{rel}} &= \text{Si}_{\text{init}} + (2.0 \times \xi) \end{aligned}$$

The cumulative release to solution is the initial moles in solution plus the stoichiometric coefficient times reaction progress ( $\xi$ ). (JS) 6/11/92

The NIADRE code was tested extensively using a trivial set of differential equations in SUBROUTINE DERIVS:

$$\frac{d\xi}{dt} = 1.0$$

$$\frac{dn_{\text{Al},E}}{dt} = 2.0$$

$$\frac{dn_{\text{Na},E}}{dt} = 3.0$$

$$\frac{dn_{\text{Si},E}}{dt} = 4.0$$

These simple differential equations can be hand calculated, using the experimental time from 0 to 5000 hrs.

$$\xi = \int_0^{5000} \frac{d\xi}{dt} dt = 5000$$

$$n_{\text{Al},E} = \int_0^{5000} \frac{dn_{\text{Al},E}}{dt} dt = 10000$$

$$n_{\text{Na},E} = \int_0^{5000} \frac{dn_{\text{Na},E}}{dt} dt = 15,000$$

$$n_{\text{Si},E} = \int_0^{5000} \frac{dn_{\text{Si},E}}{dt} dt = 20,000$$

The NIADRE runs using the trivial differential equations were hand-checked in this manner and proven to be correct. These hand calculations verify that the Runge-Kutta routines are functioning properly and producing correct results. (JS) 6/11/92

CJG 6/11/92

CJD 6/11/92



CTB  
6/11/92

## Calculations from MICROSOFT EXCEL Spreadsheet

Many data used in figures from Chapter 2 of CNWRA 91-01A were calculated using the MICROSOFT EXCEL spreadsheet software package. These data include the cumulative number of moles released and removed ( $\text{SiO}_2$  and Al) for the Analcine-Clinoptilolite Dissolution Tests (ACDT).

During the ACDT experiments, samples were taken and measurements made approximately every 50 to 100 hours for the "A" series of test. The "B" samples were measured less frequently, approximately every 300 hours. During a sampling period, measurements were taken for the mass of the sample (including bottle mass, sample mass, and water mass) before an extraction for measurement purposes and after the extraction. Sodium concentration, silica concentration, aluminum concentration, pH, and the time elapsed for the experiment were recorded. These values were entered into the EXCEL worksheet into separate columns. Thus, each sampling time contains a data set of all of the above values.

The mass of each empty bottle and the mass of the analcine added to each bottle was measured and recorded by Jim Prikrýl, who conducted the experiments. These masses were then recorded into the EXCEL files and labeled as Bottle Mass and Sample Mass, respectively.

CJD 6/16/92

A simple calculation was then performed in the EXCEL worksheet to calculate the mass of the water, before and after each extraction or sampling time. The mass of water equals the total measured mass minus the mass of the bottle minus the mass of the analcime sample added.

Concentrations of  $\text{SiO}_2$  and  $\text{Al}$  were measured in parts per billion;  $\text{Na}$  concentration was measured in parts per million. These values were converted into units of molality (moles/kg).

For some of the experimental data, it seemed probable that analytical errors had occurred in measurements, creating spurious data sets. In these instances, values for experimental concentrations were replaced with calculated values based on linear interpolation regressions. These corrected values were used in all later calculations to be discussed.

CJA 6/16/92

- All references to Microsoft Excel refer to version (updated) 4.0.

CJA 6/24/94

- All Cricket Graph data and graphs were prepared with version 1.302.

CJA 6/24/94

The cumulative number of moles of a species ( $\text{SiO}_2$ ,  $\text{Al}$ ) removed from the system during sampling was calculated at each sampling time  $t_s$  as:

$$\text{moles extracted}(t_s) = \sum_{t_p < t_s} [\text{molality}(t_p)] [\text{mass of H}_2\text{O extracted}(t_p)]$$

In other words the total amount extracted equals the molality at the sampling time in question times the mass of water extracted during that sampling time plus all previously extracted from all previous intervals of sampling.

Hand calculations were performed to verify the EXCEL calculations. For example, for the ACDT1A sample at time 48 hours, the EXCEL calculated number of moles<sub>Si</sub> extracted =  $1.1566 \times 10^{-7}$  moles.

Hand calculated:

$$\begin{aligned} \text{at time 48 hrs. moles extracted} &= (\text{molality}_{48}) (\text{H}_2\text{O extracted}_{48}) + \text{previously extracted} \\ &= \left( 2.2768 \times 10^{-6} \frac{\text{moles}}{\text{kg}} \right) (.99955 \text{ kg} - .94875 \text{ kg}) + 0.0 \\ &= \boxed{1.1566 \times 10^{-7} \text{ moles}_{\text{Si}}} \end{aligned}$$

At sampling interval #2 (time = 95 hours), moles extracted was calculated by the EXCEL spreadsheet to be  $3.4127 \times 10^{-7}$  moles<sub>Si</sub>.

Hand calculated

$$\begin{aligned} \text{at time 95 hrs. moles extracted} &= (\text{molality}_{95 \text{ hrs.}}) (\text{H}_2\text{O extracted}_{95 \text{ hrs.}}) + \text{previously extracted} \\ &= \left( 4.4587 \times 10^{-6} \frac{\text{moles}}{\text{kg}} \right) (.94865 - .89805 \text{ kg}) + 1.1566 \times 10^{-7} \text{ moles} \\ &= \boxed{3.4127 \times 10^{-7} \text{ moles}_{\text{Si}}} \end{aligned}$$

CJA 6/16/92



The cumulative number of moles of a species was calculated in two different ways. As reported in CNWRA 91-01A, the cumulative release of a species "i" is given by:

CSD 6/17/92  
mole

$$\text{at time } t_s \quad \text{moles}_i \text{ released} = (\text{molality}_i) (\text{water mass before}) + \text{previously extracted}$$

In other words, the total number of moles released at any sampling time  $t_s$  equals the measured molality at that time ( $t_s$ ) times the water mass, plus the cumulative number of moles of that species extracted from the solution during all previous sampling intervals.

Another way of calculating the cumulative release is to calculate the moles released between each sampling interval. Since concentrations and water masses (before and after 50 g samples were taken) were measured, the release between any sampling intervals "i" and "i+1" equals:

$$\text{release from } t_i \text{ to } t_{i+1} = (\text{Concentration}_{i+1}) (\text{water mass before}_{i+1}) - (\text{Concentration}_i) (\text{water mass after}_i)$$

In other words, the moles released in any interval equals the total number of moles in solution at the end of the interval minus the total number of moles in solution at the beginning of the interval.

CSD 6/17/92

Hand calculations were performed to verify the EXCEL calculations.

For sample ACDT1A, at times 48 hours and 95 hours the EXCEL worksheet calculates the moles of Si released to be  $2.2758 \times 10^{-6}$  moles and  $4.3454 \times 10^{-6}$  moles, respectively.

Hand calculations using the first method described yield:

$$\begin{aligned} \text{Si released}_{48} &= (\text{molality Si}_{48}) (\text{water mass before}_{48}) + \text{previously extracted} \\ &= (2.2768 \times 10^{-6} \text{ moles/kg}) (.99955 \text{ kg}) + (0 \text{ moles}) \\ &= \boxed{2.2758 \times 10^{-6} \text{ moles Si}} \end{aligned}$$

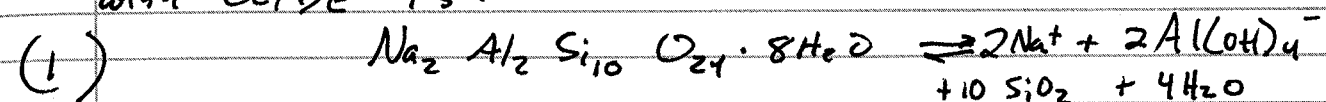
$$\begin{aligned} \text{Si released}_{95} &= (\text{molality Si}_{95}) (\text{water mass before}_{95}) + \text{previously extracted} \\ &= (4.4587 \times 10^{-6} \text{ moles/kg}) (.94865 \text{ kg}) + (1.1566 \times 10^{-7} \text{ moles}) \\ &= \boxed{4.3454 \times 10^{-6} \text{ moles Si}} \end{aligned}$$

These results also matched the EXCEL calculations made using the second method for calculating cumulative moles released for each species. CJD.

## CLIDE (CLinoptilolite Dissolution rate Equation)

This code was written to make theoretical calculations to parallel the dissolution of Clinoptilolite in the CNWRA experiments CDUSE (Clinoptilolite-Death Valley Solubility Experiments). The model solves the theoretical dissolution rate equation using numerical methods similar to those used in the code NIADRE (see p. 25-41 of this notebook).

The ideal formula for the clinoptilolite modeled with CLIDE is:



The dissolution rate equation for clinoptilolite is

$$\frac{d\xi}{dt} = k^*s \left( 1 - \left[ \frac{Q}{K} \right]^{1/5} \right)$$

where  $k^*s$  is a rate constant factor  
 $K$  is the equilibrium constant  
 and  $Q$  is the reaction quotient.

The equilibrium constant used was  $1e^{-50}$ . This value was taken from an activity diagram of  $a_{\text{Na}} \cdot a_{\text{Al}(\text{OH})_4^-} \cdot a_{\text{SiO}_2}$  (figure from

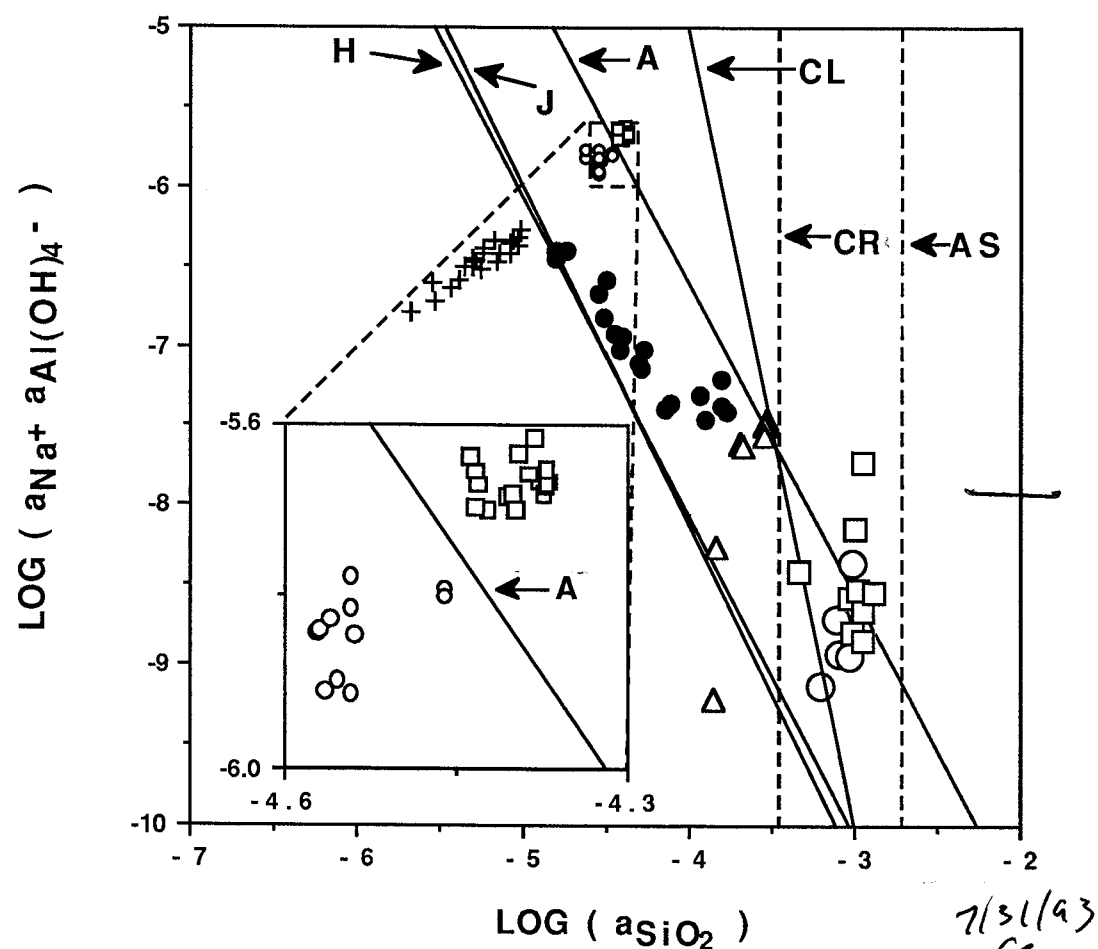
7/93 semiannual report. The line labelled CL is constrained by experimental data and has a slope corresponding to the ideal stoichiometry of Clinoptilolite.

Since  $K = [a_{\text{Al}(\text{OH})_4^-}]^2 [a_{\text{Na}}]^2 [a_{\text{SiO}_2}]^{10}$   
 can be rewritten as:



$$\log [a_{\text{Na}^+} a_{\text{Al(OH)}_4^-}] = -\frac{10}{2} \log a_{\text{SiO}_2} + \frac{\log K}{2}$$

Therefore, the equilibrium constant  $K$  can be determined from the y-intercept of the CL line in the below figure ( $K = 1e^{-50}$ )



7/31/93  
cg

cg 7/31/93

$K^*$  is a fit parameter. The value used to generate the best fit was  $8.7e^{-13}$  moles/sec.

$Q$  is the reaction quotient given by:

$$Q = [a_{\text{Na}^+} a_{\text{Al(OH)}_4^-}]^2 [a_{\text{SiO}_2}]^{10}$$

for the solution at a given value of reaction progress.

Values for  $\epsilon$ , the reaction progress are calculated in a similar manner as was  $\epsilon$  for the NIADRE code described earlier. (see p. 25-41).

Difference in the codes are in calculations of the moles released of the different species.

In CLIDE,

$$\text{Si released} = 10 * \epsilon$$

$$\text{Al released} = \text{Na released} = 2 * \epsilon$$

Clinoptilolite stoichiometry was assumed to be ideal.

activity coefficients for species were calculated using EQ3 as described in NIADRE documentation.

The stoichiometric factor,  $\sigma$ , was 20 for the CLIDE code. This was necessary since certain calculations required raising small numerical values to high powers (10). The VAX floating-point processor was unable to manipulate such numbers and was 'zeroing' out certain variables. The stoichiometric factor was implemented to retain these numerical values as well as the relative relationships between

cg 7/31/93

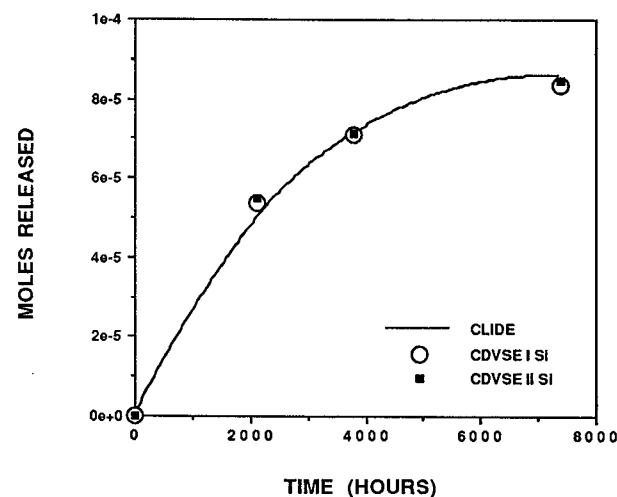
the various species concentrations.

Another difference in CLIDE is that Aluminum experimental data was used to constrain the aluminum in the system.

Aluminum data were sporadic and did not follow any obvious mechanism as silicon data did. Aluminum molality is necessary, however, to calculate  $\xi$ , and also silicon release. For this reason, a linear interpolation of aluminum molalities was used to calculate  $\xi$  at every time.

All other calculations were the same as in the analcime dissolution model NIADRE (see p. 25-41).

The final output of CLIDE is a plot of Si released (in moles) versus time with the experimental data plotted on the same graph.



CLIDE FOR  
DERIVS. FOR (SUBROUTINE)

6/21/94

7/31/93

program CLIDE

c CLinoptilolite Integrated Dissolution rate Equation

c

c revised: (1) original create, June 1993, by:

c

c Christopher J. Goulet and W. M. Murphy

c Southwest Research Institute

c Center for Nuclear Waste Regulatory Analyses

c PO Drawer 28510

c San Antonio, TX 78228 USA

c Comments: This is the integrated dissolution rate equation solver for the  
c CDVSE experiments. The program will solve for Xi, the reaction  
c progress, and total moles of Si released in the dissolution  
c reaction. A Runge-Kutta numerical integrator with an adaptive  
c stepsize mechanism has been incorporated.

implicit none

INTEGER sigma, counter

REAL\*8 exp\_time(1:50), h2o\_mass(1:50), h2o\_ext(1:50), al\_conc(1:50),

: X\_ALO2, g\_ALO2, X\_Na, g\_Na, X\_SiO2, g\_SiO2, x, ks,

: AL\_init, Na\_init, Si\_init, equilc

include 'vars.f'

external derivs, rkqc

character ustring\*80

INTEGER ii, jj, kk, Si\_file, hrsfile, infile,

: h2ofile, STDOUT, STDIN, Xi\_file,

: Na\_file, AL\_file, outfile, NVAR, temp1,

: Xi\_er, Xi\_n, AL, Na, Si, nbad, nok, AL\_rel\_file,

: Na\_rel\_file, Si\_rel\_file, AL\_con\_file, Na\_con\_file,

: SI\_con\_file, num\_int, al\_act\_file, na\_act\_file,

: si\_act\_file, DYDT\_file

PARAMETER (Si\_file=16, infile=14, h2ofile=15, STDOUT=6, STDIN=5,

: hrsfile=17, Na\_file = 18, AL\_file = 19,

: outfile=20, NVAR=5, Xi\_er=1, Xi\_n=2, AL=3, Na=4, Si=5,

: Xi\_file=21, AL\_rel\_file=22, Na\_rel\_file=23,

: Si\_rel\_file=24, AL\_con\_file=25, Na\_con\_file=26,

: Si\_con\_file=27, al\_act\_file=28, na\_act\_file=30,

: si\_act\_file=31, DYDT\_file=29 )

REAL\*8 con\_AL\_init, con\_Na\_init, con\_Si\_init,

: Y(NVAR), DYDT(NVAR), H1, HMIN, eps, HMAX, wh2o,

: con\_AL, con\_Na, con\_Si, TIME, d\_print, a\_ALO2, a\_Na, a\_SiO2, temp

REAL\*16 Q

OPEN(na\_file, file='na.rem', status='old')

OPEN(infile, file='const.in', status='old')

OPEN(h2ofile, file='water.ary', status='old')

OPEN(hrsfile, file='hours.out', status='old')

OPEN(si\_file, file='si.rem', status='old')

OPEN(al\_file, file='al.rem', status='old')

OPEN(outfile, file='clide.out', status='old')

OPEN(Xi\_file, file='Xi.out', status='old')

OPEN(AL\_rel\_file, file='al.rel', status='old')



```

OPEN(Na_rel_file, file='na.rel', status='old')
OPEN(Si_rel_file, file='si.rel', status='old')
OPEN(Al_con_file, file='al.con', status='old')
OPEN(Na_con_file, file='Na.con', status='old')
OPEN(Si_con_file, file='si.con', status='old')
OPEN(Al_act_file, file='al.act', status='old')
OPEN(Na_act_file, file='Na.act', status='old')
OPEN(Si_act_file, file='si.act', status='old')
OPEN(DYDT_file, file='dydt.out', status='old')

```

```

c =====
c enter input data file 1 (constants)

30 read (infile, '(a80)') ustring
   if (ustring(1:1).EQ. '#') goto 30

   read (ustring, *) ks, g_SiO2, X_SiO2, g_AlO2,
:       X_AlO2, g_Na, X_Na, equilK, x, sigma,
:       con_Al_init, con_Na_init, con_Si_init

   write (STDOUT, *) 'Equilibrium K = ', equilK

   write(STDOUT, *) 'THE INPUT FILE OF CONSTANTS HAS BEEN READ.'

```

```

c ks = rate constant times surface area
c g_SiO2 = activity coefficient for SiO2
c X_SiO2 = fraction of total Si as SiO2
c g_AlO2 = activity coefficient for AlO2-
c X_AlO2 = fraction of total aluminum as AlO2-
c equilK = equilibrium constant for analcime dissolution
c x = correction for variance from ideal stoichiometry for analcime
c sigma => 1/sigma is the exponent of (Q/K) in the dissolution rate eqn.
c con_Al_init = initial concentration of Al
c con_Na_init = initial concentration of Na
c con_Si_init = initial concentration of Si

```

```

c =====
c enter input data file 2 (experimental array)

```

```

counter = 0
temp1 = 1

```

```

50 do while (temp1.GE. 0)
   read(h2ofile, '(a80)') ustring
   if (ustring(1:1).EQ. '#') goto 50
   read(ustring, *) temp1, exp_time(counter+1), h2o_mass(counter + 1),
:       h2o_ext(counter + 1), al_conc(counter + 1)
   IF (temp1.GT.0) THEN
       counter = temp1
   ENDIF
enddo

```

```

write(STDOUT, *) 'THE EXPERIMENTAL INPUT FILE HAS BEEN READ.'

```

```

c counter = size of the arrays exp_time, h2o_mass, and h2o_ext
c exp_time = experimental sampling time array
c h2o_mass = water mass array
c h2o_ext = cumulative mass of water extracted array

```

```

c change time from hours to seconds to match units of integrated eqn.

```

```

do ii = 1,counter
  exp_time(ii) = exp_time(ii)*3600.0
enddo

```

```

c =====

```

```

DO jj=1,NVAR
  Y(jj) = 0.0
  DYDT(jj) = 0.0
ENDDO

```

```

Q = 0.0

```

```

Al_init = h2o_mass(1) * con_Al_init
Na_init = h2o_mass(1) * con_Na_init
Si_init = h2o_mass(1) * con_Si_init

```

```

c Al_init = initial number of moles of Al
c Na_init = initial number of moles of Na
c Si_init = initial number of moles of Si

```

```

a_AlO2 = al_init/h2o_mass(1)*g_AlO2

```

```

write(Na_file, *) 'OUTPUT: Cumulative Moles of Sodium Removed'
write(Si_file, *) 'OUTPUT: Cumulative Moles of Silicon Removed'
write(Al_file, *) 'OUTPUT: Cumulative Moles of Aluminum Removed'
write(Al_rel_file, *) 'OUTPUT: Cumulative Moles of Aluminum Released'
write(Na_rel_file, *) 'OUTPUT: Cumulative Moles of Sodium Released'
write(Si_rel_file, *) 'OUTPUT: Cumulative Moles of Silicon Released'
write(hrsfile, *) 'OUTPUT: Time in Hours'
write(Xi_file, *) 'OUTPUT: Xi'
write(Al_con_file, *) 'OUTPUT: [Al] (molality)'
write(Na_con_file, *) 'OUTPUT: [Na] (molality)'
write(Si_con_file, *) 'OUTPUT: [Si] (molality)'
write(Al_act_file, *) 'OUTPUT: Activity of AlO2-'
write(Si_act_file, *) 'OUTPUT: Activity of SiO2'
write(Na_act_file, *) 'OUTPUT: Activity of Na+'
write(DYDT_file, *) 'OUTPUT: DYDT (moles/second)'

```

```

c d_print must be in seconds

```

```

d_print = 10.0 * 3600.0
TIME = 0.0
H1 = (1.0 * 3600.0)/10.0
HMIN = 0.0
eps = 1.0e-6
HMAX = (1.0 * 3600.0)/10.0
wh2o = h2o_mass(1)
temp = 0.0

```

```

c TIME = calculated time, advanced by tiny atepsize taken during each iteration
c H1 = guessed first stepsize
c HMIN = minimum allowed stepsize
c eps = epsilon, the desired accuracy of the integration to be performed
c HMAX = maximum stepsize allowed
c wh2o = mass of water at any time t, corrected for evaporation and sampling

```

```

num_int = 0
IF (((INT(exp_time(counter)))-(10*INT(((exp_time(counter))/(100.0))))
:   .GE.((50.0)*(3600.0))) THEN
  num_int = 5
endif

```

```
num_int = num_int + 10 * INT(((exp_time(counter))/(100.0)/(3600.0)))
```

```
c num_int = number of 10-hour intervals to be integrated over, depends
c on experimental data
```

```
write(STDOUT, *) 'RUNNING. PLEASE WAIT . . . '
```

```
c =====
```

```
DO kk=1, num_int
```

```
CALL ODEINT(Y, NVAR, TIME, TIME+d_print,
```

```
: eps, h1, hmin, nok, nbad, derivs, rkqc, HMAX,
```

```
: wh2o, a_AL02, temp, Q)
```

```
c The following IF statement will control the writing of output
c to files. In this case, "MOD(kk,5)" will print every fifth value, which
c corresponds to every fifty hours.
```

```
IF (((MOD(kk,5)).EQ.0)) THEN
```

```
write(hrsfile, *) (TIME+d_print)/3600.0
```

```
write(AL_file, '(F20.8)') Y(AL)
```

```
write(Na_file, '(F20.8)') Y(Na)
```

```
write(Si_file, '(F20.8)') Y(Si)
```

```
write(Xi_file, '(F20.8)') (Y(Xi_er)+Y(Xi_n))
```

```
write(AL_rel_file, '(F20.8)') (AL_init + (2.0+x)*(
```

```
Y(Xi_er)))
```

```
write(Na_rel_file, '(F20.8)') (Na_init + (2.0+x)*(
```

```
Y(Xi_er)))
```

```
write(Si_rel_file, '(F20.8)') (Si_init + (10.0-x)*(
```

```
Y(Xi_er)))
```

```
con_AL = ((AL_init+(2.0+x)*(Y(Xi_n)+Y(Xi_er))-Y(AL))/wh2o)
```

```
con_AL = a_AL02/(X_AL02*g_AL02)
```

```
con_Na = ((Na_init+(2.0+x)*(Y(Xi_n)+Y(Xi_er))-Y(Na))/wh2o)
```

```
con_Si = ((Si_init+(10.0-x)*(Y(Xi_n)+Y(Xi_er))-Y(Si))/wh2o)
```

```
write(AL_con_file, '(F20.8)') con_AL
```

```
write(Na_con_file, '(F20.8)') con_Na
```

```
write(Si_con_file, '(F20.8)') con_Si
```

```
write(AL_act_file, '(F20.8)') a_AL02
```

```
write(Si_act_file, '(F20.8)') con_Si*g_Si02*X_Si02
```

```
write(Na_act_file, '(F20.8)') con_Na*g_Na*X_Na
```

```
write(DYDT_file, '(F20.16)') temp
```

```
write(STDOUT, *) 'Q = ', Q
```

```
ENDIF
```

```
TIME = TIME + d_print
```

```
ENDDO
```

```
end
```



```
SUBROUTINE DERIVS(TIME, Y, DYDT, wh2o, a_AlO2, temp, Q)
```

```
c   This subroutine will calculate the value of  $dx_i/dt$  at
c   each step taken.  the subroutine is called from:
c   RK4, the "algorithm" subroutine
c   RKQC, the "stepper" subroutine, and
c   ODEINT, the "driver" subroutine
```

```
implicit none
```

```
INTEGER sigma, counter
```

```
REAL*8 exp_time(1:50), h2o_mass(1:50), h2o_ext(1:50), al_conc(1:50),
:      X_AlO2, g_AlO2, X_Na, g_Na, X_SiO2, g_SiO2, x, ks,
:      Al_init, Na_init, Si_init, equilk
include 'vars.f'
```

```
INTEGER Xi, Xi_n, Xi_er, Al, Na, Si, ct, NVAR, STDOUT
```

```
PARAMETER (Xi=1, Xi_er=1, Xi_n=2, Al=3, Na=4, Si=5, NVAR=5, STDOUT=6)
```

```
REAL*8 a_Na, a_AlO2, a_SiO2, wh2o, r_h2o_ex, Al_soln,
:      Na_soln, Si_soln, Y(NVAR), DYDT(NVAR), TIME,
:      k, A, B, num, k_er, k_n, temp, Q
REAL*16 con_al
```

```
ct = 2
```

```
25 DO While((exp_time(ct).LT.TIME))
   IF (ct.GT.counter) THEN
     write(STDOUT, *) 'Time has gone past experimental boundaries.'
     write(STDOUT, *) 'Code halted in subroutine DERIVS.'
     stop
   ELSE
     ct = ct + 1
     goto 25
   ENDIF
ENDDO
```

```
c   ct = counter to iterate through experimental water file until the correct
c   experimental time interval is found
```

```
wh2o = h2o_mass(ct - 1) + ((TIME - exp_time(ct - 1))/
:      (exp_time(ct) - exp_time(ct - 1)))*
:      (h2o_mass(ct) - h2o_mass(ct - 1))
```

```
c   wh2o = mass of water at any time t, corrected for sampling and evaporation
c   by linear interpolation
```

```
r_h2o_ex = (h2o_ext(ct) - h2o_ext(ct - 1))/
:      (exp_time(ct) - exp_time(ct - 1))
```

```
c   r_h2o_ex = rate of water extraction, to be used in calculation of change
c   in number of moles extracted (Al, Na, Si)
```

```
Na_soln = Na_init + (2.+x)*Y(Xi) - Y(Na)
DYDT(Na) = Na_soln*(r_h2o_ex)/wh2o
```

```
c   Na_soln = moles of Na in solution
c   DTDt(Na) = change in moles Na extracted with time
```

```

con_al = al_conc(ct - 1) + ((TIME - exp_time(ct - 1))/
:      (exp_time(ct) - exp_time(ct - 1))) *
:      (al_conc(ct) - al_conc(ct - 1))

```

```

Al_soln = con_al*wh2o
DYDT(Al) = con_al*(r_h2o_ex)

```

```

c Al_soln = moles of Al in solution
c DYDT(Al) = change in moles Al extracted with time

```

```

Si_soln = Si_init + (10.0-x)*Y(Xi) - Y(Si)
DYDT(Si) = Si_soln*(r_h2o_ex)/wh2o

```

```

c Si_soln = moles of Si in solution
c DYDT(Si) = change in moles Si extracted with time

```

```

a_AlO2 = con_al*(X_AlO2)*(g_AlO2)
a_Na   = Na_soln*(X_Na)*(g_Na)/wh2o
a_SiO2 = Si_soln*(X_SiO2)*(g_SiO2)/wh2o

```

```

c a_AlO2 = activity of AlO2-
c a_Na   = activity of Na+
c a_SiO2 = activity of SiO2

```

```

if (a_AlO2.LT.0) Then
  write(6, *) 'a_Al < 0', a_AlO2
  write(6, *) 'wh2o = ', wh2o
  write(6, *) 'Al_soln =', Al_soln
  write(6, *) 'X_al = ', X_AlO2
  write(6, *) 'g_AL = ', g_alO2
  write(6, *) 'alal_init = ', Al_init
  write(6, *) 'x = ', x
  write(6, *) 'Y(Xi) = ', Y(Xi)
  write(6, *) 'Y(AL) = ', Y(AL)
endif

```

```

Q = ((a_Na)**(0.2+x))*((a_AlO2)**(0.2+x))*((a_SiO2)**(1.0-x))

```

```

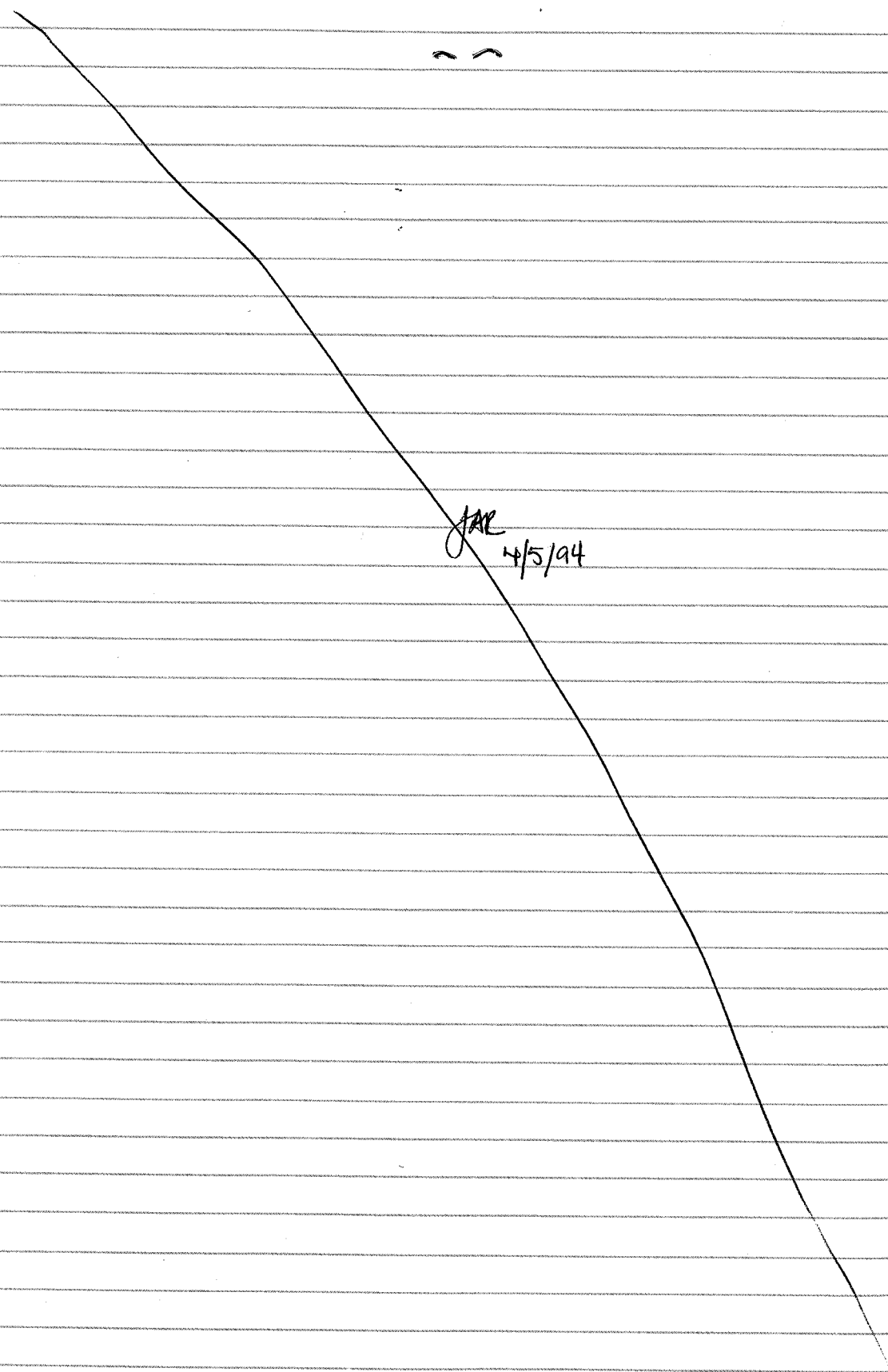
DYDT(Xi) = (ks)*
:      (1.0-((Q/equilk)**(1.0/sigma)))
temp = DYDT(Xi)

```

```

END

```



See page 81 for update UMM 4/7/95

Calculation of  $K^*$  for Al & Si in Samples ACDTIA-III A

- For samples ACDTIA, ACDTIIA and ACDTIIIA individual ~~graphs were~~<sup>figures were</sup> created, plotting the moles released of aluminium and silica versus time (hours) for each sample.

- Lines were handplotted on the figures estimating the slope of the initial mole release for Al and Si, respectively for each sample.

- Using the equations:

$$\frac{dn_{Al}}{dt} = \frac{1}{1.02} \cdot \frac{\text{moles}}{\text{Time}} = K^* \cdot \text{surface area} \cdot \text{mass}$$

$$\frac{dn_{Si}}{dt} = \frac{1}{1.98} \cdot \frac{\text{moles}}{\text{Time}} = K^* \cdot \text{surface area} \cdot \text{mass}$$

values of  $K^*$  were calculated for the six samples (ACDTIA-Al, -Si, ACDTIIA-Al, -Si, ACDTIIIA-Al, -Si).

- Mass values were obtained from Appendix ~~3.1 B~~ Table A. 'Experimental Conditions' ~~of~~ from "Geochemical Investigations Related to the Yucca Mtn. Environment and Potential Nuclear Waste Repository"
- Surface Area values were obtained from section 3.4.1 'Analogue' ~~3.1~~ Sample Characterization and preparation of the same report.

	Mesh Size	SA	Mass
ACDTIA	200-230	$0.11 \pm 0.01 \text{ m}^2/\text{g}$	3.7502g
ACDTIIA	230-325	$0.12 \pm 0.02 \text{ m}^2/\text{g}$	2.5002g
ACDTIIIA	325-450	$0.6 \pm 0.04 \text{ m}^2/\text{g}$	2.2501g



Calculations:

- ACDTIA

Al

$$\frac{dn}{dt} = \frac{1}{1.02} \cdot \frac{7 \times 10^{-6} \text{ moles}}{500 \text{ hr} (60 \text{ min}) (60 \text{ sec})} = K^* \left( \frac{11 \text{ cm}^2}{\text{g}} \right) (10^4 \text{ cm}^2) (3.7502 \text{ g})$$

$$K_{Al}^* = 9.24 \times 10^{-16} \text{ mol/s} \cdot \text{cm}^2$$

Si

$$\frac{dn}{dt} = \frac{1}{1.98} \cdot \frac{7 \times 10^{-6} \text{ mol}}{250 (3600 \text{ sec})} = K^* (1100 \text{ cm}^2) (3.7502)$$

$$K_{Si}^* = 9.522 \times 10^{-16} \text{ mol/s} \cdot \text{cm}^2$$

- ACDTIIA

Al

$$\frac{dn}{dt} = \frac{1}{1.02} \cdot \frac{6.1 \times 10^{-6} \text{ mol}}{500 (3600 \text{ sec})} = K^* (1200 \text{ cm}^2/\text{g}) (2.5002 \text{ g})$$

$$K_{Al}^* = 1.107 \times 10^{-15} \text{ mol/sec} \cdot \text{cm}^2$$

Si

$$\frac{dn}{dt} = \frac{1}{1.98} \cdot \frac{6.875 \times 10^{-6} \text{ mol}}{250 (3600 \text{ sec})} = K^* (1200 \text{ cm}^2/\text{g}) (2.5002 \text{ g})$$

$$K_{Si}^* = 1.2859 \times 10^{-15} \text{ mol/s} \cdot \text{cm}^2$$

JAR  
4/5/94

- ACDTIIIA

Al

$$\frac{dn}{dt} = \frac{1.6 \cdot 20 \times 10^{-6} \text{ mol}}{1.02 \cdot 500 (3600 \text{ sec})} = K^* (2.2501 \text{ g}) (6000 \text{ cm}^2/\text{g})$$

$$K_{Al}^* = 2.5013 \times 10^{-16} \text{ mol/cm}^2 \cdot \text{s}$$

Si

$$\frac{dn}{dt} = \frac{1.6 \cdot 875 \times 10^{-6} \text{ mol}}{1.98 \cdot 250 (3600 \text{ sec})} = K^* (2.2501 \text{ g}) (6000 \text{ cm}^2/\text{g})$$

$$K_{Si}^* = 2.858 \times 10^{-16} \text{ mol/s} \cdot \text{cm}^2$$

-  $K^*$  values for Al, and Si sample ACDTIIIA were different from the values calculated for ACDTIA and ACDTIIA by approximately a factor of 4. These values and sample ACDTIIIA were not used in the next calculation.

- The  $K^*$  value was assumed to be  $1 \times 10^{-15} \text{ mol/s} \cdot \text{cm}^2$  for Al and Si in ACDTIA and ACDTIIA. The slope of the line,  $\frac{dn}{dt}$ , was recalculated using this value.

ACDTIA

Al

$$\frac{dn}{dt} = 1.02 (1 \times 10^{-15} \text{ mol/s} \cdot \text{cm}^2) (1100 \text{ cm}^2/\text{g}) (3.7502 \text{ g})$$

$$\frac{dn}{dt} = 4.2 \times 10^{-12} \frac{\text{mol}}{\text{s}}$$

Si  
 $\frac{dn}{dt} = 1.98 (1 \times 10^{-15} \text{ mol/s} \cdot \text{cm}^2) (1100 \text{ cm}^2/\text{g}) (3.7502 \text{ g})$

$\frac{dn}{dt} = 8.1675 \times 10^{-12} \frac{\text{mol}}{\text{s}}$

ACDTIIIA

Al  
 $\frac{dn}{dt} = 1.02 (1 \times 10^{-15} \text{ mol/s} \cdot \text{cm}^2) (1200 \text{ cm}^2/\text{g}) (2.5002 \text{ g})$

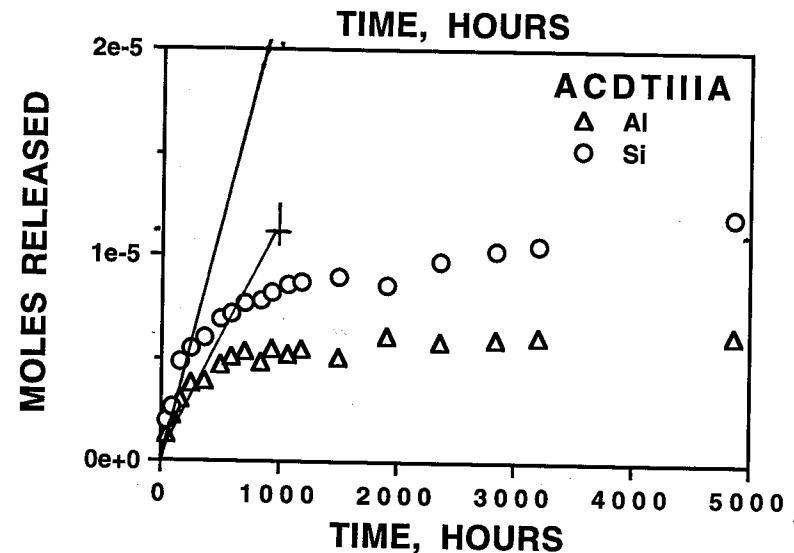
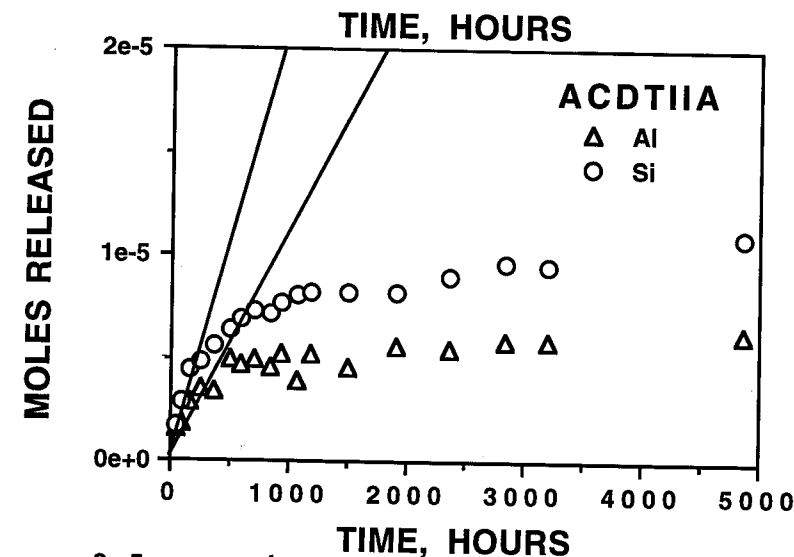
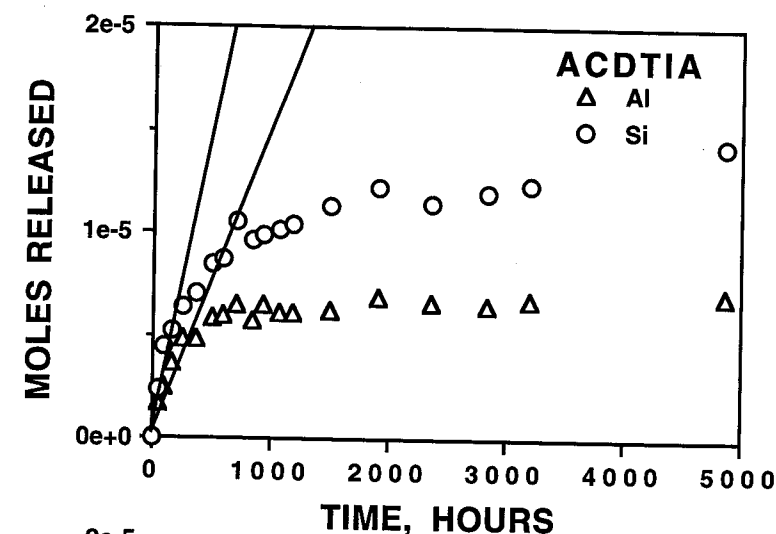
$\frac{dn}{dt} = 3.06 \times 10^{-12} \text{ mol/s}$

Si  
 $\frac{dn}{dt} = 1.98 (1 \times 10^{-15} \text{ mol/s} \cdot \text{cm}^2) (1200 \text{ cm}^2/\text{g}) (2.5002 \text{ g})$

$\frac{dn}{dt} = 5.94 \times 10^{-12} \text{ mol/s}$

- Lines with these slopes were then plotted on their respective figures.

JAR 4/5/94



See page

81

for  
update

and

4/7/95

JAR 4/5/94

## Correction for Splash - Error in data RACDTIA

When graphing Na molality vs. time for RACDTIA it was found that the experimental data did not fit the calculated data. The calculated data did not fit a straight line, but increased rapidly for the initial ~5000 hours then leveled off at a slope mirroring that of the experimental data. After consulting the analyst it was discovered that a splash had occurred during evaporation. The splash was corrected for in the following manner:

1. The original calculated data for

RACDTIA was ignored. Experimental data for the set was fit with a curve and values for Na were found from this curve (Na Molality v. Time) given the experimental times used. The percent increase of Na was calculated over the curve and Cl was assumed to have increased the same percent. The experimental data for Cl was increased by this proportion and the new splash corrected data for Na and Cl was put into EQ3 equation to calculate the activities of  $\text{Na}^+$ ,  $\text{SiO}_2$  and  $\text{Al(OH)}_4^-$ . The logs of the activities were derived from the EQ3 formula and the values were copied into a Cricket graph file. The  $\log(a_{\text{Na}^+} + a_{\text{Al(OH)}_4^-})$  was calculated by adding  $\log a_{\text{Na}^+} + \log a_{\text{Al(OH)}_4^-}$ . This data was graphed into existing figures Anal-Clinop15 copy and Analtime solubility 10 copy as  $\log(a_{\text{Na}^+} + a_{\text{Al(OH)}_4^-})$  v.  $\log a_{\text{SiO}_2}$  and compared to the original uncorrected data.

JAR 4/12/94

There was no significant difference between the two data plots. The uncorrected RACDTIA uncorrected data was removed from the plots and replaced by the corrected splash data.

JAR 4/19/94

## HISTOGRAM PLOT for Na

The difference between moles of Na for experimental and moles of Na calculated was calculated for data sets ACDTIA, -2A, -3A, ASE1, -2, -3, -4 and ASE1, -2, -3. The entire set of data was then sorted and counted on a mid range of  $-4.5 \times 10^{-3}$  to  $+11.5 \times 10^{-3}$ . The data was put into Cricket graph and a plot was made in histogram (bar) form.

JATZ 4/21/94

CS



## CLIDE - Modifications to Parameter Values

- Various changes were made to figures involving CDVSE data as a result of the discovery of an error in an array of experimental data. Recalculations were performed using the CLIDE code mentioned in this notebook.
- For CDVSE III at time 13789 hours, the measured Al mobility was entered into a spread sheet as 9.02 ppb, while the actual value was 0.0 ppb. The correction was made and Figure 3-12 of the Geochemistry Topical Report (CNWRA 94-006) was regenerated using corrected data.
- Additionally, the value of the equilibrium constant was modified to correspond to that constant drawn from Figure 3-14 of the same report. For the recalculation, a value of  $\log K = -51$  was used.
- Modifying the rate constant became necessary to produce a reasonable regression of the data. A value of  $7.2 \times 10^{-13}$  was used as an input for  $k_s$  in the data file "constin". Within the same file, the equilibrium constant  $K$  was entered as  $7.9 \times 10^{-6}$  which corresponds to the actual value,  $10^{-51}$  to the 10th power. This convention was necessary due to the nominal formula of clinoptilolite used in the rate equation derivation.

- CD 6/22/94

- The value for  $k_s$  used in CLIDE calculations corresponds to the initial rate of dissolution of Si.
- The surface area specific dissolution rate would correspond to the value of  $k_s$  entered divided by surface area and mass of material to yield units of moles/cm<sup>2</sup>/s

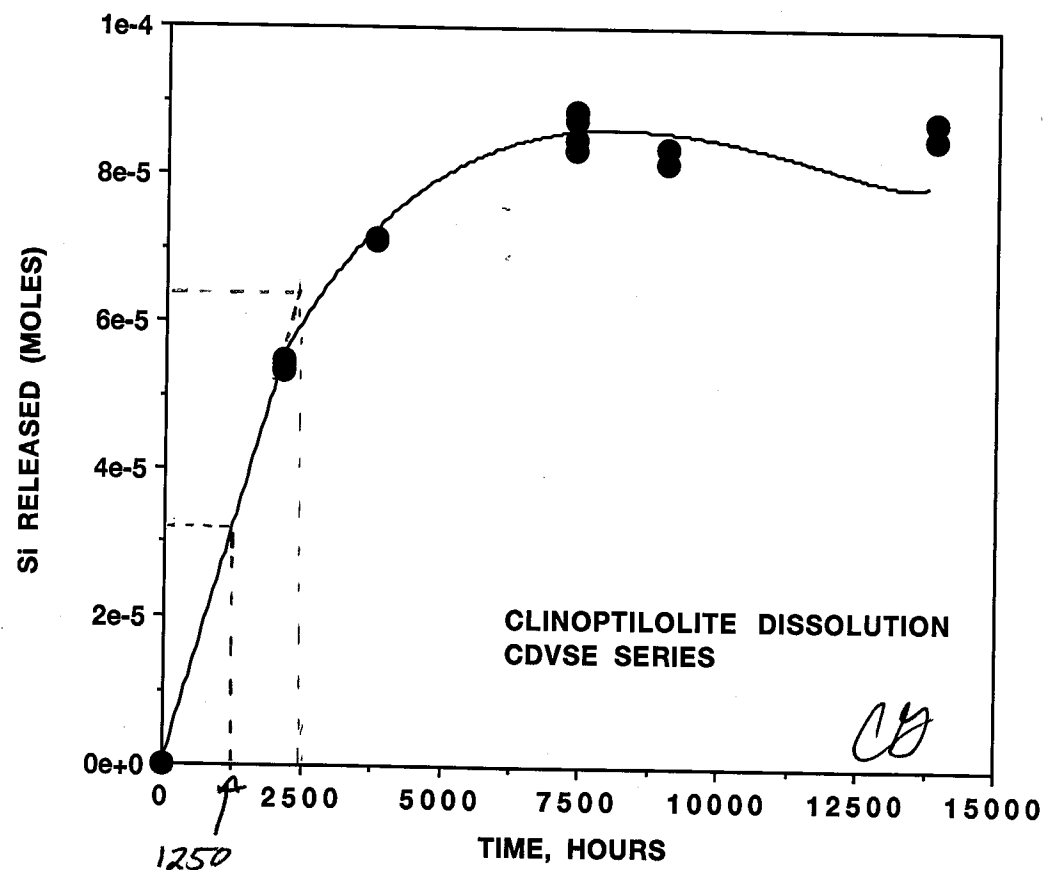
Verification of CLIDE CODE

- The CLIDE code integrates the general dissolution rate equation:

$$\frac{dQ}{dt} = k_s \left( 1 - \frac{Q}{K} \right)$$

- At conditions far from equilibrium,  $Q \rightarrow 0$  and the slope of the line representing the dissolution rate (the line generated by Clide) should equal  $k_s$ .
- A hand calculation can verify that the slope calculated by CLIDE is indeed equal to the value of  $k_s$  at conditions far from equilibrium.

- CD 6/22/94



✓ For times  $< 2500$  hours, the slope approximates the initial dissolution rate. Selecting two convenient data points, the slope can be hand calculated:

$$\begin{pmatrix} 1250 & 3.2e^{-5} \\ 2500 & 6.4e^{-5} \end{pmatrix}$$

$$\frac{dSi}{dt} \approx \frac{6.4e^{-5} - 3.2e^{-5}}{1250 \text{ h} \cdot \frac{1 \text{ h}}{3600 \text{ s}}} = 7.11e^{-12}$$

Referring to p. 43 of this notebook, the dissolution rate equation used (equation (1)) shows that the dissolution of ~~clinoptilolite~~ <sup>clinoptilolite</sup> is  $10 \times$  less than that of silica. Therefore, dividing the value hand calculated for  $\frac{dSi}{dt}$  by 10 gives  $\boxed{7.11e^{-13}}$ .

- This value corresponds almost exactly to the value input for the dissolution rate constant for clinoptilolite within an minute error range due to crudeness of hand calculations. This verifies that the code is working at conditions far from equilibrium.

- Value from code input:  $\boxed{7.2e^{-13}}$

Value from hand calculation:  $\boxed{7.11e^{-13}}$

$$\text{Error} = \frac{7.2e^{-13} - 7.11e^{-13}}{7.2e^{-13}} \times 100\% \approx 1.25\%$$

CJ 6/22/91

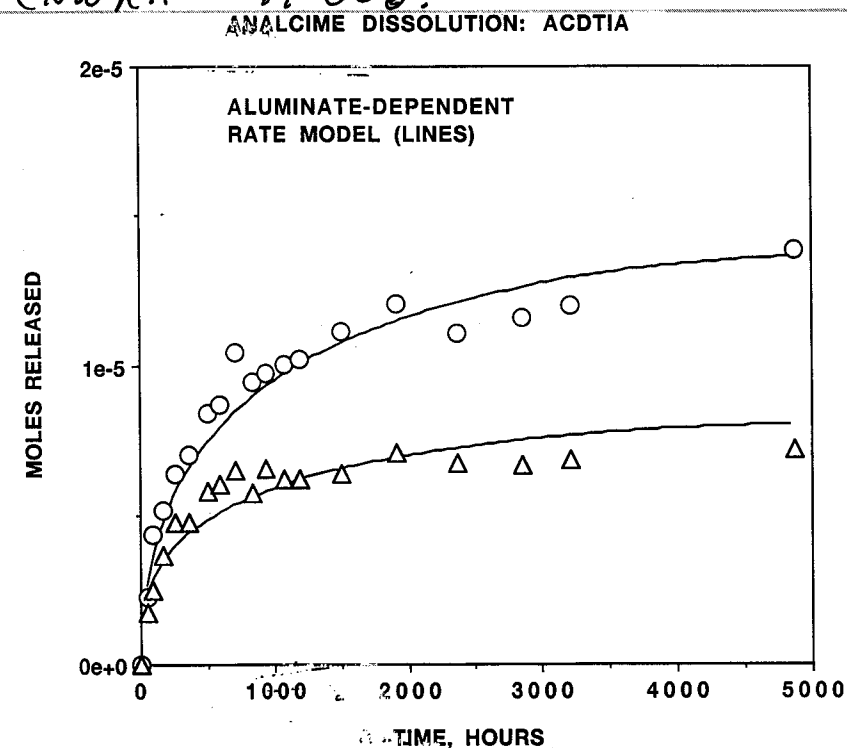
- At conditions nearing equilibrium the code can be verified by comparison with graphs illustrating evolution of the system towards equilibrium.
- Figure 3-14 of CNWRA 94-006 shows the evolution of the CDUSE samples (squares) toward equilibrium (represented by the line).
  - At time  $\sim 4000$  hours the system is still undersaturated. The figure on p. 58 shows this point on a still increasing portion of the curve, but no longer at the maximum dissolution rate (initial rate). This shows that the curve is reasonable for times through  $\sim 4000$  hrs.
- Points at times  $\sim 7000$  hr and  $\sim 9000$  h show supersaturation with respect to equilibrium of clinoptilolite dissolution. Correspondingly in the figure on p. 58 these points are at states of supersaturation ~~above~~ the curve fits the data well, and it has flattened out and begun a downswing.
- The calculated line agrees well with the interpretation on pp 3-28 and 3-29 of CNWRA 94-006 of clinoptilolite equilibrium being approached from supersaturation in the dissolution experiments. These consistencies work to verify the results of calculations made with the CDUSE code. 6/22/94

## Revisions to Niadre Input Decks

- Revisions were made to NIADRE (discussed on pp 25-33) input decks to make various parameters agree with values presented in CNWRA 94-006
- Revisions were made to both the aluminate-dependent model and the dual mechanism model

## Aluminate-Dependent Model

- The equilibrium constant  $K$  was modified to  $2.14 \times 10^{-15}$  to agree with the log value of  $-14.67$  drawn (extracted) from Figure 3-11 of CNWRA 94-006.
- The rate constant  $k_s$  was modified to  $1.3 \times 10^{-23}$  (within the file "derivs.for").  
moles/sec CD 6/23/94
- Theoretical basis of the Aluminate-dependent model are described in section 3.5.2.2 of CNWRA-94-006.



6/23/94



## Dual Mechanism Model: NIADRE

- A mechanism for modeling of dissolution rate based on two variably reactive materials was presented in section 3.5.2.1 of CWRRA 94-006.
- The rate constant of the normal material was held at  $1.98e^{-13}$  moles/sec.
- The rate constant for the ultra reactive material was initially set at  $4e^{-12}$  moles/sec but decreased according to an equation relating to  $\xi$  and surface area.
- A general equation was derived after an Helgeson, Murphy, and Agarad Geochimica et Cosmochimica Vol. 48, pp 2405-2432, 1984 article:

$$k_{s-er} = (A - B\xi)^{2/3}$$

- A and B are adjustable parameters, and good regressions were obtained with  $A = 8e^{-18}$  and  $B = 1.65e^{-12}$ .
- The ratio of  $\frac{A}{B}$  equals  $\frac{V}{V_0}$ , which is

the ratio of initial volume of ultra reactive material to the molar volume.

Since molar volume,  $V_0$ , equals  $\frac{MW}{\text{density}}$ , the equation can be solved for initial (mass/volume) of ultra reactive material:

$$\frac{A}{B} = \frac{V}{V_0}$$

$$V = \frac{A}{B} V_0 = \frac{A}{B} \frac{MW}{P} = \frac{8e^{-18}}{1.65e^{-12}} \frac{(220.2 \text{ g/mol})}{2.25 \text{ g/cc}}$$

$$= 4.7 \text{ cm}^3 \text{ analcime, or}$$

$$\frac{4.7 \text{ cm}^3}{1} \cdot \frac{2.25 \text{ g}}{\text{cm}^3} = \boxed{1e^{-3} \text{ g analcime}}$$

The sample ACDTIA was initially 3.75g

The ultra reactive material therefore corresponds to approximately

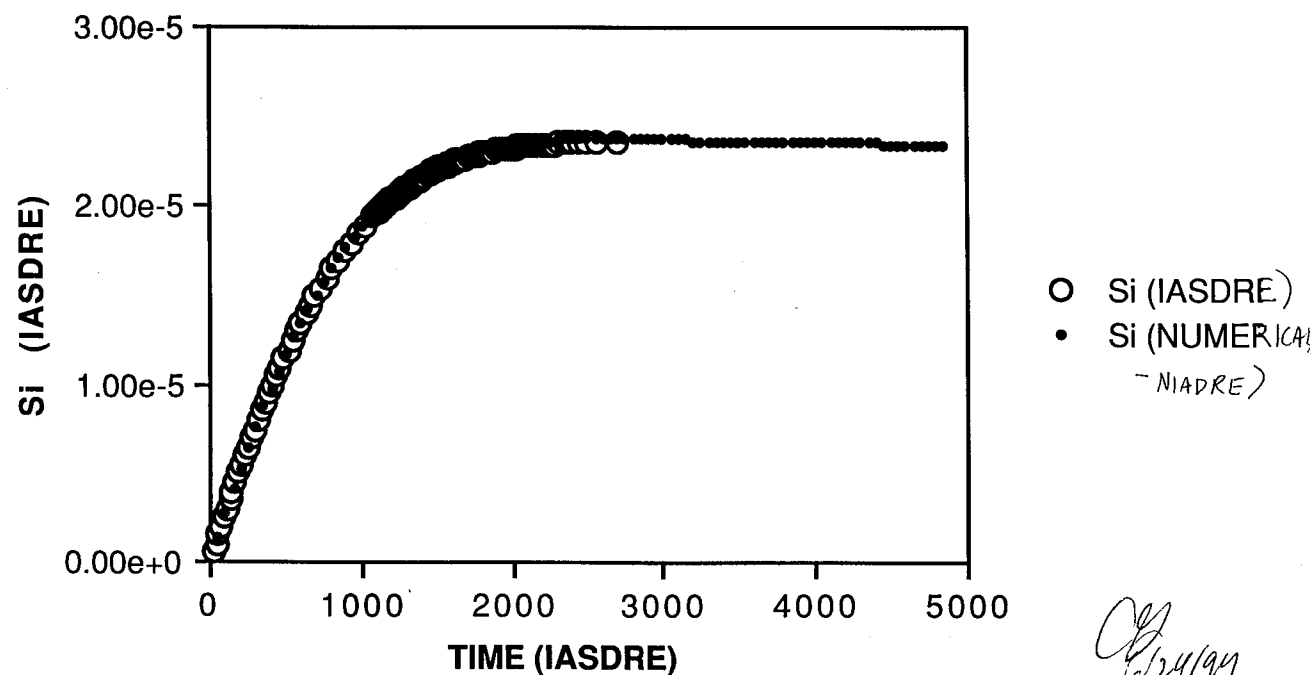
$$\frac{1e^{-3} \text{ g}}{3.75 \text{ g}} \times 100\% = \boxed{0.03\% \text{ of total sample mass (initial)}}$$

(19)  
6/24/99

## Verification of NIADRE code

- A test of the calculations made in NIADRE was performed by comparing calculations with IASDRE (pp 2-), which integrates the rate equation analytically rather than numerically as NIADRE does.
- Identical input decks produced indistinguishable output, as evidenced by the below figure. Open circles designate IASDRE calculated data while small filled circles represent NIADRE calculations. IASDRE runs only to a point near equilibrium and then halts.

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CG 6/24/94

Pages 1-64 of This notebook were reviewed for compliance to QAP-001 in response to CAE 94-02. Corrections and clarifications were made as appropriate. In some cases, the date of the change will reflect the date of This review rather than the date of the original Scientific Notebook entry.

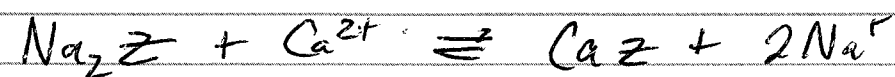
Verified by: Randy Jolch  
SWRT - QA  
7/12/94

CG 7/22/94

## CALCULATIONS ON ION-EXCHANGE (MODELING)

Na<sup>+</sup>/Ca<sup>2+</sup> system

The general exchange reaction for a Na<sup>+</sup>/Ca<sup>2+</sup> system can be written as:



where Z represents the zeolite form. For this reaction, an expression for the equilibrium constant can be written as

$$K = \frac{(a_{\text{Na}^+})^2 \lambda_{\text{CaZ}} \lambda_{\text{NaZ}}}{(a_{\text{Ca}^{2+}}) \lambda_{\text{Na}_2\text{Z}} \lambda_{\text{Na}_2\text{Z}}}$$

where  $a_i$  represents thermodynamic activities of species  $i$ ,  $\lambda_i$  represents mole fraction of endmember  $i$  in the zeolite (as opposed to aqueous) form, and  $\lambda_i$  represents non-ideality factors for species  $i$ .

By definition:

$$\lambda_{\text{Na}_2\text{Z}} + \lambda_{\text{CaZ}} = 1$$

$$a_{\text{Na}^+} = m_{\text{Na}^+} \gamma_{\text{Na}^+}$$

$$a_{\text{Ca}^{2+}} = m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}}$$

$$\text{TN} = m_{\text{Na}^+} + 2m_{\text{Ca}^{2+}}$$

where  $m$  equals the molality of species  $i$ ,  $\gamma_i$  is the activity coefficient of species  $i$  and  $\text{TN}$  is the total normality of the system (fixed for each experiment).

-CJD 7/28/94

Therefore:

$$\frac{(m_{\text{Na}^+})^2}{\text{TN} - m_{\text{Na}^+}} = \frac{K \lambda_{\text{Na}_2\text{Z}} \lambda_{\text{Na}_2\text{Z}} \gamma_{\text{Ca}^{2+}}}{2 \lambda_{\text{CaZ}} \lambda_{\text{CaZ}} (\gamma_{\text{Na}^+})^2}$$

Using the quadratic equation, it is solved that

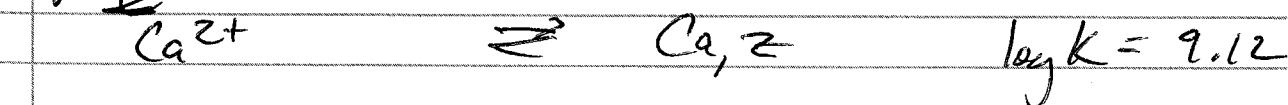
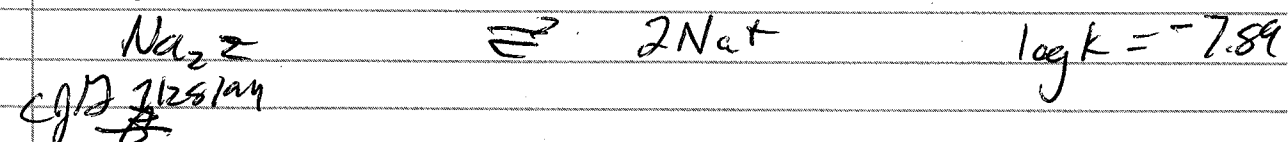
$$m_{\text{Na}^+} = \frac{-F \pm \sqrt{F^2 + 4(\text{TN} \times F)}}{2}$$

$$\text{where } F = \frac{K \lambda_{\text{Na}_2\text{Z}} \lambda_{\text{Na}_2\text{Z}} \gamma_{\text{Ca}^{2+}}}{2 \lambda_{\text{CaZ}} \lambda_{\text{CaZ}} (\gamma_{\text{Na}^+})^2}$$

Activity coefficients  $\gamma_{\text{Ca}^{2+}}$  and  $\gamma_{\text{Na}^+}$  were calculated using the aqueous speciation code EQ3NR version 7.1 with data base DATA0.COM.R16.

The Equilibrium constant,  $K$  was calculated using data from the 'database'

It equals the sum of the two reactions



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$X_{CaZ}$  was used as an independent variable and was stepped from values of 0 to 1 by increments of approximately 0.05.

The non-ideality factors  $\lambda_{CaZ}$  and  $\lambda_{NaZ}$  were calculated according to a Margules formulation:

$$RT \ln \lambda_{CaZ} = (2W_{62} - W_{61}) X_{NaZ}^2 + 2(W_{61} - W_{62}) X_{NaZ}^3$$

$$RT \ln \lambda_{NaZ} = (2W_{61} - W_{62}) X_{CaZ}^2 + 2(W_{62} - W_{61}) X_{CaZ}^3$$

where  $W_{62}$  and  $W_{61}$  are fit parameters,  $R$  is the ideal gas constant ( $= 8.314 \text{ J/Kmol}$ ), and  $T$  is temperature in Kelvin ( $= 298 \text{ K}$ ).

Values of  $m_{Na^+}$  were calculated and  $m_{Ca^{2+}}$  was subsequently solved as

$$m_{Ca^{2+}} = (TN - m_{Na^+})/2$$

The mole fraction of  $Na^+$  and  $Ca^{2+}$  in aqueous solution were then calculated as

$$X_{Na^+(aq)} = \frac{m_{Na^+}}{m_{Na^+} + m_{Ca^{2+}}}$$

$$X_{Ca^{2+}(aq)} = \frac{m_{Ca^{2+}}}{m_{Ca^{2+}} + m_{Na^+}}$$

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## CALCULATIONS WITH EXPERIMENTAL DATA

Experimental data were taken and recorded for ion-exchange experiments as initial and final aqueous concentrations of the two species in the binary exchange system (e.g.,  $Na^+/Ca^{2+}$ ,  $Na^+/K^+$ ,  $Na^+/Sr^{2+}$ ).

Values of  $\lambda_Z$  and  $X_{(aq)}$  were calculated in two distinct ways: one based on  $Na^+$  measurements, one based on the other cation measurements.

$Na^+/Ca^{2+}$  system - example of  $Na^+$ -based calculations

$$X_{CaZ} = \frac{n_{CaZ}}{n_Z}$$

where  $n_{CaZ}$  is the total moles of calcium zeolite and  $n_Z$  is the total moles of zeolite.

By definition =

$$n_Z = \frac{CEC \cdot (\text{initial sample mass})}{2}$$

where CEC is the calculated cation exchange capacity (calculated by Pabalan through separate experiments to be  $2.04 \times 10^{-3} \text{ eq/g}$ ).

Therefore, using  $Na^+$  data:

$$X_{CaZ} = \frac{\frac{1}{2} (\Delta n_{Na(aq)})}{(CEC \cdot \text{sample mass})/2}$$

assuming for every 2 moles of  $Na^+$  entering into solution, one mole of  $Ca^{2+}$  is formed.

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And:

$$X_{Ca^{2+}(aq)} = \left[ m_{Ca^{2+}}^{init} - \frac{1}{2} \left( \frac{\Delta n_{Na(aq)}}{W_{H_2O}} \right) \right]$$

$$\left[ m_{Ca^{2+}}^{init} - \frac{1}{2} \left( \frac{\Delta n_{Na(aq)}}{W_{H_2O}} \right) \right] + m_{Na^+}^{final}$$

$$X_{Na_2Z} = 1 - X_{CaZ}$$

$$X_{Na(aq)} = \frac{m_{Na^+}^{final}}{m_{Na^+}^{final} + \left( m_{Ca^{2+}}^{init} - \frac{1}{2} \frac{\Delta n_{Na(aq)}}{W_{H_2O}} \right)}$$

where  $W_{H_2O}$  is the mass of water in the solution.

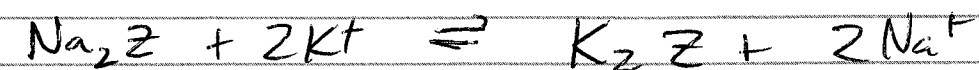
$$\Delta n_{Na(aq)} = m_{Na^+}^{final} \cdot W_{H_2O} - m_{Na^+}^{init} \cdot W_{H_2O}$$

and  $\Delta n_{Na(aq)} > 0$  since Na is being transferred from the zeolite into the aqueous solution.

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# Na<sup>+</sup>/K<sup>+</sup> System - Model Calculations

The reaction:



The equilibrium expression can be written as:

$$K = \frac{(a_{Na^+})^2 X_{K_2Z} \lambda_{K_2Z}}{(a_{K^+})^2 X_{Na_2Z} \lambda_{Na_2Z}}$$

By definition:

$$X_{Na_2Z} + X_{K_2Z} = 1$$

$$a_{Na^+} = m_{Na^+} \gamma_{Na^+}$$

$$a_{K^+} = m_{K^+} \gamma_{K^+}$$

$$TN = m_{Na^+} + m_{K^+}$$

Therefore:

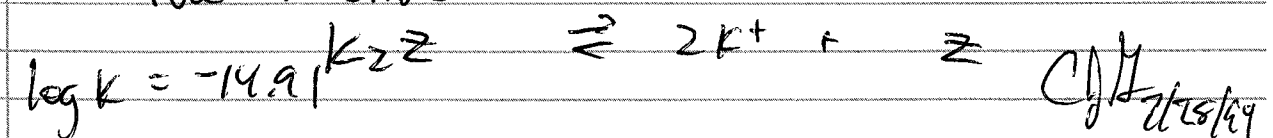
$$\frac{(m_{Na^+})^2}{(TN - m_{Na^+})^2} = \frac{K X_{Na_2Z} \lambda_{Na_2Z} (\gamma_{K^+})^2}{X_{K_2Z} \lambda_{K_2Z} (\gamma_{Na^+})^2}$$

Solving the quadratic yields the solution:

$$m_{Na^+} = \frac{-2(TN)(F) \pm \sqrt{[2(TN)(F)]^2 + 4(1-F)(F/TN)}}{2(1-F)}$$

$$\text{where } F = \frac{K X_{Na_2Z} \lambda_{Na_2Z} (\gamma_{K^+})^2}{X_{K_2Z} \lambda_{K_2Z} (\gamma_{Na^+})^2}$$

For the reaction:



therefore log k for the  $\text{Na}^+/\text{K}^+$  system equals  $-7.89 + 14.91 = 7.02$ .

Activity coefficients are reported in a summary of data to be inserted in this notebook.

### EXPERIMENTAL DATA CALCULATIONS

$$X_{Kz} = \frac{n_{Kz}}{n_z} = \frac{n_{Kz}}{(\text{CEC} \cdot \text{sample mass})/z}$$

### EXAMPLE USING $\text{K}^+$ DATA

$$X_{Kz} = \frac{(-\Delta n_{K(aq)})/z}{(\text{CEC} \cdot \text{sample mass})/z}$$

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7/28/04  
 $X_{Kz(aq)}$

$$X_{K^+(aq)} = \frac{m_{K^+ \text{ final}}}{m_{K^+ \text{ final}} + \left[ m_{\text{Na}^+ \text{ init}} - \Delta n_{K(aq)} \right] / W_{H_2O}}$$

note:  $\Delta n_{K(aq)} < 0$  since K is moving from solution into the zeolite.

$$X_{Na^+} = 1 - X_{Kz}$$

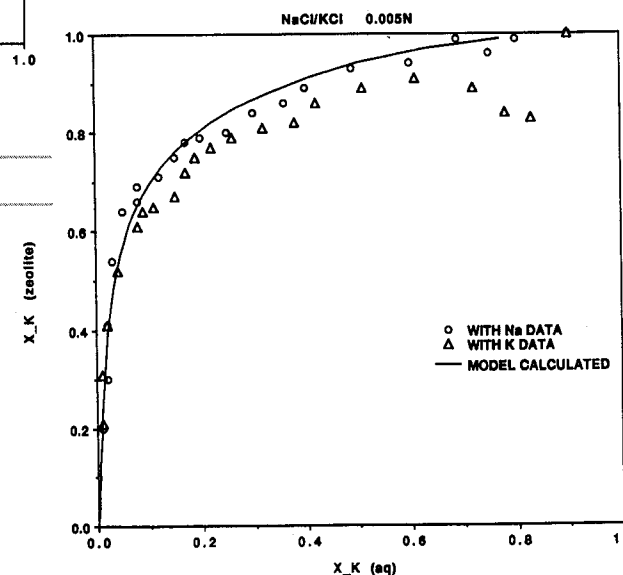
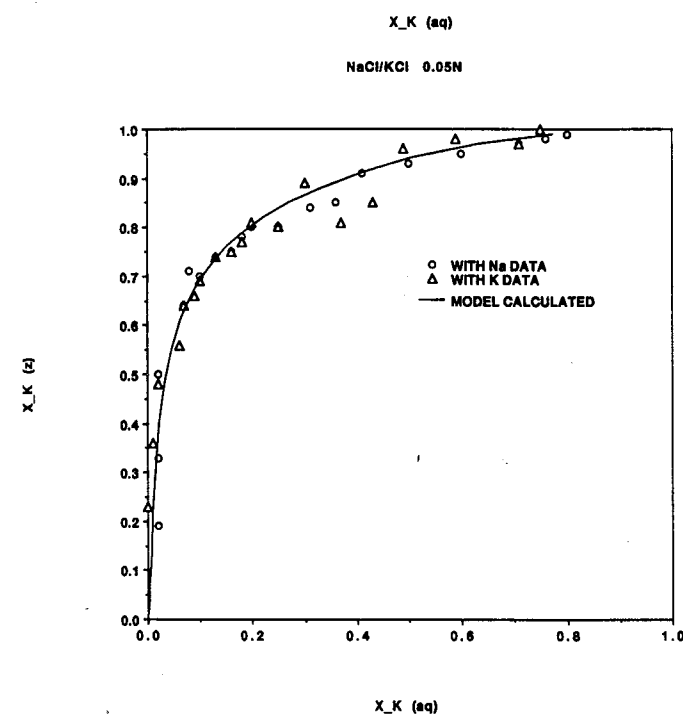
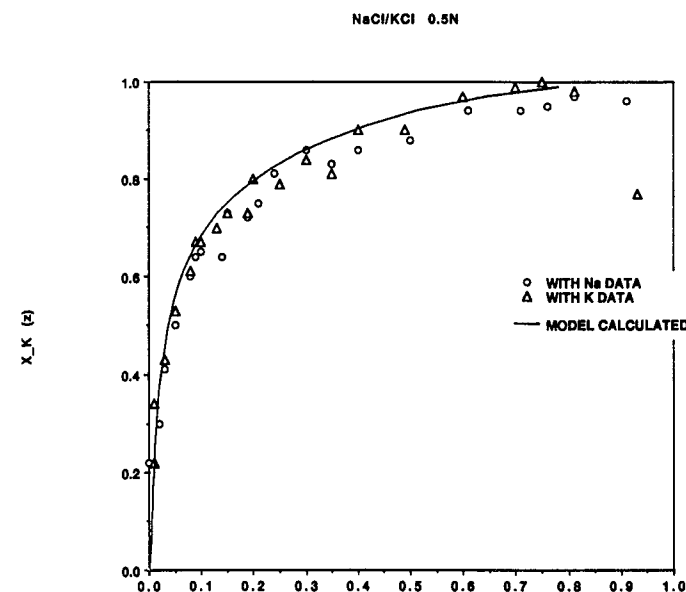
$$X_{Na^+(aq)} = \frac{(m_{\text{Na}^+ \text{ init}} - \Delta n_{K(aq)}) / W_{H_2O}}{\left[ (m_{\text{Na}^+ \text{ init}} - \Delta n_{K(aq)}) / W_{H_2O} \right] + m_{K^+ \text{ final}}}$$

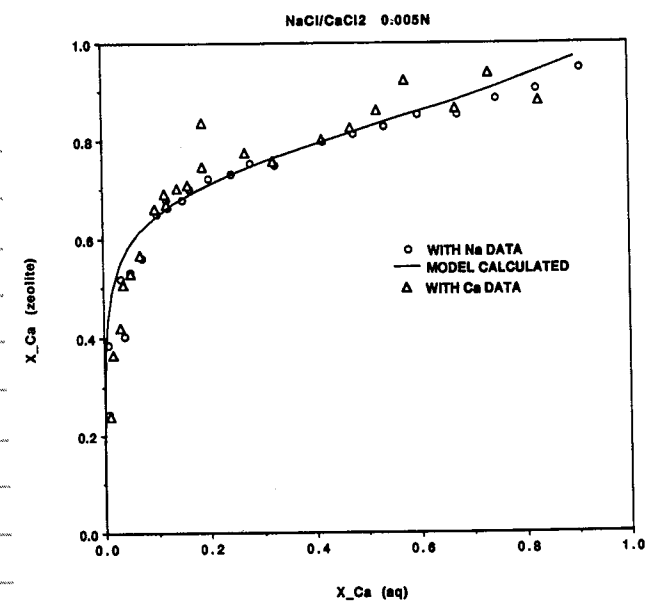
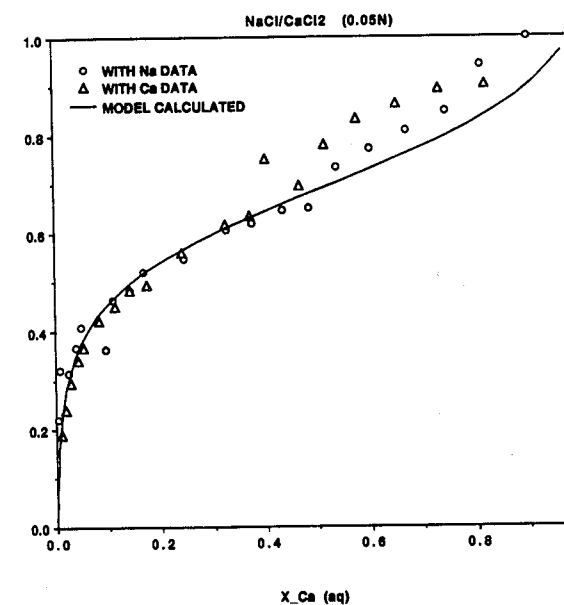
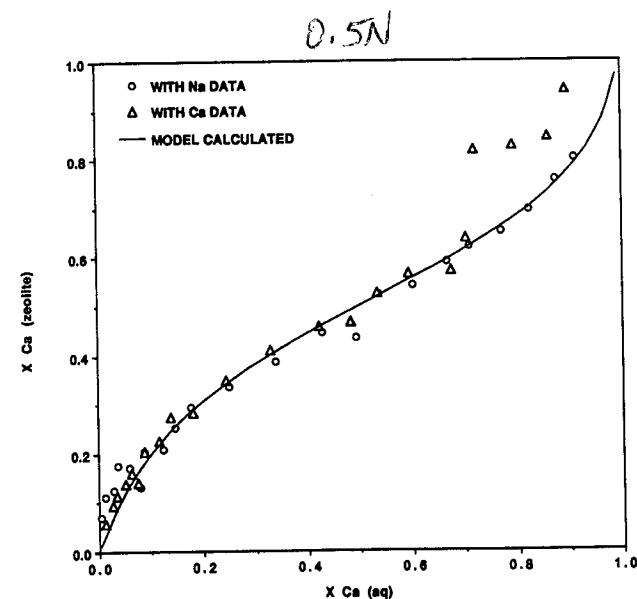
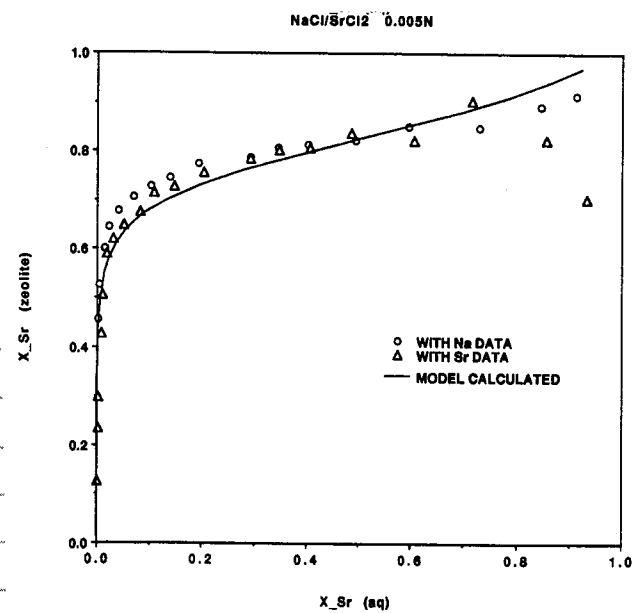
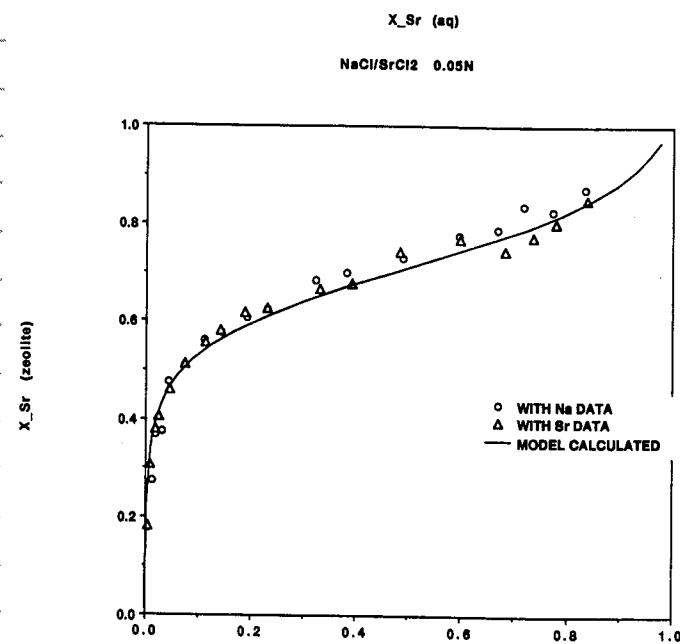
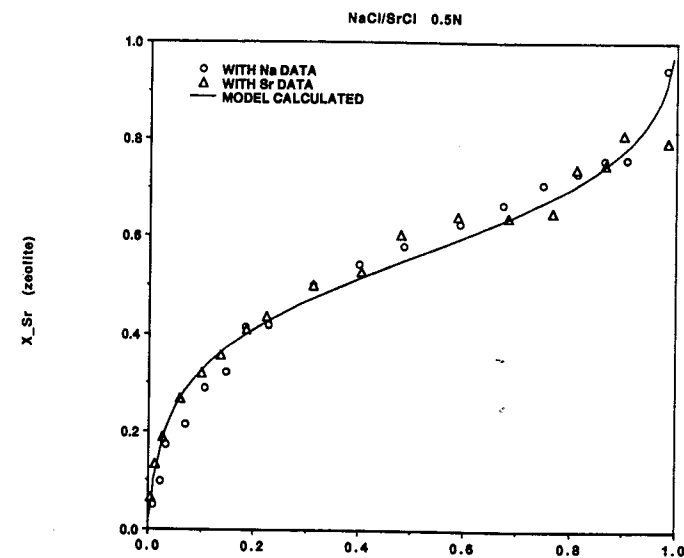
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### $\text{Na}^+/\text{K}^+$ System

Experimental data and models.

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Na<sup>+</sup>/Ca<sup>2+</sup> System

- experimental data and models

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Na<sup>+</sup>/Sr<sup>2+</sup> System

- experimental data and models

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The cation exchange capacity (CEC) equals  $2.04 \times 10^{-3}$  for all experiments.

\* estimated: No logk data for Sr-clinoptilolite in EQ36NR modified database.

Experiment	Total Normality	$\gamma_{Na+}$	$\gamma_{Cation}$	log10K	G1 (fit parameter)	G2 (fit parameter)
NaCl/CaCl <sub>2</sub>	0.5	0.67	0.248	1.23	5000	-25000
	0.05	0.80	0.46	1.23	5000	-25000
	0.005	0.92	0.72	1.23	5000	-25000
NaCl/SrCl <sub>2</sub>	0.5	0.67	0.21	0.01 *	-6000	-20000
	0.05	0.80	0.45	0.01 *	-6000	-20000
	0.005	0.92	0.72	0.01 *	-6000	-20000
NaCl/KCl	0.5	0.68	0.64	7.02	20000	-35000
	0.05	0.82	0.81	7.02	20000	-35000
	0.005	0.927	0.926	7.02	20000	-35000

## ION EXCHANGE MODELING PARAMETERS

CPG  
7/28/94

## K<sub>d</sub> Calculation for Carbon Dispersion/Diffusion Model

$$K_d = \left[ \frac{\text{mg C}}{\text{g H}_2\text{O}} \right] \left[ \frac{\text{ml gas}}{\text{mg C}} \right] = \frac{[C]_{aq}}{[C]_g}$$

- Aqueous concentrations of C were obtained from aqueous speciation calculations performed with EQ3/6 v.7.
- Data files can be found in Murphy MacIntosh directory: [Folders, Modeling VAXFiles.EQ3693, EQ6.VFUG, SE693]

$$[C]_{aq} = m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} + m_{\text{CO}_2(aq)}$$

where  $m_i$  equals the molality of the subscripted species.  $3.35 \times 10^{-3}$  ( $3.35 \times 10^{-3}$ ) moles/kg is a representative value for  $[C]_{aq}$  based on the Murphy Natural System Model (described in Murphy Focus 43 p.115, 1993). (Actual value taken from file 'species.t')

- $[C]_g$  is equal to  $\frac{RT}{P}$  according to the ideal gas law, where  $R$  is the gas constant, and  $T$  is Kelvin temperature, and  $P$  is pressure of CO<sub>2</sub> in atmospheres.
- The value of pressure used was taken from the Natural System Model calculations from the file 'gases.t' and equals  $(0.00198 \text{ bars} \cdot \frac{1 \text{ atm}}{1.01325 \text{ bars}})$

Therefore  $K_d = \frac{3.35 \times 10^{-3} \text{ moles}}{\text{kg H}_2\text{O}} \frac{(0.08206 \text{ Latm/Kmol})(298 \text{ K})}{(0.00198 \text{ bars} \cdot \frac{1 \text{ atm}}{1.01325 \text{ bars}})}$

$$K_d \approx \boxed{41.9}$$

Following notes by Murphy.

New analcime surface areas reported by Pabalan

size (mesh)	new surface area (m <sup>2</sup> /g)	former
200-230	0.103 ± 0.003	0.11 ± 0.01
230-325	0.145 ± 0.013	0.12 ± 0.02
325-450	0.183 ± 0.009	0.16 ± 0.04

Reference pg. 50 calculations (for new surface areas)

$$\frac{\text{ACDTIIA}}{\text{Al}} \quad \frac{1}{S} \frac{dn}{dt} = \frac{1}{1.02} \frac{7 \times 10^{-6} \text{ mole}}{500 \times 3600 \text{ sec}} \left( \frac{0.103 \text{ m}^2}{\text{g}} \right)^{-1} \frac{\text{m}^2}{10^4 \text{ cm}^2} \frac{1}{3.7502 \text{ g}}$$

$$= k^* = 9.87 \times 10^{-16} \frac{\text{mole}}{\text{cm}^2 \text{ sec}}$$

$$\frac{\text{Si}}{\text{S}} \quad \frac{1}{S} \frac{dn}{dt} = \frac{1}{1.98} \frac{7 \times 10^{-6} \text{ mole}}{250 \times 3600 \text{ sec}} \frac{9 \text{ mmol}_{4/7/95}}{0.145 \text{ m}^2} \frac{\text{m}^2}{10^4 \text{ cm}^2} \frac{1}{3.7502 \text{ g}}$$

$$= k^* = \frac{7.22 \times 10^{-16} \text{ mole}}{1.02 \times 10^{-15} \text{ cm}^2 \text{ sec}}$$

$$\frac{\text{ACDTIIA}}{\text{Al}} \quad \frac{1}{S} \frac{dn}{dt} = \frac{1}{1.02} \frac{6.1 \times 10^{-6} \text{ mole}}{500 \times 3600 \text{ sec}} \left( \frac{0.145 \text{ m}^2}{\text{g}} \right)^{-1} \frac{\text{m}^2}{10^4 \text{ cm}^2} \frac{1}{2.5002 \text{ g}}$$

$$= k^* = 9.16 \times 10^{-16} \frac{\text{mole}}{\text{cm}^2 \text{ sec}}$$

$$\frac{\text{Si}}{\text{S}} \quad \frac{1}{S} \frac{dn}{dt} = \frac{1}{1.98} \frac{6.875 \times 10^{-6} \text{ mole}}{250 \times 3600 \text{ sec}} \frac{9}{6.145 \text{ m}^2} \frac{\text{m}^2}{10^4 \text{ cm}^2} \frac{1}{2.5002 \text{ g}}$$

$$= k^* = 1.064 \times 10^{-15} \frac{\text{mole}}{\text{cm}^2 \text{ sec}}$$

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## ACDT III A

$$\text{Si} \quad \frac{1}{S} \frac{dn}{dt} = \frac{1}{1.98} \frac{6.875 \times 10^{-6} \text{ moles}}{250 \times 3600 \text{ sec}} \frac{\text{g}}{16 \text{ cm}^2} \frac{\text{m}^2}{10^4 \text{ cm}^2} \frac{1}{2.2501 \text{ g}}$$

$$= \frac{1.07 \times 10^{-15} \text{ moles}}{9.37 \times 10^{-16} \text{ cm}^2 \text{ sec}} \quad \text{mm 4/7/95} \quad 0.183 \text{ mm 4/7/95}$$

$$\text{Al} \quad \frac{1}{S} \frac{dn}{dt} = \frac{1}{102} \frac{6.2 \times 10^{-6} \text{ moles}}{500 \times 3600 \text{ sec}} \frac{\text{g}}{16 \text{ cm}^2} \frac{\text{m}^2}{10^4 \text{ cm}^2} \frac{1}{2.2501 \text{ g}}$$

$$= \frac{9.38 \times 10^{-16} \text{ moles}}{8.20 \times 10^{-16} \text{ cm}^2 \text{ sec}} \quad \text{mm 4/7/95} \quad 0.183 \text{ mm 4/7/95}$$

These calculations show that the surface specific analcime dissolution rate is approximately  $1 \times 10^{-15}$  moles/cm<sup>2</sup>/sec. This is the same conclusion reached previously with the old surface areas. Furthermore, Jennifer incorrectly noted the old surface area of ACDT III A as  $0.6 \times 10^4$  cm<sup>2</sup>/g rather than  $0.16 \times 10^4$  cm<sup>2</sup>/g. This is why the ACDT III A data appeared not to conform to IIA and IIA as noted in NUREG/CR-6282. With the correct updated surface area IIIA conforms well.

mm 4/7/95

Proper slopes for the log-log figure of page 53 (for ACDT III A) are

$$\text{Si} \quad 1 \times 10^{-15} \frac{\text{moles}}{\text{cm}^2 \text{ sec}} \frac{1.98 \text{ moles Si}}{\text{mole Anl}} \frac{1830 \text{ cm}^2}{\text{g}} \frac{1}{2.2501 \text{ g}}$$

$$= 8.153 \times 10^{-12} \frac{\text{moles}}{\text{sec}}$$

$$= 2.935 \times 10^{-8} \frac{\text{moles}}{\text{hr}}$$

$$\frac{2.5 \times 10^{-5} \text{ moles}}{2.935 \times 10^{-8} \frac{\text{moles}}{\text{hr}}} = 852 \text{ hr} \quad (\text{for } 2.5 \times 10^{-5} \text{ moles})$$

$$\text{Al} \quad 1 \times 10^{-15} \frac{\text{moles}}{\text{cm}^2 \text{ sec}} \frac{1.02 \text{ Al}}{\text{mole Anl}} \frac{1830 \text{ cm}^2}{\text{g}} \frac{1}{2.2501 \text{ g}}$$

$$= 4.2 \times 10^{-12} \frac{\text{moles}}{\text{sec}}$$

$$< 1.512 \times 10^{-8} \frac{\text{moles}}{\text{hr}} \quad \frac{2.5 \times 10^{-5} \text{ moles}}{1.512 \times 10^{-8} \text{ moles/hr}} = 1653 \text{ hr}$$

$$= 1.512 \times 10^{-5} \frac{\text{moles}}{1000 \text{ hr}}$$

Lines corresponding to these slopes have been plotted on page 53.

mm 4/7/95



Input files for EQ3 runs  
in support of interpretation  
of analcime clinophyllite  
experimental studies are  
contained on the disk  
attached to this page. (Mac disk)  
Primary reference and documentation  
is Murphy and Pabalan  
NUREG/CR-6288 Section 3.

Also included  
are mass  
transfer codes  
and calculations  
in support  
of data  
interpretation.

WJ 3/12/96

Input files and representative outputs for  
modeling with EQ3/6 are contained  
on the disk (Mac) attached to this  
page. These are files developed in  
research leading to results in Section  
4 of Murphy and Pabalan  
NUREG/CR-6288

WJ 3/12/96

The Geochemistry Research Project terminated. The primary documentation of research activities is Murphy, W.M. and Pabalan, R.T. Geochemical Investigations Related to the Yucca Mountain Environment and Potential Nuclear Waste Repository. NUREG/CR-6288 U.S. Nuclear Regulatory Commission, Washington DC. 1994 and the references given in that publication.

Use of this scientific notebook is terminated.

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3/12/96

**ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK #: 049 (p. 84)**

<b>Document Date:</b>	03/12/1996
<b>Availability:</b>	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, Texas 78228
<b>Contact:</b>	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, TX 78228-5166 Attn.: Director of Administration 210.522.5054
<b>Data Sensitivity:</b>	<input checked="" type="checkbox"/> "Non-Sensitive" <input type="checkbox"/> Sensitive <input type="checkbox"/> "Non-Sensitive - Copyright" <input type="checkbox"/> Sensitive - Copyright
<b>Date Generated:</b>	1996
<b>Operating System:</b> (including version number)	MAC
<b>Application Used:</b> (including version number)	NA
<b>Media Type:</b> (CDs, 3 1/2, 5 1/4 disks, etc.)	1 - 3 1/2 disk
<b>File Types:</b> (.exe, .bat, .zip, etc.)	Various
<b>Remarks:</b> (computer runs, etc.)	Media contains: Input files for EQ3 runs in support of interpretation of analcime clinophyllite experimental studies and mass transfer codes and calculations in support of data interpretation.

**ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK #: 049 (p. 85)**

<b>Document Date:</b>	03/12/1996
<b>Availability:</b>	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, Texas 78228
<b>Contact:</b>	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, TX 78228-5166 Attn.: Director of Administration 210.522.5054
<b>Data Sensitivity:</b>	<input checked="" type="checkbox"/> "Non-Sensitive" <input type="checkbox"/> Sensitive <input type="checkbox"/> "Non-Sensitive - Copyright" <input type="checkbox"/> Sensitive - Copyright
<b>Date Generated:</b>	1996
<b>Operating System:</b> (including version number)	MAC
<b>Application Used:</b> (including version number)	NA
<b>Media Type:</b> (CDs, 3 1/2, 5 1/4 disks, etc.)	1 - 3 <sup>1/2</sup> disk
<b>File Types:</b> (.exe, .bat, .zip, etc.)	Various
<b>Remarks:</b> (computer runs, etc.)	Media contains: Input files and representative outputs for modeling with EQ3/6. These are files developed in research leading to results in Section 4 of NUREG/CR-6288.