QA: QA

REQUIREMENTS DOCUMENT (RD)
for
TOUGHREACT Version 2.2

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PRELIMINARY DRAFT
INFORMATION ONLY

CHANGE HISTORY

Revision Number	Effective Date	Description of Change
00	03/12/00	Initial issue of CP1 documents prior to ITSMA review.
01	05/1/00	Initial issue of CP1 documents following ITSMA review. The changes were the addition of the "QA" designator, this Change History, extensive changes to appendices to include referenced material and the resulting change in page numbers.

This Requirements Document (RD) 10154-RD-2.2-01 is based upon Software Activity Plan (SAP) 10154-SAP-2.2-00 and the Master Planning Document (MPD) YMP-MPD-LADS-1.0, *NEPO Support for LADS FY99.* In accordance with AP-SI.1Q, Rev. 2, ICN 4, *Software Management*, this RD is followed by Design Document (DD) 10154-DD-2.2-01.

I. FUNCTIONAL REQUIREMENTS

The general requirements for this software are described in Appendix C (excerpted from Spycher et al., 1999, Sections 1, 2.1 and 2.2). The requirements specific to V2.2 are as follows:

1. All upgrades necessary for consistency with TOUGH2 EOS3 V1.4 (STN: 10007-1.4-01) (Wu et al. 1999): active-fracture model, downstream weighting option, capillary pressure linear extrapolation at low liquid saturations, changes in relative permeability based on a modified Brooks-Corey model;
2. Restart option for reactive transport;
3. New option for calculating gas diffusion coefficients as function of temperature and pressure;
4. Use input tortuosity to weight molecular diffusion coefficients;
5. New options for calculating effective surface areas;
6. New option for precipitation rate law;
7. Time dependent thermal conductivity factors;
8. New conjugate gradient stabilized solver;
9. Carmen-Kozeny porosity-permeability coupling option;
10. Modified output options and formats (separate plot ouput file for gases, option to output gas and mineral amounts in volume fraction, output additional variables such as porosity and permeability in plot files).

I.1 Scientific Approaches, Numerical Techniques, and Algorithms

The mathematical methods implemented in TOUGHREACT V2.2 are discussed in Appendix A and D.

The enhancements in TOUGHREACT V2.2 will include the testable requirements listed in Section I. Supporting information to address the points for the functional requirements in the Requirements Document Annotated Outline is discussed following sections.

I.2 Processes Supported by the Overall Nature and Purpose of the Software

This software shall be used to evaluate coupled thermal, hydrological, and chemical processes affecting the unsaturated zone around potential waste-emplacement drifts at Yucca Mountain. These analyses will be documented in Analysis /Model Reports (AMRs) and Process Model Reports (PMRs).

I.3 Input Transformation into Output

The code shall use the algorithms referred to in Section I.1 to process the inputs into the outputs.

I.4 Initiation and Receipt of Specific Information

The code is to be run in batch form, with the user supplying input files and receiving output files.

I.6 Information Required for Functions and Calculations

The information required for the functions and calculations is to be obtained by the software from its input files (including databases), which are described in Appendix F with modifications pertaining to V2.2 listed in Appendix B.

I.7 Description of Automated Inputs, Processing, Outputs and Conditions for Each Function

Once the user provides the input files and runs the code, the program automatically shall do the processing of the inputs and provide the outputs without intervention by the user. These shall be the only conditions for each function.

I.8 Description of Manual Inputs, Processing, Outputs and Conditions for Each Function

As described in Section I.6 above, the user shall create input files manually. After these files are read by the code, the rest is to be automatic.

I.9 Description of Data or Records Shared with Other Applications

There shall be no data or records shared with another application.

I.10 Hierarchical and Sequential View of System Functions Flow Diagram

The flow diagram for this software is shown in Appendix E.

II. INPUT AND OUTPUT REQUIREMENTS

For a general overview of input and output requirements, taken from predecessor code TOUGHREACT V2.1, see Appendix F. Specific formats with changes pertaining to V2.2 are listed in Appendix B.

II.1 Description of Automated Input Requirements

Once the user provides the input files and runs the code, the program automatically does the processing of the inputs and provides the outputs without intervention by the user. Required input file formats are described in Appendix B.

II.2 Description of Manual Input Requirements

The manual input consists of entering data in the prescribed format into the input files for the code.

II.3 Description of Output Requirements

The program automatically generates output files.

II.4 Description of Input/Output Requirements for Intended Use

For a general overview of input and output requirements, see Appendix F. Specific formats with changes pertaining to V2.2 listed in Appendix B.

II.5 Description of Input/Output Options

For a description of input/output options, with new options and resulting input data changes pertaining to V2.2, see Appendix B.

II.6 Description of Data Files, Input and Output Data, and File Formats

For a description of data files, see Appendix F. New options and resulting input/output data changes pertaining to V2.2 are listed in Appendix B.

II.7 Allowable Ranges of Inputs and Outputs

For a description of allowable ranges of inputs and outputs, see Appendix F. New options and resulting input/output data changes pertaining to V2.2 are listed in Appendix B.

II.8 Anticipated Errors and Method(s) of Handling

Error messages and error handling have not changed from V2.1 to V2.2. For a description of anticipated errors and method(s) of handling, see Appendix G.

III. PERFORMANCE REQUIREMENTS

The performance requirements defining how the software must function (e.g., response times, throughput under detailed load conditions, reliability, availability, and hours of operation) are not applicable to this kind of calculation. The code is to be run as a batch job without concern for response times or detailed load conditions or hours of operation. Its reliability should be basically consistent and it should be readily available. The general requirements shall be to produce its results on a Unix workstation (see System Interface Requirements in Section V below).

IV. USER INTERFACE REQUIREMENTS

IV.1 User Access and Interaction, Screen Elements

The user interface requirements describing how the user will access and interact with the software and how information will flow between the user and the software shall be that the user provides input files and the software produces output files. The means of error notification is to be the displaying of error messages in the *run_log.dat* file (errors related to reactive transport computations) and in the FLOW.OUT file (errors related to heat and fluid flow/transport computations).

IV.2 User Skill Levels

The code requires familiarity with numerical simulators in general and this software's documentation in particular; see Appendix C. It also requires familiarity with FORTRAN77 compilers if the code is to be to compiled.

IV.3 User Range of Work

The user's range of work shall be to employ the code for numerical simulation of coupled thermal, hydrological, and chemical processes in the subsurface.

V. SYSTEM INTERFACE REQUIREMENTS

V.1 Hardware Interfaces

A terminal or computer linked to the network.

V.2 Software Interfaces

A Unix workstation or equivalent system is required. Some of the output files generated are TECPLOT-compatible (®Amtec Engineering, Bellevue,WA).

V.3 Data Interfaces

There shall be no data interfaces with the system.

V.4 Timing Considerations

There shall be no system timing issues related to this software.

V.5 Development Constraints

No development constraints are anticipated for this software.

V.6 Information Architecture and Associated Hardware and Software Standards

This section is not applicable to this code because it is to be a numerical simulation code.

VI. COMMUNICATION REQUIREMENTS

The connectivity requirements shall be those of a terminal linked by a LAN to a server that runs the software or a stand alone Unix workstation.

VII. SECURITY AND ACCESS REQUIREMENTS

There is to be no sensitive information employed in this software, its inputs or its outputs, so security and access requirements to be followed are simply to have it secured by off-hours locked offices and/or buildings. For issues related to electronic management of data, the requirements of YMP-LBNL-QIP-SV.0, *Control of the Electronic Management of Data* are to be followed.

VIII. BACKUP AND RECOVERY REQUIREMENTS

The backup and recovery requirement for this software shall be for YMP-LBNL servers and stand-alone computers to have the system backup the code and any data files through an Ethernet backbone network on a routine basis. The requirements of YMP-LBNL-QIP-SV.0, *Control of the Electronic Management of Data* are to be followed.

IX. DATA REQUIREMENTS

IX.1 Stored and Processed Data Elements and Logical Data Groupings

All stored and processed data elements and their logic groupings shall reside in ASCII files associated with the code in the same directory.

IX.2 Definitions, How Data is Stored, and Data Flow and Volume

The definitions, data storage, and data flow are described in Appendix F, Section F6.2, with changes pertaining to V2.2 listed in Appendix B. The volume of the executable files is to be less than 1 MB. The output file sizes range to the tens of MB for typical problems, depending on number of elements and number of species and reactions.

X. IMPLEMENTATION REQUIREMENTS

X.1 Requirements Anticipated for Implementing the Software Product

Requirements and system limitations for V2.2 have not changed since V2.1, and are discussed in Appendix C.

X.2 User Production Cycle and Training

Implementation of the software including installation and operation should be at a level that a user familiar with this code's calculations would be able to run this software after reading the Users Manual (UM).

References:

Reed, M.H., "Calculation of Multicomponent Chemical Equilibria and Reaction Processes in Systems Involving Minerals, Gases, and an Aqueous Phase." Geochimica et Cosmochimica Acta, 46, 513-548. New York; Amsterdam: Elsevier Science, 1982. TIC: 224159.

Spycher, N., Sonnenthal, E., Ahlers, R., and Xu, T., *TOUGHREACT V2.1 Software Qualification*, 1999. MOL.20000216.0113.

Wu, Y.S., Haukwa, C., and Mukhopadyay S., *TOUGH2 V1.4 and T2R3D V1.4: Verification and Validation Report and User's Manual,* Rev 00, 1999. MOL 20000216.0111

Xu, T., and Pruess, K., *Coupled Modeling of Non-isothermal Multi-phase Flow, Solute Transport and Reactive Chemistry in Porous and Fractured Media: 1. Model Development and Validation*, Lawrence Berkeley Laboratory Report LBNL-42050, 1998.

Appendix A: Mathematical Models and Methods—Upgrades from V2.1

A.1 Upgrades necessary for consistency with TOUGH2 EOS3 V1.4 (STN: 10007-1.4-01)

The core of TOUGHREACT is the TOUGH2 code (EOS3 module) which solves the equations for the flow of water, vapor and heat under non-isothermal and variably saturated conditions. Functions that have been changed, tested and qualified in TOUGH2 EOS3 V1.4 are the option for downstream weighting of permeabilities and linear extrapolation of capillary pressure at low liquid saturations when using the Van Genuchten model. The upgrade also includes the changes in relative permeability calculations based on a modified Brooks-Corey model ((Wu et al. 1996 and 1999), and use of the active-fracture model (Liu et al., 1998). These two required functions are further described below in sections A.1.1 and A.1.2.

A.1.1 Implementation of modified Corey relative permeability function:

TOUGH2 v1.4 implements an additional function for computing the two-phase gas relative permeability. We implement a modified Brooks-Corey relative permeability function that results in lower gas mobility than the existing Brooks-Corey function, implemented in Q-code (ITOUGH2 v?, Finsterle, 1998?). The gas relative permeability K_{rg} is calculated using the following function:

$$K_{rg} = \left(1 - S^*\right)^2 \left(1 - S^{*\frac{2+n}{n}}\right) \qquad \text{(A.1.1-1)}$$

where,

$$n = \frac{m}{1-m}, \text{ and } S^* = \frac{S_l - S_r}{S_s - S_r} \qquad \text{(A.1.1-2)}$$

m is the van Genuchten parameter (same for liquid relative permeability and capillary pressure functions), S_l is the liquid saturation, S_r is the residual liquid saturation and S_s is the satiated liquid saturation.

The modifications are implemented in the EOS3 module of TOUGH2 v1.4. The available options for the gas relative permeability in TOUGH2 v1.4 are summarized in the table below:

Krg function	**TOUGH2 v1.3**			**TOUGH2 v1.4**		
	Switching Parameters	**Input test file**	**Output test file**	**Switching Parameters**	**Input test file**	**Output test file**
1-krl	RP4=0. RP5 (not used	Krg1o.dat	Krg1o.out	RP4=0. RP5=0.	Krg1n.dat	Krg1n.out
Brooks-Corey	RP4>0. RP5(not	Krg2o.dat	Krg2o.out	RP4>0.0 RP5=0.	Krg2n.dat	Krg2n.out

	used)					
Modified Brooks-Corey (new)	-	-	-	RP4=0 RP5>0	Krg3.dat	Krg3.out

Inspection of the output results show identical values for the gas and liquid relative permeability for TOUGH2 v1.3 and TOUGH2 v1.4 , output files Krglo.out & Krgln.out; Krg2o.out & krg2n.out. The values of gas relative permeability obtained using the modified Brooks Corey function (output file Krg3.out) was checked by hand calculation using the input parameters and equations A.1.1-1 and A.1.1-2 and were found to be identical.

A.1.2 Active Fracture Model: According to the active fracture conceptualization, only the fractures contributing to liquid flow are referred to as "active fractures". The Active Fracture Concept (AFC) was developed by *Liu et al.* [1998] to describe gravity-dominated, non-equilibrium, preferential liquid flow in fractures, which is expected to be similar to fingering in unsaturated porous media. AFC is based on the following hypothesis: (1) the number of active fractures is small compared with the total number of connected fractures, (2) the number of active fractures within a grid block is large so that the continuum approach is valid, and (3) the fraction of active fractures, f_a, is related to water flux and equals one for a fully saturated system, and zero if the system is at residual saturation. The following power function of effective liquid saturation, S_e, fulfills these conditions:

$$f_a = S_e^{\gamma} \qquad \text{(A.1.2-1)}$$

Here, γ is a positive constant depending on properties of the fracture network, and S_e is the effective liquid saturation given by

$$S_e = \frac{S_l - S_{lr}}{1 - S_{lr}} \qquad \text{(A.1.2-2)}$$

Capillary pressure and relative permeability functions are modified to account for the fact that the effective saturation in the active fractures, S_{ea}, is larger than the effective saturation of the total fracture continuum:

$$S_{ea} = \frac{S_e}{f_a} = S_e^{1-\gamma} \qquad \text{(A.1.2-3)}$$

Using the van Genuchten model, capillary pressure and liquid relative permeability are given, respectively, by

$$p_c = -\frac{1}{\alpha}\left[S_e^{(\gamma-1)/m} - 1\right]^{1/n} \qquad \text{(A.1.2-4)}$$

and

$$k_{rl} = S_e^{(1+\gamma)/2}\left\{1 - \left[1 - S_e^{(1-\gamma)/m}\right]^m\right\}^2 \qquad \text{(A.1.2-5)}$$

The fracture-matrix interface area reduction factor is given by

$$a_{fm} = S_e^{1+\gamma} \qquad \text{(A.1.2-6)}$$

The AFC is invoked by selecting $\gamma > 0$, which is provided as an additional parameter of the standard van Genuchten model (ICP=7) through variable CP(6, NMAT) of the fracture element. Fracture-matrix interface area reduction according to Equation. (A.1.2-6) is invoked by selecting ISOT = -10 for fracture-matrix connections in a mesh using a dual-permeability approach.

The AFC is implemented by modifying the capillary pressure and relative permeability functions. The implementation is tested by directly comparing the values (i.e., saturation, capillary pressure, and relative permeability) given in the TOUGH2 output file with the ones calculated using Equations. (A.1.2-2) through (A.1.2-5).

A.2 New option for calculating gas diffusion coefficients

A new option shall be implemented in V2.2 to compute gas diffusion coefficients as a function of temperature and pressure. Assuming ideal gas behavior, the tracer diffusion coefficient of a gaseous species is to be expressed as a function of temperature and pressure as follows:

$$D = \{R\,Tk / [(3/(2^{0.5}))\,\pi\,P\,N_A\,d_M^2]\}\ [8\,R\,Tk/(\pi\,MW)]^{0.5} \qquad \text{(A-1)}$$

where:
D = diffusion coefficient (m^2/s)
R = molar gas constant (8.31451 $m^2 kg\, s^{-2} mol^{-1} K^{-1}$)
Tk = temperature in Kelvin units
π = 3.1415926536
P = pressure ($kg\, m^{-1} s^{-2}$)
N_A = Avogadro's number (6.0221367×10^{23} molecules/mol)
d_M = molecular diameter (m)
MW = molecular weight (kg/mol)

A.3 Calculation of effective diffusion coefficients

Effective diffusion coefficients for gas and aqueous species are to be automatically calculated as:

$$D_e = D\,\tau \qquad \text{(A-2)}$$

where:
D_e = effective diffusion coefficient (m^2/s)
D = diffusion coefficient (m^2/s) calculated by Equation A-1 or directly input into the code
τ = tortuosity

A.4 New options for calculating effective surface areas

In TOUGHREACT V2.2 as well as V2.1, mineral effective surface areas are to be calculated, by default, from input surface areas in $cm^2/g_{mineral}$ as follows:

$$A_e = [A\ \rho_m\ V_f\ (1-\phi)\ /\ (S_l\ \phi\ \rho_w)\ 0.1\ ]\ \ S_l \qquad \text{(A-3)}$$

where:
A_e = effective surface area (m^2/kg_{H2O})
A = input surface area ($cm^2/g_{mineral}$)
V_f = mineral volume fraction ($V_{mineral}/V_{solids}$, excluding voids)
ϕ = porosity
ρ_w = water density (kg/m^3) (here assumed = 1000)
ρ_m = mineral density (kg/m3) computed from input molecular weight and molar volume
S_l = liquid saturation (cancels out)

The multiplication by S_l on the right-hand side of this equation reflects a correction to account for the hypothesis that wetted areas become localized at small liquid saturation values (Liu et al., 1998), therefore canceling S_l in the denominator. The equation thus yields an effective surface area per mass of water equivalent to the saturated surface area.

A new option shall be implemented in V2.2 to input surface areas in $m^2/m^3_{mineral}$ as follows:

$$A_e = [\ A'\,V_f\,(1-\phi)\,/\,(\rho_w\,\phi\,S_l)\ ]\ \ S_l \qquad \text{(A-4)}$$

where:
A' = input surface area ($m^2/m^3_{mineral}$)
Other symbols as described previously

Another option shall be added to V2.2 to make use of the active-fracture model (Liu et al., 1998) for calculating effective surface areas:

$$a_{fm} = [\ (S_l - S_{l\,min})\,/\,(1 - S_{l\,min})\ ]^{(1+\gamma)} \qquad \text{(A-5)}$$

where:
a_{fm} = active-fracture model factor
$S_{l\,min}$ = minimum liquid saturation for which water-rock reactions are considered
γ = active-fracture model parameter
Other symbols as described previously

Effective surface areas are then to be calculated as:

$$A_e = [A\ \rho_m\ V_f\ (1-\phi)\ /\ (S_l\ \phi\ \rho_w)\ 0.1]\ a_{fm} \qquad \text{(A-6)}$$

or

$$A_e = [\ A'\ V_f\ (1-\phi)\ /\ (\rho_w\ \phi\ S_l)\ ]\ a_{fm} \qquad \text{(A-7)}$$

where symbols are as described earlier.

A.5 New optional precipitation rate law

In addition to the default rate law already implemented in V2.1, a new precipitation rate law shall be implemented in V2.2 as follows:

$$\text{rate} = k\ A_e\ [\ (Q/K)^m - (\ 1/(Q/K)^{2m}\ )\ ] \qquad \text{(A-8)}$$

where:
rate = effective reaction rate (mol s^{-1} kg_{H2O}^{-1})
A_e as defined previously [m^2/kg_{H2O}]
Q/K = saturation index (supersaturated if > 1, saturated if = 1, undersaturated if < 1)
m = exponent
k = rate constant (mol s^{-1} m^{-2}) as previously implemented in V2.1

The second (Q/K) term in equation (A-7) is to be added so that the rate tends to zero as (Q/K) tends to one. At (Q/K) values greater than one, this second term quickly should become negligible.

A.6 Porosity-permeability coupling for matrix grid blocks

Matrix permeability changes are to be calculated using permeability ratios calculated from the Carmen-Kozeny relation, and ignoring changes in grain size, tortuosity and specific surface area as follows:

$$k = k_i\ [\ (1-\phi_i)/(1-\phi)\ ]^2\ (\phi/\phi_i)^3 \qquad \text{(A-9)}$$

where:
k = new permeability
k_i = initial permeability
ϕ = new porosity
ϕ_i = initial porosity

This relationship is assumed for all grid blocks that have a porosity less than 0.8 (the rationale being that matrix grid blocks typically have porosities less than 0.8 while fracture grid blocks in TOUGHREACT simulations are typically defined with porosities greater than 0.8).

For grid blocks with porosities greater than or equal to 0.8, a "cubic law" permeability-porosity relationship is assumed as in V2.1:

$$k = k_i \ (\phi^3/\phi_i^3) \qquad \text{(A-10)}$$

where symbols are as described earlier.

The computed capillary pressure is to be updated to account for changing permeability and porosity. The new capillary pressure, P_c, is derived as follows:

$$P_c = pcfact \ P_{ci} \qquad \text{(A-11)}$$

with

$$pcfact = \ (k_i/\phi_i)^{0.5} / \ (k/\phi)^{0.5} \qquad \text{(A-12)}$$

where P_{ci} is the "initial" capillary pressure and other symbols are as described earlier. Note that P_{ci} is actually to be the capillary pressure computed at the current time step (i.e. using the current liquid saturation) but computed from initial capillary pressure model parameters (e.g., Van Genuchten, Brooks-Corey, etc.) that are unchanging and calibrated from porosity and permeability values at time t=0.

A.7 New conjugate gradient stabilized solver

The conjugate gradient stabilized solver DLUSTB (Moridis and Pruess 1998) shall be implemented as an optional solver for flow and/or transport computations. Details on this solver are given in Moridis and Pruess (1998, pp. 418-419).

A.8 References

Liu, H. H.; Doughty, C.; and Bodvarsson, G.S., "An Active Fracture Model for Unsaturated Flow and Transport in Fractured Rocks." *Water Resources Research 34* (10), 2633–2646. Washington, D.C.: American Geophysical Union, 1998. TIC: 243012.

Moridis G. J. and Pruess K. "T2SOLV: An Enhanced Package of Solvers for the TOUGH2 Family of Reservoir Simulation Codes." *Geothermics 27,* 415-444, 1998. TIC: 246902.

Pruess K. *TOUGH2-A General Purpose Numerical Simulator for Multiphase Fluid and Heat Flow.* Report LBL-29400, UC-251, Berkeley, California: Lawrence Berkeley National Laboratory, 1991. NNA.19940202.0088

Spycher, N., Sonnenthal, E., Ahlers, R., and Xu, T., *TOUGHREACT V2.1 Software Qualification*, 1999. MOL.20000216.0113

Wu, Y.S.; Ahlers, C.F.; Fraser, P.; Simmons, A.; and Pruess, K., *Software Qualification of Selected TOUGH2 Modules.* Report LBNL-39490, UC-800. Berkeley, California: Lawrence Berkeley National Laboratory, 1996. MOL.19970219.0104.

Wu, Y.S., Haukwa, C., and Mukhopadyay S., *TOUGH2 V1.4 and T2R3D V1.4: Verification and Validation Report and User's Manual,* Rev 00, 1999. MOL 20000216.0111

Xu, T., and Pruess, K., *Coupled Modeling of Non-isothermal Multi-phase Flow, Solute Transport and Reactive Chemistry in Porous and Fractured Media: 1. Model Development and Validation*, Lawrence Berkeley Laboratory Report LBNL-42050, 1998. TIC: 243735.

Appendix B: Input/Output Changes from V2.1

A general description of TOUGHREACT V2.1 input and output files and formats is provided in Appendix F. Only changes from V2.1 are described here.

FORTRAN format notations are to be used to describe fixed formats (A for strings, I for integers, F for reals, X for spaces, etc.). Free formats are to be described using a modified FORTRAN notation, with format letters specified without a length. Free formats for arrays may be preceded by a variable (e.g. ntmp*F) which indicates the maximum dimension of the array. These dimensions are generally to be defined in the PARAMETER.INC source file. Character strings in free format must be enclosed in single-quotes. As a reminder, free format string variables below are listed with names between quotes.

B.1 FLOW.INP input file

This file is to be in standard TOUGH2 input format (Pruess 1991) and to be consistent with EOS3 V1.4 input formats (Wu et al. 1996 and 1999), except for different assigned ISOT values, as noted below.

The following new flag values shall be implemented in the ROCKS input block:

ICP = 10	Flag for capillary pressure function (see TOUGH2 user's guide): same function as with ICP = 7 (van Genuchten model), but the capillary pressure is linearly interpolated at liquid saturations below $S_{residual}$ + ($S_{residual}$ x *factor*), using the slope of the capillary pressure-saturation curve at that point. $S_{residual}$ is entered as CP(2) (as in V2.1) and *factor* is entered as CP(4) (in place of P_{max} in use if ICP = 7).
CP(6)	Active-fracture model parameter γ as defined in equation A-4 (only effective if ICP = 7 or ICP = 10). Leave blank or zero to disable the active-fracture model, and specify this parameter only for fracture rock types.

The following new flag values shall be implemented in the CONNE input block:

ISOT = -10	Enables the active-fracture model (in conjunction with non-zero CP(6) values) for the specified connection. Set ISOT = -10 only for fracture-matrix connections.
ISOT = -15	Enables downstream weighting of permeabilities at the specified connection (Note!!!: the same option in EOS3 V1.4 is enabled with ISOT = -2)

The following new flag values shall be implemented in the PARAM input block:

MOP(21) = 5	New solver (for flow computations): conjugate gradient stabilized (preconditioned) with LU factorization.

A new flag (*ktab*) shall be added to the first record of the GENER input block to implement time-varying thermal conductivities:

- 1st record of GENER block (A3,I2,A3,I2,4I5,5X,A4,A1,3E10.4,I2): EL, NE, SL, NS, NSEQ, NADD, NADS, LTAB, TYPE, ITAB, GX, EX, HG, *ktab*

  EL, NE, SL, NS, NSEQ, NADD, NADS, LTAB, TYPE, ITAB, GX, EX, and HG are as previously defined for V2.1 (see TOUGH2 users' guide, Pruess 1991).

ktab	If non-zero or non-blank, *ktab* enables input of thermal conductivity factors into the GENER block. With this option, LTAB must be blank or zero and TYPE must be set to "HEAT". *ktab* must be set equal to the number of time-variable conductivity factors that need to be input. Time values in the GENER block are then input as standard TOUGH2 generation times (F1(L), L = 1, ktab), and corresponding thermal conductivity factors are input as standard TOUGH2 generation rates (F2(L), L = 1, ktab). With this option, the thermal conductivity (input in the ROCKS block) is multiplied by the factors F2 at corresponding times F1.

B.2 SOLUTE.INP input file

Input formats are to be the same as for V2.1, but a record is to be added to the file. This file is therefore not backward compatible with V2.1 without some minor editing.

Records 1 to 10 are the same as in V2.1. A new record is then to be inserted as follows:

- 11th record (A20,A60): OUTGAS, TITLE
  Name of file for output of gas plot data (TEC_GAS.DAT) and any title

Next records are the same as in V2.1 (but offset by one record) until record 18 (corresponding to record 17 in V2.1), where a new flag (MINFLAG) is to be added:

- 18th record (7I5): NWTI, NWNOD, NWCOM, NWMIN, IWCOMT, MINFLAG

  NWTI, NWNOD, NWCOM, NWMIN, IWCOMT are to be as previously defined for V2.1. MINFLAG is to be a new flag to indicate output units for gas and mineral amounts: MINFLAG = 0 or blank, no change from V2.1 (output in bars for gases and moles/m^3_{medium} for minerals); MINFLAG = 1, gas and mineral amounts are to be output in volume fractions (of the medium).

A new solver is to be available by setting ISOLVC, in the third record of this file, as follows:

ISOLVC = 5 New solver (for transport computations): conjugate gradient stabilized (preconditionned) with inprilete LU factorization.

A new option for gas diffusion coefficients is enabled by setting DIFUNG, in the 13th record of this file, as follows:

DFFUNG = -1.0	Enables calculation of the gas diffusion coefficients as a function of temperature and pressure using Equation A-1.
DFFUNG > 0	In this case DFFUNG is the gas diffusion coefficient (not multiplied by tortuosity, as was the case in V2.1).

B.3 CHEMICAL.INP input file

Input formats are to be the same as for V2.1, but a few flags are to be added to the file. This file is therefore not backward compatible with V2.1 without some minor editing.

All record formats and variables are to be the same as in V2.1, except for the mineral records and initial mineral zones records.

In the mineral records, a flag (NPLAW) is to be added to specify the precipitation rate law as follows:

- 3nd mineral record, only if IKIN > 0 and IDSPRE = 2 or 3 (F,I,7F,I): RKPREC, IDEPREC, CK1PREC, CK2PREC, EAPREC, ACFPREC, BCFPREC, CCFPREC, RNUCL, NPLAW

  RKPREC, IDEPREC, CK1PREC, CK2PREC, EAPREC, ACFPREC, BCFPREC, CCFPREC, and RNUCL are to be as previously defined for V2.1. Specify NPLAW = 0 (cannot be left blank) for the default rate law (same as in V2.1), and NPLAW = 1 for the new rate law (equation A-7).

In the initial mineral zones records, a flag (IMFLG) is to be added to specify the units of input surface area as follows:

- 2nd mineral record (in mineral zones), only if IKIN4 = 1 (2F,I): RAD, AMIN, IMFLG

  RAD is as previously defined for V2.1. AMIN is the mineral surface area in [$cm^2/g_{mineral}$] if IMFLG = 0 (cannot be left blank), and in [$m^2/m^3_{mineral}$] if IMFLG = 1.

B.4 THERMOK.DAT input file (thermodynamic database)

Input formats are to be the same as for V2.1, but a few variables were added/changed in the gas records. This file is therefore not backward compatible with V2.1 without some minor editing.

All record formats and variables, except for the first record of each gas entry and the last record of the gas block, are to be the same as for V2.1. Two variables (DMOLWT and DMDIAM) are to be added to the third gas records as follows:

- 1st record (A,2F,I,mpri*(F,A)): 'NAME', DMOLWT, DMDIAM, NCPG, (STQG(i), 'NAM(i)', i=1,NCPG)

NAME, NCPG, STQG, NAM, and NCPG are to be as defined for V2.1. DMOLWT is the gas molecular weight in [kg/mol] and DMDIAM is the gas molecular diameter in [m]. These two variables are to be used to compute the gas diffusion coefficient according to equation A-1 if DFFUNG (the gas diffusion coefficient variable) in the SOLUTE.INP file is set to -1.0.

The maximum total number of gases allowed in the program is to be *mgas* (defined in source file PARAMETE.INC). After the data for all gases have been listed (three records per gas), the last record to end the gas data must be as follows:

- Last record (A,F,I): 'null' 0. 0. 0 (where 'null' is the actual string in quotes)

B.5 Output files

Output files are to be the same as in V2.1, except that the TEC_MIN.DAT file of V2.1 (which then included gas data) is to be split into two files with V2.2: TEC_MIN.DAT (without gas data) and TEC_GAS.DAT for the gas data. Also, compared to V2.1, additional variables are to be output in plot files as follows: porosity and permeability (m^2) in TEC_MIN.DAT and total pressure (Pa) in TEC_GAS.DAT. Mineral and gas amounts in these files are to be output in units that are set by the value of MINFLAG (see Section B.2).

B.6 References

Pruess K., *TOUGH2-A General Purpose Numerical Simulator for Multiphase Fluid and Heat Flow.* Report LBL-29400, UC-251, Berkeley, California: Lawrence Berkeley National Laboratory, 1991. NNA.19940202.0088.

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Wu, Y.S.; Ahlers, C.F.; Fraser, P.; Simmons, A.; and Pruess, K., *Software Qualification of Selected TOUGH2 Modules.* Report LBNL-39490, UC-800. Berkeley, California: Lawrence Berkeley National Laboratory, 1996. MOL.19970219.0104.

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Appendix C: General Description of Requirements for TOUGHREACT V2.2 (excerpted from Spycher et al., 1999, Sections 1, 2.1, and 2.2)

C.1 Introduction

TOUGHREACT was developed by Tianfu Xu and Karsten Pruess at Lawrence Berkeley National Laboratory. The original computer code was modified (TOUGHREACT V1.0) for simulations of the Drift Scale and Single Heater Tests, to simulate boiling conditions and fracture-matrix interactions (diffusion and advection of aqueous and gaseous species across fracture-matrix interfaces). The core of TOUGHREACT is the TOUGH2 V1.11 code (EOS3 module) which solves the equations for the flow of water, vapor and heat under non-isothermal and variably saturated conditions.

In TOUGHREACT, a transport module and a geochemical speciation module are sequentially coupled to the TOUGH2 V1.11 module. The transport module solves for transport of dissolved species in water, and transport of gases such as CO_2 and O_2 in a "carrier" gas phase consisting of H_2O and air (transport of the latter two gas phases is computed by the TOUGH2 V1.11 module). The geochemical module incorporated in TOUGHREACT solves simultaneously a set of chemical mass-action and mass-balance equations to compute the extent of reaction and mass transfer between a set of given aqueous species, minerals, and gases at each grid block of the flow model.

C.2.2 User Requirements

The correct implementation, setup, problem formulation, and interpretation of the results of TOUGHREACT requires knowledge of the basic equations of fluid and heat flow and transport in porous media and a basic understanding of the numerical solution of the partial differential equations that are used to describe these processes. In addition, the formulation of the geochemical problem requires familiarity with geochemical modeling and an in-depth understanding of the system that is being modeled and of the data used for input to the model. The model boundary conditions, time step length, convergence criteria, and grid properties are crucial elements to providing a realistic and accurate solution to a problem. Numerical models can produce erroneous results and therefore must be interpreted with caution.

Appendix D: General Description of Mathematical Model and Numerical Methods for TOUGHREACT V2.2 (excerpted from Spycher et al., 1999, Section 3)

D.3 Mathematical Model and Numerical Methods

Versions V1.0 (and above) of TOUGHREACT have been modified to incorporate the water chemical mass balance scheme of Reed (1982).

The coupling of porosity to permeability and capillary pressure has been implemented in version V2.1. At each time step, for each grid block, a new porosity (ϕ) is calculated from computed minerals amounts:

$$\phi = 1 - \sum (V_i) - V_{unreact} \qquad \text{(D3-1)}$$

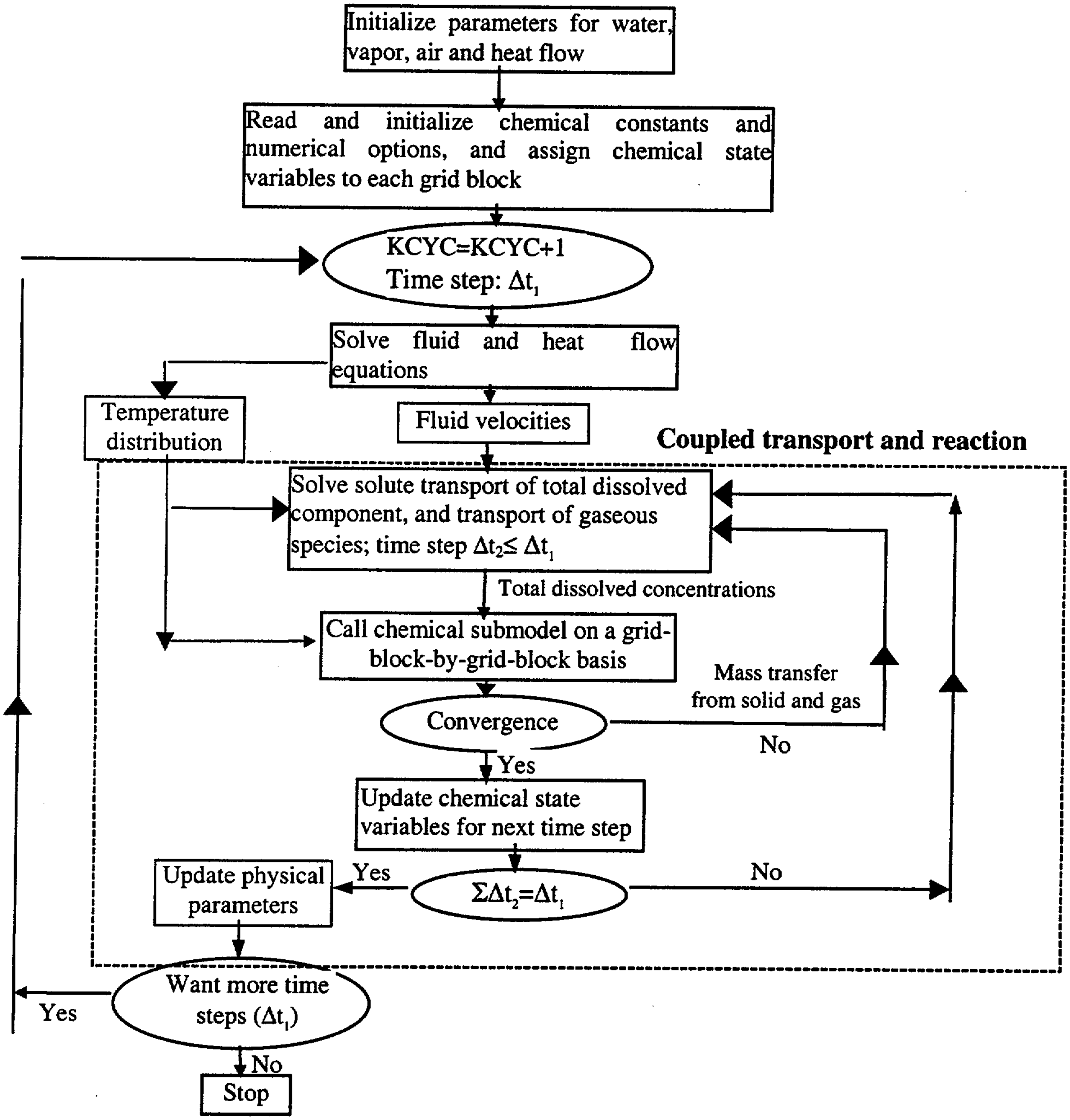
where V_i are the current volume fractions of reactive minerals present in the system ($V_{mineral}/V_{medium}$), and $V_{unreact}$ is the total volume fraction of unreactive solids (if any).

After changing porosity, a new permeability is derived as follows:

$$k = k_0 \ (\phi^3/\phi_0^3) \qquad \text{(D3-2)}$$

where k and ϕ are the permeability and porosity, respectively, at the present time step and k_0 and ϕ_0 are the same parameters at time t=0. This formulation is based on the Cubic Law for plane parallel fractures.

Appendix E: Simplified Flow Chart for TOUGHREACT V2.2



Appendix F: General Overview of Input and Output for TOUGHREACT V2.2 (excerpted from Spycher et al., 1999, Section 6.1)

F.6 TOUGHREACT V2.1 Data Input and Output

This section discusses the program data input and output, including file formats, default parameters, and allowable and tolerable ranges of input parameters.

Input/output files and their formats are generally the same for V2.1 as for V1.0, with a few important changes in the formats of files THERMOK.DAT, SOLUTE.INP, and CHEMICAL.INP. Important changes have also been made in the units of mineral volume fractions and surface areas specified in file CHEMICAL.INP. In addition, in V2.1, the name of the THERMOK.DAT file is no longer fixed and needs to be specified in the SOLUTE.INP file. For these reasons, input files of V1.0 are not upward compatible with V2.1, and vice versa.

F.6.1 General Description of Input and Output Files

F.6.1.1 Input Files

Several data files are used to input data into TOUGHREACT V2.1. All but one input file have fixed file names (i.e. names that cannot be specified by the user).

Fixed-name input files

FLOW.INP - Hydrological and thermal parameters. These data include rock properties, initial boundary conditions, time-stepping information, initial conditions of gas and liquid saturations, temperature, and pressure, and all other grid data for hydrological and thermal calculations. The format of this file is identical to the regular TOUGH2 V1.11 input file (Pruess et al. 1996).

SOLUTE.INP - Transport and other run parameters. This file contains various flags and input parameters for calculations of reactive transport, such as diffusion coefficients, tolerance limits for convergence of transport and chemical iterations, printout flags for mineral and aqueous species, and the configuration of model zones with different chemical compositions (the compositions of each zone, however, are defined in file CHEMICAL.INP).

CHEMICAL.INP - Chemical parameters and initial water/rock/gas compositions. This file is used to define the chemical system (i.e. the type and number of aqueous component species, minerals, and gases considered in the simulation). It also includes the initial compositions of water, mineral, and gas zones configured in file SOLUTE.INP, and kinetic data for minerals (rate constants, surface areas, etc.).

User-specified input files

The names of these files must be specified in the SOLUTE.INP input file, and cannot be left blank. The name of the thermodynamic data base file needs to be specified as follows:

THERMOK.DAT (or any other name) - Thermodynamic database for aqueous species, minerals, and gases. This file contains reaction stoichiometries, dissociation constants (log(K)), and regression coefficients of log(K)'s as a function of temperature.

F.6.1.2 Output Files

Several output files are generated by TOUGHREACT V2.1. These include files with fixed file names, and other files with user-specified names.

Fixed-name output files

FLOW.OUT - Ouput of thermal and hydrological data (no chemical information). This file is identical to a TOUGH2 V1.11 output file, including data on temperature, pressure, liquid and gas saturations, liquid and gas (steam+ air) fluxes, and velocities for all grid blocks of the model.

CHEMICAL.OUT - Echo of chemical input data. This file lists the data read from input files CHEMICAL.INP and THERMOK.DAT, including initial water rock, and gas compositions, equilibrium constants and stoichiometries of chemical reactions, and kinetic data.

SOLUTE.OUT - Echo of transport and other run parameters. This file lists the data read from input file SOLUTE.INP, including all transport parameters, chemical zone configuration, and other run-specific parameters.

run_log.dat - Log of the simulation progress. This file is constantly updated during a simulation. It lists some run input parameters and all run-related messages, including error messages (Section 7). It also contains mass balance and other data whose printout is enabled by setting specific MOP parameters to non-zero values in the FLOW.INP file

chdump.dat - chemical speciation data. This file contains results of geochemical speciation calculations for each initial water composition input into the model. It also lists these data for grid nodes where chemical convergence fails. The results are computed for an original 1 liter of liquid. They include a printout of chemical mass balances (total mass balance and aqueous species mass balance) which must always remain zero or very small. For debugging purposes or for small grids, if the flag ICHDUMP in the SOLUTE.INP input file is set equal to 1, geochemical speciation results will be output in the *chdump.dat* file for every grid node at every time step (!). As a precaution to avoid filling up disk space, results of speciation calculations are output only for the first thousand grid nodes and/or time steps, after which the program will abort.

User-specifed output files

The names of these files must be specified in the SOLUTE.INP input file, and cannot be left blank. The file names currently specified and the file contents are as follows:

ITER.DAT - Iteration Data. This file lists the number of flow, transport and chemical iterations used to reach convergence at each simulation time step. The number of transport iterations in this file indicate the number of iterations between flow, transport and chemical computations at each time step (not the actual number of iterations required to reach convergence during calculations of aqueous species and gas transport). It is always equal to 1 with this version of the program (no iteration between flow, transport, and chemistry).

TEC_CONC.DAT - Aqueous species plot data. This file contains time (s), grid block coordinates (m), liquid saturation, temperature (°C), pH, and aqueous species concentrations ($\text{mol/liter}_{\text{liquid}}$) at all grid blocks for time steps specified in the FLOW.INP file. The number and type of species to output in the TEC_CONC.DAT file is specified by flags in the input file SOLUTE.INP. This file is in a TECPLOT-compatible format, although some editing of this file will be required to import data for dual permeability grids into TECPLOT. Note: there is a field for oxygen fugacity in this file. This field is padded with zero values unless a redox system is considered. However, redox simulations have not been tested with this version of the program.

TEC_MIN.DAT- Mineral and gas plot data. This file contains time (s), grid point coordinates (m), temperature (°C), changes in mineral amounts ($\text{mol/m}^3_{\text{medium}}$), and gas pressures (bars) (e.g. CO_2) at all grid blocks for time steps specified in the FLOW.INP file. Currently, mineral amounts are output in moles per cubic meter of rock medium (i.e. matrix or fracture), and gas pressures in bars. The mineral amounts represent the change between the amount at the current time step and the initial amount (at time zero). Negative amounts indicate overall dissolution, and positive amounts overall precipitation. The number of minerals in the TEC_CONC.DAT file are specified by flags in the input file SOLUTE.INP. Gas pressures for all gases specified in the CHEMICAL.INP file are output following the mineral data. This file is in a TECPLOT-compatible format, although some editing of the file will be required to import data for dual permeability grids into TECPLOT.

TIME.DAT - Plot data at specified grid blocks. This file contains grid block identifier, time (days), liquid saturation, temperature (°C), pH, aqueous species concentrations ($\text{mol/l}_{\text{liquid}}$), mineral amounts ($\text{mol/m}^3_{\text{medium}}$), and gas pressures (bars) for specific grid blocks and time step intervals, as specified in the input file SOLUTE.INP. This file can be used to generate time-profiles at specified locations. Note: there is a field for oxygen fugacity in this file. This field is padded with zero values unless a redox system is considered. However, redox simulations have not been tested with this version of the program.

F.6.2 Input/Output File Formats and Contents

Required formats for each input file are described below. FORTRAN format notations are used to describe fixed formats (A for strings, I for integers, and F for reals, X for spaces, etc.). Free formats are described using a modified FORTRAN notation, with format letters specified without a length. Free formats for arrays may be preceeded by a variable (e.g. ntmp*F) which indicates the maximum dimension of the array. These dimensions are generally defined in the PARAMETER.INC source file. Character strings in free format must be enclosed in single-quotes. As a reminder, free format string variables below are listed with names between quotes.

F.6.2.1 FLOW.INP - Hydrological and thermal parameters

Format: fixed

No changes since V1.0. The format of this file is identical to the regular TOUGH2 input file (Pruess 1991). However, a few MOP parameters have been assigned new functions, as follows:

MOP(20)	= 0 for reactive transport = 1 no reactive transport, but input files with chemical data are read > 1 no reactive transport, no chemical data files are read
MOP(22)	> 0 writes the transport coefficient matrix, Darcy velocities, porosities, and other transport data in the *run_log.dat* file during calculations of aqueous species and gas transport. For debugging only.
MOP(23)	> 0 writes source terms, right-hand side, old and new aqueous concentrations, and various other parameters in the *run_log.dat* file during transport calculations. Also outputs the permeability, porosity, and capillary pressure correction factor at each grid block in the *run_log.dat* file. For debugging purposes only.
MOP(24)	=1 does not force at least one transport step to be calculated (can be useful to compute chemical reaction only in single-grid node problems).

F.6.2.2 THERMOK.DAT - Thermodynamic data for aqueous species, minerals, and gases.

Format: free

The format of this file has changed since version V1.0. Mineral molecular weights have been added to the first record of entries for these components. Otherwise, entries in this file have remained unchanged since V1.0. The new file version is not backward compatible with TOUGREACT V1.0, nor is the old file version upward compatible with TOUGHREACT V2.1.

Initial records:

- First record (A,I,ntemp*F): 'DUMMY', NTEMP, (TEMPC(i), i=1,NTEMP)

  DUMMY is a label used to describe the data for this record. NTEMP is the number of TEMPC values to read. TEMPC are temperatures (°C) at which the log(K) data are listed in this file. TEMPC values must be listed in order of increasing temperature. Only the first (minimum) and last (maximum) temperatures are used by the program. These values are used to constrain log(K) extrapolation within this temperature range. Log(K)'s are not extrapolated outside this temperature range! For example, if the maximum TEMPC is 150 °C but the computed system temperature is 250 °C, log(K)'s will be extrapolated only to 150 °C (i.e. the geochemical speciation will be computed at 150 °C, not 250 °C)! Therefore, users must make sure that simulation temperatures are within the range of thermodynamic data temperatures.

Component species records. These data immediately follow the initial file record, as follows:

- Each record (A,2F): 'NAME', A0, Z

  For each component species, NAME is the name, A0 the Debye-Huckel a0 parameter (ion effective or hydrated radius), and Z the ion electric charge. The maximum length of NAME is 20. The maximum number of records is *mpri* (defined in source file PARAMETE.INC)

- Last record must be (A,2F): 'null' 0.0 0.0 (where 'null' is the actual string in quotes)

Derived species records. These must directly follow the component species records. The data for each derived species is given by 3 records, which are as follows:

- 1st record (A,2F,I,mpri*(F,A)): 'NAME', A0, Z, NCPS, (STQS(i), 'NAM(i)', i=1,NCPS)

  NAME, A0, and Z are as defined for the component species. NCPS is the number of component species defining the derived species. STQS contains the stoichiometric coefficient of component species NAM included in the dissociation reaction of the derived species (negative and positive values for reactants and products, respectively). The maximum value for NCPS is *mpri* (define in source file PARAMETE.INC).

- 2nd record (A,ntemp*F): 'NAME', (DUMMY(i), i=1,ntemp)

  NAME is as defined above. DUMMY contains the dissociation constants (log(K) in base 10) for the given reaction at each discrete temperature listed in the initial file record. These data are skipped on input, because all log(K) values are computed as a function of temperature using the regression coefficients that follow (below). The discrete log(K) values should, however, always be included in the file to provide for an easy reference of the data.

- 3rd record (A,5E): 'NAME', (AKCOES(maqx,i), i=1,5)

  NAME is as defined above. AKCOES contains regression coefficients a, b, c, d, and e to calculate log(K) as a function of temperature (within the range of temperatures listed on the first record of the file) such that $\log(K) = a*\ln(Tk) + b + c*Tk + d/Tk + e/Tk^2$, where Tk is absolute temperature (K), and *log* and *ln* stand for base-10 and natural logarithms, respectively.

The maximum total number of derived species allowed in the program is *maqx* (defined in source file PARAMETE.INC). After the data for all derived species have been listed (three records per species), the last record to end the derived species data must be as follows:

- Last record (A,2F,I): 'null' 0. 0. 0 (where 'null' is the actual string in quotes)

<u>The mineral records</u>. These must directly follow the derived species records. The data for each mineral is given by 3 records, which are as follows:

- 1st record (A,2F,I,mpri*(2F,A)): 'NAME', MOLWT, VMIN, NCPM, (STQM(i), 'NAM(i)', i=1,NCPM)

  NAME, MOLWT and VMIN are the name of the mineral, its molecular weight (g/mol) and molar volume (cm^3/mole), respectively. NCPM is the number of component species defining the mineral. STQM contains the stoichiometric coefficient of component species NAM in the dissociation (hydrolysis) reaction of the mineral (negative and positive values for reactants and products, respectively). The maximum value for NCPM is *mpri* (defined in source file PARAMETE.INC).

- 2nd record (A,ntmp*F): 'NAME', (DUMMY(i), i=1,ntmp)

  NAME is as defined above. DUMMY is the dissociation constants (log(K) in base 10) for the given reaction at each discrete temperature listed in the first record of the file. These data are skipped on input, because all log(K) values are computed as a function of temperature using the regression coefficients that follow (below). The discrete log(K) values should, however, always be included in the file to provide for an easy reference of the data.

- 3rd record (A,5E): 'NAME', (AKCOEM(mmin,i), i=1,5)

  NAME is as defined above. AKCOEM contains regression coefficients a, b, c, d, and e to calculate log(K) as a function of temperature (within the range of temperatures listed on the first record of the file) such that $\log(K) = a*\ln(Tk) + b + c*Tk + d/Tk + e/Tk^2$, where Tk is absolute temperature (K), and *log* and *ln* stand for base-10 and natural logarithms, respectively.

The maximum total number of minerals allowed in the program is *mmin* (defined in source file PARAMETE.INC). After the data for all minerals have been listed (three records per mineral), the last record to end the mineral data must be as follows:

- Last record (A,2F,I): 'null' 0. 0 (where 'null' is the actual string in quotes)

The gas records. These must directly follow the mineral records, and have a format identical to that of minerals. The data for each gas is given by 3 records as follows:

- 1st record (A,F,I,mpri*(F,A)): 'NAME', DUMMY, NCPG, (STQG(i), 'NAM(i)', i=1,NCPG)

  NAME is the name of the gas. DUMMY is molar volume but this value is not used (the molar volume of gases are computed by the program assuming the ideal gas law). NCPG is the number of component species defining the gas. STQG contains the stoichiometric coefficient of component species NAM in the dissociation reaction of the gas (negative and positive values for reactants and products, respectively). The maximum value for NCPG is *mpri* (defined in source file PARAMETE.INC).

- 2nd record (A,ntmp*F): 'NAME', (DUMMY(i), i=1,ntmp)

  NAME is as defined above. DUMMY is the dissociation constants (log(K) in base 10) for the given reaction at each discrete temperature listed in the first record of the file. These data are skipped on input, because all log(K) values are computed as a function of temperature using the regression coefficients that follow (below). The discrete log(K) values should, however, always be included in the file to provide for an easy reference of the data.

- 3rd record (A,5E): 'NAME', (AKCOEG(mgas,i), i=1,5)

  NAME is as defined above. AKCOEG contains regression coefficients *a*, *b*, *c*, *d*, and *e* to calculate log(K) as a function of temperature (within the range of temperatures listed on the first record of the file) such that $\log(K) = a{*}\ln(Tk) + b + c{*}Tk + d/Tk + e/Tk^2$, where Tk is absolute temperature (K), and *log* and *ln* stand for base-10 and natural logarithms, respectively.

The maximum total number of gases allowed in the program is *mgas* (defined in source file PARAMETE.INC). After the data for all gases have been listed (three records per gas), the last record to end the mineral data must be as follows:

- Last record (A,F,I): 'null' 0. 0 (where 'null' is the actual string in quotes)

The adsorbed species records (surface complexes). This feature of TOUGHREACT has not been tested in V2.1 and therefore no data should be entered, except for the termination record:

- Last record (A,F,I): 'null' 0. 0 (where 'null' is the actual string in quotes)

F.6.2.3 SOLUTE.INP - Transport and other run parameters

Format: fixed

The format of this file has changed since version V1.0. The name of the thermodynamic database must now be entered in this file, and a new factor is read in the fifth record. In other respects, entries in this file have remained unchanged since V1.0. The new file version is not backward compatible with TOUGHREACT V1.0, nor is the old file version upward compatible with TOUGHREACT V2.1.

- 1st record (A76): TITLE

  Run title

- 2nd record ( ): skipped on input; can be used to define the data that follows

- 3rd record (3I5,F5.3,3I5): ISPIA, INIBOUND, ISOLVC, ICOUR, NGAS1, ICHDUMP, KCPL

  ISPIA is a flag to define the sequential iterative approach between computations for transport and for chemistry, as follows:

0	sequential iteration between transport and chemistry (if MAXITPTR > 1)
1	partial sequential iteration (do not use, not tested!)
2	no sequential iteration (fully explicit reaction source terms)
3	sequential iterations between transport, chemistry, and flow (do not use, not tested!)

INIBOUND is a flag for enabling the use of different recharge water compositions (0=disabled, 1=enabled)

ISOLVC is a flag for the type of transport solver to use. Always use ISOLVC = 3 (default) with this version of the program. Other options have not been tested.

RCOUR is both a variable and a flag to limit the time step size. RCOUR > 0.0 limits the maximum time step size to RCOUR x Courant Number. This option is disabled if RCOUR = 0.0.

ICHDUMP is a flag to enable printing of chemical speciation results at each grid node and each time step (0 = disabled, 1=enabled). It should be enabled for debugging purposes only, or to track small problems. If this option is enabled, the program will abort after outputting speciation results for the first 1000 grid nodes and/or time steps, to avoid accidentally filling up disk space.

KCPL is a flag to enable coupling porosity, permeability, and capillary pressure changes as described in Section 3 (0 = disabled, 1=enabled).

- 4th record ( ): skipped on input; can be used to define the data that follows.

- 5th record (3E10.4): SL1MIN, D1MIN, STIMAX, CNFACT

The first three parameters are used for skipping the chemical solver (i.e. skip geochemical speciation calculations) at grid nodes where conditions of saturation, inter grid block distance, or ionic strength are outside of the valid ranges of the model. The geochemical calculations are skipped at grid blocks where: the liquid saturation is less than SL1MIN; the minimum distance to the center of any adjacent block is less than D1MIN; or the stoichiometric ionic strength is more than STIMAX. For typical boiling simulations, use SL1MIN less or equal to 10^{-3}. Set D1MIN = 0.0 (disabled) unless absolutely necessary. With this program version, STIMAX should not be greater than 2.0 (preferably 1.0) because of limitations regarding the calculation of activity coefficients at elevated ionic strength.

CNFACT is a weighting factor for mineral and gas reaction source terms in the transport equations (1.0 = fully implicit source terms, 0.0 = fully explicit source terms). This parameter has an effect only if sequential iterations are enabled (ISPIA = 0 or 1). In this program version, CNFACT always defaults to 1.0 if a non-zero value is input (implicit only). Simulations with CNFACT = 0.0 using sequential iterations will produce the same results as simulations without sequential iterations (explicit source terms) but requires increased computing time and therefore should be avoided.

- 6th record ( ): skipped on input; can be used to define the data that follows

- 7th record (A20,A60): OUTITER, TITLE
  Name file for output of iteration data (ITER.DAT), and any title

- 8th record (A20,A60): OUTPLOT, TITLE
  Name of file for output of aqueous species plot data (TEC_CONC.DAT) and any title.

- 9th record (A20,A60): OUTSOLID, TITLE
  Name of file for output of mineral and gas plot data (TEC_MIN.DAT) and any title

- 10th record (A20,A60): OUTTIME, TITLE
  Name of file where to output time profile plot data (TIME.DAT) and any title

- 11th record ( ): skipped on input; can be used to define the data that follows

- 12th record (2F10.0,2E10.3): WTIME,WUPC,DIFUN,DIFUNG

  WTIME is an interface weighting factor. Always set WTIME = 1 (other values not tested). WUPC is an upstream weighting factor. Always set WUPC = 1 for full upstream weighting (other values not tested). DIFUN and DIFUNG are the products of the diffusion coefficient and tortuosity of the medium (m^2/sec) for aqueous species and gases, respectively.

- 13th record ( ): skipped on input; can be used to define the data that follows

- 14th record (I5,E10.3,I5,E10.3,I5,E10.3,I5,E10.3): MAXITPTR, TOLTR, MAXITPCH, TOLCH, MAXITPAD,TOLAD

  MAXITPTR is the maximum number of iterations for solving the sequential transport/chemistry iterative procedure. If MAXITPTR=1, no sequential iteration will take place even if ISPIA <> 2. TOLTR is the relative concentration tolerance for convergence during sequential iterations (difference between the concentrations at the current and previous and sequential iterations, divided by the arithmetic average of these concentrations).

  MAXITPCH is the maximum number of iterations for solving geochemical speciation (typically 200). TOLCH is the relative concentration tolerance for solving geochemical speciation (concentration change from the previous iteration to the current one, divided by the current concentration). Set TOLCH $\leq 10^{-4}$.

  MAXITPCH and TOLAD are maximum number of iterations and tolerance for solving adsorption. This version of the program was not tested with surface complexes. These parameters are not used if no adsorption species are entered in the CHEMICAL.INP file (do not enter any).

- 15th record ( ): skipped on input; can be used to define the data that follows

- 16th record (7I5): NWTI, NWNOD, NWCOM, NWMIN, IWCOMT

  NWTI is a flag for writing data in the TIME.DAT file. Data will be written at every NWTI time steps.

NWNOD is the total number of grid blocks at which to output data in the TIME.DAT file. It should correspond to the number of nodes listed on record 18.

NWCOM is the total number of aqueous species for which to output concentrations in the TIME.DAT and TEC_CONC.DAT files. It should correspond to the number of species listed on record 20.

NWMIN is the total number of minerals for which to output amounts in the TIME.DAT and TEC_MIN.DAT files. It should correspond to the number of species listed on record 22.

IWCOMT is a flag to indicate the type of aqueous species concentration to output in the TIME.DAT and TEC_CONC.DAT files. IWCOMT=0 for concentrations of individual aqueous species. IWCOMT=1 for total aqueous concentrations (i.e. the sum of concentrations of a component species and all derived species that contain this component).

- 17th record ( ): skipped on input; can be used to define the data that follows

- 18th record (15A5): ELEMW(i), i = 1,NWNOD

ELEMW contains the list of grid node names for which to output data in the TIME.DAT file. If NWNOD is greater than 15, an additional record of must inserted, which offsets all following records. The maximum number of node names is 30. Leave the record blank if NWOD = 0.

- 19th record ( ): skipped on input; can be used to define the data that follows

- 20th record (15I5): IWCOM(i), i = 1,NWCOM

IWCOM contains the list of species indexes for which to output data in the TIME.DAT file and TEC_CONC.DAT file. The indexes correspond to the species order in the list of component species entered in CHEMICAL.INP. For derived species (if IWCOMT = 0) indexes above those of component species can be determined from the chdump.dat file by aborting a run after the first time step. If NWCOM is greater than 15, an additional record must be inserted, which offsets all following records. The maximum allowed number of species indexes is 30. Leave this record blank if NWCOM=0.

- 21th record ( ): skipped on input; can be used to define the data that follows

- 22th record (20I5): IWMIN(i), I = 1,NWMIN

IWCOM contains the list of mineral indexes for which to output data in the TIME.DAT file and TEC_CONC.DAT file. The mineral indexes correspond to the order in the list of minerals entered in CHEMICAL.INP. The maximum allowed number of mineral indexes is 20. Leave this record blank if NWMIN=0.

- 23th record ( ): skipped on input; can be used to define the data that follows

- 24th record (6I5): IZIWDF, IZBWDF, IZMIDF, IZGSDF, IZADDF, IZEXDF

  The first four parameters are the default initial waters, boundary waters, mineral zones, and gas zones, respectively, to assign to each grid node. Values of IZIWDF and IZBWDF must each correspond to one of the water composition indices (IWTYPE) specified in CHEMICAL.INP. Similarly, values of IZMIDF and IZGSDF must correspond to one of the mineral and gas zone indices (IMTYPE and IGTYPE, respectively) specified in CHEMICAL.INP. The last two parameters are not used with this version of the program and must be set to zero.

- 25th record ( ): skipped on input; can be used to define the data that follows

- Next records (one per grid block) (A5,8I5): EL, NSEQ, NADD, IZIW, IZBW, IZMI, IZGS, IZAD, IZEX

  These records are used to assign initial waters, boundary waters, mineral zones, and gas zones to specific grid nodes of the model (maximum allowed is *mnod*, defined in source file PARAMETE.INC). These records can be omitted (in this case all grid blocks are assigned the defaults specified on record 24). Parameters as follows for each grid block:

EL	grid node name
NSEQ	= 0 (always, with this version of the program)
NADD	= 0 (always, with this version of the program)
IZIW	initial water index (one of the IWTYPE values in CHEMICAL.INP)
IZBW	boundary water index (one of the IWTYPE values in CHEMICAL.INP)
IZMI	mineral zone index (one of the IMTYPE values in CHEMICAL.INP)
IZGS	gas zone index (one of the IMTYPE values in CHEMICAL.INP)
IZAD	= 0 (always, with this version of the program)
IZEX	= 0 (always, with this version of the program)

- End record for zone assignments (A5,8I5): (must be blank)

- Next record ( ): skipped on input; can be used to define the data that follows

- Next record (A5,5E10.3): EL, DISG(i), (PFUGB(i,ig), ig = 1,NGAS)

  This record is to specify nodes connected to a gas supply (i.e. atmosphere). This option has not been tested and this record must be left blank.

Final file record (optional): end ('end' is the actual string, without quotes)

F.6.2.4 CHEMICAL.INP - Chemical parameters and initial water/rock/gas compositions
Format - free

The units of mineral surface areas and initial volume fractions specified in this file have changed since version V1.0. Also, a variable was added to the record specifying parameters for minerals precipitation rates. Therefore, this file is not backward compatible with V1.0 (or vice versa).

<u>Initial records</u>

- 1st record (A): 'LABEL'

- 2nd record (A): 'LABEL'

- 3rd record (A): 'LABEL'

  LABEL is a character string (maximum length 100) currently used to define the run title (1st and 2nd record) and to describe the data that follows (3rd record).

<u>Component species records</u>. These define the chemical system in the simulation, and must be entered directly following the initial records. One record must be entered per component species, in any order, as follows:

- Initial record (A): 'LABEL'

  LABEL is a character string (maximum length 100) used to describe the data that follows.

- Each following record (A): 'NAPRI'

  NAPRI is the name of each selected component species (20 characters maximum). These names must match exactly the names of component species in the THERMOK.DAT file.

The maximum total number of component species allowed in the program is *mpri* (defined in source file PARAMETE.INC). After the selected component species have been listed (one record per species), the last record to end the component species list must be as follows:

- Last record (A): '*' (where '*' is the actual string in quotes)

The program selects automatically in the file THERMOK.DAT all derived species that contain the selected component species.

Mineral records. These contain the minerals desired in the simulation, and must directly follow the component species records. Minerals can be entered in any order as long as the minerals at equilibrium precede those under kinetic constraints. The specified minerals consist of reactants and any possible products. Their names must match exactly the names of minerals in the THERMOK.DAT file. Also, all component species used in the mineral reaction stoichiometry in the THERMOK.DAT must be included in the list of component species above.

Minerals can be specified to react either at equilibrium with the aqueous phase, or under kinetic constraints. Minerals with identical stoichiometries (i.e. quartz and cristobalite) cannot both be specified at equilibrium (use kinetic constraints in this case). Minerals specified to be at equilibrium are equilibrated with the solution only if these are calculated to be supersaturated (no forced equilibrium). If undersaturated, these minerals are assumed to be totally dissolved and remain as possible products (inactive bystanders) until they reach saturation.

- Initial record (A): 'LABEL'

  LABEL is a character string (maximum length 100) used to describe the data that follows.

Minerals at equilibrium are defined with one record (per mineral). Minerals under kinetic constraints require one or two more records (per mineral). Minerals at equilibrium must always be listed preceding those under kinetic constraints. The following record(s) must be specified for each mineral:

- First mineral record (A, 2I): 'NAMIN', IKIN, IDISPRE

  NAMIN is the mineral name (20 characters maximum). IKIN is a flag for the type of mineral: 0 for minerals at equilibrium, and 1 for those under kinetic constraints. IDSPRE is a flag for the type of kinetic constraints: 1 for dissolution only, 2 for precipitation only, and 3 for both (mineral can either precipitate or dissolve). Always set IDSPRE = 0 if IKIN = 0 and IDISPRE > 0 if IKIN = 1.

- 2nd mineral record, only if IKIN > 0 (F,I,6F): RKF, IDEP, CK1, CK2, EA, ACFDISS, BCFDISS, CCFDISS (mineral dissolution rate parameters)

RFK is the coefficient a in the expression $k = a \cdot \exp(EA/RT)$, where k is the rate constant (in mol/m^2/sec), EA is the activation energy in kJ/mol, R the ideal gas constant ($8.3144 \cdot 10^{-3}$ kJ/°K/mol), and T absolute temperature (°K). The form of the rate law is:

$$\text{rate} = k \cdot S \cdot (1-(Q/K)^m)^n$$

where the rate is in mol/sec/kg$_{H2O}$, Q/K is the mineral saturation index, and S the effective surface area (in m^2/kg$_{H2O}$) specified later.

IDEP is a flag for rate dependence on pH. Always use IDEP=0 with this version of the program (no pH dependence).

CK1 and CK2 are the exponents n and m, respectively in the above rate expression. Always use CK1=1 and CK2=1 with this version of the program.

ACFDISS, BCFDISS, and CCFDISS should be set to zero, unless a different form of rate constant dependence with temperature is desired. This alternate form is: $\log(k) = a + b \cdot T + c/T$, where T is absolute temperature in K and *log* is in base 10. To enable this option, RFK must be set to 1.0, EA must be set to zero and ACFDISS, BCFDISS, and CCFDISS must be specified as the coefficients a, b, and c, respectively, in the above expression.

- 3nd mineral record, only if IKIN > 0 and IDSPRE = 2 or 3 (F,I,6F): RKPREC, IDEPREC, CK1PREC, CK2PREC, EAPREC, ACFPREC, BCFPREC, CCFPREC, RNUCL

  (mineral precipitation rate parameters)

  These input parameters, except for the last one, are listed in the same order and have the same functions as those described above for mineral dissolution (2nd record), except that the parameters apply to mineral precipitation instead of dissolution.

  RNUCL contains the initial volume fraction ($V_{mineral}/V_{solid}$) to be assumed for calculating initial effective surface area (Equation 3-4) if the mineral is not present at the start of a simulation but precipitates as a new reaction product. If zero, RNUCL is assumed to be 10^{-5}.

The maximum total number of minerals allowed in a simulation is *mpri* (defined in source file PARAMETE.INC). After the selected minerals have been listed (one record per mineral), the last record to end the minerals list must be as follows:

- Last record (A,2I): '*' 0 0 (where '*' is the actual string in quotes)

Gas records. These contain gas species desired in the simulation (besides H_2O, which is treated independently in the flow routines). The gas names must match exactly the names of gases in the THERMOK.DAT file. Also, all component species used in the gas reaction stoichiometry in the THERMOK.DAT must be included in the list of component species above. The gas records must be entered directly following the mineral records, in any order, as follows:

- Initial record (A): 'LABEL'

  LABEL is a character string (maximum length 100) used to describe the data that follows.

- Each gas record (A): 'NAGAS'

  NAGAS is the gas name (20 characters maximum). The maximum total number of gases allowed in the program is *mgas* (defined in source file PARAMETE.INC). The last record to end the gas list must be as follows:

- Last record (A): '*' (where '*' is the actual string in quotes)

Adsorbed species records (surface complexes). These directly follow the gas records. This feature of TOUGHREACT has not been tested with surface complexes in V2.1 and therefore no data should be entered, except for a termination record:

- Last record (A): '*' (where '*' is the actual string in quotes)

Initial, boundary, and recharge water compositions. These data directly follow the gas records, and are headed by two label records as follows:

- Initial record (A): 'LABEL'
- Next record (A): 'LABEL'

  LABEL is a character string (maximum length 100) used to describe the data that follows.

- Next record (3I): NIWTYPE, NBWTYPE, NRWTYPE

  These parameters indicate the number of different sets of initial water compositions, boundary water compositions, and recharge water compositions to read in, respectively. The maximum number of different water compositions is *mnel* initial waters, *mbound* boundary waters, and *mrech* recharge waters (these parameters are defined in source file PARAMETE.INC).

Sets of water compositions follow. A total of NIWTYPE + NBWTYPE + NRWTYPE sets must be entered. These sets must be listed in order of first, initial waters, then boundary waters, then recharge waters. Each water composition set has the following format:

- 1st record (I,F): IWTYPE, TC2

IWTYPE is an index for the water composition set. It must be 1 for the first set, 2 for the second set, and so on, but must be reset to 1 at the start of each different water type (i.e. for the first initial, first boundary, and first recharge water). This index is used in file SOLUTE.INP to assign water compositions to grid blocks. TC2 is the initial temperature of the water (°C) at which the initial geochemical speciation is calculated. This temperature does not affect flow/thermal calculations and will be overwritten by the initial system temperature specified in the FLOW.INP file. If TC2 is much different than the latter temperature, the program may have difficulty in reaching convergence when computing geochemical speciation during the first time step.

- 2nd record (A): 'LABEL'

LABEL is a character string (maximum length 100) used to describe the data that follows.

- Following records (one record per species) (A,I,2F,A,I): 'NAME', ICON, CGUESS, CTOT, 'DUM', ICTOT2

NAME is the name of component species as specified in the component species list in the first part of the file, but not necessarily in the same order. ICON is a flag which indicates the type of concentration to be entered. It must be either 1 or 3, as described below.

CGUESS is the trial molality of the component species, for use as a starting point for Newton-Raphson iterations necessary to solve geochemical speciation. CGUESS can take any value, but should be as close as possible to the actual molality of the species (the calculated solution) or convergence may not occur.

CTOT stores the species concentration (i.e. the analyzed water composition) and takes different input depending on the value of ICON:

If ICON=1: CTOT for all components except water is total concentration (component + derived species) in moles per specified liter of liquid. For water, the amount entered is the volume of liquid in liters (generally one liter so that CTOT for other components is in moles/liter).

If ICON=3: CTOT is the activity of the individual component species (for example 10^{-pH} for H^+). Do not use this option for water.

DUM is an unused dummy string variable. Always leave as one or more blanks between quotes.

ICTOT2 is currently unused. Always set ICTOT2 = 0

Each water composition set must be terminated with the following record:

- End record (A,I,2F,A,I): '*' 0 0.0 0.0 '' 0

  (where '*' and '' are a star and a blank string in quotes)

Initial mineral zones. These records directly follow the water composition sets and are headed by two label records as follows:

- Initial record (A): 'LABEL'
- Next record (A): 'LABEL'

  LABEL is a character string (maximum length 100) used to describe the data that follows.

- Next record (I): NMTYPE

  This parameter indicates the number of mineral zones to read in (maximum is *mnel*, defined in source file PARAMETE.INC).

  Records for mineral zones follow. A total of NMTYPE mineral zones must be listed. Each mineral zone has the following format:

- 1st record (I): IMTYPE

  This is the index of the mineral zone. It must be 1 for the first zone, 2 for the second zone, and so on. This index is used in file SOLUTE.INP to assign the mineral zones to grid blocks.

- 2nd record (A): 'LABEL'

  LABEL is a character string (maximum length 100) used to describe the data that follows.

Each mineral at equilibrium is then defined with one record. Minerals under kinetic constraints require one more record. Minerals can be listed in any order as long as those at equilibrium precede those under kinetic constraints. Mineral spelling and designation (equilibrium or kinetic) must be the same as defined previously. The following record(s) must be specified for each mineral:

- 1st mineral record (each mineral) (A,F,I): 'NAME', VOL2, IKIN4

  NAME is the name of the mineral (20 characters maximum). VOL2 is the initial volume fraction of the mineral, excluding liquid (mineral volume divided by total volume of solids). The sum of VOL2's need not add up to 1. The remaining solid volume fraction is considered unreactive. IKIN4 is a flag to indicate whether the mineral is to be treated at equilibrium (IKIN4=0) or under kinetic constraints (IKIN4=1). IKIN4 must be consistent with previously defined IKIN for each mineral.

- 2nd mineral record, only if IKIN4 = 1 (2F): RAD, AMIN

  RAD is the grain radius, which is currently not used (set to zero or any value). AMIN is the mineral surface area in [cm^2/g] (i.e. square centimeters per gram of mineral). AMIN is not the effective reactive surface area (see Section 3).

After all the minerals in the zone have been listed (one record per mineral), the last record to end the mineral zone must be as follows:

- Last record (A,F,I): '*' 0.0 0 (where '*' is the actual string in quotes)

Initial gas zones. These records directly follow the mineral zones and are headed by two label records as follows:

- Initial record (A): 'LABEL'

- Next record (A): 'LABEL'

  LABEL is a character string (maximum length 100) used to describe the data that follows.

- Next record (I): NGTYPE

  This parameter indicates the number of gas zones to read in (maximum is *mnel*, defined in source file PARAMETE.INC).

Records for each gas zone follow if NGTYPE > 0. A total of NGTYPE gas zones must be entered. Each gas zone has the following format:

- 1st record (I): IGTYPE

  This is the index of the gas zone. It must be 1 for the first zone, 2 for the second zone, and so on. This index is used in file SOLUTE.INP to assign the gas zones to grid blocks.

- 2nd record (A): 'LABEL'

  LABEL is a character string (maximum length 100) used to describe the data that follows.

- Each following record (one per gas) (A,F): 'NAME', CGNOD

  NAME is the name of the gas (20 characters maximum). Gas names must be the same as defined previously (in any order). CGNOD is the gas initial partial pressure (in bars) in the fraction of pore spaces that are not filled with water. If this pressure is not the same as the partial pressure reflecting the initial composition of the pore water, a new initial partial pressure will be calculated to reflect chemical equilibrium between pore gas and pore water. If the initial gas fraction in pore spaces is small, CGNOD has little effect on calculation results. However, if the initial gas fraction is large, the value of CGNOD may contribute significantly to the total initial mass of the gas in the system.

After all the gases in the zone have been listed, the last record to end the gas zone must be as follows (also needed if NGTYPE=0):

- Last record (A,F): '*' 0.0 (where '*' is the actual string in quotes)

Initial adsorption zones. This feature of TOUGHREACT was not tested in V2.1. Therefore, these data must be left blank. However, for the program to finish reading the file correctly, several records must be included directly following the gas zone data:

- Initial record (A): 'LABEL'

- Next record (A): 'LABEL'

  LABEL is a character string (maximum length 100) used to describe the data that follows.

- Next record (I): NDTYPE

  Set NDTYPE = 0 (no surface complexes).

- Next record (A): 'LABEL' (as above)

Last two records of file. These must be present to avoid input errors:

- Last before final record (A): 'LABEL' (as above)

  LABEL is any character string (maximum length 100)

- Final record in file (A): 'end' (where 'end' is the actual string in quotes).

Appendix G: Error Messages and Error Handling for TOUGHREACT V2.2 Excerpted from Description of TOUGHREACT V2.1, Section 7

G.7 Anticipated Error Messages

All execution stops built into TOUGHREACT V2.1 are accompanied by a message indicating why the execution was aborted. Other error messages do not lead to a program interruption. Only messages related to the reactive transport part of the program are reviewed below. Error messages originating during heat or fluid flow calculations are the same as for TOUGH2 V.1.11 (Pruess et al., 1991).

G.7.1 From routine: INIT (reads the CHEMICAL.INP file)

Most of these messages are self explanatory and refer to exceeded array dimensions or other error encountered when reading the CHEMICAL.INP file. Array dimension problems can be corrected by reducing the problem size or changing array dimensions in the source file PARAMETE.INC and recompile the program.

Error: maximum number of component species (MPRI) was exceeded. Current max= ____
Execution stop: yes. Self explanatory.

Error: maximum number of minerals (mmin) was exceeded. Current max= ____
Execution stop: yes. Self explanatory.

Error: maximum number of gases (mgas) was exceeded. Current max= ____
Execution stop: yes. Self explanatory.

Error: maximum number of ads. species (mads) was exceeded. Current max= ____
Execution stop: yes. Self explanatory.

*Error: MBOUND(parameter of adjustable array) should be great than*____
Execution stop: yes. Too many boundary waters were specified.

*Error: MRECH (parameter of adjustable array) should be great than*____
Execution stop: yes. Too many recharge waters were specified.

error in number of primary species in zone= ___ (iwtype)
Execution stop: yes. One of the initial, boundary, or recharge waters does not have data for one of the component species specified in system, or has more components than specified for the simulation. All species listed in the first part of the CHEMICAL.INP file must have a concentration defined for each specified initial, boundary, or recharge water.

error reading chemical control parameters
Execution stop: yes. Error while reading the CHEMICAL.INP file at one of the following locations: initial title; number of initial, boundary, and recharge waters (niwtype,nbwtype,nrwtype); number of sorptions zones (ndtype).

error reading aqueous species of the system
Execution stop: yes. Self explanatory.

error reading minerals of the system
Execution stop: yes. Self explanatory.

error reading gases of the system
Execution stop: yes. Self explanatory.

error reading surface complexes of the system
Execution stop: yes. Self explanatory.

error reading the model of surface complexes
Execution stop: yes. Self explanatory.

*error reading initial water zone=*___ (iwtype)
Execution stop: yes. Self explanatory.

error reading initial mineral zone= ____ (imtype)
Execution stop: yes. Self explanatory.

error reading initial gas zone= ___ (imtype)
Execution stop: yes. Self explanatory.

error reading initial surface adsorption zone= ___ (idtype)
Execution stop: yes. Self explanatory.

G.7.2 From routine: NRINIT (initial Newton-Raphson iterations)

ERROR (convergence problem in initialization of water composition)
Please adjust convergence criteria regarding chemical iteration
and initial guess of concentration of primary species
Execution stop: yes. Self explanatory. This error results in calling routine chdump for troubleshooting (i.e. the last chemistry calculation data are output in the *chdump.dat* file). This error occurs during the initial geochemical speciation of waters specified in CHEMICAL.INP (no minerals, before the first time step). Check the *chdump.dat* file for clues, and also check that

water temperatures specified in CHEMICAL.INP data are not too different than the initial condition of temperature specified in the FLOW.INP file.

G.7.3 From routine: READTHERM (reads the database THERMOK.DAT)

All these messages occur while reading the thermodynamic database and are self explanatory. These indicate improperly-formatted records in the THERMOK.DAT file. All errors result in a program execution stop

Error reading temperature data: stop

Error reading primary species: stop

Error reading secondary species: stop (followed by the species name)

Error reading minerals: stop (followed by the mineral name)

Error reading gases: stop (followed by the gas name)

Error reading adsorbed species: stop (followed by the species name)

Error in opening database file: stop

G.7.4 From routine: READSOLU (reads the file SOLUTE.INP)

There are currently no specific error messages generated while reading the file SOLUTE.INP. The unit number of this file 31. System error messages relating to this I/O number originate while reading this file. Make sure the fixed formats of this file are respected.

G.7.5 From routine: CR_CP (kinetic data calculations)

error in data option for mineral (kinetic)= ____
Execution stop: yes. This message occurs if the flag IDEP for any of the kinetic minerals is not set to either 0 or 1. With this program version, IDEP must always be zero (this flag is specified in the mineral section of the CHEMICAL.INP file).

G.7.6 From routine: NEWTONEQ (Newton-Raphson iterations after 1st time step)

ERROR: chemistry did not converge at node ____ (routine NEWTONEQ)
Species: ____ Error=____ Error limit= ____ relative
Node temperature (C): ____
Program execution was not aborted. Check results!
Execution stop: only if this error occurs at more than fifty grid blocks at any given time step. This error also calls routine chdump for troubleshooting (i.e. the last chemistry calculation data

are output in the *chdump.dat* file). This error occurs during the node-by-node geochemical speciation computations after the first time step (complete system, with minerals and gases if any). Check the *chdump.dat* file for clues on why convergence was not reached. You may need to increase the loop limit (MAXITCH) and/or tolerance (TOLCH) in the SOLUTE.INP file. If boiling occurs, you may try increasing ST1MIN or decreasing STIMAX. Chemical convergence may also fail because of errors during transport, resulting in erroneous system compositions which cannot yield a solution to geochemical speciation calculations. In this case, the time step may be decreased and/or the Courant number option enabled (ICOUR=1). Depending on the type of problem, chemical speciation in closely spaced grid blocks can be skipped by setting D1MAX > 0 (last resort).

Error: Negative concentration for species ____
Execution stop: no. Self explanatory. A concentration may temporarily become negative during the chemical Newton-Raphson iterations, but should not remain negative. This error may indicate problems to come. It is rarely encountered.

G.7.7 From routine: LUDCMP (linear equation solver)

This routine is called during the Newton-Raphson iterations to compute geochemical speciation.

Singular Matrix in Chemical Solver, STOP
Execution stop: yes. Self explanatory. This indicates an ill-defined chemical system. This error results in calling chdump to output the last geochemical speciation data in the *chdump.dat* file. A phase-rule violation or inclusion of minerals (at equilibrium) with identical stoichiometries in the simulation will cause this error. In some cases, divergence and over/underflows during Newton-Raphson iterations (sometimes related to transport problems) may cause this error even though a true singularity has not occurred. Check the *chdump.dat* file for clues on why the error happened.