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H2O_TREAT USERS' MANUAL: AN AID FOR EVALUATING WATER TREATMENT REQUIREMENTS FOR AQUIFER THERMAL ENERGY STORAGE SYSTEMS

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SUMMARY

This manual addresses the use of a public-domain software package developed to aid engineers in the design of water treatment systems for aquifer thermal energy storage (ATES). The software, H2O_TREAT, which runs in the DOS or UNIX Environment, was developed by the Pacific Northwest Laboratory and targeted to engineers possessing limited or no experience in geochemistry. To do this, the software provides guidance on geochemical phenomena that can cause problems in ATES systems (i.e., the formation of scale in heat exchangers, clogging of wells, corrosion in piping and heat exchangers, and degradation of aquifer materials causing a reduction in permeability). Preventing such problems frequently requires the use of water treatment systems. Because individual water treatment methods vary in cost, effectiveness, environmental impact, corrosion potential, and acceptability to regulators, proper evaluation of treatment options is required to determine the feasibility of ATES systems.

The software is available for DOS- and UNIX-based computers. It uses a recently revised geochemical model, MINTEQ, to calculate the saturation indices of selected carbonate, oxide, and hydroxide minerals based on water chemistry and temperature data provided by the user. The saturation index of a specific mineral defines the point at which that mineral is oversaturated and hence may precipitate at the specified temperature.

Cost calculations are not performed by the software; however, treatment capacity requirements are provided. Treatments include Na and H ion exchanger, fluidized-bed heat exchanger or pellet reactors, and CO_2 injection. The H2O_TREAT software also provides the user with warning of geochemical problems that must be addressed, such as Fe and Mn oxide precipitation, SiO_2 precipitation at high temperatures, corrosion, and clay swelling and dispersion.

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1.0 INTRODUCTION

The chemistry of aquifers often represents a significant design consideration for aquifer thermal energy storage (ATES) systems. The precipitation of minerals in heat exchangers can result in significant scale formation that can make the heat exchanger less efficient or even inoperable. Many ground waters are naturally corrosive to many common materials used in heat exchangers, pumps, and pipes. Changes in temperature may make such waters even more corrosive. In addition, precipitation of minerals within the aquifer or precipitates transported into the aquifer can clog the aquifer.

Water treatment technologies are available that can mitigate these problems. The cost, effectiveness, and environmental consequences of these treatment technologies vary considerably. The selection and sizing of the appropriate treatment technology for a specific situation (aquifer chemistry and design temperature) require significantly more expertise in geochemistry than most design engineers who are making a feasibility assessment for ATES are likely to possess.

This software was designed to aid engineers who may have limited or no experience in geochemistry at the feasibility analysis and preliminary design stages in designing ATES water treatment systems. Although H2O_TREAT does not perform cost calculations, treatment capacity requirements are provided as is guidance on other geochemical problems that must be addressed (e.g., SiO_2 precipitation, corrosion, and environmental considerations). It is expected that this software will also be useful in evaluating the new or supplemental water supplies for municipality or industrial use.

The Thermal Energy Storage Program at the Pacific Northwest Laboratory[a] supported development of the public-domain software package H2O_TREAT as a contribution to Annex VI of the International Energy Agency.

This manual contains four sections. Following the Introduction, two sections provide background information and guidance on Geochemical Problems (Section 2.0) and Treatment Methods (Section 3.0). The narrative that explains step-by-step operation of the code is presented in Section 4.0. References cited in the text are listed in Section 5.0. The appendix provides the DOS batch file for H2O_TREAT.

(a) The Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute.

2.0 GEOCHEMICAL PROBLEMS

The most common geochemical problem encountered in ATES systems is the precipitation of calcium carbonate (e.g., scale formation) on heat exchangers. The clogging of the injection wells by Fe and Mn oxides and/or carbonates is also a significant concern. Use of Na-exchange water treatment to avoid carbonate precipitation may cause clays within aquifers to swell as the sodium concentrations within the aquifer increase, possibly resulting in clogging of the aquifer. Degassing of oversaturated gases during reinjection may also result in clogging of the aquifer because of the formation of a separate gas phase. The corrosive nature of natural aquifer waters will often be enhanced by heating and by some treatments used to prevent scale formation.

2.1 Carbonate Precipitation

Significant scale formation on heat exchangers greatly reduces their thermal transfer efficiency. Precipitation on the well screen, in the gravel pack, or in the aquifer markedly decreases the injection rate at a fixed pressure (Jenne et al. 1992). Because the solubility of carbonate minerals decreases with increasing temperature, the higher the storage temperature, the more likely is carbonate scale formation. Although calcite (a common calcium carbonate mineral) is the predominate carbonate mineral formed, ferrous carbonate (siderite) is suspected as the cause of reduced permeability in some Swedish ATES systems.[a]

The departure from equilibrium with respect to a specified solid phase can be calculated by determining the aqueous speciation of the dissolved components (e.g., Ca, dissolved carbonate) and calculating the ion activity product, e.g., activity of Ca^{2+} x activity of CO_3, which at equilibrium is equal to the solubility product of the mineral at the temperature of the water. The logarithm of the ratio of the ion activity product to

[a] Olöf Andersson, personal communication.

the solubility product is known as the saturation index (SI). At SI values of less than 0.3, carbonate precipitation appears to be too slow to pose a problem anywhere in the ATES system (Willemsen and Appelo 1985; Banck 1989; van Dijk and Wilms 1990; Griffioen 1992) because of the interference of components such as dissolved organic carbon (DOC), Mg, and PO_4 with the precipitation process (Jenne 1990; Griffioen 1992). Another factor that affects precipitation and SI values is the formation of solid solutions of Mg, Fe, and Mn with $CaCO_3$. If the SI estimated at the temperature to which the water is to be heated is at or below zero, no water treatment is required. For SI ≥ 0.3, water treatment is indicated. Because storage at a temperature lower than originally contemplated might remove the necessity for water treatment, it is important to estimate the temperature at which $SI_{calcite}$ is <0.3. Errors in calculated SI values for carbonate minerals may result from errors in the water chemistry analysis caused by the loss of CO_2 during pumping and sampling, and while awaiting analysis.

2.2 Oxide Precipitation

The hydroxides and oxides of Fe and Mn, respectively, hereafter referred to as oxides, precipitate upon reaction with air as a consequence of oxidation of the reduced metal. Fe2[a] and Mn2 are the dominant valence states of dissolved Fe and Mn in aquifers that are depleted of oxygen. This is primarily a result of microbial processes that deplete the oxygen as surface water infiltrates. Because every oxygen molecule that comes into contact with reduced ground water can oxidize four Fe2 to Fe3 or two Mn2 to Mn4 atoms, the entry of even small amounts of air may cause considerable oxide precipitation. ATES systems should preclude air entry if the source water concentration of Fe or Mn is >0.1 mg/L, because O_2 entry and resultant oxide precipitation may cause scaling and clogging and may also increase corrosion rates.

[a] The number following the chemical symbol specifies a valence.

2.3 Sodium Hazard

The dispersion of fine-grained sediment and the swelling of clays may also reduce aquifer permeability. Dispersion may occur as a result of physical disturbance (Molz et al. 1981), but more generally from increased sodium saturation of expandable clays caused by use of Na-exchange water treatment or a significant reduction in ionic strength, as when a foreign water of lower ionic strength water is introduced into a saline aquifer (Jones 1964). The likelihood of clay dispersion, swelling, and reduced permeability is characterized by the "sodium hazard." Sodium hazard is a function of conductivity and the sodium adsorption ratio, which is the ratio of Na to the square root of the sum of the Mg and Ca concentrations in milli equivalents (Richards 1954, p. 80; Jackson 1958, p. 258).

2.4 Degassing

Gases are often present in ground water in amounts greater than would be in equilibrium with atmospheric pressure. If, during injection, the pressure on the water is reduced as a result of inadequate back pressure, the gases may come out of solution and create a discrete gas phase that can block aquifer pores, greatly decreasing permeability and causing a system to fail. If the concentration of CO_2 is greater than the value in equilibrium with the atmosphere, then a partially open system may allow degassing and a pH increase with resultant precipitation of Ca, Fe, or Mn carbonates.

2.5 Corrosion

Metal surfaces commonly react with constitutents in the medium with which they are in contact to form corrosion products such as oxides or sulfide. This has the undesirable effect of reducing the thickness of the unoxidized metal leading to leakage. Corrosion is enhanced by strongly reducing conditions. Elevated temperatures also increase the rate of corrosion. Oxygen is significantly more corrosive in the presence of elevated chloride; the corrosion rate produced by O_2 alone increases up to about 5.5 mg/L of O_2 (Andersson 1991, p. 30). Chloride and sulfate each increase the corrosion

rate rapidly up to individual concentrations of 10 to 20 mg/L. CO_2 is more aggressive in soft water (i.e., water with low Ca and Mg concentrations); corrosion rate increases up to about 150 psi (Andersson 1991, p. 31). The presence of H_2S at concentrations greater than a fraction of a mg/L may cause corrosion; corrosion is more severe in high-salt water (Andersson 1991, p. 36). Assuming oxygen is excluded, significant corrosion potential exists if any of the following conditions occur: the pH is below 5.5; H_2S concentrations are greater than 0.1 mg/L; CO_2 partial pressure is greater than 150 psi; either Cl or SO_4 concentrations exceed 20 mg/L; or microbiological growth on or adjacent to the metal.

3.0 TREATMENT METHODS

Sodium- and H-exchange, CO_2 injection and fluidized-bed heat exchanger treatment methods to avoid carbonate precipitation are considered here. Nitrate injection and cascade treatment methods to mitigate Fe and Mn oxide precipitation are also considered.

3.1 Ion Exchange

H2O_TREAT estimates the fraction of water that must be treated by either Na or H exchange to prevent carbonate scale formation in the heat exchanger.[a] To perform this calculation, H2O_TREAT starts at the High Temperature with essentially 100% treatment and successively increases the fraction of the total relevant cations (Ca, Mg, Fe, and Mn) present in the sample analysis until the SI for any of the specified carbonate precipitates exceeds 0.3. The treatment fraction immediately greater than the fraction resulting in precipitation is the estimated treatment fraction required. If the user elects to evaluate the tradeoff between temperature and treatment requirements (by selecting a Low Temperature of treatment), these calculations are repeated over the range of temperatures specified by the user. The ion exchange process is assumed to be ideal (i.e., all relevant cations are replaced with an equal molar amount of either Na or H). To anticipate the extent of treatment that will be required for the heat-extracted water when it is recovered from storage, the user will need to sample this water before its recovery and heating or perform laboratory experiments to anticipate the changes in composition that will occur during storage of the heated water.

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[a] Treatment levels are computed for temperatures ranging from High Temperature to Low Temperature. If High Temperature and Low Temperature are equal, only one temperature level will be computed. The High Temperature should reflect the highest temperature any water in the heat exchanger will experience. Typically, the highest temperatures occur at the wall of the heat exchanger. Some heat exchanger designs may actually involve wall temperatures significantly higher than the design bulk injection temperature. H2O_TREAT will provide the treatment data required to quantify the tradeoffs between treatment costs and heat exchanger costs.

Either NaCl brine or HCl solutions are used to recharge the cation exchanger. Na exchange is to be generally preferred over H exchange, because the H-saturated exchanger results in lower pH and additional carbonate mineral dissolution during heated water storage. Additionally, the fraction of storage water that must be treated is expected to decrease with each cycle when Na exchange is used,[a] but is expected to increase if H exchange is used. However, H exchange may be the method of choice if the aquifer contains a significant amount of expansible clays, particularly if poorly cemented, or if only traces of carbonate minerals are present and degassing can be facilitated. Where siderite ($FeCO_3$) clogging may occur, acidification without degassing may decrease the concentration of CO_3 enough to bring the $SI_{siderite} \leq 0.3$ with minimal increase in dissolved Fe concentration at pH values above 5.

3.2 CO_2 Injection

H2O_TREAT starts with a high partial pressure of CO_2 and decreases the partial pressure until the partial pressure of CO_2 in equilibrium with the original sample is found. Then, the partial pressure of CO_2 is increased until the $SI_{calcite}$ is below 0.3. The difference in moles of CO_2 between these two points is then converted to the amount of CO_2 that must be dissolved (in mg/L) to avoid calcite precipitation. Because the dissolution of CO_2 is sensitive to total pressure as well as to the partial pressure of CO_2, the total pressure in the heat exchanger is a required input with a default of 1.5 atm.

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[a] The fraction of water requiring treatment, hence reduction in treatment capacity, on subsequent storage cycles at the same or higher temperatures can be approximated by calculating the composition of the water at a given fraction of treatment, entering the estimated temperature of this source water as Sample Temperature, and the entering temperature at which the water is to be injected as High Temperature. The approach is not conservative in that it does not account for dissolution of minerals during the storage of the heated water.

3.3 Fluidized-Bed Heat Exchanger

In the fluidized-bed reactor, where high pumping rates cause fine-grained sand to be fluidized, calcite precipitation is enhanced by the high surface area of the fine sand (van Dijk and Wilms 1990). If an SI for calcite in excess of 2.5 occurs, very fine-grained precipitates may form in the aqueous phase and require sand filtration. If the water is still significantly oversaturated when it is injected, further precipitation may occur and may clog the aquifer. The amount of $CaCO_3$ to be removed is estimated from the initial concentration of Ca (in meq/L), and the fraction of water that must be treated at the respective temperatures in the Na-exchange treatment is output as mg/L of $CaCO_3$.

3.4 Nitrate Injection

In a low-nitrate environment, the in situ oxidation of reduced Fe and Mn can be accomplished with nitrate injected upgradient from a source well. This occurs as a result of the stimulation of microbial growth when nitrate is added to low-nitrate environments. The increased microbial growth results in Fe2 and Mn2 oxidation (Vanek 1990). The lack of detailed data on Fe and Mn precipitation rates under such conditions and the significant impact of DOC on the oxidation of Fe suggest that it is wise to treat all of the water to be used in an ATES system. H2O_TREAT identifies those cases where $Fe(OH)_{3(a)}$ and/or birnessite (δ-MnO_2) are oversaturated.

3.5 Cascade and VYREDOX Treatments

In the cascade treatment, water is aerated by dropping it on a cement apron partially covered with small rocks that provide oxide-coated surfaces to catalyze the oxidation of Fe2 and Mn2. Suspended precipitates are removed by passing the water through a slow sand filter. The treated water infiltrates the aquifer and creates a local body of treated water that is used as the source water for heating and storage at a different location in the aquifer.

In the VYREDOX treatment (Hallberg and Martinel 1976), ground water is extracted, aerated, and reinjected in an outer circle of four to six wells. The water flows toward the source well, and although there is some mixing with local ground water, the water reaching the source well is sufficiently low in Fe. In the case of eskers-type aquifers, the air-saturated water can be injected upgradient of the source well, as in the nitrate method. H2O_TREAT identifies those cases where $Fe(OH)_{3(a)}$ and/or birnessite (δ-MnO_2) are oversaturated.

4.0 RUNNING THE CODE

H2O_TREAT allows a user to perform the complex geochemical calculations required to design ATES water treatment systems using a general-purpose geochemical model without mastering the input and output data structures of the geochemical code. A data entry menu system is available for H2O_TREAT on DOS-based computers to create the data input file. The setting of screen colors (see Appendix) by the menu system requires that the DOS device driver, ANSI.SYS, be included in the users CONFIG.SYS file.

The geochemical code used in H2O_TREAT is the MINTEQ code (Felmy et al. 1984). The MINTEQ code is a thermodynamic model used to calculate solution equilibria for geochemical applications. Version 4.00 contains formulations for correcting equilibrium constants for the effect of temperature (from 0° to 300°C) and pressure. The MINTEQ User's Manual (Peterson et al. 1987) describes the input files, input options, database files, and methodology for using the MINTEQ code. Necessary modifications to the MINTEQ 4.00 input file are given by Eary and Jenne (1992).[a] However, this information is not necessary for the operation of H2O_TREAT.

4.1 Data Requirements

Because the quantity of available water chemistry data varies widely, data input requirements have been divided into "Required" and "Optional" (Table 1). "Required" data are considered essential for a meaningful analysis to be performed. Inclusion of certain "Optional" data may result in a significant improvement in the reliability of the analysis. Both "Required" and "Optional" data are indicated in Table 1. "Saving" a file without one of the required values brings the cursor to the entry showing "missing*value."

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[a] Further modifications in MINTEQ version 4.01 used in H2O_TREAT are that either 0.0 or a second temperature must to be entered after the Sample Temperature and use of alkalinity option "1" (total titration alkalinity) does not require division by two.

TABLE 1. H2O_TREAT "Required" and "Optional" Data (brackets signify concentrations)

"Required"	"Optional"
[Ca]	[K]
[Mg]	[NH_4]
[Na]	[Mn]
[SO_4]	[Fe2]
[Cl]	[Fe3]
pH	[F]
Conductivity	[PO_4]
Physical Properties	[NO_2]
Sample Temperature	[NO_3]
High Temperature[a]	[Si]
Low Temperature	[S]
Alkalinity	[DOC]
Heat Exchanger Pressure	Eh
	Partial Pressure CO_2
	Partial Pressure CH_4
	Percent Carbonate Minerals in Aquifer
	Percent Expansible Clays
	Degassing Observed?

(a) Wall temperature or plate temperature in the case of the fluidized-bed and pellet reactors, respectively.

The pH and temperature must always be specified for the aqueous speciation calculations; hence, also for the solubility calculations. Alkalinity (CO_3, HCO_3, H_2CO_3) must be included because of the major importance of the carbonates of Ca, Fe, and Mn and oxides of Fe and Mn as scale-forming agents. The second temperature allows the speciation and solubility to be computed at some expected storage temperature.

Conductivity is required because it is needed in calculating the Na hazard for the Na-exchange treatment. The major cations (Ca, Mg, and Na) and major anions other than CO_3 (Cl and SO_4) must be specified for the speciation calculations to be meaningful. It is important that the concentration of Si be included if the storage temperature exceeds 100°C. The head should be provided if the water comes from

depths of 500 ft (150 m) or more. For shallower depths, the value entered is of little consequence.

Iron and Mn may not be important in the case of carbonate scaling, and therefore are not specified as required for the general case. However, recent observations in Sweden indicate that well clogging is increasingly being attributed to siderite, an Fe carbonate. In many waters, Fe and Mn oxides represent the only important scale-forming agents; therefore, it is always desirable to include Fe and Mn, and it is essential to include them in areas where red or black precipitates are observed in water samples. It is doubtful that air can be totally excluded from the ATES system; it is advisable to rerun the data set with an elevated redox potential (Eh).

Providing "Optional" chemical components is likely to increase the accuracy of the calculations. Potassium, NH_4, PO_4, and F are not required because they are infrequently present in sufficiently high concentrations in ground water to exert a significant effect on Ca or CO_3 speciation. For example, the calculated calcite is decreased by indicating that the mode of alkalinity determination is by acid titration rather than combustion, because MINTEQ makes a correction for non-carbonate forms of alkalinity when alkalinity is determined by acid titration. The concentrations of F and K are useful in that their presence increases the accuracy of the speciation calculations because of complex formation with metals and ionic strength effects, respectively. Similarly, although NH_4, NO_3, and NO_2 are not involved in any SI used to trigger the treatment requirement and have minimal effect on speciation calculations, they do provide valuable corroboration of a measured Eh value. The concentrations of Cl, S-2 (i.e., H_2S, HS^-, S^{2-}), and CO_2 are important in the evaluation of corrosion potential. The concentrations of CO_2 and CH_4 are useful in that they may indicate the need for an increased back pressure to avoid degassing during injection.

If a required constituent is not available, a value from other analyses of the same aquifer can be used, recognizing that the results will be significantly less reliable.

4.2 Input File

Saving from the data entry menu creates the TREAT.OUT file, which contains the default forms of those input variables that have alternative forms (e.g., well depth will be in feet). The structure of this file is illustrated in Table 2.

TABLE 2. Structure of TREAT.OUT File (All concentrations [shown in square brackets] are in mg/L; all temperatures are in °C; variables 36 through 41 and 44 not used in this version).

Line No.	Value	Comments[a]
1	1	Units: 1 = mg/L; 0 = mmol/L
2	[Ca]	Calcium
3	[Mg]	Magnesium
4	[Na]	Sodium
5	[SO_4]	Sulfate
6	[Cl]	Chloride
7	pH	pH
8	*blank*	*Conductivity as
9	Conductivity	in μmho/cm
10	Combustion or Titration[b]	
11	*blank*	*Alkalinity as
12	[Alk]	Alkalinity as CO_3
13	*blank*	Temperature as
14	Stemp	Temperature of aquifer water sample
15	LowT	Lowest value of temperature range
16	HighT	Highest value of temperature range
17	*blank*	*Heat exchanger pressure as
18	HxP	Heat exchanger pressure in feet
19	*blank*	*Ammonium as
20	[NH_4]	Ammonium
21	*blank*	*Nitrite as
22	[NO_2]	Nitrite
23	*blank*	*Nitrate as
24	[NO_3]	Nitrate
25	'Fe(tot)_&_Eh'; 'Fe2_&_Fe3'	
26	[Fe2] or [Fe2]+[Fe3]	
27	[Fe3] or Eh	Eh in millivolts
28	*blank*	*Sulfur as
29	[S]	Sulfur as HS
30	*blank*	*Silicon as
31	[Si]	Silicon as H_4SiO_4

TABLE 2. (cont'd)

32	[K]	Potassium
33	[Mn]	Manganese
34	[PO_4]	Phosphate
35	[F]	Fluoride
36	PCO_2	Partial pressure CO_2 in mbar
37	PCH_4	Partial pressure CH_4 in mbar
38	Pcarb	% Carbonate minerals
39	Pexpa	% Expansible clays
40	DOC	Dissolved organic carbon
41	'maybe', 'yes' or 'no' degassing observed[c]	
42	*blank*	*Head units
43	head	Head in aquifer in feet or meters
44	*blank*	*Total iron
45	*blank*	*Sodium adsorption ratio
46	*blank*	*Sum of base cations
47	*blank*	*Sodium hazard

(a) The asterisk designates switches controlling the form of chemical species; in the manual creation of a TREAT.OUT file, as is necessary for Unix-based computers, the line would be left blank. If the method of alkalinity analysis is not known, use the default choice of acid titration, which is the more common method.

(b) The geochemical model makes a correction for non-carbonate alkalinity when the alkalinity is determined by acid titration. If the method of alkalinity is not known, use the default choice of acid titration, which is the more common method of alkalinity determination.

(c) Oversaturation of the aquifer with CO_2 may be indicated by observations of an increase in pH immediately following sample collection or a significantly higher laboratory pH than that found in the field. Conversations with drilling personnel or the on-site geologist may indicate that gas bubbles were observed immediately after water samples were retrieved. If there is a significant possibility that the aquifer is over pressured with CO_2, it is advisable to run a sensitivity analysis by incremental increase in the partial pressure of CO_2. The partial pressure is entered as the decimal value in mbar.

4.3 Menu Input

DOS-based computers provide H2O_TREAT users the option of a menu system to create the main data input file. Formatted data screens are accessed by pressing

ENTER when the proper selection is highlighted. Toggles are operated with the right and left arrow keys. All other entries are actual data values. There are 13 toggles available (see Table 3). When the component form is changed, all other values are converted.

When starting H2O_TREAT on a DOS-based system, type TREAT or TREAT <*filename*> at the DOS prompt. Entering a file name is optional but necessary to allow the input data file to be saved. If a file name is given, it must be without a DOS extension as adding a DOS extension will result in a "file creation error." Calling

TABLE 3. Toggles

Menu	Name	Choices
Main	Units	mg/L; mM/L
"Required" Components	Conductivity as	µmho/cm; mS/m
	Alkalinity by	Titration; Combustion
	Alkalinity as	HCO_3; CO_3
	Temperature as	Fahrenheit; Celsius
	Heat exchanger pressure	mbar; psi
"Optional" (Alternative Form) Components	Ammonium as	N; NH_4
	Nitrite as	N; NO_2
	Nitrate as	N; NO_3
	Iron as	Fe(tot)_&_Eh; Fe2 and Fe3
	Sulfur	H_2S; HS; S
	Silicon as	Si; SiO_2; H_4SiO_4
	Degassing	Yes; No; Maybe
Physical & Aquifer Properties	Head as	meters; feet

TREAT will bring up a screen with default and blank values whereas TREAT <*filename*> will bring up the file if it has been previously saved. In either case, the TREAT.OUT file is created that the MINDRIVE component of H2O_TREAT uses to create an input file for MINTEQ. As shown in Exhibit 1, the first selection on the main menu controls the concentration units used. It allows the user to toggle between units of mg/L and mmol/L. Move up and down the menu by using the up and down arrow keys or entering the first letter of the specific selection. Use the ESCAPE key to return to the main menu screen. The current units are provided on each of data screens; previously entered values will be converted to the new units if the originally selected unit is changed. The next five menu items are used to access the formatted data screens. When the desired menu selection is highlighted, press ENTER and the appropriate screen will be displayed. The data currently displayed will be saved for future modifications until the file is saved or the session is aborted.

As one moves down the data screens, the current prompt is highlighted and one can either enter the value of the selected parameter or toggle between component forms. Only alkalinity and Eh are allowed to have negative values. Four components have preset limits: pH, Eh, partial pressure of CO_2, and head. If the limit is exceeded, the value will not be accepted and the program will replace the entry with "missing*data" and await a within-range value. The limits are set to reduce the likelihood of causing the geochemical model to iterate indefinitely in a futile effort to solve the speciation problem or to terminate without finding a solution. The limits are: 800 > Eh > -400, 10 > pH > 0, 3500 > feet of head > 0.1, and 1 > partial pressure CO_2 > 0.00001. Multiple pressure units are used to allow the unit commonly used in the particular field, e.g., feet or meters are used for well depth, mbar or partial pressure of CO_2. Unit conversions are given in Table 4.

Main Menu

UNITS: mg/L or mmol/L (milligram/liter or millimole/liter)
Required Components
Optional (Alternative Form) Components
Optional (Fixed Form) Components
Physical and Aquifer Properties
View Calculated Values
FINISHED
ABORT
Use arrows or First letter to move to selection
Hit ENTER to make your choice

Use the right/left arrows to choose the chemical units

"Optional" (Alternative Form) Components
"Optional" (Alternative Form) Components (mg/L or mmol/L)

Ammonium		
Ammonium as	-	NH4 (or N)
Ammonium	:	1.4
Nitrite		
Nitrite as	-	NO2 (or N)
Nitrite	:	.02
Nitrate		
Nitrate as	-	N03 (or N)
Nitrate	:	.90
Iron		
Iron as	-	Fe2_&_Fe3 (or Fe(tot)_&_Eh)
Ferrous	Fe2:	.015
(or Total Iron Fe)	:	—
Ferric	Fe3:	.0007
(or Redox Potential	mV)	
Sulfur		
Sulfur as	-	H2S (or HS, or S)
Sulfur	:	.02
Silicon		
Silicon as	-	Si (or H4SiO4, or SiO2)
Silicon	:	8.52

Use ESCape to leave entry screen

Selected Aquifer and Physical Parameters Menu
Selected Aquifer and Physical Properties

Carbonate Minerals	%:	.5
Expansible Clays	%:	3
Dissolved Organic Carbon	mg/L:	3
Degassing Observed		maybe (or yes/no)
Head		
Head as	-	meters (or feet)
Head	:	45

Use ESCape to leave entry screen

"Required" Parameters Menu
"Required" Parameters (mg/L or mmol/L)

Calcium	Ca:	12.2
Magnesium	Mg:	missing*data
Sodium	Na:	12
Sulfate	SO4:	7.7
Chloride	Cl:	9.9
pH	:	8.01
Conductivity		
Conductivity as	-	µmho/cm (or mS/m)
Conductivity	:	200
Alkalinity		
Alkalinity by	:	Titration (or Combustion)
Alkalinity as	-	HCO3 (or CO3)
Alkalinity	:	75.2
Temperature		
Temperature as	:	Celsius (or Fahrenheit)
Sample Temperature	:	9.5
Low Temperature	:	20
High Temperature	:	40
Heat Exchanger Pressure		
Pressure as	-	psi (or mbar)
Pressure	:	22

Use ESCape to leave entry screen

"Optional" (Fixed Form) Components Menu
"Optional" (Fixed Form) Components (mg/L or mmol/L)

Potassium	K:	1.4
Manganese	Mn:	.0044
Phosphate	PO4:	.21
Fluoride	F:	.1
Partial Pressures	mbar	
Carbon dioxide	CO2:	—
Methane	CH4:	—

Use ESCape to leave entry screen

View Calculated Values Menu

Calculated Values

Total Iron	:	0.015700
Sodium Adsorption Ratio	:	0.0663949
Sum of Base cations	meq:	1.796273
Sodium Hazard	:	Medium

Use ESCape to leave entry screen

EXHIBIT 1. H2O_TREAT Menus

TABLE 4. Unit Conversions

Pressure

1 psi = 6.895×10^{-3} Pa (Pascal)
1 atm = 1.013×10^{-5} Pa
1 bar = 10^5 Pa

Length

1 ft = 0.3048 m (meter)

Conductivity

1 mS/m (milli Siemens/meter) = 10 μmho/cm (micro mho/centimeter)

When all components have been entered, select FINISHED from the main menu. If all "Required" components have been entered, this selection will save the data to a file, exit the data entry program, and proceed with the calculation phase of H2O_TREAT. If all "Required" data has not been entered, the "Required" data screen will be redisplayed. The user may exit the program at any time by choosing ABORT from the menu.

The user can go back and forth between input screens any number of times by pressing ESCAPE to return to the main menu and reselect a screen. "As" switches (identified in the input screens by "as" followed by a "-" rather than being followed by a ":") are provided so that the user is rarely required to make conversions in the form of chemical components, which must be passed to th geochemical model (MINTEQ) in a particular form before data entry. The switch that the code will use is the one shown on the screen. "As" switches are provided for alkalinity, sulfur, silicon, head, and temperature because these components require the passing of concentration data in a specific form. Iron concentrations may be entered either as Fe total (Fe3 plus Fe2 and an associated Eh value) or as Fe3 and Fe2 separately. In the latter case, MINTEQ calculates the Eh of the Fe couple. The maximum concentration of dissolved Mn3 or Mn4 is so small that dissolved Mn is entered as Mn2. In the absence of an input Eh value or of paired Fe3 and Fe2 values, H2O_TREAT will assume that the entered Fe and Mn values are the concentrations of the lower valence state, speciate Fe and Mn

among the Fe2 and Mn2 complexes, and calculate SI for Fe2 and Mn2 solids only.

Although the SI calculations of Fe and Mn carbonates are initially made at the measured Eh value, if the waters contain elevated levels of Fe and Mn, the prime concern is likely to be the possible precipitation of oxides/hydroxides of these metals. With Mn or Fe concentrations of >0.1, sensitivity analyses on oxide precipitation is advisable. This can be performed by increasing the Eh (in 50- or 100-mV increments).

4.4 Output File

Exhibit 2 is an example of the output generated by H2O_TREAT. The output file is named *<filename.H2O>*. The extent of each treatment required for each of the design temperatures is provided. "N," "H," or "C" are used to indicate that Fe, Mn, and/or Si (when temperatures are above 100°C) oxides are calculated to be oversaturated for the various temperatures of Na-exchange, H-exchange, and CO_2 treatment, respectively. The same symbols indicate if corrosion is likely. If no oxides calculate to be oversaturated or if corrosion is not likely, a dash is inserted instead of N, H, or C under the Fe, Mn, Si, or Corrosive headings. If no treatment is required for the highest temperature, the output file contains the words "No treatment is required."

				Fluidized	Hazard				
Temp	Na	H	CO2	Bed	Fe	Mn	Si	Corrosive	Na
°C	%	%	mg/L	mg/L					
120.	85.	20.	0.70	122.	---	---	---	NHC	low
100.	75.	10.	0.42	108.	-HC	---	---	NHC	low
80.	45.	5.	0.26	65.	NHC	---	---	NHC	low

EXHIBIT 2. Sample Output Generated by H2O_TREAT

4.5 Sensitivity Analysis

A sensitivity analysis was carried out using plus and minus values that represent, for the most part, common analytical uncertainties in the input values. As can be seen in Table 5, the resultant changes in percent treatment required all appear reasonable.

TABLE 5. Sensitivity Analysis Results

Treat-ment	Temp °C	Na %	H %	CO_2 mg/L	Fluidized Bed mg/L	Hazard Fe	Mn	Si	Corrosive	Na
Ca -15%	120.	94.	36.	310	143	--C	---	---	NHC	low
	20.	74.	36.	7	113	N--	---	---	NHC	low
Ca +15%	120.	96.	34.	302	194	-HC	---	---	NHC	low
	20.	82.	4.	7	165	NH-	---	---	NHC	low
Mg -15%	120.	96.	36.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
Mg +15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
Na -15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
Na +15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
SO_4 -15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
SO_4 +15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
Cl -15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
Cl +15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low

TABLE 5. (cont'd)

Treat-ment	Temp °C	Na %	H %	CO_2 mg/L	Fluidized Bed mg/L	Hazard Fe	Mn	Si	Corrosive	Na
Mn -15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
Mn +15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
PO_4 -15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
PO_4 +15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
F -15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
F +15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
temp -2.5	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	76.	4.	7	133	NH-	---	---	NHC	low
temp +2.5	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	80.	4.	7	140	NH-	---	---	NHC	low
head -250 ft	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
head +250 ft	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
pH -0.15	120.	94.	34.	303	165	-HC	---	---	NHC	low
	20.	62.	2.	7	109	NH-	---	---	NHC	low
pH +0.15	120.	96.	36.	303	168	-HC	---	---	NHC	low
	20.	86.	4.	12	151	NH-	---	---	NHC	low
Eh -15 mV	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	N--	---	---	NHC	low
Eh +15 mV	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low

TABLE 5. (cont'd)

Treat-ment	Temp °C	Na %	H %	CO_2 mg/L	Fluidized Bed mg/L	Hazard Fe	Mn	Si	Corrosive	Na
Cond -5 mS	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
Cond +5 mS	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low
CO_3 -15%	120.	94.	30.	300	165	-HC	---	---	NHC	low
	20.	76.	2.	7	133	NH-	---	---	NHC	low
CO_3 +15%	120.	96.	40.	327	168	--C	---	---	NHC	low
	20.	80.	4.	18	140	NH-	---	---	NHC	low
Fe -15%	120.	96.	34.	302	168	--C	---	---	NHC	low
	20.	78.	4.	7	137	N--	---	---	NHC	low
Fe +15%	120.	96.	34.	302	168	-HC	---	---	NHC	low
	20.	78.	4.	7	137	NH-	---	---	NHC	low

The dependence of calcite saturation on temperature is illustrated by taking a water analysis that has a saturation index of about 0.2 at ambient ground water temperature and calculating the calcite SI at progressively higher temperatures. As shown in Figure 1, the extent of oversaturation increases several fold at 100°C. The effect of pressure is much less than temperature, amounting to an increase in calcite SI of about 0.1 as the water head increases from 10 to 3000 feet (Figure 2).

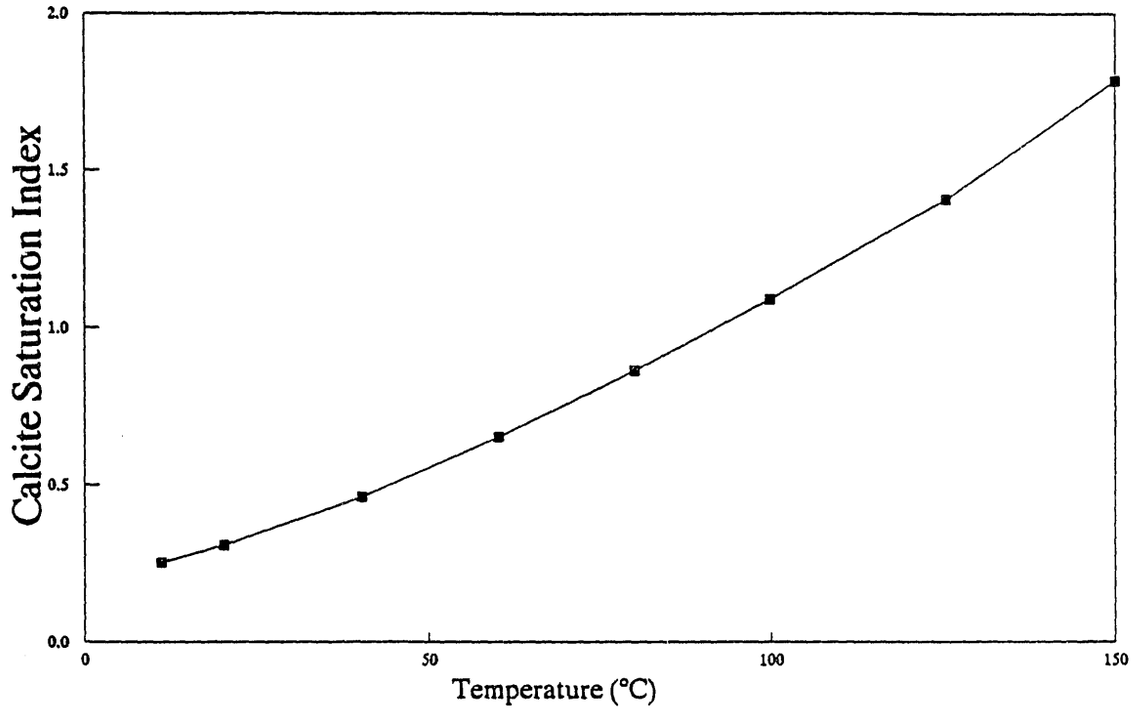

Figure 1 Variation in Calcite Saturation Index with Temperature.

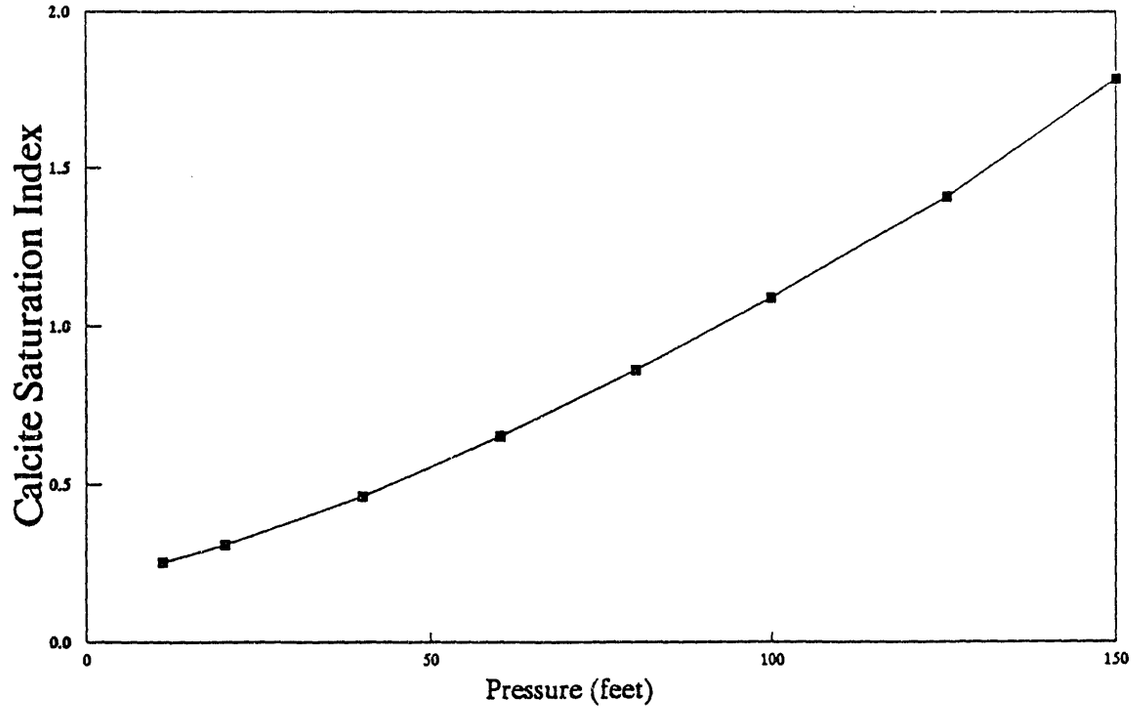

Figure 2. Variation in Calcite Saturation Index with Pressure (depth of water column in feet).

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APPENDIX

DOS BATCH CONTROL FILE TREAT.BAT

APPENDIX

DOS BATCH CONTROL FILE TREAT.BAT

```
@ echo off
REM   set color to white on blue
ECHO ←[2;44;37m
cls
echo+
echo+
echo+
echo+
echo    H2O_TREAT
echo+
echo    An Aid for Selecting ATES Water Treatment
echo       For further information contact:
echo          Lance Vail
echo          Pacific Northwest Laboratory
echo          Richland, Washington  99352
echo+
echo+
echo       Version: 1.0
echo       Date: 1 Nov 1992
echo+
echo+
echo+
pause
REM
REM   there are 3 cases:
REM       no filename was entered on the command line
REM       entered an existing filename for retreival & possible update
REM       entered a new filename to save data
REM

IF %1x == x goto noparam
code\screen %1
goto end
REM no filename entered by the user
:noparam
  code\screen
  goto end
:end
del debug.h2o
del toss.out
```

```
del scratch
del sum.h2o
del %1.tbl
ren treat.out scratch
copy start.ctl control.fil
REM    TREAT.BAT
REM    TREAT file
if not exist scratch goto stop
:start1
if not exist control.fil goto stop
code\mindrive > toss.out
code\minteq4
type minout.dat >> debug.h2o
type toss.out   >> debug.h2o
type toss.out   >> sum.h2o
goto start1
:STOP
code\table sum.h2o scratch %1.tbl
type %1.tbl
```

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