2

Conf-920501--27

PNL-SA--20388

DE93 001551

H_2O TREAT: AN ACID FOR EVALUATING WATER TREATMENT REQUIREMENTS FOR AQUIFER THERMAL ENERGY STORAGE

L. W. Vail
E. A. Jenne
L. E. Eary

August 1992

Presented at the
Aquifer Thermal Energy Storage
August 3-4, 1992
San Diego, California

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ABSTRACT

A public-domain software package is available to aid engineers in the design of water treatment systems for Aquifer Thermal Energy Storage (ATES). Geochemical phenomena that cause problems in ATES systems include formation of scale in heat exchangers, clogging of wells, corrosion in piping and heat exchangers, and degradation of aquifer materials. Preventing such problems frequently requires employing water treatment systems. Individual water treatment methods vary in cost, effectiveness, environmental impact, corrosion potential, and acceptability to regulatory bodies. Evaluating these water treatment options is generally required to determine the feasibility of ATES systems. The H2O*TREAT* software was developed by Pacific Northwest Laboratory for use by engineers with limited or no experience in geochemistry. At the feasibility analysis and design stages, the software utilizes 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 whether that mineral is oversaturated, hence may precipitate at the specified temperature. The saturation indices of key calcium, iron, silica, and manganese carbonates, oxides, and hydroxides (calcite, rhodochrosite, siderite, $Fe(OH)_3$[a], birnessite, chalcedony, and SiO_2) are calculated. User input is separated into "required" and "optional" data (Table 1). Currently, H2O*TREAT* does not perform cost calculations; however, treatment capacity requirements are provided. Treatments considered include 1) Na and H ion exchangers and pellet reactors to avoid calcite precipitation, and 2) *in situ* nitrate addition and cascade precipitators to prevent Fe and Mn oxide precipitation. The H2O*TREAT* software also provides the user with guidance on other geochemical problems that must be considered, such as SiO_2 precipitation, corrosion, and environmental considerations. The sodium adsorption ratio and sodium hazard are calculated to evaluate the likelihood of clay swelling and dispersion caused by high Na concentrations (e.g., as a result of Na ion exchange water treatment used to prevent calcite precipitation). H2O*TREAT* is available for DOS and UNIX computers.

INTRODUCTION

The chemistry of aquifers often represents a significant problem in the design of 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 inoperable. Many ground waters are naturally corrosive to many common materials used in heat exchangers, pumps, and pipes. Changes in temperature may make these 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 background in geochemistry than most design engineers who are making a feasibility assessment for ATES are likely to possess.

A public-domain software package is now available to aid engineers in the design of water treatment systems for ATES. The H2O*TREAT* software was developed for use by engineers

with limited or no experience in geochemistry at the feasibility analysis and design stages. The software was developed by Pacific Northwest Laboratory for the U. S. Department of Energy as part of the United States' contribution to Annex VI of the International Energy Agency.

GEOCHEMICAL PROBLEMS

The most general geochemical problem encountered in ATES systems is that of precipitation of carbonate on heat exchangers and clogging of the injection well and/or storage aquifer by Fe and Mn oxides or by carbonates. The deposition of a significant amount of scale on heat exchangers greatly reduces their thermal transfer efficiency and deposition on the well screen, gravel pack, or in the aquifer markedly decreases the injection rate at a fixed pressure.

The major geochemical reactions of concern in ATES are:

- precipitation (scale formation, aquifer clogging),
- dissolution,
- redox transformations (oxidation of reduced Fe and Mn),
- cation exchange,
- swelling of expandable clays,
- dispersion of fine-grained sediments, and
- degassing (formation of gas phase).

The solubility of carbonate minerals decreases with increasing temperature. Although calcite is the predominate carbonate mineral formed, ferrous carbonate (siderite) is suspected as the cause of reduced permeability in Swedish ATES systems. 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 (IAP). The logarithm of the ratio of the IAP to the solubility value (K_{sp}) is known as the saturation index (SI); i.e., IAP = A_{Ca} A_{CO3} and $SI_{calcite} = \log_{10} (IAP/K_{sp})$, where A_{Ca} = activity of Ca and A_{CO3} = activity of CO3. At $SI_{calcite}$ values of less than 0.3, calcite precipitation appears to be too slow to pose a problem (van Dijk and Wilms 1990; Banck 1989; Griffioen 1992; Willemsen and Appelo 1985) because of the interference of components such as dissolved organic carbon (DOC), Mg, and PO_4 with the precipitation process (Jenne 1990; Griffioen 1992). Other factors that affect precipitation and calculation of SI's include the formation of solid solution of $CaCO_3$ with Mg, Fe, and Mn. If $SI_{calcite}$, correctly 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 lower temperature than originally contemplated might remove the necessity for water treatment, it is important to estimate the temperature at which $SI_{calcite}$ is ≤ 0.3. It is also important to note that errors in calculated SIs for carbonate minerals may result from the loss of CO_2, with resultant rise in pH, during pumping, sampling, and while awaiting analysis.

The hydroxides and oxides of Fe and Mn, respectively, hereafter referred to as oxides, precipitate upon reaction with atmospheric O_2 as a consequence of oxidation of the reduced metal. Ferrous iron, Fe^{II}, and Mn^{II} are commonly the dominant forms of dissolved Fe and Mn in aquifers that are depleted of O_2. This is primarily a result of microbial processes that deplete the oxygen as surface water infiltrates and moves down gradient from a recharge area. When O_2 is depleted, then NO_3, NO_2, Mn^{IV}, Fe^{III}, and then SO_4 serve in turn as electron receptors. Because every oxygen molecule that comes into contact with reduced ground water can oxidize 4 Fe^{II} to Fe^{III} or 2 Mn^{II} to Mn^{IV} atoms, the entry of even small amounts of air may cause considerable oxide precipitation. ATES systems should preclude air entry if 1) the source water concentration of Fe or Mn is >0.1 mg/L because O_2 entry may cause oxide precipitation with resultant scaling and clogging and may also increase corrosion rate, or 2) if pCO_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, and Mn carbonates.

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 Na saturation of expandable clays caused by use of Na-exchange water treatment or a significant reduction in ionic strength as when a foreign, lower ionic strength water is introduced into a saline aquifer (Jones 1964). The likelihood of clay dispersion, swelling, and reduced permeability is characterized by a high, medium, or low Na hazard (Richards 1954, p. 80; Jackson 1958, p. 258).

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.

TREATMENT METHODS

Sodium exchange, hydrogen exchange, and the pellet reactor treatment methods are considered here to avoid carbonate precipitation whereas nitrate injection, cascading, and air-saturated water or peroxide injection treatments are included to avoid iron and manganese oxide precipitation.

Either NaCl or HCl are used to recharge the cation exchanger. Use of the H-saturated exchanger results in lower pH and additional carbonate mineral dissolution during heated water storage. Therefore, Na exchange is to be preferred to H exchange. Additionally, the fraction of storage water that must be treated is expected to decrease with each cycle when Na exchange is used, but is expected to increase if H exchange is used. The pellet reactor has been used to soften domestic water supplies since the mid-seventies in The Netherlands (van Dijk and Wilms 1990), achieving very rapid but not excessive over saturation with respect to calcite in the reactor by injecting and

rapidly mixing alkali with the water. In the fluidized bed reactor where high pumping rates cause fine sand to be fluidized, calcite precipitation is enhanced by the high surface area of the fine sand (van Dijk and Wilms 1990). If an $SI_{calcite}$ in excess of 2.5 occurs, very fine grained precipitates may form that may pass the rapid sand filter and clog the aquifer.

In a low-nitrate environment, the *in situ* oxidation of reduced Fe and Mn may be accomplished with nitrate injected upgradient from a source well. High nitrate concentrations stimulate microbial growth, which results in Fe^{II} and Mn^{II} oxidation (Vanek 1990). A cascade treatment can be used when the aquifer is relatively shallow and unconfined. The ground water is aerated by cascading from a trough onto a surface covered with small rocks that promote oxidation and further aeration. The precipitated oxides are removed by passing the water through a slow sand filter. The treated water infiltrates to 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 4-6 wells. The water flows towards 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.

Acidification is generally the least desirable means of avoiding carbonate scaling because acidification of the water 1) causes increased corrosion during heating as a result of both increased Cl and H concentrations and injection, and 2) it must be added each cycle before heating of water resulting in an increased Cl concentration with each cycle. However, acidification may be the method of choice if an aquifer contains only traces of carbonate minerals and degassing can be facilitated. Similarly, where siderite ($FeCO_3$) clogging may occur, acidification and degassing may decrease the concentration of CO_3 enough to bring the $SI_{siderite}$ to zero with little increase in dissolved iron concentration.

There are three means of reducing the required cation exchange treatment capacity for a given water and specified megawatts of energy storage. One means is to condition the water by withdrawing water from the source well, passing it through the exchanger and injecting it into the source well. The second is to increase the storage temperature in one or more storage-recovery cycles until the design temperature is reached (van Loon and Holde 1992). The third is to reduce the storage temperature and increase the stored volume.

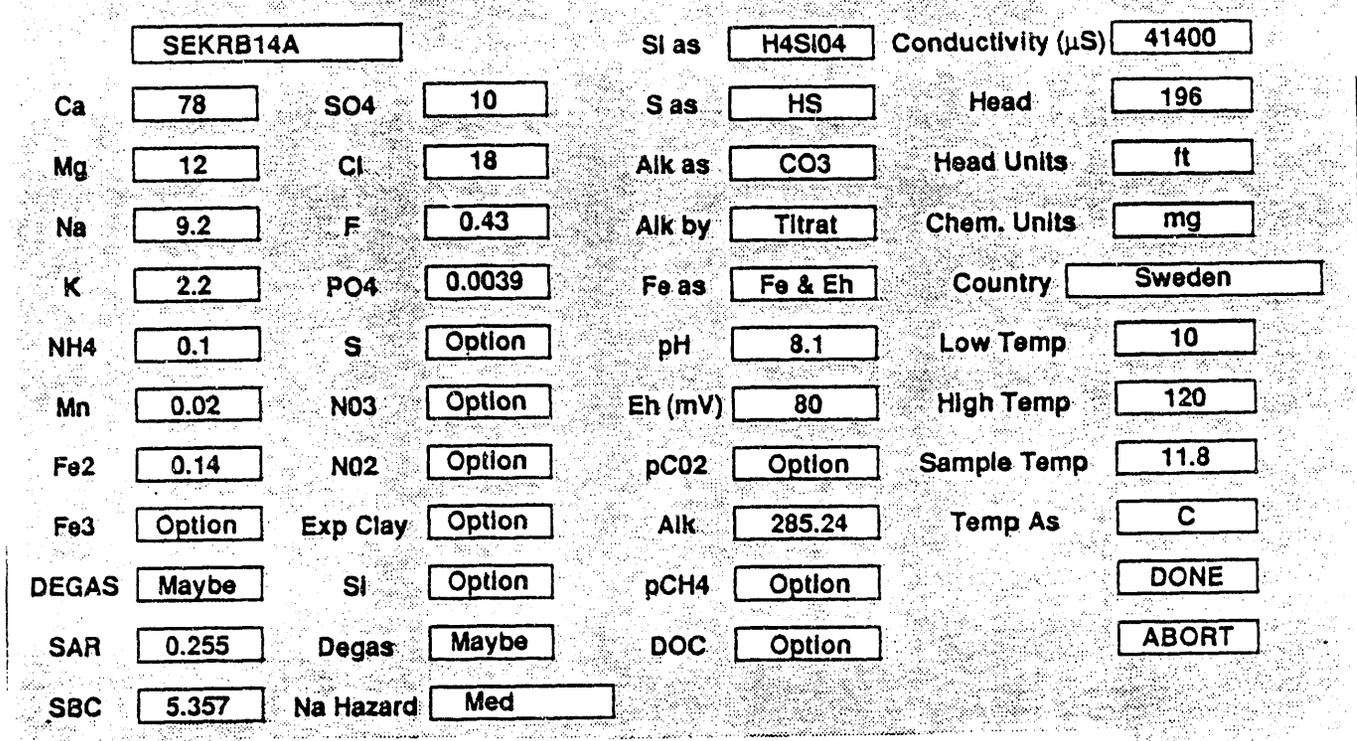

Figure 1. Example data input screen for DOS version of H2OTREAT.

H2O*TREAT*

H2O*TREAT* allows a user to perform the complex geochemical calculations that are required to design ATES water treatment systems using a general-purpose geochemical model, MINTEQ, without mastering the somewhat complex input and output data structures of the geochemical code. A point and click screen menu is available for H2O*TREAT* on DOS machines. An example of an input data screen is shown in Figure 1. For non-DOS machines the FORTRAN source codes, the geochemical database files, and a UNIX control script are available.

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.

Table 1. H_2O*TREAT* Input Data

Required	Optional
[Ca]	[K]
[Mg]	[NH_4]
[Na]	[Mn]
[SO_4]	[Fe^{II}]
[Cl]	[Fe^{III}]
pH	[F]
Conductivity	[PO_4]
Head	[NO_2]
Sample Temperature	[NO_3]
Low Temperature	[Si]
High Temperature	Eh
Alkalinity	pCO_2
	pCH_4
	DOC

H2O*TREAT* estimates the fraction of water that must be treated by Na-exchange and by H-exchange to prevent carbonate scale formation in the heat exchanger. To perform this calculation, H2O*TREAT* successively increases the fraction of the total relevant cations (Ca, Mg, Fe, and Mn) until the saturation index for one of the significant carbonate solids exceeds 0.3. The fraction immediately greater than the fraction resulting in a saturation index that exceeds 0.3 is the estimated treatment fraction required. These calculations are repeated for the range of high to low temperatures specified by the user. Figure 2 illustrates the change in treatment requirements as a function of temperature for a water chemistry controlled by calcite saturation. 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^+. H2O*TREAT* does not consider the change in treatment requirements that will occur after several cycles of treatment because of the change in water chemistry caused by the treatment process or by the change in aquifer temperature.

The MINTEQ code (Felmy et al. 1984) is included in H2O*TREAT*. The MINTEQ code is a thermodynamic model used to calculate solution equilibria for geochemical applications. Version 3.00 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. However, this information is not necessary for the operation of H2O*TREAT*.

CONCLUSION

H2O*TREAT* is a public-domain software package to aid engineers in the design of water treatment systems for aquifer thermal energy storage. H2O*TREAT* was developed for use by engineers with limited or no experience in geochemistry.

This work was supported by the U.S. Department of Energy (DOE) under Contract DE-AC06-76RLO 1830. Pacific Northwest Laboratory is operated for DOE by Battelle Memorial Institute.

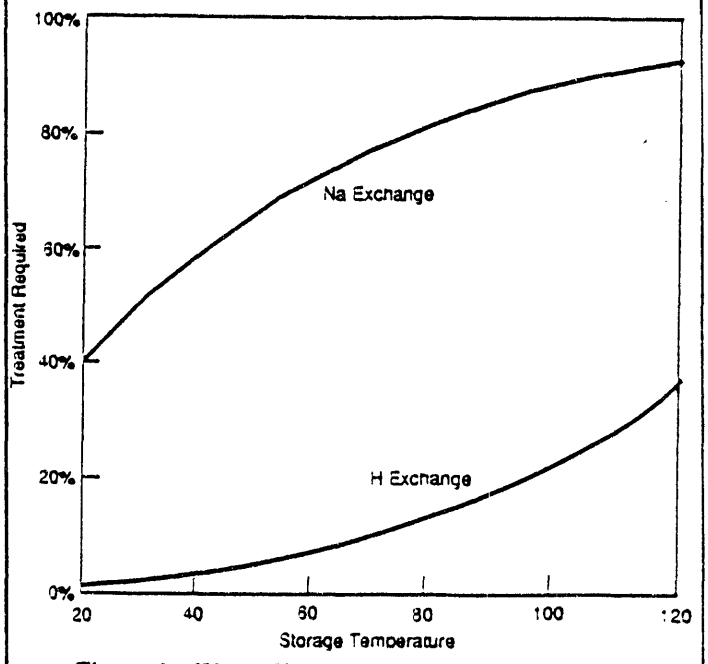

Figure 2. Water Treatment requirements for Na and H exchange as a function of temperature.

REFERENCES

Banck, A. 1989. Lomma Pilot ATES Plant: Experiences and Results. International Energy Agency, Annex VI, Report 29-E.

Dijk, J.C. van and D. Wilms. 1990. "Water Treatment Without Waste Material: The Dutch Experiences with Pellet Reactors. " Ontharding van drinkwater, in Proceedings of a Studieday in Antwerpen, Belgium, December 11, 1990. Technologish Institute KVIV Genootschap Milieutechnologie, Antwerpen, Belgium.

Felmy, A. R., D. C. Girvin, and E. A. Jenne. 1984. MINTEQ: A Computer Program for Calculating Aqueous Geochemical Equilibria. EPA-600/3-84-032 (NTIS PB84-157148), National Technical Information Service, Springfield, Virginia.

Griffioen, J. 1992. Cation-Exchange and Carbonate Chemistry in Aquifers Following Groundwater Flow. Jasper Griffioen, Amsterdam.

Hallberg, R.O. and R. Martinel. 1976. "VYREDOX-*In situ* Purification of Ground Water." Ground Water 14:88-93.

Jackson, M.L. 1958. Soil Chemical Analysis. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Jenne, E.A. 1990. "Aquifer Thermal Energy Storage: The Importance of Geochemical Reactions." Hydrochemistry and Energy Storage in aquifers, Proceedings and Information No. 43, eds. J.C. Hooghart & C.W.S. Posthumus, pp. 19-36.

Jones, F.O. 1964. "Influence of Chemical Composition of Water on Clay Blocking of Permeability." J. Petroleum Technology 16:441-446.

Loon, L.J.M. van and K. van der Holde. 1992. "High Temperature ATES at the State University of Utrecht, The Netherlands" (this proceedings).

Molz, F.J., A.D. Parr, and P.F. Angersen. 1981. "Thermal Energy Storage in Confined Aquifer: Second Cycle." Water Resours. Res. 17:641-645.

Peterson, S. R., C. J. Hostetler, W. J. Deutsch, and C. E. Cowan. 1987. MINTEQ User's Manual. NUREG/CR-4808, PNL-6106, prepared by Pacific Northwest Laboratory for the U.S. Nuclear Regulatory Commission, Washington, D. C.

Richards, L.A. (ed). 1954. Diagnosis and Improvement of Saline and Alkali Soils. U.S. Department Agriculture, Handbook no. 60, U.S. Government Printing Office, Washington, D. C.

Vanek, V. 1990. "*In situ* Treatment of Iron-Rich Groundwater by the Addition of Nitrate," Department of Ecology, Univ. Lund., ISSN 1100-6366, 33 pp.

Willemsen, A. and C.A.J. Appelo. 1985. "Chemical Reactions During Heat Storage in Shallow Aquifers in the Netherlands: Laboratory Experiments and Geochemical Modeling," In Hydrogeology in the Service of Man, Memoirs of the 18th Congress of the International Association of Hydrology, pt. 4:68-78.

END

DATE FILMED

12 / 23 / 92