Environment Canada
Water Science and Technology Directorate

Direction générale des sciences
et de la technologie, eau
Environnement Canada

Predicting the behaviour of thermal energy and
temperature-dependent reactive mass transport in shallow
aquifers
By:
J. Molson, E. Frind, D. Blowes, C. Ptacek

94-46

Management Perspective

The efficiency of an aquifer thermal energy storage (ATES) system depends strongly on
the characteristics of the host aquifer, the geochemistry of the injection water, and the
geochemistry of the resident groundwater. Chemical precipitation of solids, and an
associated reduction in permeability, has been identified as the most important technical
problem facing the success of these operations. This paper describes a new computer model
that was developed to simulate the effects of changing temperature on geochemical
processes occurring during operation of ATES systems. In the model, transient
groundwater flow is fully coupled with thermal energy processes, in three dimensions,
using the Galerkin finite element method. Further coupling of mass transport with an
equilibrium geochemical speciation/mass transfer code, also in three-dimensions, is
accomplished using a sequential two-step procedure. The model was used to simulate
physical and chemical changes occurring during a thermal injection experiment. In this
experiment 37°C water was injected into a shallow aquifer and monitored over a several
month period. The model predicts precipitation of $CaCO_3$ and $FeCO_3$ directly at the
injection well due to changing equilibrium constants which favour the formation of these
solids at higher temperatures. Potential applications of this model include predictions to
assist in the design of new ATES systems and predictions of the role of chemical
precipitates on the long term efficiency of sites already in operation.

Proceedings: CALORSTOCK '94, 6ᵗʰ International Conference on Thermal Energy Storage, Espoo, Finland, August 1994.

PREDICTING THE BEHAVIOUR OF THERMAL ENERGY AND TEMPERATURE-DEPENDENT REACTIVE MASS TRANSPORT IN SHALLOW AQUIFERS

J.W. Molson[1], E.O. Frind[1], D.W. Blowes[1] and C.J. Ptacek[2,1]

(1) Waterloo Centre for Groundwater Research, University of Waterloo
Waterloo, Ontario, Canada N2L 3G1 (Fax 519-725-8720)

(2) National Water Research Institute, Environment Canada,
Burlington, Ontario, Canada L7R 4A6

ABSTRACT

Temperature-dependent reactive mass transport is simulated numerically in three dimensions. The multicomponent chemistry and heat transport model is based on the Galerkin finite element technique with symmetric time-weighting and uses a preconditioned conjugate gradient matrix solver. The groundwater geochemistry, assumed governed by equilibrium reactions, is coupled with mass transport using a sequential physical-chemical approach. A large-scale 3D simulation of the Borden thermal injection experiment helps illustrate the complex reactions associated with shallow ATES systems, including changes in groundwater pH and temperature-induced carbonate precipitation.

1. INTRODUCTION

The efficiency of an aquifer thermal energy storage (ATES) system depends strongly on the characteristics of the host aquifer and geochemistry of the resident groundwater. Of critical importance are those temperature-dependent reactions which induce carbonate and hydroxide mineral precipitation or dissolution within the aquifer. These reactions can significantly affect aquifer permeability, thereby changing the flow system dynamics and behaviour of the thermal plume. Environmental impacts are also a concern.

Geochemical reactions associated with low-temperature ATES systems have been well documented. Palmer and Cherry (1984), for example, showed that the reactions are dependent on several factors including heating and cooling, equilibration with CO_2 and O_2, and mixing of injection and ambient waters. Perlinger et al. (1987) discuss variations in groundwater geochemistry observed at a field-scale ATES facility. In these and other documented cases, the behaviour of calcite was of prime concern because of its potential to precipitate at high temperatures, and clog injection wells. Indeed, Snijders (1991) identifies the chemical precipitation of solids as the most important technical problem facing most ATES installations.

Batch geochemical equilibrium models, such as MINTEQ and PHREEQE, are often used to help understand the reactions involved. Recently, coupled models of multicomponent reactive transport have also been developed (see, for example, Kinzelbach et al., 1991; and Walter et al., 1994). Coupled heat and mass transport models are presented by Willemsen et al. (1988) and by Kangas and Lund (1991).

In order to investigate some of the controlling factors on ATES geochemistry, a new three-dimensional numerical model has been developed which solves for both the density-dependent transport of thermal energy and multicomponent mass transport governed by temperature-dependent equilibrium reactions. The 3D simulations provide a new perspective into the influence of temperature on geochemical reactions associated with the transport of thermal energy in porous media.

2. MODEL DEVELOPMENT

2.1 Thermal Energy Transport

The continuity equation for density-dependent flow can be written as

$$\frac{\partial}{\partial x_i}\left[K_{ij}\left(\frac{\partial \psi}{\partial x_j}+\rho_r \bar{n}_j\right)\right] - \sum_{i=1}^{N} Q_i(t) = S_s\frac{\partial \psi}{\partial t} \tag{1}$$

where x_i are the 3D spatial coordinates, K_{ij} is the temperature-dependent hydraulic conductivity tensor, ψ is the equivalent freshwater head, ρ_r is the temperature-dependent relative density of water, Q_i is the fluid volume flux for a source or sink, S_s is the specific storage, and t is time. The thermal transport equation is written as

$$\frac{\partial}{\partial x_i}\left[\left(\kappa + \frac{D_{ij}}{R}\right)\frac{\partial T}{\partial x_j}\right] - \frac{\partial}{\partial x_i}\left(\frac{v_i}{R}T\right) + \sum_{i=1}^{N}\frac{Q_i(t)T_i(t)}{R\theta} = \frac{\partial T}{\partial t} \tag{2}$$

where D_{ij} is the hydrodynamic dispersion tensor, v_i is the average linear groundwater velocity, R is the thermal retardation, N is the number of sources or sinks, T is the temperature, T_i is the source injection temperature, and κ is the aquifer thermal diffusivity. Further details are provided by Molson et al. (1992).

2.2 Geochemical Mass Transport and Speciation

The equation governing advective-dispersive mass transport of an aqueous component k can be written as

$$\frac{\partial}{\partial x_i}\left[D_{ij}\frac{\partial C_k}{\partial x_j}\right] - \frac{\partial}{\partial x_i}(v_i C_k) + \sum_{i=1}^{N}\frac{Q_i(t)C_{ki}(t)}{\theta} + R_k = \frac{\partial C_k}{\partial t} \qquad k = 1, ..., N_c \tag{3}$$

where C_k is the concentration of component k in the aqueous phase, and R_k is the chemical source/sink term representing the changes in aqueous component concentrations caused by heterogeneous chemical reactions. The mass continuity equation for solid component k of a system of N stationary solid components is:

$$\frac{\partial S_k}{\partial t} - R_k^S = 0 \qquad k = 1, ..., N_c \qquad (4)$$

where S_k is the solid phase concentration and R_k^S represents the change in solid component concentration due to precipitation/dissolution and sorption/desorption reactions.

Speciation of the hydrogeochemistry is provided by the geochemical equilibrium model MINTEQA2 (Allison et al., 1990). The model considers chemical speciation, acid-base reactions, mineral precipitation-dissolution, oxidation-reduction, and adsorption. In this study, temperature corrections to the equilibrium constants within MINTEQA2 were calculated using the Van't Hoff equation.

3. NUMERICAL SOLUTION

The above equations governing fluid flow, thermal and mass transport are solved using the Galerkin finite element method with the symmetric-matrix time integration scheme of Leismann and Frind (1989). The Leismann scheme generates a symmetric coefficient matrix while retaining effective second-order accuracy, thereby providing significant savings in computer memory and execution time. The algorithm accounts for the temperature-dependent fluid density and viscosity by coupling the transient flow and thermal transport processes.

Coupling of mass transport with geochemical speciation is accomplished using a sequential two-step procedure where, in the first (physical) step, the components are advected and dispersed in space and time without reacting, and in the second (chemical) step, the components react instantaneously without being transported. The physical-chemical coupling is therefore linear, although the equilibration reactions remain nonlinear. A full development is provided by Walter et al. (1994).

The flow and transport matrices are solved using an efficient preconditioned conjugate gradient (PCG) solver. Currently, porosity or permeability changes due to mineral precipitation or dissolution are not considered.

4. THERMAL CHEMISTRY SIMULATIONS

The new 3D thermal chemistry model is applied to simulate the Borden thermal injection experiment where water at 37 °C was injected for 6 days at a rate of 0.1 L/s into a shallow sand aquifer. The injection well was screened from 2 to 4 m below the watertable. The temperature field was simulated in three dimensions by Molson et al. (1992); however, mass transport and geochemical reactions were not considered at that time. Although changes in the groundwater chemistry during the 141-day experiment were not monitored, the 3D temperature field and background water chemistry is well known making this a suitable site for model evaluation.

The model domain and boundary conditions for the thermal chemistry simulation are identical to those used in the original thermal simulation. The domain, measuring $40 \times 30 \times 20$ m in the x, y and z directions respectively, is resolved with a grid containing 29,760 nodes. The natural background horizontal flow velocity is approximately 10 cm/day.

In our initial conceptual model, we consider the simplified set of chemical components listed in Table 1. Concentrations were derived from a shallow piezometer as reported by Dickin (1980), with the exception of adding a small amount of Fe(II), determined by assuming the water was initially at equilibrium with ferrihydrite. The given component concentrations will serve as both the initial background and source water concentrations, with the exception of Na and Cl which were both increased by 10^{-3} moles/L in the injection water to simulate a non-reactive tracer. In the field experiment, the injection water was obtained from the same aquifer; we will assume a closed system with no changes in PCO_2 and PO_2 and we neglect redox reactions. We also assume the aquifer initially contains calcite ($CaCO_3$), siderite ($FeCO_3$) and ferrihydrite ($Fe(OH)_3$) at concentrations of 0.02, 6.1×10^{-5} and 0.0019 moles/L respectively.

Simulation results are provided within the central longitudinal (xz) plane at the end of the 6-day injection period (Figure 1), and at 24 days (Figure 2). Time steps during the simulation varied from 0.25 days during injection to 2 days at later times. For clarity, only a 13m $\times$ 8m sub-domain is shown; the top surface is the watertable boundary.

Comparing the temperature and non-reactive Cl profiles at 6 days (Figure 1), we observe that the temperature gradients are much less than the Cl concentration gradients due to the high thermal diffusivity relative to hydrodynamic dispersion. The effect of thermal retardation is also immediately evident from the relatively smaller size of the peak temperature plume (at 37 °C) compared with the peak Cl plume (at 0.002 moles/L).

Because the injection water is identical to the background water (with the exception of temperature, Cl and Na) all reactions are temperature-induced. The low-pH plume is due to a combined effect of temperature on the dissociation constant of H_2O and other dissolved species, and on the loss of aqueous CO_3 to $CaCO_3$ and $FeCO_3$ precipitation. The loss of CO_3 reduces the pH because at neutral pH levels, the dominant form of CO_3 is HCO_3^-, and a reduction in CO_3 leaves an excess of H^+. This process is balanced, however, because further decreases of pH will cause dissolution of $CaCO_3$ and $FeCO_3$, reversing the above reactions.

The carbonates $CaCO_3$ and $FeCO_3$ precipitate directly at the well due to changing equilibrium constants favouring the formation of these solids at higher temperatures. Shells of depleted calcite and siderite surround the precipitates because the water here is undersaturated, having lost the Ca and Fe(II) at the well. A second shell of siderite forms at the leading edge of the thermal plume where the Fe(II) concentrations are high. Depletion plumes of Ca, CO_3, and Fe(II) are consistent with carbonate precipitation. Because of the limited extent of carbonate precipitation in this example, our assumption of uniform porosity is valid.

After 24 days (Figure 2), the temperature, pH and Cl plumes have dispersed and migrated downgradient from the injection well. The CO_3, Ca and Fe(II) depletion plumes have significantly recovered due to lower thermal plume temperatures and dissolution of calcite and siderite. Siderite first begins to dissolve at the upgradient boundary where temperatures are coolest and Fe(II) concentrations are low.

Temperature

37

10

Chloride

0.002

0.001

pH

6.8

7.2

Carbonate

0.0038

0.0040

Calcium

0.0041

0.0043

Calcite

0.023

0.020

Fe(II)

2.8e-5
3.3e-5

3.0e-5

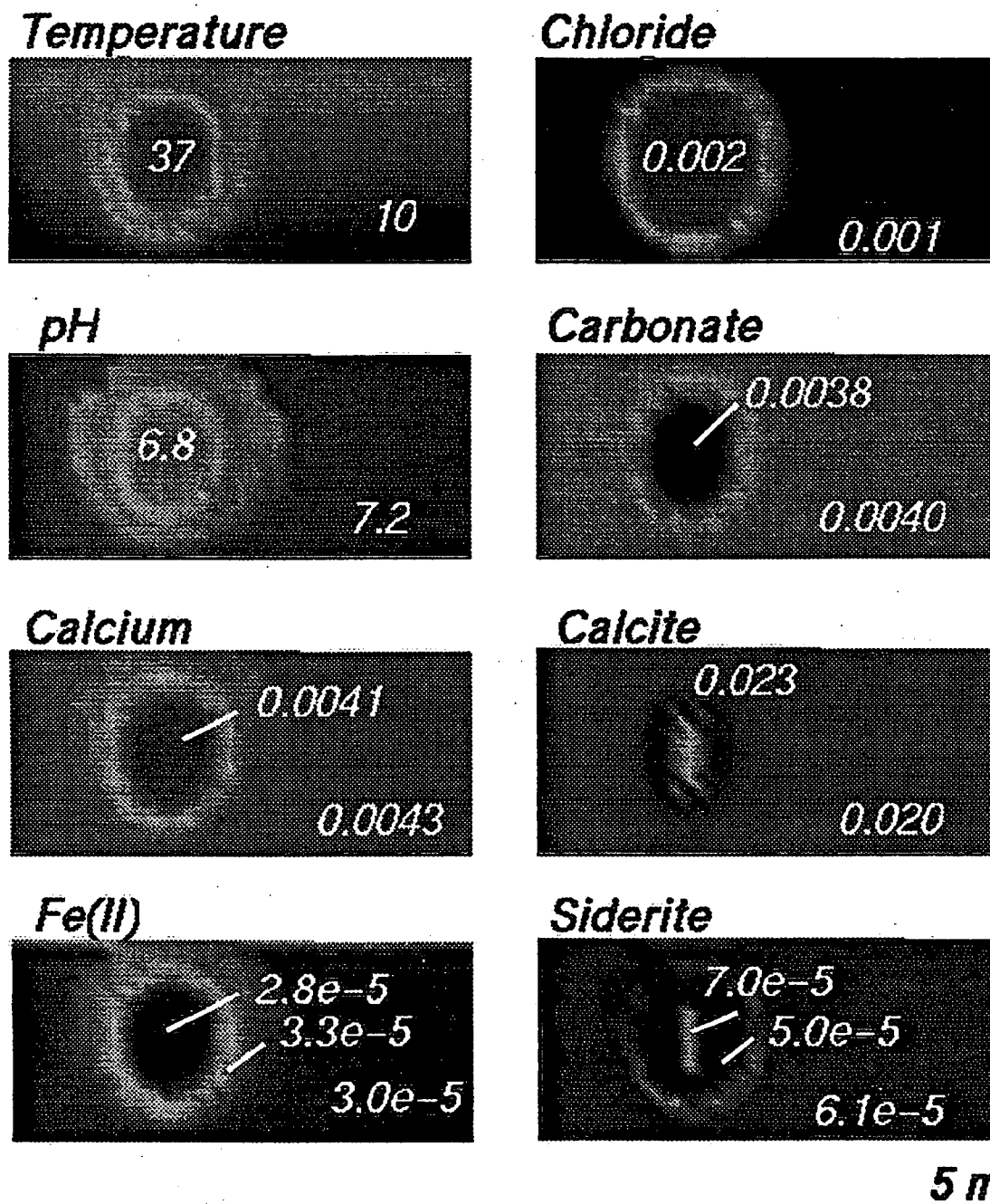## Siderite

7.0e-5
5.0e-5

6.1e-5

5 m

Figure 1. Simulated temperature, pH and selected aqueous component and solid-phase mineral concentrations in the longitudinal cross-section after 6 days of injection at 37 °C. Temperatures in °C, concentrations in moles/L. Background flow is left to right.
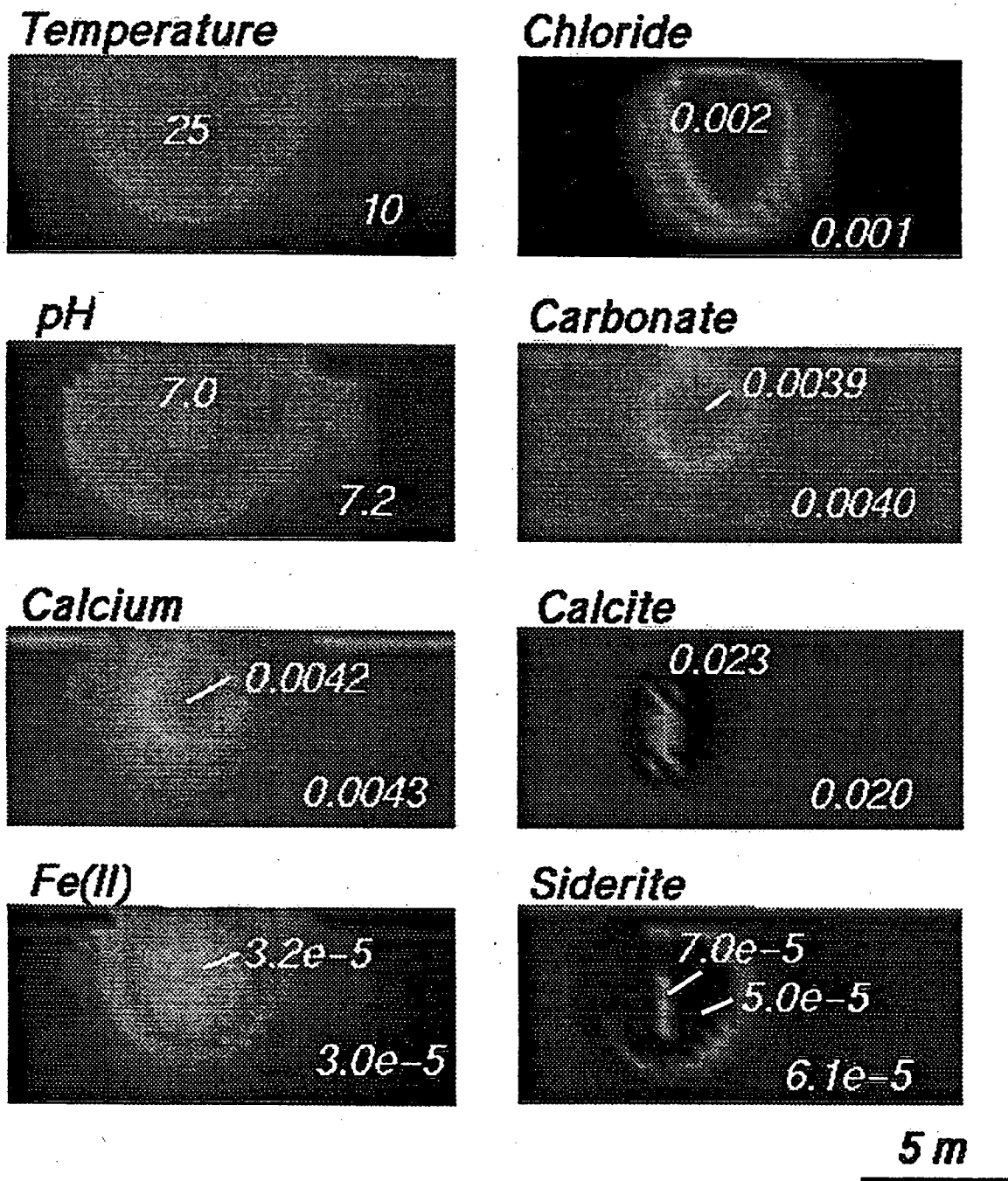
Temperature

25

10

Chloride

0.002

0.001

pH

7.0

7.2

Carbonate

0.0039

0.0040

Calcium

0.0042

0.0043

Calcite

0.023

0.020

Fe(II)

3.2e-5

3.0e-5

Siderite

7.0e-5

5.0e-5

6.1e-5

5 m

Figure 2. Simulated temperature, pH and selected aqueous component and solid-phase mineral concentrations in the longitudinal cross-section after 24 days. Temperatures in °C, concentrations in moles/L. Background flow is left to right.

Some questions relating to the geochemistry remain to be addressed. The shell of relatively higher Fe(II) concentration surrounding the injection well is currently being investigated. The simulation approach assumes separate pure phases of calcite and siderite whereas in reality a solid solution would be expected. Furthermore, mineral precipitation and dissolution may not always occur to the extent predicted by equilibrium thermodynamics. Griffioen and Appelo (1993) for example, found 12-fold supersaturation with respect to calcite. Although the supersaturation was attributed to the presence of organic acids and phosphates which are negligible at the Borden thermal injection site, the general implications of assuming equilibrium geochemistry must be addressed.

This 3D simulation required the solution of over 267,840 unknowns at each time step. The 24-day simulation required approximately 60 Mbytes and 2 hours of CPU time on an IBM RISC 6000/560.

Table 1. Aqueous component concentrations for the Borden thermal injection simulation. Solution is in equilibrium at 10 °C with respect to $CaCO_3$, $FeCO_3$ and $Fe(OH)_3$.

Component	Concentration (moles/L)	Component	Concentration (moles/L)
Ca	4.273×10^{-3}	Cl	9.874×10^{-4}
Mg	1.234×10^{-4}	CO_3	3.959×10^{-3}
Na	4.351×10^{-5}	Fe(II)	2.909×10^{-5}
K	2.558×10^{-5}	Fe(III)	1.480×10^{-8}
pH	7.156 pH units		

5. CONCLUSIONS

The 3D thermal chemistry model represents a first step in simulating the coupled processes of groundwater flow, heat and mass transport, and chemical reactive processes in shallow aquifers. The simulations show that coupled problems of this type can be simulated in three dimensions for realistic scenarios, taking advantage of efficient numerical techniques such as the Leismann scheme, sequential physical-chemical coupling, and a robust PCG matrix solver. Important processes that must still be incorporated to make the model more generally applicable include chemical kinetics, the formation of solid solutions, and the effect of mineral precipitation and dissolution on the porosity and permeability. These processes will be considered in the future.

ACKNOWLEDGEMENTS

REFERENCES

Allison, J.D., Brown, D.S. and Nova-Gradac, K.J. (1990). MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: Version 3.0 User's Manual. Environmental Research Laboratory, U.S. E.P.A., Athens, Georgia, 105p.

Dickin, R.C. (1980). Landfill leachate contaminant patterns and soil-water geochemistry at Canadian Forces Base Borden. MSc. Project, University of Waterloo, Waterloo, Ont.

Griffioen, J. and Appelo C.A.J. (1993). Nature and extent of carbonate precipitation during aquifer thermal energy storage. Applied Geochemistry, 8, 161-176.

Kangas, M.T. and Lund, P.D. (1991). Microcomputer design tool for aquifer thermal energy storage. In: Thermastock 91, 5th International Conference on Thermal Energy Storage, Scheveningen, Netherlands, 3.3.1-3.3.6.

Kinzelbach, W., Schäfer, W. and Herzer, J. (1991). Numerical modeling of natural and enhanced denitrification processes in aquifers. Water Resour. Res., 27(6), 1123-1135.

Leismann, H.M. and Frind E.O. (1989). A symmetric-matrix time integration scheme for the efficient solution of advection-dispersion problems. Water Resour. Res., 25(6), 1133-1139.

Molson, J.W., Frind E.O. and Palmer C.D. (1992). Thermal energy storage in an unconfined aquifer 2. Model development, validation and application. Water Resour. Res., 28(10), 2857-2867.

Palmer, C.D. and Cherry J.A. (1984). Geochemical reactions associated with low-temperature thermal energy storage in aquifers. Can. Geotech. J., 21, 475-488.

Perlinger, J.A., Almendinger, J.E., Urban, N.R. and Eisenreich, S.J. (1987). Groundwater geochemistry of aquifer thermal energy storage: Long-term test cycle. Water Resour. Res., 23(12), 2215-2226.

Snijders, A.L. (1991). IEA Energy storage programme - Annex VI: Environmental and chemical aspects of ATES and research and development of water treatment methods. In: Thermastock 91, 5th International Conference on Thermal Energy Storage, Scheveningen, Netherlands, 4.13.1 - 4.13.7.

Walter, A.L., Frind E.O., Blowes D.W., Ptacek C.J. and Molson J.W. (1994). Modelling of multicomponent reactive transport in groundwater: 1. Model development and evaluation. Water Resour. Res., (in press).

Willemsen, A., Buitenkamp, J., v.d. Weiden, M.J.J., Nienhuis, P.R., and Appelo, C.A.J., (1988). Chemical reactions and effects of water treatment during ATES experiments and coupled chemical transport modelling. In: Jigastock 88, 4th International Conference on Energy Storage for Building Heating and Cooling, Versailles, France.

Environment **Environnement**
Canada **Canada**

Canadä